LUMINESCENCE INDUCED IN LIQUIDS AND GASES

BY ALPHA PARTICLE EXCITATION

Thesis

Submitted by

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PART I

THE ROLE OF LUMINESCENCE IN THE RADIATION CHEMISTRY OF WATER

CHAPTER I

INTRODUCTION

1.1. Radiation Chemistry of Water and Aqueous Solutions.

The action of ionizing radiations on water and aqueous solutions has been the subject of investigation for many years. In that time a considerable amount of quantitative evidence has been accumulated, but agreement between different authors is limited. The chemical effects produced by radiation are fairly well known, but the physical action which produces the reactive species is not very well understood. Theoretical work is based mainly on results obtained in the gas phase and the extrapolation to the condensed state is not necessarily valid. The following brief survey covers the most generally accepted evidence and the theories which have been developed from it.

Because ionization is the most conspicuous feature of the radiations involved, emphasis has been directed on the ions as the source of the chemical action, although, depending on the system, only about half the energy of the radiation is used in their production. The possible role of excitation, although recognized, has received much less attention.

The most recent survey of the present position in the radiation chemistry of water and aqueous solutions is presented

by Dewhurst, Samuel and Magee[1]. There is general agreement that the products of irradiation of water are H_2, H_2O_2, and H and OH radicals. The chemical action on solutes is ascribed principally to the reactive H and OH radicals. A suggested mechanism for their formation is as follows[2].

$$H_2O \longrightarrow H_2O^+ + e \longrightarrow H^+ + OH + e$$

$$H_2O + e \longrightarrow H_2O^- \longrightarrow H + OH^-$$

The net reaction is known as the radical reaction

$$H_2O \longrightarrow H + OH \qquad (R)$$

The distribution of the free radicals about the site of the original ionization depends on the fate of the free electron which is emitted. This is uncertain. The fate of the free radicals depends to a large extent on this distribution and on the density of ionization produced by the radiation.

The molecular products, H_2 and H_2O_2, may be produced from recombination of the free radicals, or by a separate process.

$$H_2O \longrightarrow \tfrac{1}{2}H_2 + \tfrac{1}{2}H_2O_2 \qquad (F)$$

This is known as the "forward" reaction[3]. The ratio of molecular products to free radicals increases as the ion density increases.

A.O. Allen[4] has suggested a third reaction in order to account for the excess of the yield of H_2O_2 over H_2.

$$2H_2O \longrightarrow H + H + H_2O_2 \qquad (E).$$

In pure water a chain back-reaction occurs between the free radicals and the molecular products, but

$$H + H_2O_2 \longrightarrow H_2O + OH$$
$$OH + H_2 \longrightarrow H_2O + H$$

this is suppressed by the addition of suitable solutes which react with the free radicals[5].

The chemical action on a solute is usually independent of the concentration of the solute over wide limits, and of the rate of irradiation. The action of the radiation on the water predominates over any direct action on the solute. The number of water molecules dissociated per unit of energy absorbed by the solution is fairly constant for all types of radiation.

One of the aqueous systems which has received most attention is ferrous sulphate in 0.8N H_2SO_4. In aerated solutions the reaction involves dissolved oxygen as well as the Fe^{2+} ion. The accepted mechanism gives a good picture of the chemistry involved in the reactions of the products of irradiation[6].

$$H + O_2 \longrightarrow HO_2$$
$$Fe^{2+} + OH \longrightarrow Fe^{3+} + OH^-$$
$$Fe^{2+} + HO_2 \longrightarrow Fe^{3+} + HO_2^-$$
$$HO_2^- + H^+ \longrightarrow H_2O_2$$
$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH$$

The chemical yield of such a reaction is given in terms

of a G-value, the number of molecules oxidised or reduced for each 100 e.v. of absorbed energy. The G (Fe^{3+}) value of the above system is not agreed upon, but the figure of 15.5 molecules per 100 e.v.[7] is gaining acceptance for irradiation with γ-rays and fast electrons, and 5.9 for irradiation with natural α-particles[8]. From such reactions, may be calculated values for G_F and G_R, the number of water molecules which react according to equations (F) and (R).

Irradiation of water vapour indicates that other ions such as H^+ & OH^+ may be involved in the chemical action in addition to the H_2O^+ ions which are the probable parents of the free radicals[9]. As they are formed with zero kinetic energy, it is unlikely that they would separate in liquid water owing to caging effects.

The aspects of the subject to which the present work has contributed will be discussed in more detail in Chapter III.

1.2. Luminescence of Water.

Measurements of the ionization currents due to α-particle irradiation of liquid argon[10] and hexane[11] indicated that columnar recombination of ions and electrons was very rapid. Richards developed this result into the suggestion that collapse of the ion track in water was so rapid that dissociation into free radicals (time about 10^{-11} sec.) could not occur. It was suggested that the recombination of the H_2O^+ ion and the electron produced ultraviolet photons

which were absorbed by water molecules at some distance from the track, and gave rise to free radicals. The distribution of these free radicals was more diffuse than that of the ions in the α -track. The probability of recombination was reduced and reaction with solutes could take place to give the chemical action associated with α -particle irradiation of water.

In experiments designed to test this theory Dee and Richards[12], [13] were able to detect chemical action due to ultraviolet radiation transmitted by quartz from a thin film of water irradiated with α -particles. They reported that all the chemical action of α -particles could be accounted for by this process of light emission and reabsorption.

There has been further theoretical support for this process. An investigation by Magee and Samuel[14], on a classical model, into the motion of a slow electron away from its parent ion, found that the Coulomb field of the ion was strong enough to prevent the escape of the electron. Although this did not constitute a proof, it seemed possible that the production of free radicals from ions was not necessarily correct. On the other hand, according to Massey[15] radiative recombination of an ion and an electron has a low probability, although excitation to a triplet state may occur by this process.

Luminescence of water with ultraviolet excitation has been observed[16]. Distillation in vacuo reduced it, but it did not disappear. Kallman[17] found γ -ray irradiation also produced luminescence in water, but some of this would be due

to Cerenkov radiation. Belcher[18] in his studies of Cerenkov emission from solutions of β -emitting isotopes found excitation of the water when using β -emitters with energies less than the Cerenkov threshold. This visible luminescence would have no chemical effect on water, but ultraviolet luminescence which may have been present would have been undetected in the above investigations.

On the evidence it seemed that the mechanism proposed by Dee and Richards may have been correct, and certainly warranted further investigation.

1.3. The Experiment of Dee and Richards.

The experimental assembly was as shown in Figure 1, except that instead of a photomultiplier coated with Apiezon grease as a detector of the ultraviolet light, a solution of sodium iodide, chloracetic acid, or ferrous sulphate was maintained in close contact with the underside of the quartz slide. Because of the high absorption of the emitted light by water, the water film had to be of a thickness less than the range of an α -particle in water. It was found that the chemical change produced in the detecting solution amounted to about one-twentieth of that produced by the α -particles when directly incident on the solution.

An attempt to repeat the experiment by Miller and Wilkinson[8] was unsuccessful. The experiment differed from that of Dee and Richards in that it was found impossible to

maintain on the quartz slide, a film of water thinner than the range of an α -particle in water, and a film of sulphuric acid of such strength as to suit the humidity of the room was used instead. This film was maintained intact for 24 hours. The experiment showed that less than $^{1}/_{300}$th part of the chemical action caused by direct irradiation with α -particles was induced by light transmitted by the quartz.

The present work is concerned with the search, by physical means, for light emitted by α -particles from water.

CHAPTER II.

LUMINESCENCE EXCITED IN WATER BY ALPHA-PARTICLE IRRADIATION.

2.1. The Problem.

Although the experiments carried out by Miller and Wilkinson indicated that light emission from water was less than that found by Dee and Richards, they were much too insensitive to exclude light emitted in regions of very high absorption.

The most reliable results[19] on the absorption of water vapour in the vacuum ultraviolet show a continuum in the region 1860 - 1430A with a maximum at 1650A, and a banded region at 1430 - 1150A. The maximum at 1650A corresponds with the first singlet excited level of water (7.5 e.v.) and is above the dissociation energy. Spectroscopic studies of polyatomic molecules[20] indicate that higher excited levels are usually internally converted to the first excited level of the same multiplicity. Excitation by slow electrons and recombination of ions and electrons may lead to triplet states[21] but very little is known about these states in water. Inter-system crossing may occur in the absence of quenching. Emission in the regions of high absorption probably corresponds to the chemically active light found by Dee and Richards. Fluorescent light is usually of a longer wavelength than that of the exciting absorption band and to be chemically effective on water

it must have a wavelength less than 1860A. The light emission which is to be sought, if it lies in this region, must have a wavelength between 1650 and 1860A. The absorption coefficients for water vapour found by Watanabe and Zelikoff[19] are 124 cm^{-1} and 387 cm^{-1} at the maximum of the continuum and for the absorption of the Lyman alpha line. If there is no change in the mass absorption coefficient in the condensed state, the absorption coefficients for liquid water at 1650A and for the Lyman alpha line are 1.5×10^5 cm^{-1} and 4.8×10^5 cm^{-1} respectively.

The G value for alpha-particle irradiation of deaerated ferrous sulphate solution is about 4 molecules decomposed per 100 e.v. of absorbed energy.[8] If a photon emission and reabsorption process accounted for the chemical change, there would have to be 4 ultraviolet photons emitted per 100 e.v. of alpha-particle energy, or for a 5.3 Mev. alpha-particle from polonium, 2.1×10^5 photons. This is approximately the number of ion pairs which would be produced in water by a 5.3 Mev. alpha-particle (W value of 30 e.v. per ion pair). If the alpha-particle were incident normally on the surface and the absorption coefficient were large, there would be only a small error in assuming the alpha-track to be infinitely long for purposes of integration of the light emission from it. The number of photons escaping from a surface is given by

$$\frac{N}{2} \int_0^{\infty} \int_0^{\sin^{-1}\frac{1}{R}} \sin\theta \, e^{-\mu x \sec\theta} \, dx \, . \, d\theta .$$

$$= \frac{N}{4 \mu R^2}$$

N is the number of photons emitted per centimetre of path in the water, and R is the refractive index. R comes into the equation because of internal reflection at the surface. Because of internal reflection and the greater absorption path of obliquely emitted light, most of the photons will be confined to a fairly narrow cone about the normal to the surface. If the range of a polonium alpha-particle in water is taken as 38μ [22], the number of photons of wavelengths in the region of 1650A which escape from the surface is 55 per alpha-particle, and in the Lyman region, 17 per alpha-particle. For comparison, a a 5.3 Mev. alpha-particle excites the emission of 9,000 photons from an anthracene crystal [22a].

2.2. Experimental

2.2.1. Light detection.

An E.M.I. 5311 photomultiplier was used as the light detector. The output current could be measured directly on a Cambridge Spot Galvanometer, full scale deflection $\sim$ 1μA, or if necessary the output could be switched to a cathode follower and amplifier and the counting rate measured in the usual way. With the aid of shunts the output current could be measured over a range from 0 to 100μA. The gain of the photomultiplier was constant at light intensities covering this range. The mains supply for the counting assembly and the stabilized high voltage unit was kept constant with the aid

of an inefficient constant voltage transformer and a "Variac" transformer. It was possible to repeat measurements at long intervals with a reproducibility of 2%.

Light connections between apparatus, light guides, and the photomultiplier were made with medicinal paraffin.

The sensitivity curve of the photomultiplier has a broad maximum in the region of 4,000A and falls off on the short wavelength side to zero at 3,000A. In order to make the photomultiplier sensitive to ultraviolet light, the glass surface of the photocathode was coated with fluorescent materials such as Apiezon "L" grease [23] or sodium salicylate [24], which have a constant photon conversion efficiency from 3,400A to about 850A, and which emit in the region of maximum sensitivity of the photomultiplier.

The photon conversion efficiency, or the number of ultraviolet photons required to produce one fluorescent photon, was important in determining the minimum levels of ultraviolet emission which could be detected by this means. Measurements of it were made with a Unicam spectrophotometer in order that values might be related to the particular photomultiplier used in the experiments, and to the material which might not be of the same degree of purity as that used by other workers -- not that there were any reliable values. The photocell assembly was removed from the spectrophotometer and the photomultiplier attached in its place. The photomultiplier current was measured as a function of the wavelength of the light from 4,000A to lower wavelengths at a constant slit width. The photomultiplier detected no light below 3,100A. The fluorescent material was

then deposited on the surface of the photocathode and the same measurements were repeated. From the ratio of the photomultiplier current at 3,000A with the fluorescent material applied, and the current at 4,000A when the photocathode was clean, the photon fluorescent efficiency of the fluorescent material could be calculated, by assuming half of the emitted light was detected by the photomultiplier. This method measured a practical fluorescent efficiency and any self-absorption was taken into account by the method.

The fluorescent efficiency of Apiezon "L" grease was 20%, and that of sodium salicylate 35%. There was a transparency in the sodium salicylate absorption curve at 2,600A, but this did not affect the fluorescence excited by this wavelength if a sufficiently thick layer was deposited on the photocathode. The value of 35% for the fluorescence efficiency of sodium salicylate does not compare well with the measurement of 70% by Dubouloz[25]. It could probably be improved with further purification but in a practical instrument it would be unlikely that this higher efficiency could be maintained even if it could be reached.

2.2.2. Purification of Water.

The luminescence of water may be reduced by purification. The water used in the following experiments was distilled in a commercial still, then redistilled from alkaline permanganate and the vapour passed through about one metre of quartz tubing at 800°C. This water has been found to be sufficiently pure

for work in radiation chemistry [26].

2.2.3. Alpha particle sources.

Polonium is the best readily available source of natural alpha-particles, as it is almost a pure alpha-emitter. About one γ-ray is emitted per 10^5 alpha-particles. It suffers from the disadvantage that it readily contaminates apparatus by aggregate recoil. The sources used were prepared by the Radiochemical Centre, Amersham, and consisted of polonium electrodeposited on platinum. These sources emit light of their own even in a vacuum. This has been ascribed to luminescence of adsorbed gases but such an interpretation does not seem likely [28]. In the work on gases described in later chapters, the sources were kept under high vacuum for long periods and exposed to a considerable variety of gases. The light emission remained very constant when allowance was made for the decay of the polonium. The light emission was too weak to be measured with a spectrograph.

2.2.4. Sodium salicylate.

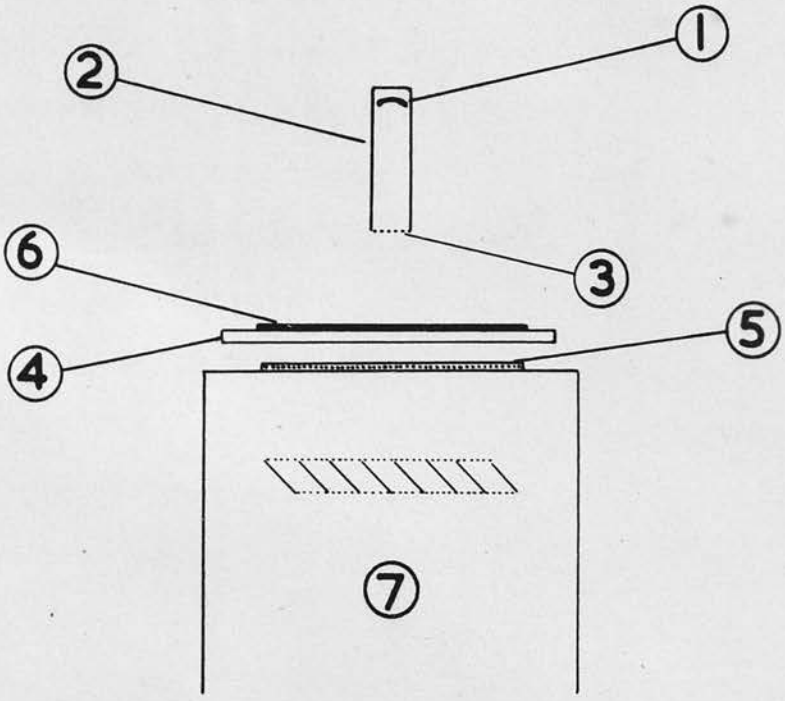
The sodium salicylate was purified by two recrystallizations from alcohol.

2.2.5. Cleaning.

Glassware and quartz was cleaned with concentrated sulphuric acid containing chromic oxide and rinsed with a small amount of water to make use of the heat of dilution. Sometimes an alcohol rinse followed by concentrated nitric acid was used.

2.3. Light transmitted by quartz.

The experimental assembly was as in Figure 1. The quartz slide was placed in contact with the Apiezon grease so that there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6
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FIGURE 1.

Irradiation of a thin film of water with P_o alpha-particles, as it slowly evaporated.

1. P_o alpha-particle source.
2. Collimating tube.
3. Nylon film, coated with aquadag.
4. Quartz slide.
5. Apiezon "L" grease.
6. Water film.
7. Photomultiplier.

was no absorption of ultraviolet light in the air gap. The quartz slide was 0.5 mm. in thickness, and showed over 90% transmission at 2,000A, the limit of our spectrophotometer. The polonium source was contained in a collimating tube and to eliminate, as far as possible, light from the source and from air excited by alpha-particles between the source and the slide, the end of the collimating tube was closed with a thin nylon film coated with aquadag. The quartz slide was vigorously cleaned in hot cleaning mixture and washed in distilled water. On removing it from the water and drying the underside with filter paper the film of water on the upper side slowly evaporated and withdrew across the plate. Interference fringes could be seen at the edges. At some stage of the evaporation the film must have been thinner than the range of an alpha-particle in water. Such a film would not be replaced on the dry slide unless the cleaning procedure was repeated.

The photomultiplier was kept in a dark box in a dark room with the high voltage applied, in order that counting might begin immediately the apparatus was assembled without having to wait for the voltage to settle to its steady value. The quartz slide with its film of water was placed on the Apiezon grease surface and the alpha-source was mounted above it. Counting was carried out continuously until the water film had evaporated, and a steady counting rate showed that the dry quartz slide was being irradiated.

The graph of counting rate against time is shown in Figure 2. Initially, the amount of light AB, was due to

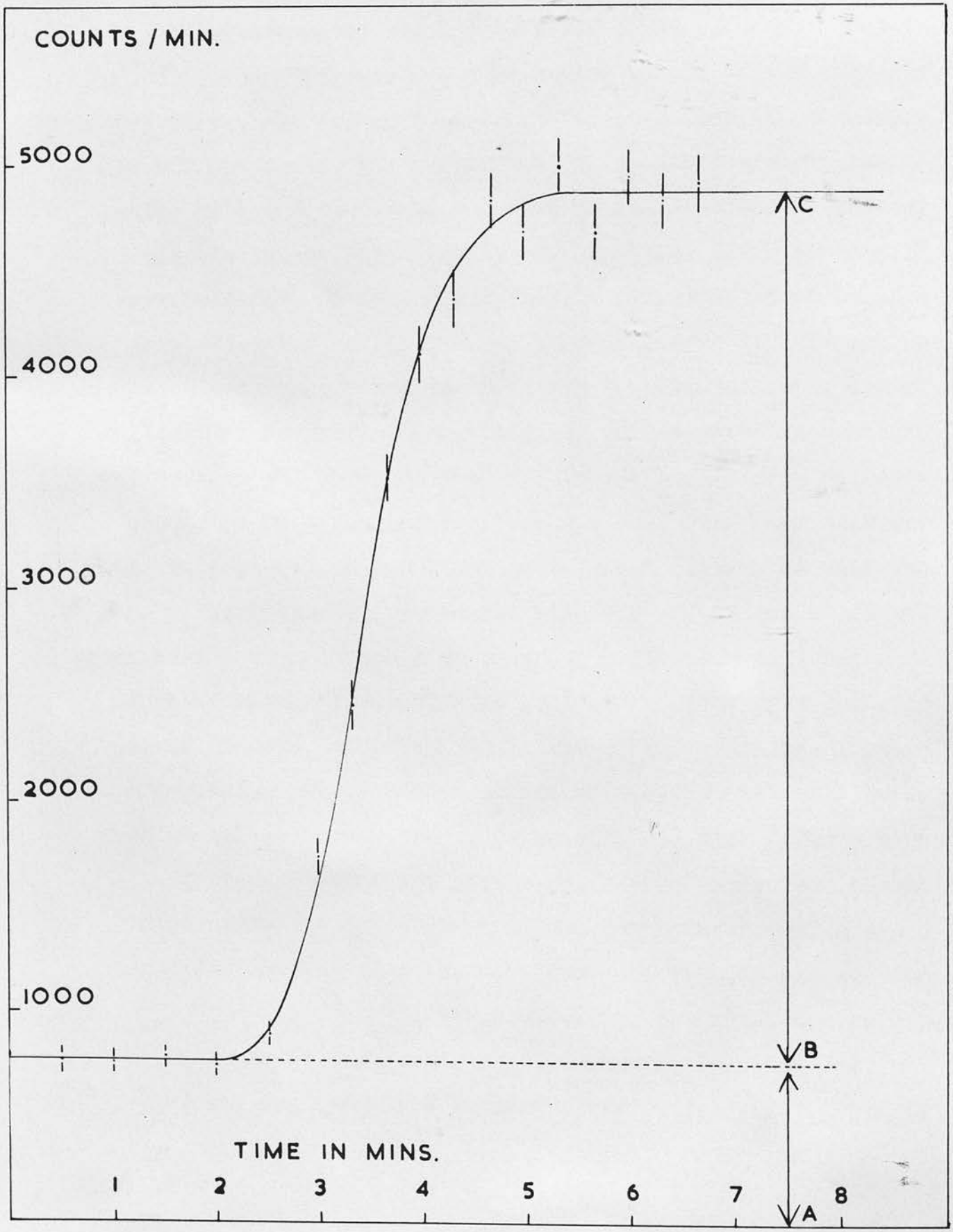

COUNTS / MIN.
5000
4000
3000
2000
1000
C
B
A
TIME IN MINS.
1
2
3
4
5
6
7
8

FIGURE 2.

Change in the counting rate from irradiation of a thin film of water evaporating from a quartz slide.

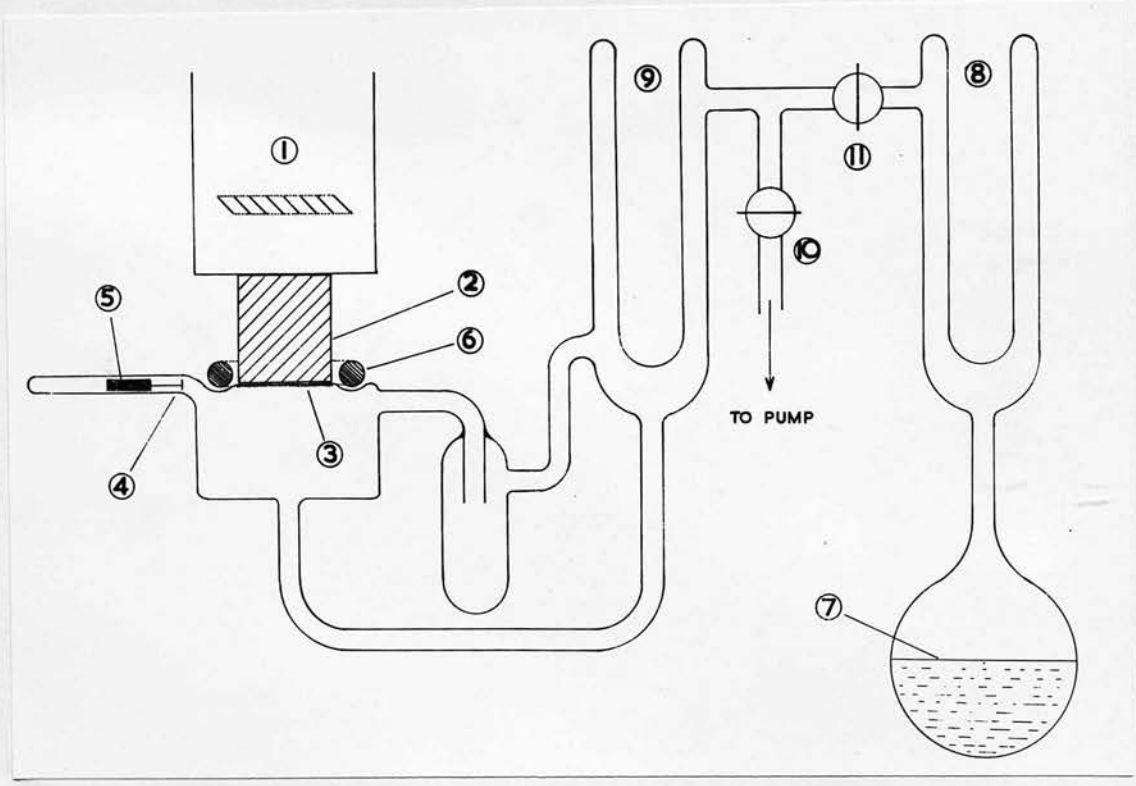
AB. Counting rate when the water film was thicker than the range of an alpha-particle.

AC. Counting rate when the water film had evaporated from the quartz slide.

(1) luminescence of the air in the gap between the end of the collimating tube and the water film, and (2) light emitted by the "thick" water film. By varying the air gap it was shown that most of the light was due to luminescence of the air. As the water film evaporated, alpha-particles of increasing residual energy were able to penetrate to the quartz until light from the air gap and the quartz gave the deflection AC. If ultraviolet light had been emitted from the thin film of water during the time the alpha-particles were reaching the water-quartz interface, the graph would have shown a maximum before falling to a steady value for dry quartz. As no maximum was observed it can be concluded that if there was any light it was (1) of a wavelength not highly absorbed by water and so made a contribution to the amount of light AB, or (2) of a wavelength not transmitted by quartz. Only in the second case could the light have had any chemical significance. It was found that a thin film of water could not be maintained on fluorite and further experiments could not be made by this method.

2.4. Light emitted directly from water.

In order to detect light of a wavelength shorter than that transmitted by quartz, an attempt was made to measure the light as it was emitted from the surface on which the alpha-particles were incident. As such light would be strongly absorbed by oxygen in the air between the water surface and the detector, it was necessary to carry out the experiment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②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
TO PUMP

FIGURE 3.

Apparatus for measuring the light emission from a water surface irradiated with alpha-particles.

1. Photomultiplier.
2. Perspex light guide.
3. Sodium salicylate crystals.
4. P_o source.
5. Soft iron.
6. Heater.
7. Purified and deaerated water.

in the absence of air. The apparatus is shown in Figure 3. The cell viewed by the photomultiplier was silvered on the inside in order to prevent light from the irradiation of the glass from obscuring the light from the water. But in order to reduce the reflection into the photomultiplier of light emitted by the polonium source, the silvered surface was left with a dull finish. A one-inch window in the upper side of the cell was coated on the inside with sodium salicylate. The polonium source was attached to a piece of iron so that it could be withdrawn into the side arm between experiments and so reduce the possibility of contamination of the cell. The window was screened by the construction of the cell from the direct impingement of alpha-particles and from direct light from the source. Because sodium salicylate is deliquescent, the window was kept a few degrees warmer than the rest of the cell with a small heater, and this also prevented condensation on the source.

The experimental procedure was as follows. Distilled water in (7) was deaerated by evacuating the system while trap (8) was cooled with liquid air. It was found that the light from the polonium source in the evacuated chamber was greater than had been expected, amounting to about 100 times the noise value. It was this background which set a limit to the sensitivity of the experiment. When stopcock (10) had been closed water vapour at room temperature was admitted to the cell. No increase in the light was detected. Light due to excited OH radicals is emitted from an arc in water

vapour[29], but any such light in this experiment was below the detection limits of the apparatus. Water was condensed into trap (9) with liquid air, and when sufficient had accumulated, the ice was allowed to melt slowly into the light chamber.

As the surface of the water rose in the cell the following factors would control the intensity of light emission.

1. The variation in the flux of alpha-particles producing detectable light could be estimated from the change in the solid angle subtended at the source by a circular area one inch in diameter beneath the window as the water surface rose. This solid angle is given by the equation

$$\text{Solid angle} = \frac{\pi r^2 \sin\theta}{4\pi (h/\sin\theta)^2}$$

$$= \frac{r^2}{4R^2} \sin\theta . \cos^2\theta$$

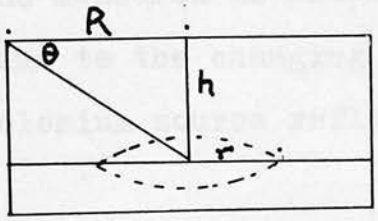


Figure 4.

2. As θ decreased the end of the alpha-track lay closer to the surface. The number of photons which escaped from the surface would increase as $1/\sin\theta$.

3. The absorption path of the light in water vapour was decreased. The vapour space above the water should have been in equilibrium with the melting ice in the trap, but because the upper surface of the cell was slightly warm, it probably was not. The pressure may have been as high as 10 mms. The absorption coefficient for water vapour at N.T.P. is 124 cm^{-1} at 1650A. The fraction of the light emitted from the surface which reached the window was $e^{-\frac{124h}{76}}$, which increased from 0.038 at 20 mms. to 0.27 at 8 mms.

The broken line in Figure 5 is the theoretical graph for light from water superposed on a steady background of 70 divisions, which gave a deflection of 80 divisions when the water level had risen to its final position 8 mms. from the window.

In the experiment the rate at which the water rose in the cell was not quite uniform, but a fairly smooth fall in the light emission was measured as shown in Figure 5. This fall could have been due to the changing detection geometry for light from the polonium source reflected by the walls of the cell.

The detection efficiency of the photomultiplier was determined in a separate experiment by measuring the Cerenkov emission from a solution of P^{32}. Belcher found that an average of 51 Cerenkov photons were emitted between 3,000 and 7,000A for each P^{32} β-particle[30]. This figure cannot be used directly to standardize the photomultiplier for measurement of fluorescent

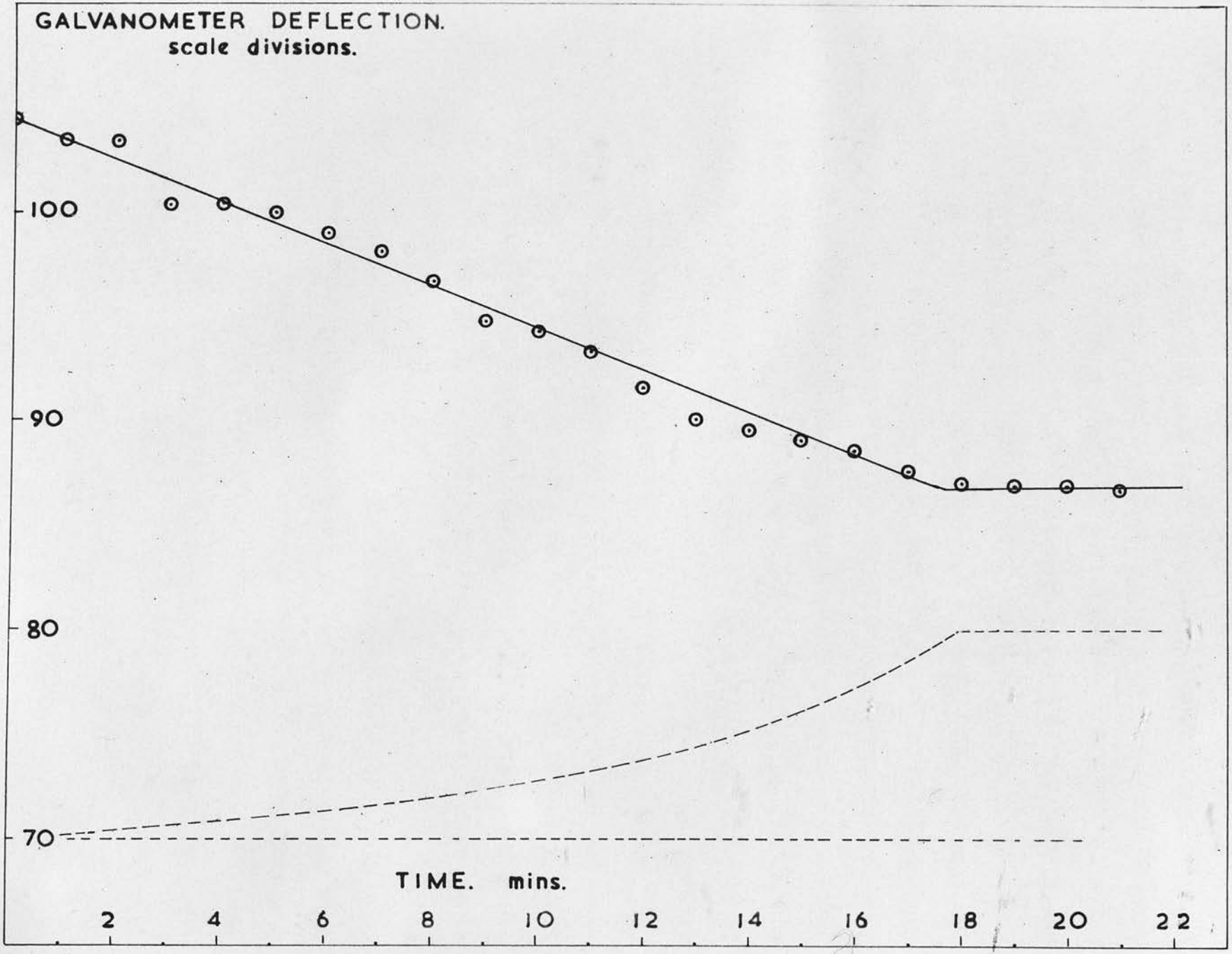

GALVANOMETER DEFLECTION.
scale divisions.
100
90
80
70
TIME. mins.
2
4
6
8
10
12
14
16
18
20
22

FIGURE 5.

Light emission from a water surface slowly rising towards an alpha-particle source.

Theoretical curve for the change in light emission on a steady background of 70 scale divisions.

light. Sodium salicylate fluoresces in the wavelength region of maximum sensitivity of the photomultiplier, and from the above figure of 51, must be calculated the equivalent number of photons in the region of maximum sensitivity. From Franck and Tamm's formula[31] the Cerenkov emission at wavelength between 3,000 and 7,000A can be calculated and the integrated curve was the equivalent of 51 photons. From the published graphs of quantum efficiency of the photomultiplier against wavelength and the above formula a graph of photomultiplier current against wavelength can be drawn. By graphically integrating this curve it was found that 29 photons emitted in the region of maximum sensitivity of the photomultiplier were equivalent to Belcher's figure of 51 photons emitted between 3,000 - 7,000A.

Light from water, if in the region of strong absorption could be considered to be emitted normally to the surface. It was assumed that all the light emitted from the projection of the window on the water surface reached the window. The fluorescent light excited in the salicylate would be emitted in all directions and the solid angle of detection would be determined by the maximum angle of internal reflection of the light guide. The Cerenkov emission of the standard light source would also be emitted in all directions. The P^{32} solution of known strength (Radiochemical Centre measurement) was contained in a small Perspex beaker which sat in medicinal paraffin in a cup on the end of a Perspex light guide, so the collection geometry should have been the same for the fluorescent

light and the standard source. As the photon conversion efficiency of sodium salicylate had been measured as 35% the light emission from water corresponding to any galvanometer deflection could be determined.

A comparison of the experimental and theoretical curves in Figure 5 indicated that a light emission less than the theoretical curve would have been obscured by the background of light from the polonium source. Hence the limit of light emission from water which would have been detectable in this experiment was such as would have given a deflection of 10 galvanometer divisions when the water surface had risen to within 8 mms. from the window. The measurements made with the P^{32} solution showed that 3.08×10^8 photons gave a deflection of 234 divisions. The number of photons which would have given a deflection of 10 divisions was therefore 1.32×10^7. Taking into account the fluorescence efficiency of sodium salicylate and the absorption path of 8 mms. of water vapour at 10 mms. pressure, the minimum number of photons emitted from the water surface in the region of 1650A which could have been detected was 1.4×10^8.

The source strength was 9.2 mc. It was calculated from the geometry of the cell that the alpha-particle flux on the water surface beneath the window was 6.4×10^6 per second. Because of the oblique angle of incidence of the alpha-particles, the light emission would have been 180 photons per alpha-particle if all the chemical action on water were due to

light emission in the region of 1650A, which corresponded to a total light emission of 1.15×10^9 photons per second. The detection limit of the experiment would therefore indicate that less than 12% of the chemical action of alpha-particles was due to light in the region of 1650A. Light in the Lyman region would have been undetectable.

This experiment was not sufficiently sensitive to give any significant evidence on the emission or otherwise of light from water in the regions of highest absorption. It is of interest because of the similarity to experiments by Richards which will be discussed in section 2.7.

2.5. Detection of light with a fluorescent solute.

In the last few years a considerable amount of work has been done on the luminescence of organic solutions, and it has been established that energy transfer may occur from the solvent to the solute, which then emits its own fluorescence[32]. One of the mechanisms which have been proposed for this transfer, is that it takes place by luminescence of the solvent which is absorbed by the solute[33], [34]. It was thought that by immersing an alpha-particle source in an aqueous solution of a fluorescent solute, it might be possible to detect transfer of energy from the water to the solute. Because the radiations which were being sought were highly absorbed by water, it was necessary to find a solute which was very soluble and had a sufficiently high absorption cross-section for light of

wavelengths in the regions of 1650A or 1200A, for the light to be absorbed by the solute rather than reabsorbed by the water.

Sodium salicylate was found to be a suitable solute. Its molar absorption coefficient was found to be 1.02×10^5 cm^{-1} at 2,000A, the limit of our spectrophotometer. There was no information available for the absorption of salicylates in the vacuum ultraviolet, but the absorption curve for phenol has broad peaks in the region of 1,800A and in the Lyman region[35]. From the evidence it was thought very reasonable to assume a molar absorption coefficient of 5×10^5 cm^{-1} for sodium salicylate in these regions. However, even with an absorption coefficient of this magnitude, only half of the light emitted by water in the Lyman region would be absorbed by salicylate molecules in a 1M solution, hence the requirement of good solubility as well as a high absorption coefficient.

Preliminary experiments were carried out with ultraviolet excitation of sodium salicylate solutions. The photomultiplier was attached to a Unicam spectrophotometer in place of the photocell compartment as described in section 2.2.1. In front of the photocathode a one centimetre quartz cell of sodium salicylate solution could be placed. The fluorescence of solutions of different concentrations was excited by wavelengths between 2,000A and 3,000A. At concentrations of salicylate greater than 10^{-2}M the exciting light was absorbed in the first millimetre of the solution. The geometry for measurement of fluorescence at higher concentrations remained constant. In this way the self-absorption of sodium

salicylate for its own fluorescent light could be found. In addition to self-absorption of fluorescent light, it was possible that self-quenching, i.e. quenching of excited molecules of salicylate by unexcited molecules might have occurred. The light detected by the photomultiplier would have been related to the incident light as in the following equation:

$$I = \frac{I_0 \, e^{-kcd}}{1 + mc}$$

where k is the self-absorption constant and m is the self-quenching constant. I_0 is the intensity of exciting light, and I the intensity of the light transmitted by solution of thickness d and concentration c.

The experimental plot of log $\frac{I_0}{I}$ against concentration in moles/l. was a straight line of slope 4.2. As this graph was taken to concentrations of 0.5M without a departure from linearity being apparent, the self-quenching constant m must have been small, so that the factor $(1 + mc)^{-1} \approx e^{-mc}$

The fluorescence of a 10^{-2}M sodium salicylate solution was found, in the experimental arrangement described, to be about 12% of that of a layer of solid salicylate deposited on the photocathode. A large part of this reduction could be accounted for by the poorer collection geometry for the fluorescent light from the solution. It seemed that solvent quenching of the fluorescence was small.

Alpha-particle irradiation of sodium salicylate solutions would be expected to excite two contributions to the emitted

luminescence.

(1) Direct excitation of the sodium salicylate which would be proportional to the concentration.

(2) Excitation of water, which if it resulted in fluorescence, would excite luminescence of the sodium salicylate. Transfer of energy from water to salicylate by any process other than photon emission and absorption would add to this luminescence.

The light emission would be given by the following equation:

$$L = K_1 c + K_2 f \frac{\epsilon c}{\mu + \epsilon c}$$

ϵ is the molar absorption coefficient of sodium salicylate which has been estimated as 5×10^5 cm^{-1}, μ is the absorption coefficient of water, f the fraction of excited water molecules which emit light. k_1 and k_2 are the relative excitation probabilities of sodium salicylate and water by an alpha-particle, and would be proportional to the excitation cross-sections and to the relative number of molecules present. The molecule ratio of salicylate to water is approximately 0.018 of the molarity. The relative alpha-particle excitation cross-sections for salicylate and water can only be guessed at, but if it is assumed that they are proportional to the collision cross-sections, the excitation cross-section for salicylate would be about 4 times that of water. From these estimates $k_1 = 0.072\ k_2$., but to be on the safe side, in the calculations k_1 has been taken as

equal to 0.1 k_2.

$$\therefore \quad L = K_1\left(c + 10f\,\frac{\epsilon c}{\mu + \epsilon c}\right)$$

$$\epsilon = 5 \times 10^5$$

$$\mu = 1.5 \times 10^5 \text{ at } 1650A$$

$$\text{and} = 5 \times 10^5 \text{ at } 1200A.$$

The experimental arrangement was as shown in Figure 6. Solutions of sodium salicylate from 10^{-4}M to 0.8M were placed in the beaker and the source was fitted in position. Because the quantum efficiency of the photocathode varied over the surface, care had to be taken to replace the beaker in the same position for each reading. Readings were easily taken and reproducible to better than 1%. In pure water a small amount of light was detectable, and at salicylate concentrations of about 10^{-4}M, the light emission rose steeply. This light was assumed to come from the polonium source and if it included some ultraviolet light, the effect at low concentrations would have been a sharp rise in light emission due to the fluorescence of the salicylate, as was actually found. The effect amounted to about 5% of the light emission at 0.1M salicylate and was subtracted from the readings at higher concentrations.

The graph of light emission against concentration was linear from 10^{-3}M up to 10^{-1}M, when it began to sag below the line of initial slope. The concentration at which the sag became apparent was lower, the greater the distance of the

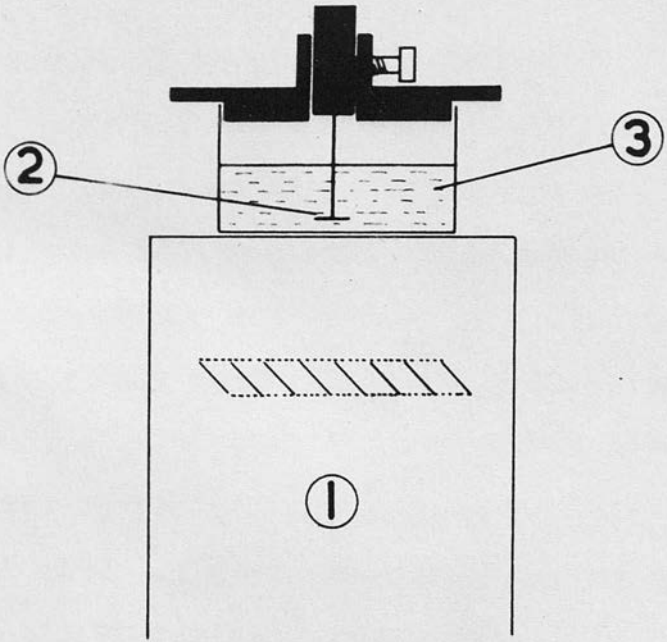

2
3
1

FIGURE 6.

Apparatus for measuring the light emission from an alpha-particle source immersed in a solution of sodium salicylate.

1. Photomultiplier.
2. P_o alpha-particle source.
3. Sodium salicylate solution.

source from the bottom of the beaker, which indicated that it was due to self-absorption of the luminescence. However it was found that a correction made from the results of the experiments with ultraviolet excitation would compensate for the "sag" over a small concentration range. At concentrations in the region of 0.4M the graph became horizontal. If experiments carried out with different sources and with the source at varying distances from the bottom of the beaker were all normalized to the same initial slope, the final value of the light emission at high concentrations was approximately the same. It was therefore concluded that a bimolecular quenching effect between excited salicylate molecules in the alpha-track, occurred at high concentrations of salicylate. At concentrations around 0.4M each molecule of salicylate in the solution was separated from its nearest neighbour by about four or five water molecules, so it was possible that some interaction could occur. The reduction in fluorescence efficiency of anthracene when the excitation was changed from fast electrons to heavy particles has been accounted for in this way [36]. Because of the difficulty of correcting for such an effect, combined with self-absorption of luminescence, it was thought that it would be more convincing to get as much information as possible from the experiment without applying any corrections. Measurements were made up to concentrations at which a departure from linearity became apparent. The source was supported at a distance of 0.45 mms. from the bottom of the beaker in order to reduce any effects of self-

absorption. Light emission was proportional to the concentration up to 0.13M as shown in Figure 7. The correction for self-absorption at this concentration was calculated to be 2.4%. Included in the graph are the theoretical curves which would have been expected for the same initial slope as the experimental curve, if the absorption coefficients of water, and the fluorescent efficiencies of water had been as indicated.

It can be seen that in the region of 1650A, if 1% of the excited water molecules emitted light, the effect would have been easily detectable by this method. The maximum number of water molecules which could be excited to this level (7.5 e.v) by a 5.3 Mev. alpha-particle, if all the energy went into excitation of this level, would be 7×10^5 and to account for all the chemical action by a photon emission and reabsorption process 2.1×10^5 photons would be required. Hence it could be concluded that less than 3.3% of the chemical action was due to emission in this region. It can be seen from Figure 7 that the detection limit would be less than the curve for f = 1%, and it is unlikely that all the energy of the alpha-particles would go into excitation of the 7.5 e.v. level by the most efficient path. Hence it is probable that the limit of the contribution to the chemical action of light in the region of 1650A would be considerably less than 3%.

In the region of 1200A the detection limit was higher. The curve for $\mu = 5 \times 10^5$, f = 5% lies 3.5% below the experimental line at a concentration of 0.13M, and this is probably the smallest deviation from a linear graph which could be

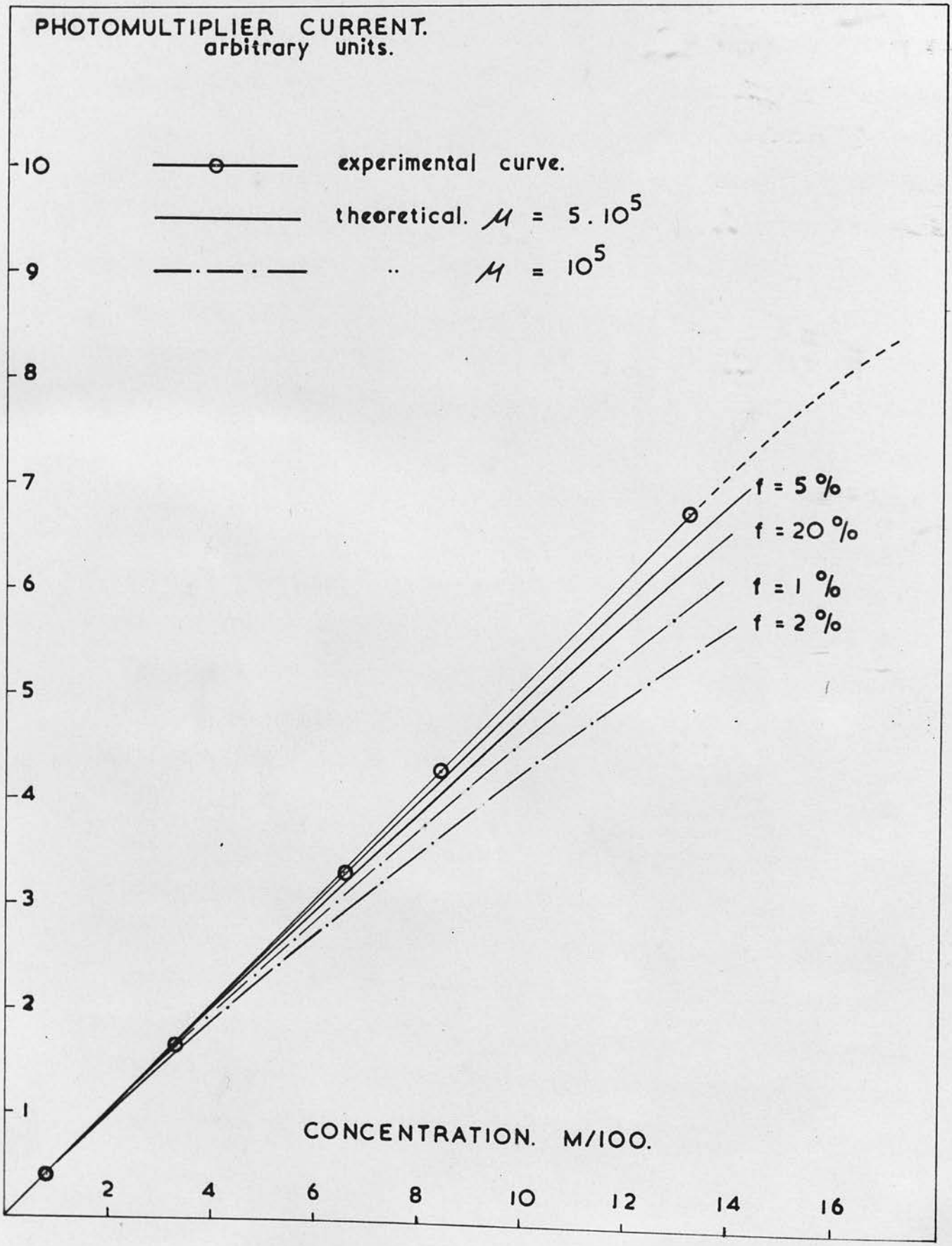

PHOTOMULTIPLIER CURRENT.
arbitrary units.
10
9
8
7
6
5
4
3
2
1
experimental curve.
theoretical. μ = 5 . 10^5
.. μ = 10^5
f = 5 %
f = 20 %
f = 1 %
f = 2 %
CONCENTRATION. M/100.
2
4
6
8
10
12
14
16

FIGURE 7.

Light emission from alpha-particle irradiation of sodium salicylate solutions.

detected. By a similar reasoning to that above, and taking into account the fact that excitation to a 1200A level would require 10.3 e.v., it could be concluded that less than 12% of the chemical action of alpha-particles was due to light emitted in this region.

An approximate calculation based on the light yield from gases, reported in later chapters, of this thesis, showed that the light emission from solutions of sodium salicylate was no more than would be expected from direct excitation of the solute. It could be concluded that transfer of energy from the solvent to the solute by any means other than a photon emission process had a probability of less than 10^{-3}.

2.6. Luminescence of ice.

The light emission from many liquid organic compounds is increased considerably in the solid state. Avery and Grossweiner[37] have described a weak fluorescence of ice at $-120^{\circ}C$ after irradiation with X-rays, and it was thought that any light emitted from water by alpha-particles might be increased by freezing.

The experiments were carried out in the apparatus shown in Figure 8. The central tube could be attached to a vacuum line so that air-free water, or other liquids, could be condensed into the irradiation cell, which could then be sealed off. Ice was formed by adding liquid air to the annular space around the central tube. The contraction of

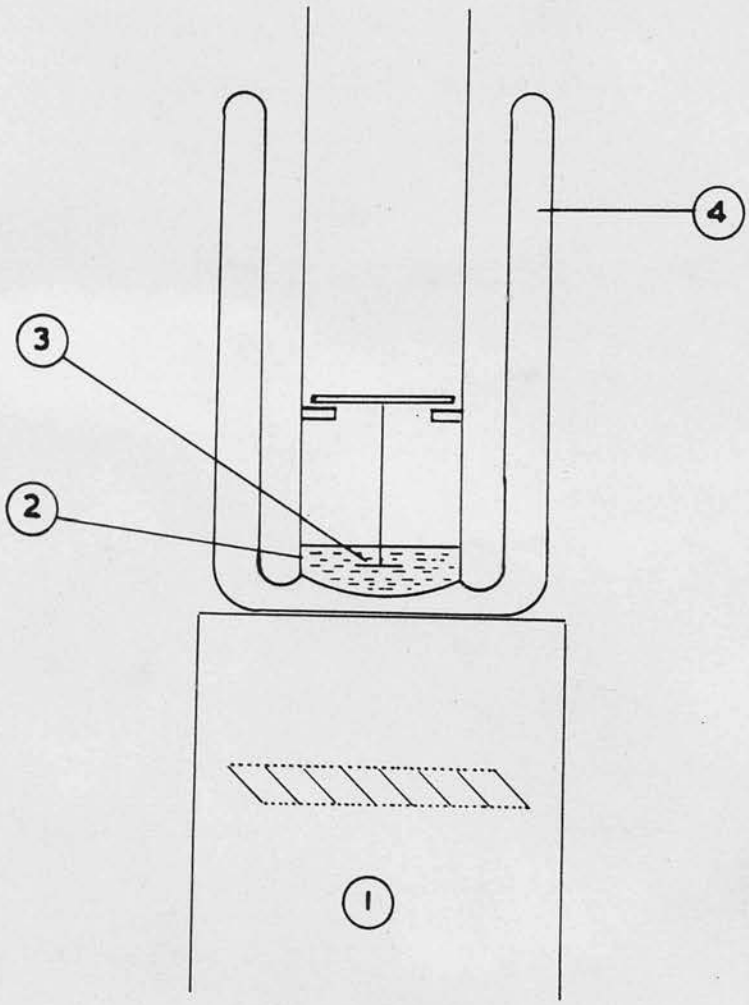

4
3
2
1

FIGURE 8.

Apparatus for measuring the light emission from ice and frozen solutions of sodium salicylate irradiated by alpha-particles.

1. Photomultiplier.
2. Ice.
3. Po alpha-particle source.
4. Vacuum jacket.

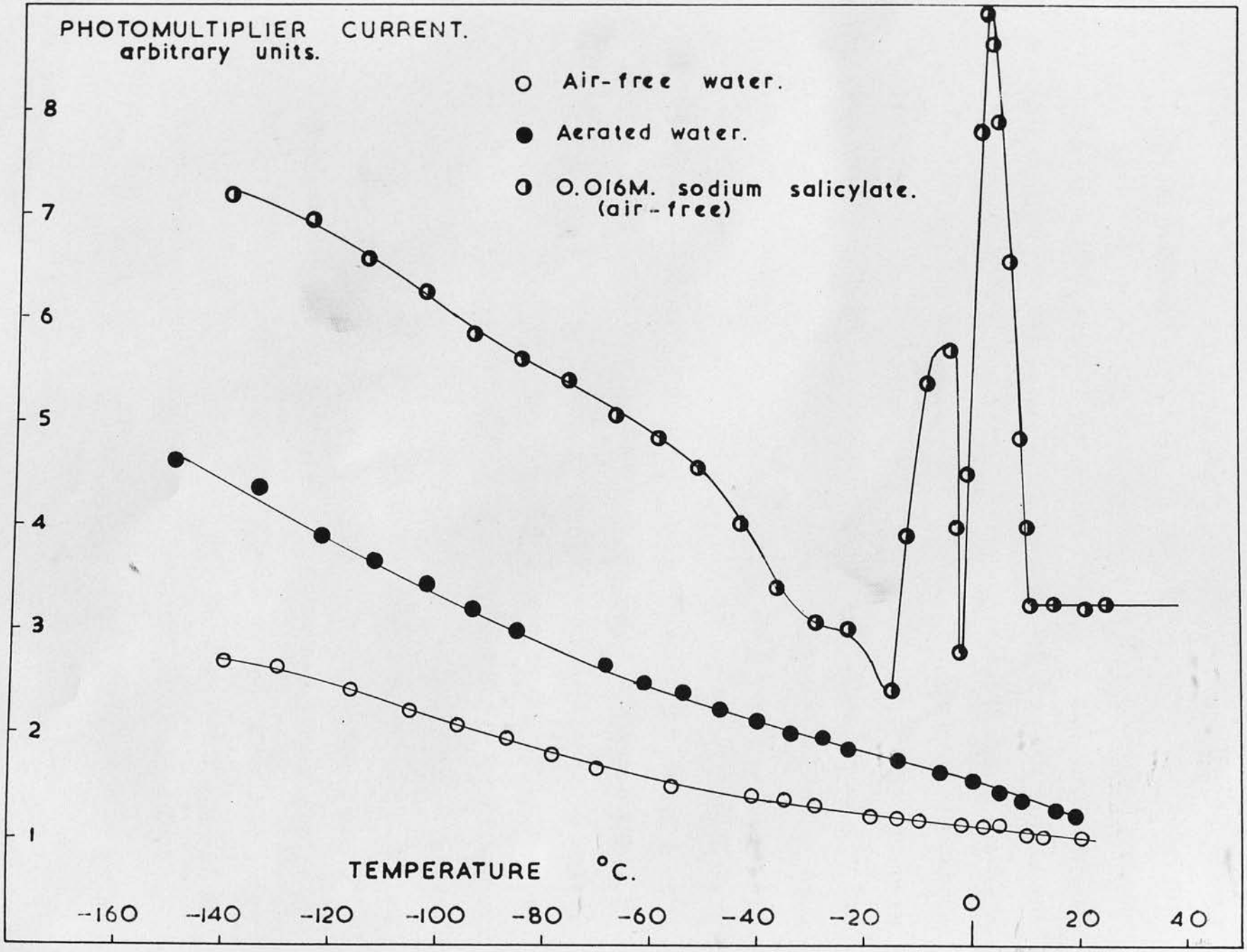

PHOTOMULTIPLIER CURRENT.
arbitrary units.
Air-free water.
Aerated water.
O.016M. sodium salicylate.
(air-free)
8
7
6
5
4
3
2
1
TEMPERATURE °C.
-160
-140
-120
-100
-80
-60
-40
-20
0
20
40

FIGURE 9.

Light emission from ice and frozen sodium salicylate solutions irradiated with alpha-particles as the temperature was slowly raised.

amounted to considerably less than one photon per alpha-particle and was of the same order of magnitude as the light emitted from the source. Frozen air-free solutions of 10^{-2}M sodium salicylate showed relatively large fluctuations in the light emission as the temperature rose, the largest occurring at -8°C and 0°C. Aerated solutions showed additional peaks at -32°C and -17°C. The light emission remained constant after the ice had melted. The level to which the light emission fell between peaks indicated that there was no significant ultraviolet emission at temperatures above -40°C. Below this temperature the light emission was higher but could have been accounted for by the reduced quenching at low temperatures.

The investigation was not taken further than these qualitative results as although they were interesting in connection with the storing of energy by ice, it did not appear that any further information would be gained on the part played by light emission in the chemical action of alpha-particles.

2.7. Other evidence on light emission.

In a recent paper Richards[38] found more evidence for the emission of light from water. The experimental arrangement was similar to that described in section 2.4, but the experiment was carried out in air. It was stated that scintillations from water decayed with a mean lifetime of 10^{-7} seconds and those from gases with a mean lifetime of 10^{-5} seconds. The background of light emission due to excitation of the air between the

source and the water surface was greatly reduced by counting the scintillations with the integration and differentiation time constants of the amplifier set at 0.2 microseconds.

There are many aspects of this work which require further explanation. The method described for separating the luminescence of water and air would be valid but for the following facts.

1. The light emission from most gases is very weak, amounting to about 10 photons per alpha-particle for air, and less for carbon dioxide. The number of electrons emitted from the photocathode of a photomultiplier viewing such light would be expected to be less than the number of alpha-particles, and in the work described in later chapters of this thesis, this has been found to be so, even with a high collection geometry for the light. The strength of the source used by Richards, the degree of collimation, and the counting rates which were found, indicated that less than one photoelectron was emitted from the photocathode for each alpha-particle incident on the surface of the water, and this was mentioned in the paper. Thus the light emission from neither gases nor water would produce pulses of electrons which could be separated by adjustment of the time constants of the amplifier, but only a succession of isolated pulses due to the amplification of single electrons, such as would be obtained from a steady illumination. The graphs of counting rate against amplifier time constants which were given by Richards for the emission from gases, were just what would be expected from single

photoelectron emission, counted at a fixed discriminator bias, and do not indicate a mean life-time for emission of 10^{-5} seconds.

2. The mean life-time for emission of light in allowed transitions is of the order of 10^{-8} seconds. Light emission of longer mean life-time is however well known. If quenching of the light is large, the mean life-time is reduced to the life-time before a quenching collision occurs [39]. The nitrogen light from air is quenched by oxygen, and at atmospheric pressure an excited nitrogen molecule would have a mean life-time of 10^{-9} seconds before a collision with an oxygen molecule occurred. Carbon dioxide is self-quenching and the mean life-time before a quenching collision occurred would be even less. With these gases, which are efficient quenchers, nearly every kinetic collision results in quenching. Therefore in these gases at least, the mean life-time for emission of light would be nearer 10^{-9} seconds than 10^{-5} seconds.

3. Richards found that carbon dioxide, water vapour, and alcohol vapour absorbed the light emitted from the water surface, but it was not absorbed by air. It is difficult to reconcile these results with the absorption coefficients of these gases in the ultraviolet [40], [41], [42]. Richards' estimate of the wavelength as 1900A must be wrong as carbon dioxide is transparent in this region. Oxygen is transparent to the Lyman alpha line where water vapour and probably alcohol absorb strongly, but carbon dioxide is relatively transparent in this region.

The author does not think that the evidence presented by Richards is sufficiently convincing to alter the conclusions drawn from his own work which are as follows:

1. Light emission from the first excited level of water accounts for less than 3% of the chemical action of alpha-particles.

2. Light emission in the region of 1200A accounts for less than 12% of the chemical action.

3. Transfer of energy from excited water molecules to a solute by means other than light emission has a probability of less than 10^{-3}.

It should be emphasized that no evidence for light emission from water has been found and that the figures for the detection limits have been estimated by assuming the most efficient excitation conditions and the least favorable regions for detection.

CHAPTER III.

DISCUSSION

From the results presented in Chapter II it can be concluded that ionizing radiations do not excite levels in water from which transfer of energy is probable, by light emission or any other means. The most probable result of excitation of water is therefore dissociation into radical pairs. This is in accordance with the view that dissociative recombination of an ion and an electron is more probable than radiative recombination[15], and that excitation of higher levels of polyatomic molecules is internally converted to the lowest level of the same multiplicity[20]. This lowest level must be repulsive because the first absorption region in water vapour is a continuum[19].

The peak of the first absorption region occurs at 1650A, corresponding to an excitation energy of 7.5 e.v. The strength of the H - OH bond is 5.15 e.v.[43]. Dissociation of a water molecule raised to the first excited level would produce a radical pair sharing an energy of 2.35 e.v. The "cage" effect of the water molecules would then determine whether those free radicals were able to separate to react with solutes or recombined. Noyes[44] measured the photochemical yield of iodine atoms formed by photolysis of iodine. When the wavelength of the incident light was 4360A, the atoms shared an energy of 1.3 e.v. The quantum yield in hexane was 59% of that in the

gas phase, when no cage effect would occur. The H and OH radicals formed by dissociation of water are lighter than iodine atoms, more energy is available as kinetic energy of the fragments, and because of the difference in mass most of it would be concentrated on the H atom. Thus the percentage of free radicals which escape from the solvent cage would be considerably greater than that found for iodine atoms. The H atoms would move further from the site of the excitation than the OH radicals, but not as far as was proposed in Lea's theory, in which the mobility of the slow electron was expected to lead to a separation of over 100A[45]. Ewell and Eyring[46] found the energy required to move a water molecule past another was 0.22 e.v. at 0°C. The expected separation of a radical pair sharing 2.35 e.v. of kinetic energy would be about 20 to 30A, and would be effective in any chemical action with dissolved solutes.

It can be seen that the processes in water of ionization, recombination of ions and electrons, and excitations would all be expected to produce radical pairs, but an analysis of the expected distribution of the radicals formed by these processes indicates that those formed from excited water molecules may be of greater chemical significance than those formed from ions. Observations on gases and vapours irradiated by ionizing particles showed that ionizations occur in small clusters of an average size of about three ion pairs. It is fairly well established that this clustering of ions is present in liquid water[47]. A reasonable picture of the track of a fast electron

in water would be as follows. The primary particle produces random ionizations and excitations in its path. The slow secondary electron ejected at the ionization, produces one or two more ions close to the parent ion and probably one or more excited water molecules would be ~~excited~~ produced as well. If both ions and excited molecules produce radical pairs, the net result would be a cluster of radical pairs at the site of the primary ionizations, and isolated radical pairs at random intervals along the track of the fast electron. The diameter of the cluster would be about 30A, and for a 0.5 Mev. electron, the clusters would be separated from each other by an average distance of about 5,000A (48). Intercombination of the radicals in a cluster would be probable, but reaction between clusters or between isolated radical pairs formed from primary excitations would not be likely. It seems a reasonable hypothesis that the radicals in the clusters give rise to the molecular products and the isolated radical pairs react with solutes. Some free radicals will, of course, escape from the clusters and contribute to the free radical yield. As the ionization density of the primary particle increases, so clusters will be able to react with each other, and with the radicals formed from excited water molecules between the clusters. According to Allen (49), this interaction becomes important when the energy of the primary electron has fallen to 1.4 kev. and clusters are formed about 60A apart, a distance of the same order as the estimated size of a cluster. With alpha-particle irradiation the distinction between clusters

and isolated radical pairs disappears.

It is significant that the highest value for the radical yield (G_R) of 13.4 per 100 e.v. has been found by Dainton and Rowbottom[50] using solutions of H_2O_2 from 1M to 22M. In such solutions, solute molecules are at a concentration of the same order as the estimated local concentration of free radicals in a cluster. So reaction between solute molecules and free radicals would effectively compete with free radical intercombination.

There is as yet so little quantitative evidence on such quantities as the relative cross-sections for excitation and ionization in water that it would be unwise to develop the theory further, and the above discussion is not intended to substitute a mechanism based on excitation processes for one involving ions, but merely to indicate that radicals formed from excited water molecules may play a more significant part in the chemical action of ionizing radiations than has been recognized.

PART II

LUMINESCENCE OF GASES EXCITED BY ALPHA-PARTICLE IRRADIATION

CHAPTER IV.

REACTIONS OF EXCITED SPECIES IN GASES.

In recent years research in radiation chemistry has been directed on the condensed states of matter and gases have been comparatively neglected. As work on the radiation chemistry of gases and vapours was being initiated in the laboratory in which the author was working, and research on the luminescence of organic solutions and polymers was already in progress[51], a study of the luminescence of gases formed a useful related subject for investigation, particularly as Grün and Schopper[52] had drawn attention to the limited amount of work which had been done on the luminescence of gases excited by alpha-particle irradiation. The work undertaken was primarily a physical study of the luminescence of gases and the measurement of quenching and sensitised fluorescence reactions. No chemical analyses of the products of reactions of the excited species were made, and in view of the low light intensities which were involved, spectroscopic analysis of the light emission was not possible.

4.1. Mechanism of Excitation and Ionization.

Excitation and ionization in atoms and molecules are produced by interactions of the bound electrons with incident photons or particles which raise the bound electron to a higher quantum level. The particles producing excitation

may consist of electrons, ions or, in collisions of the second kind, excited and ionized atoms and molecules. Photochemistry is generally confined to the region where the energy of the exciting electromagnetic radiation is a few electron volts, and usually less than the ionization potential of most atoms and molecules. Excitation is confined to discrete energy levels and determined by spectroscopic selection rules. With higher energy radiations and particles both ionization and excitation occur, and depending on the system about half of the absorbed energy appears as ionization. Excitation by high energy radiations is not as selective as photoexcitation and the variety of excited species and the interpretation of the results of their interaction are more complicated.

In the present work, polonium alpha-particles have been used to produce excitation and ionization, but as a large part of energy goes into production of secondary electrons, the greater amount of theoretical work on collisions between electrons and atoms is applicable. In gases, as in the previous investigation of the radiation chemistry of water, the process of primary luminescence producing photoexcitation is possible.

Theoretical studies of the cross-sections of elastic and inelastic collisions between electrons and atoms are well established and in good agreement with experimental results. The Born approximation[53] predicts the magnitude of the reaction cross-sections with considerable accuracy when the velocity of the incident particle is much greater than that

of the bound electron which it excites, but at lower energies of the incident particle the agreement with experiment is poor. The formula is derived from a wave-mechanical analysis of the collision, and is applicable to both elastic and inelastic collisions by electrons and alpha-particles.

Massey and Burhop[54] have summarized the general properties of inelastic collisions which are supported by experiment.

(a) At electron energies much greater than the threshold, all inelastic cross-sections fall off with electron energy E. For optically allowed transitions the rate of fall is as E^{-1} log E. For transitions which are optically forbidden but do not involve a change of multiplicity the decrease is as E^{-1}. It is much more rapid if a change of multiplicity is involved.

The process of ionization behaves as an optically allowed transition.

(b) Cross-sections for transitions involving a change of multiplicity are only large near the threshold.

(c) At electron energies for which electron exchange is negligible the cross-sections for optically allowed transitions are larger than for any others.

(d) The strongest intercombination transitions are those in which there is no change in the azimuthal quantum number. Electron exchange reactions are important near the threshold energy for the process.

Excitation by alpha-particles can similarly be estimated from the Born approximation[55] when the energy is sufficiently

high. Excitation is, however, dependent on velocity rather than energy, and because of the greater mass of an alpha-particle the energy of maximum excitation cross-section is much greater than for an electron. For singlet excitation by an electron the maximum cross-section is observed at an incident energy of about 100 e.v., but for an alpha-particle at about 750 kev. The cross-sections for excitation are of the same order for alpha-particles and for electrons.

While excitation by an electron cannot occur unless $\frac{V^2}{U^2} > 1$, where V is the velocity of the incident particle and U is the velocity of the bound electron which is excited, excitation by alpha-particles and positive ions in general can occur when $V^2/U^2 < 1$. It is only in the high velocity region that the behaviour of electrons and alpha-particles is similar.

Excitation and ionization of molecules is governed by the Franck-Condon[56] principle, which states that in an electronic transition the nuclear separation and velocity of relative motion alter to a negligible extent. Because of this, the products of an electronic transition can be estimated from the shape and relative positions of the potential energy curves of the initial and final states. Transitions are represented on diagrams of potential energy against nuclear separation by vertical lines. Excitation of a diatomic or a polyatomic gas may result in excited or ionized molecules, which may be stable or dissociate. Dissociation may lead to unexcited atoms or radicals, or the

products may be excited or ionized. It can be seen that when a molecule has a large number of excited levels and the energy of the incident radiation is high, a large variety of products of irradiation is possible.

4.2. Radiation Chemistry of Gases.

In a field of study such as radiation chemistry where the large number of excited reactants which are possible makes the elucidation of a reaction mechanism difficult, it was natural for the early workers in the field to turn their attention to the study of gas phase reactions in the search of simplicity. In spite of much skilful work using frightening sources of alpha-particles a great deal yet remains to be discovered in this subject. The earlier work has been reviewed by Lind[57].

Some simplification of gaseous systems can be made by applying an electric field across the reaction vessel[58, 59]. By variation of the field the contribution made by ions to the reaction may be measured although the interpretation of the results may be subject to ambiguity because of surface reactions at the electrodes. Perhaps surprisingly, in view of the attention which has been directed on ionization effects, a large number of reactions have been found to be unaffected by the application of a field, which indicated that neither ions nor recombination of ions and electrons are responsible in most cases for the initiation of the reactions. The electric shutter technique has been used in order to separate the effect of free electrons

from that of negative ions and produce a further simplification in the reaction mechanisms.[60]

Initiation reactions for all gas-phase radiation chemical processes have been classified by Essex[61] under the following headings.

1. Recombination of ions

$$AB^+ + e \longrightarrow A + B$$

$$AB^+ + AB^- \longrightarrow 2A + 2B$$

2. The molecule splits with attachment of an electron.

$$AB + e^- \longrightarrow A + B^-$$

The probable mechanism is the following one.

$$AB + e^- \rightarrow AB^- \rightarrow A + B^-$$

3. The molecule splits without attachment of an electron.

$$AB + e^- \longrightarrow A + B + e^-$$

The process is probably one of excitation followed by dissociation.

$$AB + e^- \rightarrow AB^* + e^- \longrightarrow A + B + e^-$$

4. The molecule splits on ionization.

$$AB + e^- \longrightarrow A^+ + B^-$$

or $$AB + e^- \longrightarrow A^+ + B + 2e^-$$

The initiation reactions may be complicated by cluster formation[62], and the secondary processes by chain reactions[63] and free radical reactions[64].

4.3. Luminescence of Gases.

4.3.1. Photoluminescence.

The method by which a species is excited has no effect on the subsequent de-excitation processes, although mutual reactions between excited species may depend on the density of excitation. For this reason, the results of studies of photoluminescent processes may be extended to cover luminescence produced by other means. As in the chemical work which has already been briefly surveyed, the complexity of the study is increased if the excitation is carried out with high energy radiation.

The substances which have been most intensely studied are those which are excited to luminescence by the more easily accessible regions of the spectrum, the visible and near ultra-violet. These substances include the vapours of a number of metals, particularly those of the first two groups of the periodic classification, and some polyatomic gases, and vapours of organic liquids and solids.

Luminescence is only one of the ways in which an excited species may lose its energy. The changes in luminescence which are produced by changes in the pressure and constituents of gas mixtures may give information on the luminescent process and on the competing de-excitation processes. These include processes of internal de-excitation in the molecule itself and external collision reactions with

the walls of the containing vessel or other molecules present. If luminescence does occur, the emitted light may be absorbed, or modified in its path through the gas.

The reactions of electronically excited species may be summarized as follows[65].

1. Unimolecular reactions.
   - (a) Luminescence.
   - (b) Spontaneous dissociation.
   - (c) Spontaneous isomerization.
   - (d) Internal degradation of energy.
2. Bimolecular reactions.
   - (a) Physical quenching.
   - (b) Transfer of electronic energy to a colliding molecule. This produces quenching of the original excited molecule but may excite emission characteristic of the colliding molecule, or sensitized luminescence[66].
   - (c) Quenching with dissociation of the quencher.
   - (d) Quenching with dissociation of the excited molecule.
   - (e) Quenching with isomerization of the quencher.
   - (f) Association between the excited and colliding molecules.

The reactions which produce quenching of the luminescence in a collision process cannot be differentiated in a physical study of the light emission.

The more important aspects of luminescence of gases and vapours, and the energy transfer processes resulting in quenching and sensitized fluorescence are given below.

1. The half-value period for emission of luminescence in an allowed transition is of the order of 10^{-8} to 10^{-7} seconds. If the luminescence is emitted from a resonance level and no intermediate levels exist between it and the ground state, the emission may be "imprisoned", or absorbed and emitted in a cascade process the length of which depends on the pressure of the gas, and the size of the vessel[67, 68]. This process increases the effective emission time and so also the probability of quenching by collision with an impurity. The quenching of resonance luminescence has been studied quantitatively for sodium[69], cadmium[70], mercury[71], but is of course a general phenomenon.

2. Energy transfer from an excited molecule may occur in a collision with an unexcited molecule of the same kind, or with a molecule of another kind in a gas mixture. The effectiveness of energy transfer in a two-body collision depends on the following conditions.

(a) The closer the energy resonance, the greater the cross-section for the transfer process between the two levels. This factor of resonance is of great importance and for an energy defect in the transfer of 50 mev, the cross-section may be fifty times the gas kinetic cross-section, and even larger for closer resonance[72].

Such resonance would also occur in a mechanism involving emission of luminescence and absorption of the light by a "solute" molecule. In such a process the half-value period

for emission would be independent of the pressure of the quencher, whereas if the transfer occured by a collision process the half-value period would be decreased and the emission line broadened. Otherwise the dependence of light emission on pressure, and concentration of the quencher would be very similar. There is a considerable amount of evidence for the collisional transfer mechanism in gases[73], but this does not exclude the possibility of a photon transfer where transfer by collision is small or not possible.

It is important not to carry the concept of resonance too far in collision processes. It does not apply to a three-body collision nor to exchange reactions, and it applies principally to the transfer of electronic energy[74].

(b) The quenching cross-section increases as the number of internal degrees of freedom of the quenching molecule is increased[75].

(c) The probability of transfer of excitation energy is proportional to the number of collisions with quenching molecules and so is greater for long-lived species, other factors being equal.

(d) There is some evidence that in a collision the total spin is conserved, but this factor seems to be less important in determining the cross-section of a process than the factors given in 2(a) and 2(b)[76].

4.3.2. Luminescence excited by alpha-particles.

The excitation of luminescence by alpha-particle irradiation has not lead to any fundamentally new knowledge on luminescence and energy transfer processes. It is a convenient method for exciting species whose absorption bands lie in the far ultra-violet. A large amount of energy is dissipated in a short track and the sources are not affected by high pressures of oxygen and other gases in which an electron source could not operate. Because of the high excitation density in an alpha-particle track, there is the possibility of mutual reactions between excited or ionized species.

There has been comparatively little attention given to the study of luminescence excited by alpha-particles in gases, and there is very little agreement between the results of different authors. This is partly due to the very weak luminescence which can be excited by easily available alpha-particle sources, but, as in so much work on gases, much more due to the very important effects of small amounts of impurities, and the need for the most careful experimental techniques.

Early workers[77] used photographic means of detection, and because of the weak light emission, long exposures and high pressures of gas were required. The introduction in recent years, of photomultipliers as very sensitive light detectors, has enabled these studies to be extended. Even

so, until the recent paper of Grün and Schopper[78], this work has been largely qualitative.

The two most important results on which there is general agreement are as follows.

1. The light intensity from an alpha-particle track varies in accordance with the intensity of ionization; it follows the normal Bragg curve for ionization and is more intense near the end of the alpha-particle track[79].

2. The application of an electric field across the excited gas has no effect on the light intensity, showing that the light emission does not involve ions, either directly or in a recombination process. It has been found that weak first negative bands due to excited N_2^+ ions occur in the light from nitrogen excited by intense beams of fast electrons and protons[80], but the intensity was presumably too small to be detected in the work with alpha-particle excitation.

The most recent studies in this field by Ward[79], and by Grün and Schopper[78], which have paralleled the present investigation have made useful contributions to an analysis of the secondary processes which occur in luminescence at high pressures, but their measurements will be discussed in the appropriate sections of Chapter VII.

CHAPTER V.

THEORETICAL.

It has been shown that irradiation of gases by alpha-particles produces excitation, and that the energy of excitation may be lost by a number of processes such as luminescence, internal quenching, and reactions with the walls of the containing vessel or other unexcited species in the gas phase. In the analysis presented below it has been assumed that the luminescence of the irradiated gas is emitted from a constant length of alpha-particle track which is determined by the geometry of the vessel. The measurements were made at pressures at which the vessel was completely traversed by the alpha-particles. It has also been assumed that there was no effect of excitation density along the track. This qualification was realised experimentally by using only the initial high energy part of the track where the linear excitation density was almost constant. With these assumptions the number of atoms or molecules excited by the passage of an alpha-particle would be proportional to the pressure.

Of the large number of secondary reactions which could occur, only those producing simple collisional quenching, and sensitized fluorescence by a collisional transfer of energy, have been analysed. More complicated reaction schemes can usually be recognized as one of, or a combination

of, these two simple reactions.

5.1. Quenching.

1.	A	$\xrightarrow{\alpha}$	A^*	Excitation.
2.	A^*	$\longrightarrow$	$A + h\nu$	Luminescence.
3.	$A^* + Q$	$\longrightarrow$	$A + Q$	Quenching.

Using steady-state kinetics, or from the probabilities of each reaction it can be shown that,

$$[A^*] = \frac{k_1 [A]}{k_2 + k_3 [Q]}$$

or Light emission $L = k_2 [A^*]$

$$= \frac{k_1 k_2 [A]}{k_2 + k_3 [Q]}$$

where k_1, k_2, and k_3 are the reaction rate constants for the three processes.

In the experiments which are described later, the luminescence of mixtures of known composition was measured over a range of pressures.

The total pressure $p = [A] + [Q]$

$$[Q] = a\,p$$

where a is a known fraction.

$$\therefore [A] = p(1 - a)$$

$$\therefore L = \frac{k_1 k_2 p(1 - a)}{k_2 + k_3 a p} \quad \ldots\ldots\ldots (1)$$

The graphs of light emission against pressure derived from such an equation are shown in Figure 10 for different values of a. If the quenching is sufficiently great, the graph at high pressures becomes horizontal. The constants in the equation may be evaluated from the "saturation" light emission, and the value of the pressure when the light emission is half the "saturation" value.

$$L_{max} = \frac{k_1 k_2 (1 - a)}{k_3 a}$$

At $L = \frac{1}{2} L_{max}$

$$k_2 = k_3 a p.$$

A better method is to plot P/L against p.

$$P/L = \frac{1}{k_1(1 - a)} + \frac{k_3 a p}{k_1 k_2 (1-a)} \quad \ldots\ldots \quad (2)$$

In this way, for different values of a, a series of straight lines is obtained with intercepts on the P/L axis of $\frac{1}{k_1 (1-a)}$ and slopes of $\frac{k_3 a}{k_1 k_2 (1-a)}$.

It is obvious that only the ratio of k_3/k_2 can be found, that is the ratio of the probabilities of de-excitation by collision and by luminescence. If the half-life period for the luminescence can be measured independently, k_3 can be calculated.

The gas-kinetic collision rate constant (k_3') can be calculated from published data and the ratio of k_3/k_3' is a

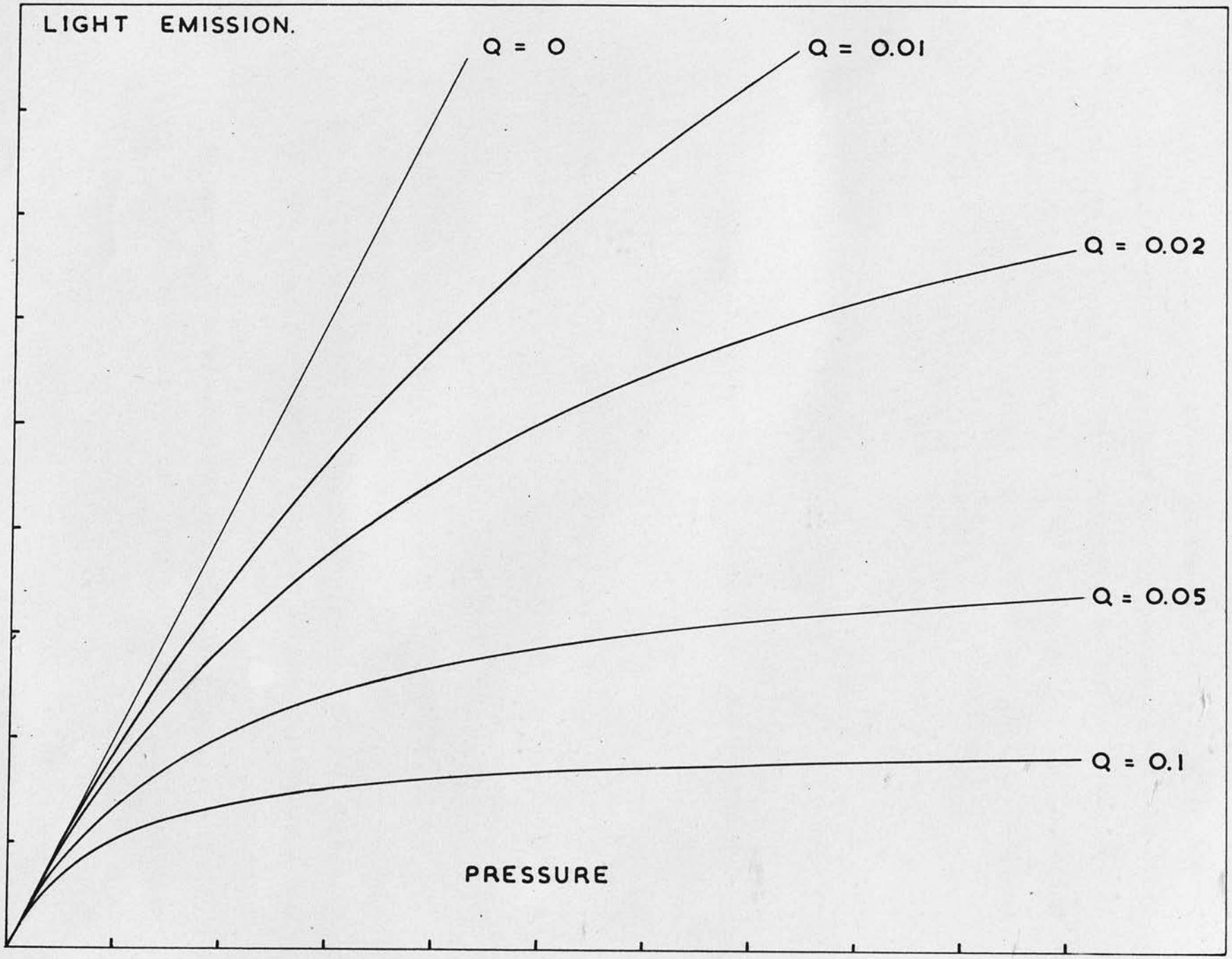

LIGHT EMISSION.
Q = 0
Q = 0.01
Q = 0.02
Q = 0.05
Q = 0.1
PRESSURE

FIGURE 10.

Quenching.

$$\text{Light Emission} = \frac{k_1 k_2 [A]}{k_2 + k_3 [Q]}$$

Theoretical quenching curves where $[Q]$ is the indicated fraction of the total pressure $[A] + [Q]$.

measure of the ratio of the quenching cross-section to the gas-kinetic cross-section σ_a^2/σ_k^2.

Quenching may occur in a pure gas as well as in a gas mixture, more usually in a molecular gas but even in an atomic gas if the reaction of an excited atom and an unexcited one can form a molecule.

1. $AB \xrightarrow{\alpha} AB^*$
2. $AB^* \longrightarrow AB + h\upsilon$
3. $AB^* + AB \longrightarrow 2AB$.

$$\text{Light emission} = \frac{k_1 k_2 P}{k_2 + k_3 P}$$

5.2. Sensitized Fluorescence.

1. $A \xrightarrow{\alpha} A^*$ Excitation
2. $A^* \longrightarrow A$ Internal quenching or luminescence which is not detected.
3. $A^* + S \longrightarrow A + S^*$ Transfer of excitation.
4. $S^* \longrightarrow S + h\upsilon$ Luminescence .

From steady state kinetics

$$\text{Light emission} = k_4 [S^*] = k_3 [A^*][S]$$

$$\text{But } [A^*] = \frac{k_1 [A]}{k_2 + k_3 [S]}$$

$$\therefore \text{Light emission} = \frac{k_1 k_3 [A][S]}{k_2 + k_3 [S]}$$

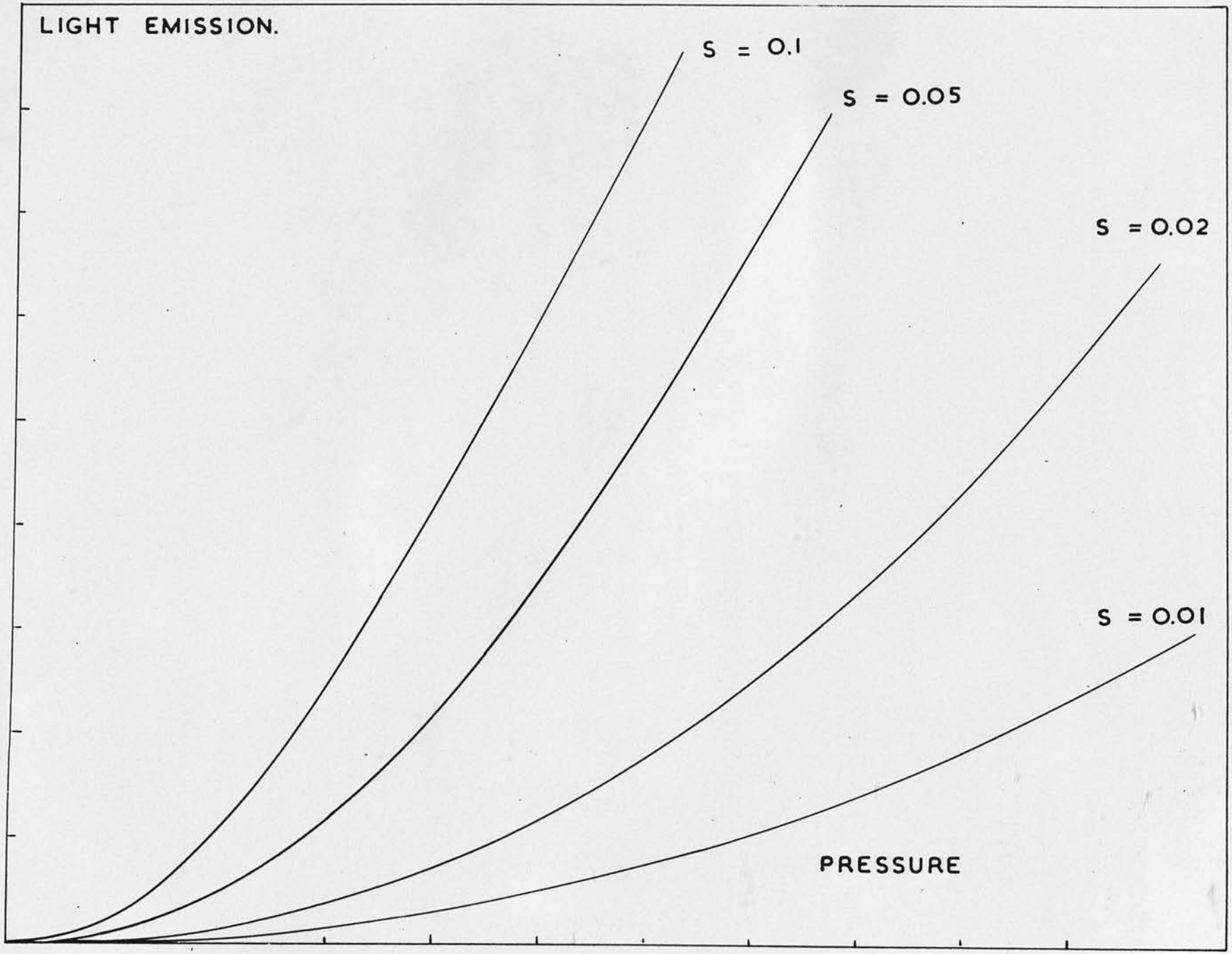

LIGHT EMISSION.
S = 0.1
S = 0.05
S = 0.02
S = 0.01
PRESSURE

FIGURE 11.

Sensitized Fluorescence.

$$\text{Light Emission} = \frac{k_1 k_3 [A] [S]}{k_2 + k_3 [S]}$$

Theoretical curves for sensitized fluorescence where $[S]$ is the indicated fraction of the total pressure, $[A] + [S]$.

Again $[S] = a\,p.\quad [A] + [S] = p.$

$$\therefore \quad Ls = \frac{k_1 k_3 p^2 a(1 - a)}{k_2 + k_3 a p}$$

As $\underline{a}$ is usually small, $\underline{a}^2$ is negligible

$$\therefore \quad Ls = \frac{k_1 k_3 a p^2}{k_2 + k_3 a p}$$

The curves for this equation are shown in Figure 11 for different values of $\underline{a}$. It can be seen that at high pressures the light emission becomes proportional to the pressure, i.e. the transfer of energy from A to S is virtually complete.

In this analysis the contribution to the light emission of directly excited S atoms has been neglected.

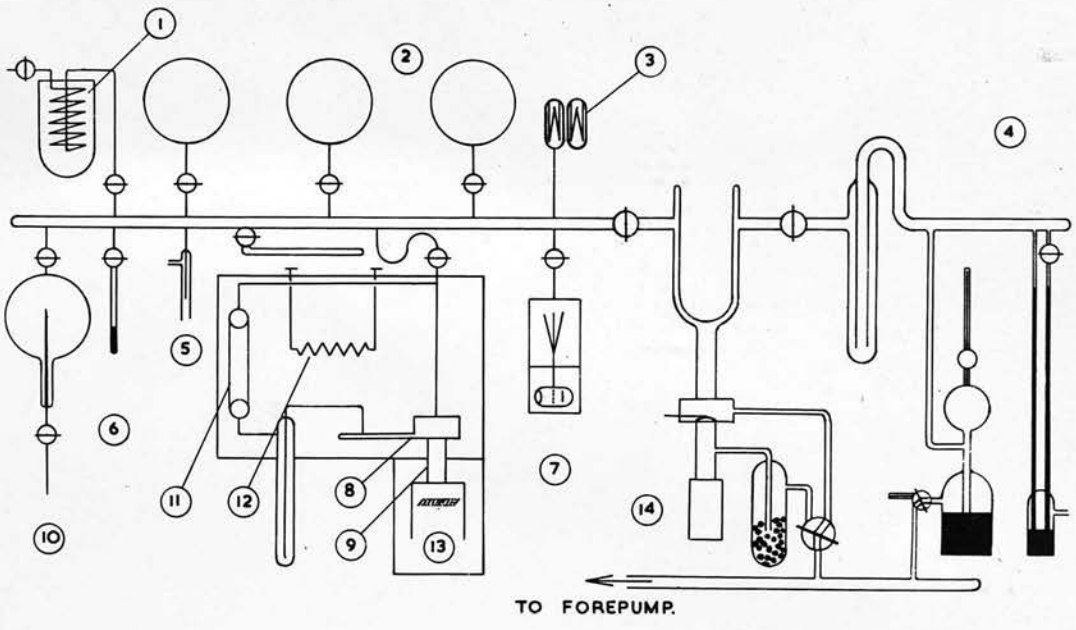
CHAPTER VI.

EXPERIMENTAL.

6.1. Vacuum line.

In preliminary experiments, reported in Chapter VII, it was found that the presence of mercury in the system interfered with the light emission measurements from most of the gases which were used. Accordingly a vacuum line was constructed which was free from mercury. Because of the great difficulty in removing mercury once the line had become contaminated it was not thought to be a sufficient precaution to isolate the mercury diffusion pump and mercury manometers by means of a liquid air trap. The line was constructed of Pyrex glass as shown in Figure 12. The mercury manometers were kept isolated from the rest of the system by a stop-cock which was opened only during the occasional pressure calibration, and only after the trap had been immersed in liquid air for some time. Two traps were actually used although only one is shown in the diagram. An amalgamated copper trap was placed between the forepump manifold and the reservoir of the Macleod gauge.

An Edwards oil-diffusion pump with an ice-cooled trap produced a vacuum of 10^{-6} mms. The speed of the pump was sufficiently high in spite of the presence of the trap, which was used in order to prevent any possible contamination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11
12
13
14
TO FOREPUMP.

FIGURE 12.

The vacuum line used in the experiments on luminescence of gases.

1. Carbon dioxide still.
2. Storage flasks.
3. Pirani gauge.
4. Mercury manometers for calibration.
5. Palladium thimble.
6. Activated charcoal.
7. Alphatron gauge.
8. Irradiation cell.
9. Perspex light guide.
10. Storage flask with capilliary leak from purification line.
11. Circulating pump.
12. Heater.
13. Photomultiplier.
14. Oil diffusion pump and calcium chloride trap.

of the line with oil which is highly fluorescent.

An "Alphatron" gauge (Section 6.4) and a Pirani gauge were used for pressure measurements.

Mercury contamination of the line never caused any interference with the light emission measurements.

The exposed glasswork was outgassed by strongly heating it with a torch flame while the line was under high vacuum. The circulating pump and irradiation cell in the light-tight box were heated to about 100°C. by means of the electric heater (12). The apparatus was connected to the high vacuum pump at all times other than when an experiment was in progress. No contamination of gases in the line was apparent in a time much longer than that required for a complete experiment.

Where it was not convenient to introduce small quantities of freshly prepared gases for immediate use, they were stored in one-litre bulbs (2). These were strongly heated and evacuated for several days before filling. The gases stored in them suffered some contamination in time, but as the stored gases were used in small proportions in a mixture with a freshly prepared gas, the impurities in the stored gas constituted a negligible fraction of the mixture, and light emission measurements were quite reproducible.

6.2. Light detection.

As in the experiments on luminescence of water, an E.M.I. 5311 photomultiplier was used for the detection of light

emission. The photocathode was maintained at-1400 volts and the collecting electrode was connected to earth through a galvanometer. The photomultiplier was housed in a light-tight box and connected to the irradiation cell by a light-guide of one-inch polished Perspex rod. The irradiation cell was screened from the high voltage applied to the photocathode by an earthed aluminium shield. The high voltage supply connections to the photocathode were coated with paraffin wax in order to reduce corona discharge. As the light emission from the polonium source gave a much larger current than the noise emission of the photomultiplier no other precautions to keep the noise value low were taken.

The photomultiplier current produced by the light emission from the polonium source was biased off by the current from a lead accumulator through a partially variable high resistance.

6.3. Irradiation cell.

The irradiation cell is shown in Figure 13(c) and consisted of a flat glass cylinder painted black on the outside and aluminized on the inside apart from a one-inch window in the lower end through which light was transmitted to the light-guide. The window projected into the cell a little way so that direct impingement of alpha-particles on the glass was not possible. The aluminium deposited on the inner surface of the cell was necessary in order to prevent light emission produced in the glass by the alpha-particle irradiation from

being detected, and in order to increase the detection efficiency for the light from the gases in the cell. The application of the aluminium surface was difficult, more so than the chemical deposition of silver, but was worth the effect because of the greater resistance of an aluminized surface to corrosion which caused changes in the detection efficiency for light. Aluminium is also a better reflector than silver for ultra-violet light.[81]

The aluminium was evaporated from a tungsten hairpin-shaped filament which was introduced through the central glass tube into the cell. The leads to the filament passed through a water-cooled wax seal on a ground-glass cone which fitted into a socket attached to the irradiation cell. The aluminium was fused on to the filament in a separate evacuated chamber, and then introduced into the irradiation cell which had been chemically cleaned. The cell was further cleaned by passing a discharge through it from the filament for some time before the evaporation of the aluminium was carried out. After the deposition of the aluminium, the window was made by removing a one-inch circle of the film with a pad soaked in caustic soda.

When measurements of the ultra-violet emission were to be made, the window was coated on the inside with Apiezon "L" grease[23] by means of a pad of cotton wool impregnated with grease. This was introduced into the irradiation cell through a tube of paper, in order that other parts of the cell should not be contaminated with the grease.

An estimate had to be made of the comparative detection efficiencies of such an apparatus for visible and ultra-violet light. All light of a wavelength greater than about 3300A which was incident on the window should theoretically be refracted into the light guide and transmitted to the photomultiplier where the quantum efficiency would depend on its wavelength. The same proportion of any ultra-violet emission which occurs in the irradiation cell should be incident on the window as the reflection coefficient for aluminium is almost independent of the wavelength. If the ultra-violet light had a wavelength less than 3300A it would excite luminescence of the Apiezon grease which has a fluorescence efficiency of 20% (Section 2.2.1). This luminescent light would be emitted in all directions and there would be little refraction in its path to the light guide. So the detection efficiency for the fluorescent light would be determined by the minimum angle for internal reflection in the light guide. Some of the fluorescent light would be reflected from the aluminium surface back to and through the window.

If the refractive index of Perspex is taken as 1.5^{82}, the fraction of the fluorescent light excited in the grease which would be transmitted by the light guide would be $\frac{1}{6}$. The fluorescence efficiency of the grease is 20% so only $\frac{1}{30}$ of the ultra-violet light incident on the grease would be directly detected. If all the fluorescence from the grease which is emitted into the irradiation cell were reflected

back to the window, the detection efficiency would be increased to $\frac{4}{30}$ of the incident light. From qualitative experiments with sources of visible light, with and without an aluminium reflector it would seem that $\frac{2}{30}$ would be a reasonable estimate for the fraction of the incident ultraviolet light which would be detected.

The alpha-particle source consisted of about 8 millicuries of polonium deposited on platinum. It was attached to a piece of soft iron so that it could be withdrawn from the irradiation cell during outgassing and so reduce the contamination of the cell due to aggregate recoil of the polonium. A considerable amount of contamination of the cell and the circulation system did occur, fairly obviously due to polonium carried by the circulating gas. This did not affect the light emission measurements, but constituted a health hazard when parts of the glass system had to be changed.

The irradiation cell, trap, and circulating pump were constructed as an all-glass unit, the only grease exposed to the system being on the inlet stop-cock. The system was contained in a light-tight box, and the connection to the outer line was made through a loop of glass tubing which, with the inlet tap, was painted black and covered with a black cloth in order to exclude light from the box. The trap which protruded through the floor of the box was painted black.

6.4. Circulating Pump.

The pump was used for circulating gases through the irradiation cell, and for homogenizing mixtures of gases. It was magnetically operated. The pump and the operating switch are shown in Figures 13(a) and 13(b). The soft iron armature of the pump consisted of a cylindrical tube which made a good sliding fit with the glass tubing. It was originally enclosed in glass in order to reduce contamination of the gases due to impurities absorbed in the iron. However, owing to wear, glass dust was circulated. Absorbed gases in the iron were considered a lesser hazard and the uncovered iron armature, well outgassed, was used without any harmful effects. The valves consisted of thin glass globes which were seated into the top of the armature and into a ground seat in the glass tubing. In order that outgassing of the body of the pump should not be hindered by the resistance of the valves, a by-pass to one of the valves was introduced. This could be closed with the steel ball (4) when the pump was in action.

At a stroke rate of about 2 per second, the pump circulated about one litre of gas per minute down to a few centimetres pressure if the impedance in the system was low. At 5 mms. pressure the pump ceased to operate.

The switch which operated the solenoid of the pump is shown in Figure 13(b). This switch was found to be more

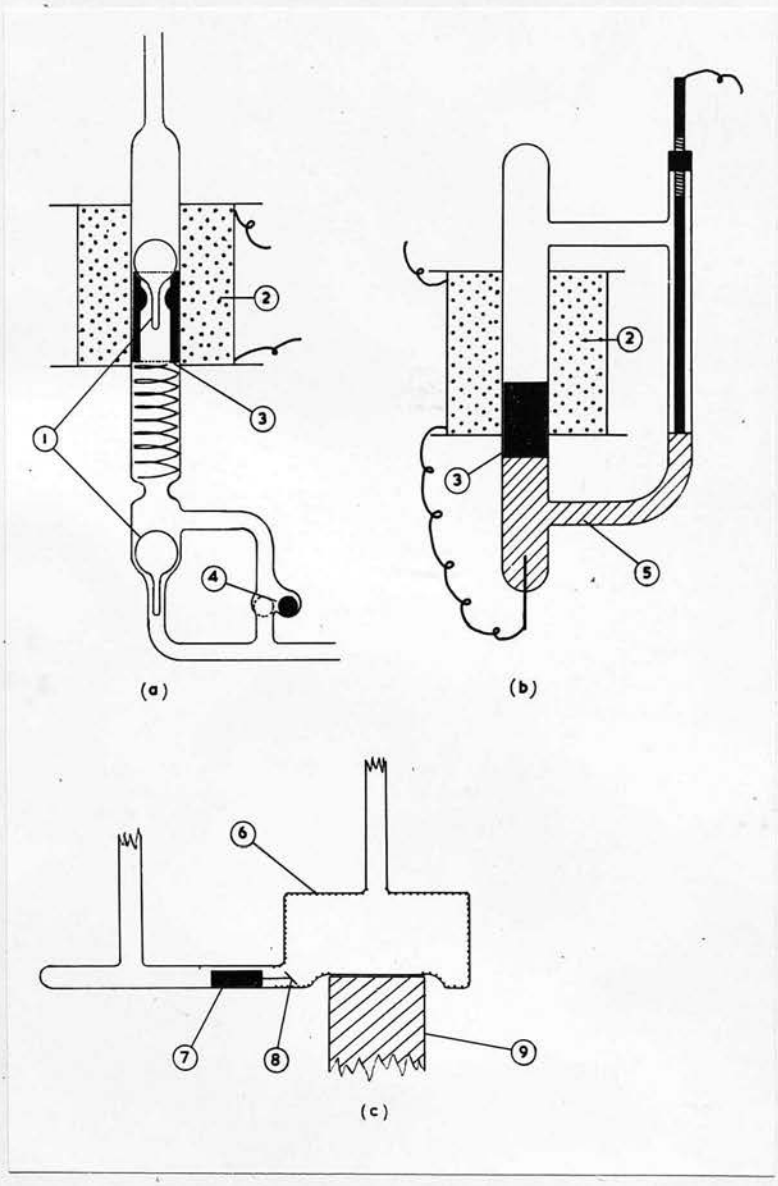

1
2
3
4
(a)
2
3
5
(b)
6
7
8
9
(c)

FIGURE 13.

(a) Circulating pump.

1. Glass valves.
2. Solenoid.
3. Soft iron armature.
4. Steel ball.

(b) Operating switch for pump.

5. Mercury.

(c) Irradiation cell.

6. Aluminized inside surface.
7. Soft iron.
8. Polonium source.
9. Perspex light guide.

reliable than a multivibrator and relay. The gas space above the mercury was filled with argon and a condenser was connected across the terminals to prevent arcing. The two solenoids of the pump and the switch, and a 200 ohm resistance were connected in series to the 240 volts mains. The length and frequency of the stroke of the pump could be adjusted by altering the series resistance in the circuit and the length of the terminal rod which dipped into the mercury in the side-arm of the switch.

6.5. Pressure Measurement.

The pressure had to be measured without using mercury manometers, and for the light emission measurements were made over a range of from about 10^{-2} mms. to 100 mms. The lower limit was set by the minimum pressure at which light emission by alpha-particle excitation became too small to be measured accurately in the presence of the light emission from the polonium source. The upper limit was set at a pressure at which the light emission against pressure measurements for gases would not be complicated by the increased excitation density at the end of an alpha-track.

It was decided that an "Alphatron" gauge[83] would be the most suitable as it was possible to measure the pressure over the required range on one instrument. An attempt to make an ionization chamber with aluminized glass electrodes and quartz insulators in order to allow easy outgassing was

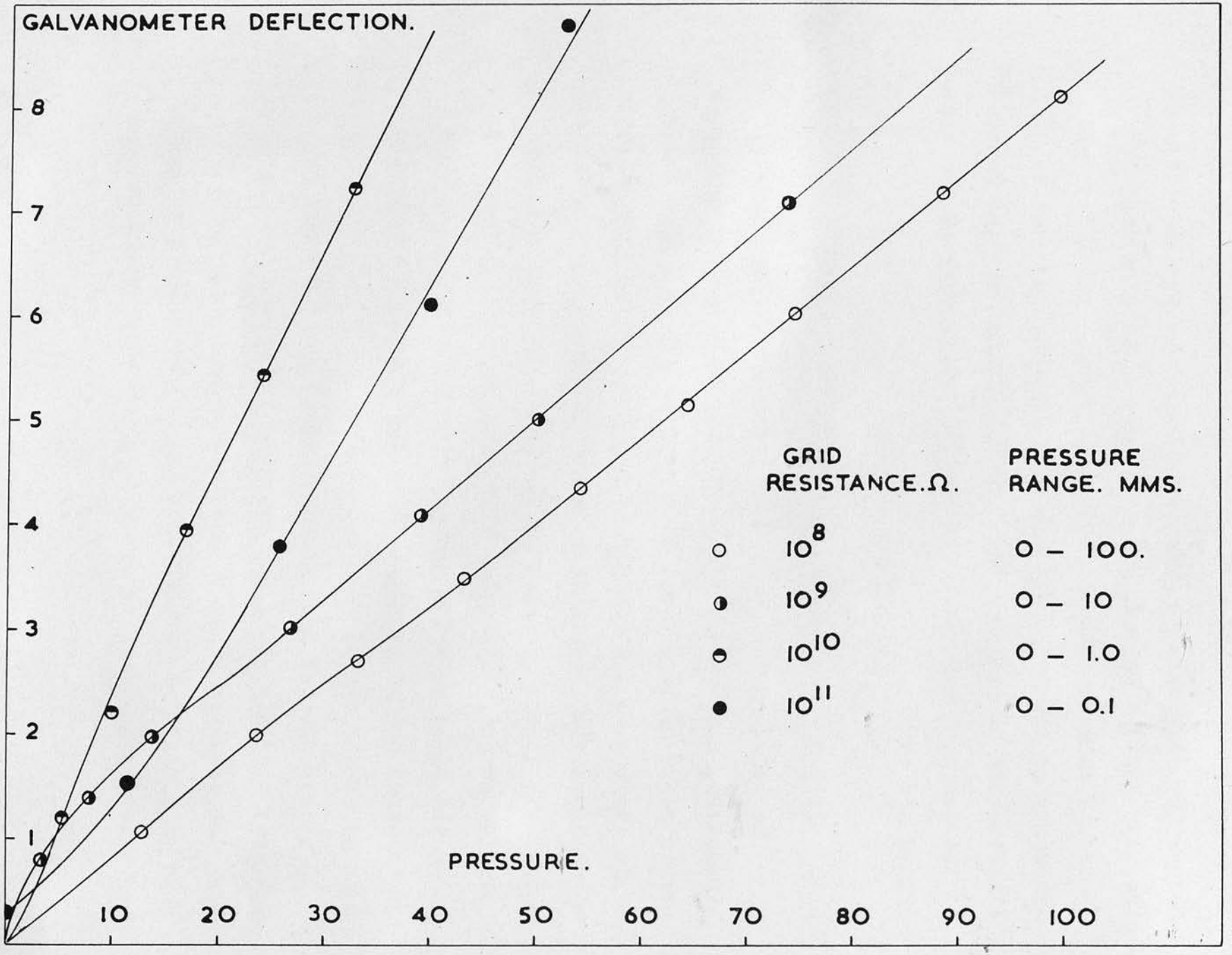

GALVANOMETER DEFLECTION.
8
7
6
5
4
3
2
1
PRESSURE.
10
20
30
40
50
60
70
80
90
100
GRID RESISTANCE.Ω.
PRESSURE RANGE. MMS.
10^8
0 – 100.
10^9
0 – 10
10^{10}
0 – 1.0
10^{11}
0 – 0.1

FIGURE 14.

Curves for galvanometer current against pressure for oxygen as measured with the Alphatron gauge.

not successful as, even at low electrode voltages, saturation effects occurred at low pressures. Accordingly an ionization chamber similar to that described by Downing and Mellen was constructed. The polystyrene insulation which was the best available gave some difficulties due to gassing, but by reducing to a minimum the surface exposed to the vacuum, and by continual pumping when not in use, this did not interfere with the measurements.

A one millicurie polonium alpha-particle source was used and the voltage applied to the outer electrode of the ionization chamber was + 120 volts. Polonium was the only readily available alpha-particle source and had the disadvantage that after calibration, a correction for decay had to be applied. This correction could have been carried out by adjusting the galvanometer shunt, but as fairly frequent calibration checks were carried out it was as easy to draw new graphs of ion current against pressure from time to time and to make the small corrections required for the decay over a few days.

The ion current was passed to earth through a selected resistance of four Victoreen standard high resistances and the voltage was applied to the grid of an Osram ET3 electrometer triode which was attached to the end of the ion chamber. The associated circuit shown in Figure 15 was fitted to a control panel on the bench. The ion chamber, standard resistances, and the electrometer valve were enclosed in an earthed metal box. The leads to the control panel were also

screened. This screening was sufficiently effective for most interference but not for a Tesla spark.

The grid resistance of the ET3 valve was stated to be 10^{14} ohms, but the associated switches and insulators lowered this to an estimated value of 2×10^{13} ohms.

The circuit was simple but sufficiently stable for the purpose. Lead accumulators, in good condition, were used for the filament and anode supplies to the valve. The floating potential of the grid was -2 volts with respect to the filament. The filament biassing resistor maintained the filament at about +2 volts with respect to earth, so the grid and the collecting electrode of the ion chamber were approximately at earth potential, the same as that of the guard ring.

The operation of the Alphatron was as follows. With the grid earthed, the filament current was switched on, then the anode voltage of the valve and at the same time the bias current through the galvanometer to oppose the anode current of the valve. The filament current was adjusted to give an anode current of about 100 μA, in the middle of the range of the bias adjustment. When a series of experiments was in progress the Alphatron was left switched on for several days and very little adjustment was necessary. If a large current were drawn from the valve for too long, on returning the grid switch to the earthed position it was found that the anode current had fallen slightly, and the zero required adjustment.

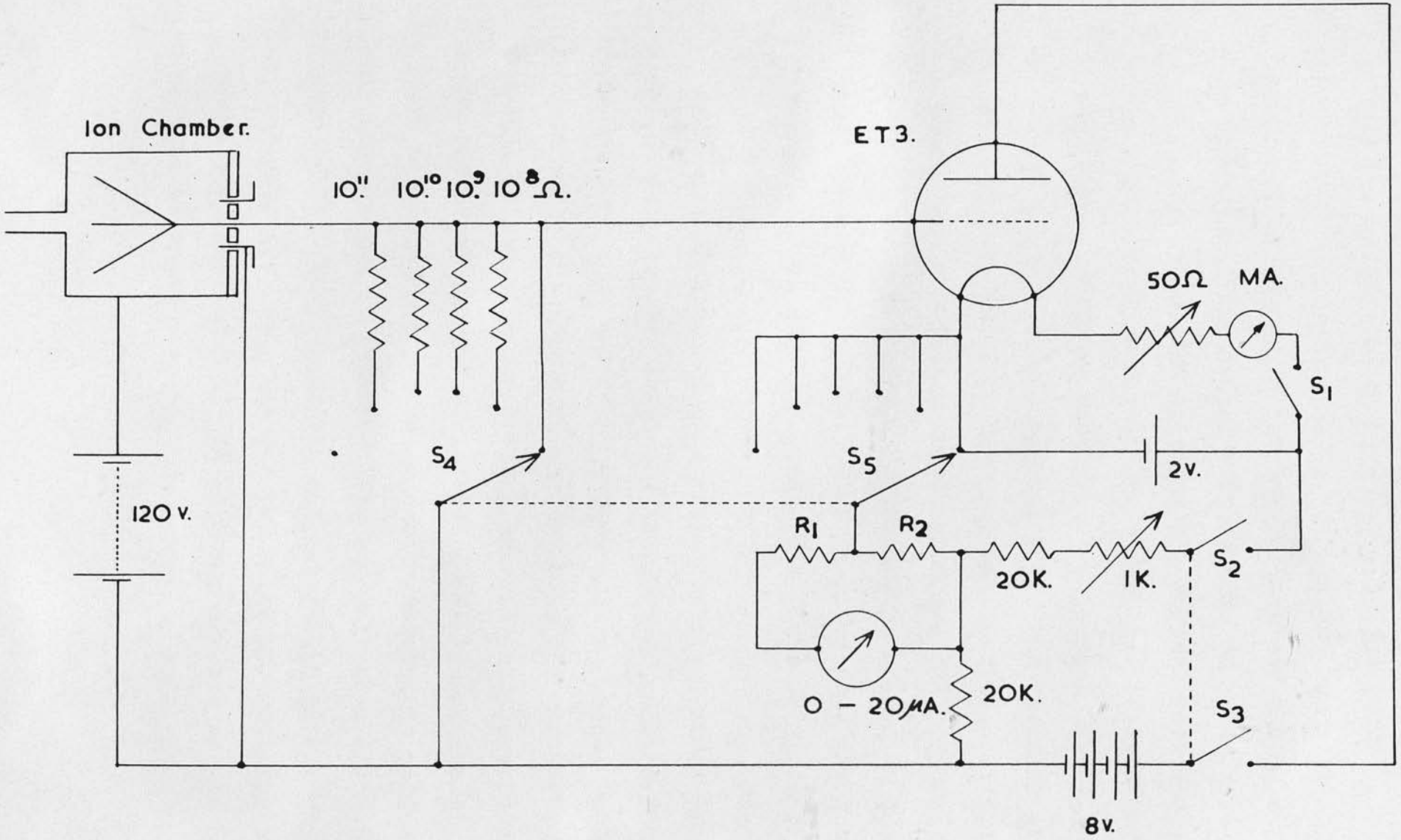

Ion Chamber.
10^{11} 10^{10} 10^{9} $10^{8}\Omega$.
ET3.
50Ω MA.
S_1
S_4
S_5
2v.
120 v.
R_1
R_2
20K.
1K.
S_2
0 – 20μA.
20K.
S_3
8v.

FIGURE 15.

Circuit for Alphatron Gauge.

However by taking measurements quickly at the high pressure end of the ranges, and returning the grid to the earthed position the effect did not interfere with the accuracy of the measurements. The circuit could have been improved by the introduction of more valves and negative feed-back, but as it was, the instrument was simple, with very little to go wrong and very suitable for the purpose. Using a Cambridge Spot galvanometer which gave a full scale deflection of 100 divisions for a current of 20μA, it was possible to measure the pressure in the four ranges, 0 - 100 mms., 0 - 10 mms., 0 - 1 mm., and 0 - 0.1 mms., with an accuracy of better than 3% except at the low pressure end of the 0 - 0.1 mm. range.

Calibration of the Alphatron gauge was carried out with the mercury manometer and the Macleod gauge isolated from the line by two liquid air traps, or for a calibration with carbon dioxide, by a dry-ice bath. A typical series of curves for oxygen is shown in Figure 14. The standard resistances were not accurate powers of ten, and were rather old, so a calibration was made for each pressure range. The curvature of the graphs at low pressures was probably due to secondary ionization but did not interfere with the calibration and measurements. A comparison of the curves for different gases agreed well with those calculated from the energy required per ion pair, and the stopping power of the gases. The change in ion current with time agreed with the half-value period for polonium of 138 days. Nevertheless calibrations were carried out before any series of experiments, for each gas, rather than rely on

large corrections to the original calibration.

A Pirani gauge was used for measuring the vacuum attained and for checking the condition of the vacuum line.

6.5. Temperature Measurement.

The temperatures of furnaces used in the purification of the gases, and of the irradiation cell during measurements of the temperature coefficient of light emission, were measured with copper-constantan thermocouples and a Cambridge Spot galvanometer, 30 ohm resistance, and a full scale deflection of 20 μA. The sensitivity of the thermocouples was adjusted by means of the series resistance. The calibration of the thermocouples was carried out in the usual way with liquid oxygen, solid carbon dioxide, ice, boiling water, and molten lead as the fixed points on the temperature scale.

6.6. Purification of Gases.

6.6.1. Argon.

Commercial argon was passed through columns of soda-lime and magnesium perchlorate, then over spongy uranium at 200°C followed by spongy uranium at room temperature[84, 85]. The uranium furnace consisted of a Pyrex tube surrounded by an electric heater. It was charged with uranium swarf which had been washed with 10% nitric acid. Hydrogen was then passed through the uranium at a temperature of about 200°C until the hydride had been formed. The temperature was raised to 400°C

and the furnace was evacuated. The hydride was decomposed at this temperature and the uranium was left in a finely divided and highly active form. Uranium so prepared combines with all except the noble gases at 200°C. The dissociation pressure of the hydride is considerable at this temperature so the argon was passed through a tube of cold uranium which had been activated in the same way, to remove the remaining hydrogen. This method was used in preference to other possible methods because of the low temperature at which the purification of the argon could be carried out. The experimental assembly was in rather cramped quarters and for the sake of the greased stop-cocks and the operator's comfort it was desirable to keep the air temperature at a reasonable level. The method had the disadvantage that once the uranium had been prepared in its active state, any accidental introduction of air into the purification line was dangerous.

After such an accident the purification of argon was carried out by passing the argon over a mixture of barium and magnesium in a steel furnace at a temperature of 800°C [86]. The gas in the purification line was kept a few centimetres above atmospheric pressure and was introduced into the vacuum line through a fine capillary. While a series of measurements were made with one gas mixture, a flask (10; Figure 12) was slowly filled with pure gas through the capillary. In this way the gas flow through the purification line was kept at a slow rate so that the gas remained for some time in contact with the furnace filling, and yet a sufficient volume of gas accumulated in the flask for the next experiment to be carried

out without delay.

After argon had been introduced into the vacuum line from which the irradiation cell had been closed off, it was adsorbed on active charcoal by cooling with liquid air[87]. The line was then pumped out for a few minutes in order to remove any of the lighter rare gases which may have been introduced with the argon. Evaporation and re-adsorption of the argon was repeated twice, and then the argon was allowed to evaporate into the irradiation cell.

Argon purified in this way on excitation by alpha-particles, gave light emission measurements which were reproducible to within 10%. Although no analysis of the purity was possible, it seemed that nitrogen was the most persistent impurity and it was found to increase the light emission from argon by about three times in concentrations of 100 parts per million. It would seem that the irreproducibility of the light emission measurements with purified argon was due to variations in the nitrogen concentration of a few parts per million.

Helium, similarly purified but without adsorption on active charcoal, gave irreproducible light emission measurements.

6.6.2. Nitrogen

Commercial nitrogen was passed through columns of soda-lime and magnesium perchlorate and then over a bath of molten potassium at 340°C[88]. This should have removed all the expected impurities except the rare gases and hydrogen which

would have been formed in the potassium furnace from any water vapour which was not removed by magnesium perchlorate. When the nitrogen had been admitted to the vacuum line it was adsorbed on active charcoal and the line evacuated as in the purification of argon. This should have removed any hydrogen or helium in the nitrogen. It had been found that argon as an impurity did not affect the light emission measurements. Measurements with nitrogen purified this way were reproducible although this was not of course a sufficient criterion of purity.

6.6.3. Carbon dioxide.

A low temperature distillation was used to purify carbon dioxide. Commercial carbon dioxide was washed with concentrated sulphuric acid and then condensed into a trap which could be connected to the still. The still (1; Figure 12) consisted of a long helix of glass tubing which was immersed vertically in a bath of liquid air. The carbon dioxide was evaporated from the trap and condensed in the upper end of the helix. The helix was then evacuated and pumping was continued during the distillation. As the liquid air evaporated, the level in the bath fell and the carbon dioxide distilled slowly down the helix leaving less volatile impurities behind and allowing any non-condensible gases which might have been occluded to be pumped off. When the level of the liquid air fell below the lowest loop of the helix, the vacuum line was closed off from the pump and carbon dioxide distilled into

the line as the temperature of the helix rose. When the liquid air in the bath was almost exhausted the helix was closed off from the vacuum line.

6.6.4. Oxygen.

Oxygen was prepared by gently warming a tube containing "Analar" potassium permanganate crystals which had been kept under high vacuum.

6.6.5. Hydrogen.

Hydrogen was diffused into the line from coal-gas passing over a heated palladium thimble. It had been shown that no other gases diffused through in measureable quantities[89]. The thimble was heated under vacuum for some time before hydrogen was admitted to the line.

6.6.6. Vapours.

Water vapour, alcohol vapour, and benzene vapour were introduced from purified supplies which had been deaerated by evaporating under vacuum on to a finger cooled with liquid air. Their pressure in the vacuum line was adjusted by immersing the reservoir in a bath at a suitable temperature, which of course had to be less than room temperature.

6.7. Preparation of Gas Mixtures.

The light emission from mixtures of gases was measured in the following way. One of the constituents of the proposed gas mixture, usually the one whose concentration was being varied in a series of measurements, was admitted to the vacuum line and the irradiation cell to the desired pressure. The inlet stop-cock to the irradiation cell was closed and the vacuum line was evacuated. The second gas was then admitted to the vacuum line to a pressure in excess of the pressure finally required after mixing. The inlet stop-cock to the irradiation cell was then opened slowly and the pressure measured. The concentrations in the mixture could then be calculated. With the inlet stop-cock closed the circulating pump was started and circulation continued until the light emission as measured by the photomultiplier remained constant. The mixture was then homogeneous. The length of glass tubing from the inlet stop-cock to the direct path of the circulation was kept as short as possible so that no dead space was left to cause errors in the calculation of the concentrations in the mixture.

Measurements of the light emission were made at different pressures by withdrawing gas from the irradiation cell. It can be seen that the Alphatron gauge contained only the second pure gas which had been added, and thus the pressure measurement was simplified. If a mixture of gases had been introduced into

the Alphatron a different calibration curve would have been required for each mixture.

A complete series of measurements of the light emission from gas mixtures at a number of pressures could be quickly and accurately taken. With mixtures containing hydrogen or helium, if the stop-cocks were left open, the effect of diffusion from the irradiation cell and into the Alphatron could be detected at low pressures by slow changes in the light emission and the ion current. With other gases no separation of the constituents of the mixtures could be detected.

CHAPTER VII.

RESULTS AND DISCUSSION.

7.1. Luminescence due to mercury vapour.

The luminescence of mercury vapour has been studied more thoroughly than that of almost any other gas or vapour, and many energy transfer reactions involving it have been reported[90, 75, 71]. It seemed that interference from mercury vapour in a study of the luminescence of gases was very likely.

In the early stages of the experimental work a search was made for luminescence produced by mercury vapour in the system, and because the problem of removing mercury vapour from a vacuum line was under-estimated, it at first appeared that mercury was not interfering. However it was soon found that liquid air traps between the irradiation cell and the mercury manometers did not provide a sufficient safeguard. By circulating the gases through the irradiation cell protected on either side by a liquid air trap it was found that the light emission from the three gases examined, carbon dioxide, nitrogen, and argon, was increased by the presence of mercury vapour.

The increase in light emission was greatest with argon, and the curves of light emission against pressure which were obtained when the traps were maintained at the temperature indicated are shown in Figure 16. The light emission cannot

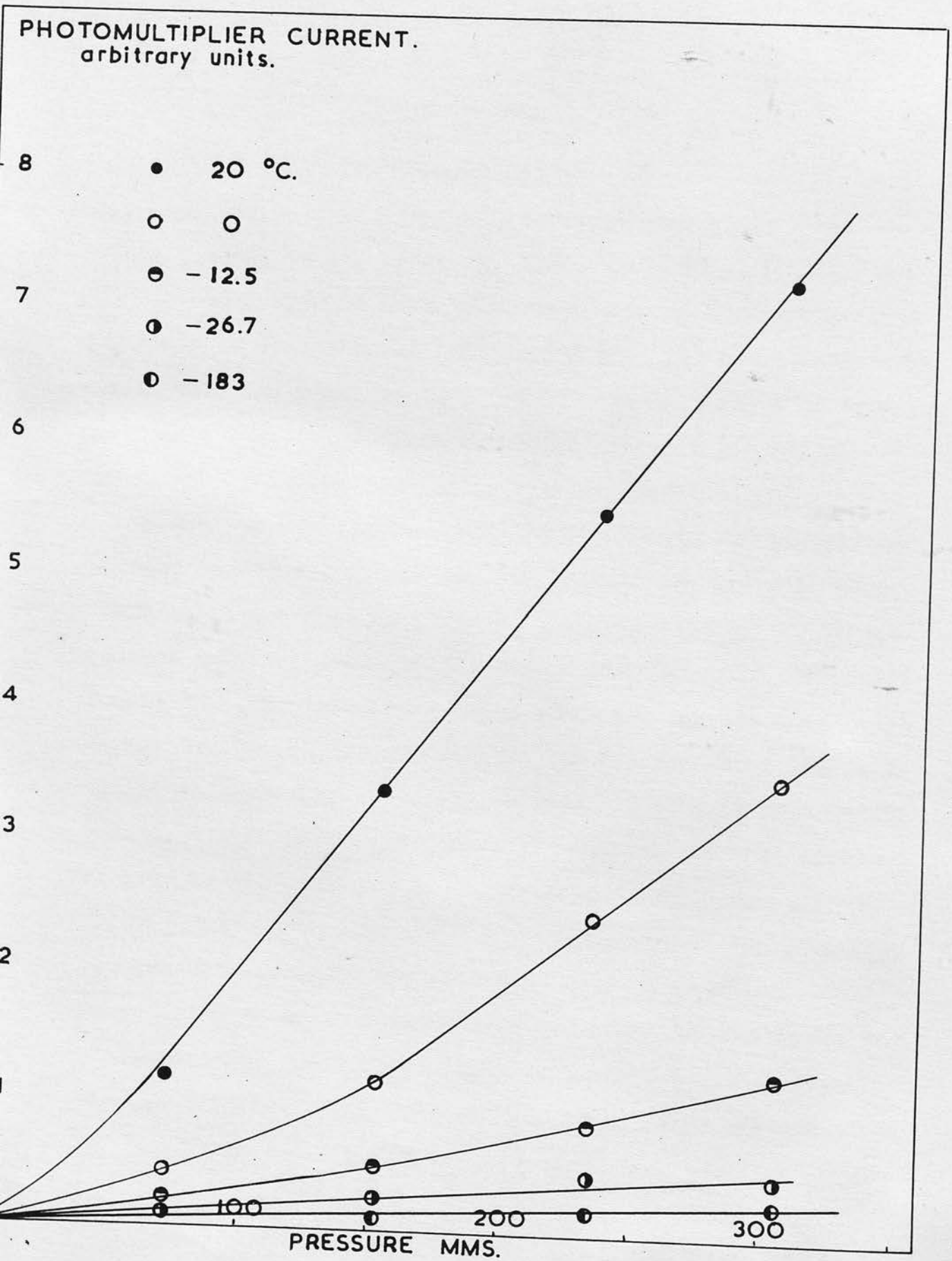

PHOTOMULTIPLIER CURRENT.
arbitrary units.
8
7
6
5
4
3
2
20 °C.
0
−12.5
−26.7
−183
100
200
300
PRESSURE MMS.

FIGURE 16.

Light emission from argon and mercury vapour which was circulating through traps at the temperature indicated.

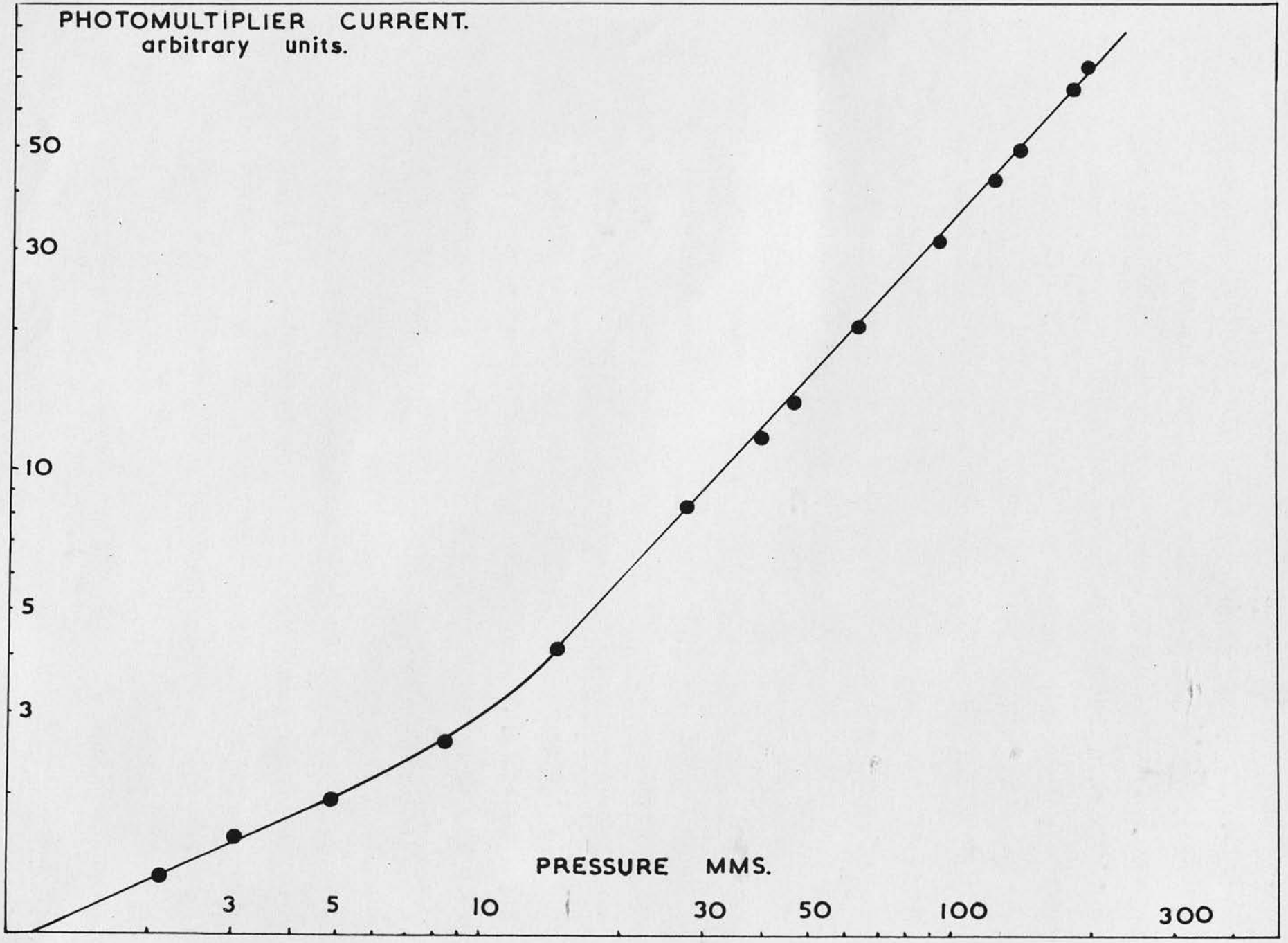

PHOTOMULTIPLIER CURRENT.
arbitrary units.
50
30
10
5
3
PRESSURE MMS.
3
5
10
30
50
100
300

FIGURE 17.

Light emission from nitrogen containing mercury vapour at 20°C.

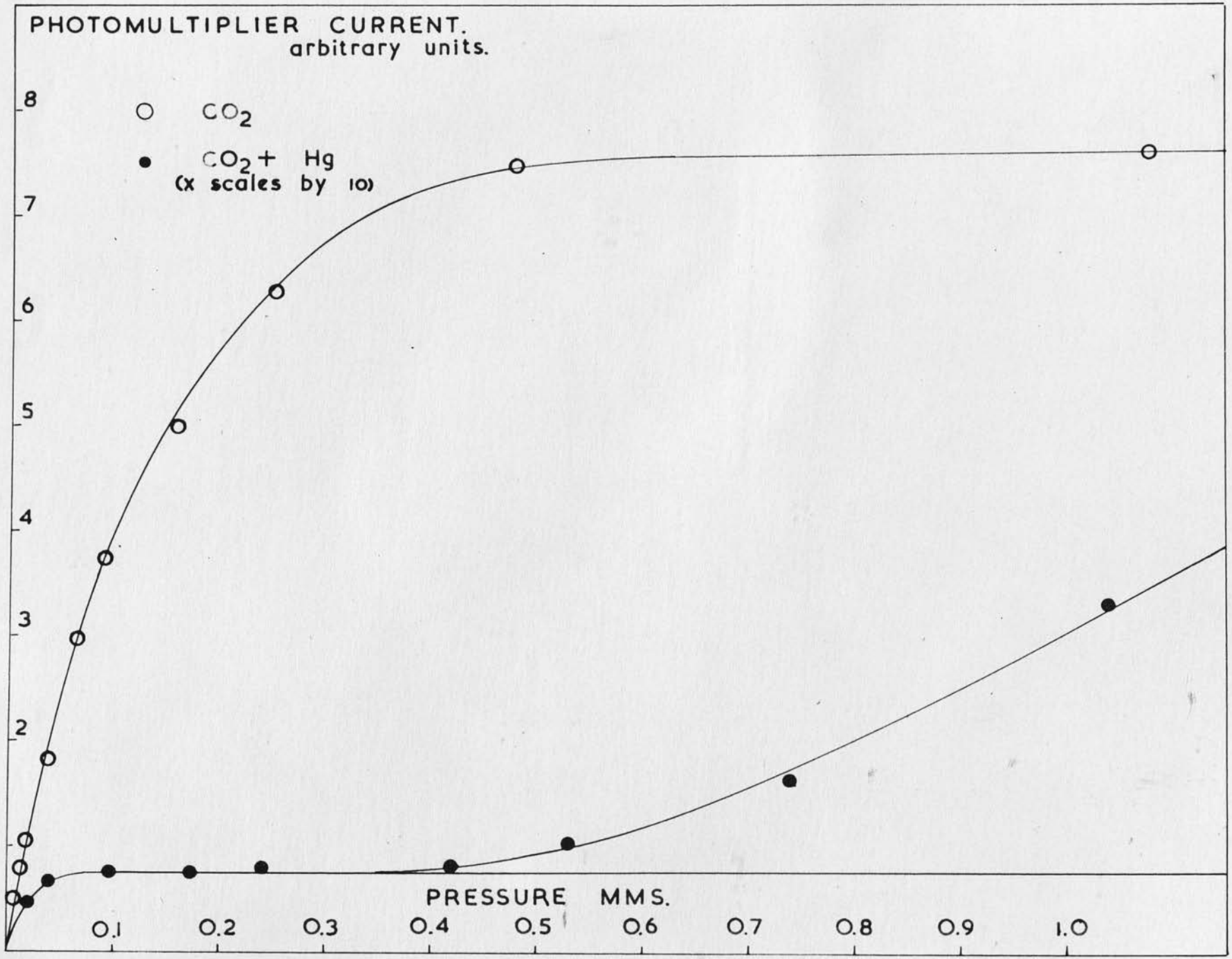

PHOTOMULTIPLIER CURRENT.
arbitrary units.
○ CO_2
● CO_2 + Hg
(x scales by 10)
8
7
6
5
4
3
2
PRESSURE MMS.
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

FIGURE 18.

Light emission curves for

(a) Carbon dioxide

(b) Carbon dioxide containing mercury vapour at 20°C. The scales have been reduced by a factor of 10.

From these rather approximate measurements it was obvious that an energy transfer from the excited gas to mercury was taking place, but not necessarily from the levels of excitation which gave the light emission in the absence of mercury. However these results will be discussed in more detail in connection with other energy transfer processes in the sections on the respective gases.

As a result of these experiments, a mercury-free vacuum line was constructed as has been described in Section 6.1.

7.2. Intensity of Light Emission from Gases.

It is noticeable that comparative measurements reported in the literature of light emission from gases excited by alpha-particles show little agreement[91, 78, 79]. This is for the following reasons.

1. The light emission can be critically dependent on the purity of the gases, particularly if the impurities present are such as to convert ultra-violet light which is not normally detected, into luminescence to which the light detector is sensitive. For this reason the light emission from argon in particular has been over-estimated.

2. The light emission from different gases does not depend on pressure in the same way, and so the pressure at which measurements are made should be specified.

3. The wavelength sensitivity curve of the photo-multiplier, or the photomultiplier and filter system should be specified. If for instance a 1 P 28 photomultiplier which

has a quartz envelope is used with a light guide of Perspex which does not transmit below 3000A, the sensitivity curve of the photomultiplier will not correspond with that published by the makers. In the present work a Perspex light guide for light transmitted by the Pyrex envelope of the irradiation cell was used with an E.M.I 5311 photomultiplier.

The gases and vapours which have been examined are carbon dioxide, nitrogen, argon, helium, oxygen, hydrogen, water vapour, benzene vapour, and alcohol vapour. Of these only the first four show sufficient luminescence for accurate measurement. The light emission from helium was irreproducible to a degree which did not warrant a detailed study. It was found that helium did not quench argon light, although argon, oxygen, and hydrogen quenched the light emission from it. The light emission from oxygen and hydrogen was small but greater than that from any of the vapours.

The relative light emissions from the gases at the pressures indicated are given in Table I. The gas mixture of 1.4% nitrogen in argon had the highest light yield at high pressures of any gas which was measured, and is included for comparison.

In the same units, the light from the polonium source gave a deflection of 35.0 divisions when the irradiation cell was evacuated. As it was not certain that all this light came from the polonium source, and not partially from the alpha-particles incident on the walls of the irradiation cell, the fall off in the light emission values for hydrogen and oxygen

TABLE I

Light emission from gases excited by alpha-particles.

(1 unit 0.15 photons per alpha-particle.)

Pressure mms.	Air	A + 1.4% N_2	A	N_2	CO_2	H_2	O_2
0.01	2.2	0.2	0.2	2.2	2.6	0.2	0.7
0.10	11.9	9.1	5.1	13.6	16.0	1.8	2.1
1.00	40.0	118	17.2	54.2	30.4	3.1	3.1
10.0	76.0	590	41.5	140	31.2	3.6	1.8
100	110	4560	97.0	460	31.8	1.6	1.4

at high pressures may have been due to the reduction in energy of the alpha-particles reaching the walls after traversing the gas volume. Such an effect would not be large at the lower pressures but nevertheless no significance was attached to the measurements of light emission from these gases.

The units in which the light emission values in Table I are given can be expressed in terms of photons per ion pair by a calibration with a standard solution of P^{32} as a light source as described in Section 2.4. A large number of approximations enter into the calculation, and although the relative values are accurate to better than 5%, the absolute values might be in error by a factor of two. The approximations are as follows.

1. The geometry for detection of light from a gas in the irradiation cell and from the Cerenkov emission from a solution of P^{32} would not be the same. The emission spectra of the gases would be different from each other and from the Cerenkov emission, and so the quantum efficiency for detection of the light would be different in each case. The light was too weak to allow spectroscopic measurements. These differences have been ignored and the figures given in Table II represent the light emissions between 3000A and 7000A, related to the Cerenkov emission between the same wavelength limits, and assuming the detection geometry was the same for all the gases and the Cerenkov emission.

2. The alpha-particle flux which produces excited species can only be estimated very approximately. The detection

TABLE II

Light emission from gases - photons per ion pair x 10^4.

Pressure mms.	Air	A + 1.4% N_2	A	N_2	CO_2	H_2	O_2
0.01	1460	100	100	1540	1120	860	410
0.10	795	460	260	950	685	710	120
1.00	270	600	88	380	130	120	18
10.0	51	300	21	99	13	14	1.0
100	7.4	230	4.9	32	1.4	0.6	0.1

geometry for light emitted from different parts of the irradiation cell would not be constant. From the cell geometry and the known strength of the polonium source it was estimated that a flux of 2.7×10^7 alpha-particles per second was effective in producing excited species, in the "view" of the photomultiplier. An effective track length in the cell of 40 mms. was estimated. The number of ion pairs produced per alpha-particle in this distance is given by the following formula.

$$\text{No. of ion pairs per alpha-particle} = \frac{7300\ sp}{W}$$

where p = pressure in mms.

s = stopping power of the gas relative to air.

W = energy required per ion pair[93, 94].

The energy of a polonium alpha-particle was taken as 5.3 Mev. and the range in air as 38.3 mms. at N.T.P.

Table II shows the number of photons emitted per ion pair from the indicated gases. This seems to be a suitable way of indicating the fluorescence efficiencies of the gases.

It can be seen that the fluorescence efficiencies of all the gases are quite high at pressures less than 0.1 mms. but fall rapidly with increase of pressure due to secondary processes which compete with the fluorescence. A mixture of argon + 1.4% nitrogen maintains a fairly high efficiency at all pressures.

The energy efficiency is of course lower than the

efficiency per ion pair. The emitted photons are probably in the blue part of the spectrum (second positive bands for nitrogen and argon-nitrogen mixtures[80]) with an energy of about 3 ev. per photon which is about one-tenth of the average energy required to form an ion pair in these gases. The energy efficiency for argon + 1.4% nitrogen at 100 mms. pressure on this calculation is about 0.23%. For comparison the energy efficiency for an anthracene crystal for polonium alpha-particles is 0.324%[92]. It would seem from this that highly fluorescent gas mixtures may be suitable in certain applications for counting high energy particles.

7.3. Carbon Dioxide.

Measurements of the light emission from pure carbon dioxide and from mixtures of carbon dioxide with hydrogen, nitrogen, oxygen and argon were made over a wide pressure range and the results are as follows.

7.3.1. Pure carbon dioxide.

The graph of light emission against pressure for pure carbon dioxide is shown in Figure 18. The plateau in the curve remained constant within a few per cent up to 100 mms. pressure. The resemblance of the curve to the theoretical curves for quenching (Figure 10) is at once obvious. A plot of pressure/light emission $\frac{P}{L}$ against pressure gave a straight line graph with an intercept on the P/L axis. Therefore the light emission from carbon dioxide fits an equation of the

following form.

$$\text{Light emission } (L) = \frac{k_1 k_2 p}{k_2 + k_3 p}$$

and the constants were evaluated from the graph of P/L against p.

k_1 = 249 divisions per mm.

Slope = 2.55×10^{-2} div^{-1}

$$= \frac{k_3}{k_1 k_2}$$

$$\therefore \frac{k_3}{k_2} = 6.35.$$

Therefore at 1 mm. pressure the probability of quenching by collision is greater than the probability of de-excitation by light emission. The cross-section for the quenching collision can be calculated if the half-value period for emission by carbon dioxide is known. This value has not been measured but if the light emission arises from an allowed transition it would probably be about 10^{-8} seconds. Assuming this value,

$k_2 = 6.93 \times 10^7$ sec^{-1}

$\therefore k_3 = 4.40 \times 10^8$ collisions/sec.

From the formula for gas-kinetic collisions, the number of collisions per second which an excited carbon dioxide molecule would make with unexcited molecules at 1 mm. pressure can be calculated. The concentration of excited molecules will be very small and mutual collisions can be neglected.

k_3' (kinetic collisions) = $4 n \sigma_k^2 (\pi RT/M)^{\frac{1}{2}}$

σ_k^2 = Cross section for a kinetic collision (σ = collision diameter)

= 21.2×10^{-16} cm^2 for CO_2.

n = no. of molecules per c.c. at 1 mm. pressure.

= 3.54×10^{16}.

R = Gas constant.

T = Absolute temperature.

M = Molecular weight.

For CO_2 k_3' = 1.27×10^7

Therefore the cross-section for quenching of excited carbon dioxide by unexcited carbon dioxide is equal to

$$\frac{k_3}{k_3'} \sigma_k^2 = 34.6 \sigma_k^2$$

7.3.2. Temperature coefficient for light emission

The variation with temperature of the luminescence of carbon dioxide was too small to be measured over the range of temperature from 20°C to 100°C. The light emission from the polonium source varied much more than that from the carbon dioxide. This result indicated that the activation energy for the quenching collision was less than 1000 calories per mole, and that the probability of quenching occurring in a kinetic collision was high.

7.3.3. Carbon dioxide and Hydrogen.

The shape of the light emission curves for mixtures of hydrogen and carbon dioxide was similar to that obtained from pure carbon dioxide. The initial slope of the curves was the same but they flattened off at lower values of the light emission. It appeared that hydrogen was quenching the carbon dioxide light. If the light emission, at pressures where it was independent of pressure, was plotted against the percentage of hydrogen in the mixture the graph of Figure 19 was obtained.

From the following series of reactions an equation for the light emission can be found.

1.	$CO_2 \xrightarrow{\alpha} CO_2^*$		Excitation
2.	$CO_2^* \longrightarrow CO_2 + h\nu$		Luminescence
3.	$CO_2^* + CO_2 \longrightarrow 2CO_2$		Self-quenching
4.	$CO_2^* + H_2 \longrightarrow CO_2 + H_2$		Quenching by H_2

$$\text{Light emission} = \frac{k_1 k_2 [CO_2]}{k_2 + k_3[CO_2] + k_4[H_2]}$$

If $[H_2]$ constitutes a fraction a of the total pressure -

$$\text{Light emission} = \frac{k_1 k_2 p(1 - a)}{k_2 + k_3\, p(1 - a) + k_4\, ap}$$

When the light emission of the mixture is one-half of the light emission from pure carbon dioxide

$$\frac{k_1 k_2\, p}{k_2 + k_3\, p} = \frac{2\, k_1 k_2\, p(1 - a)}{k_2 + k_3\, p(1-a) + k_4\, ap}$$

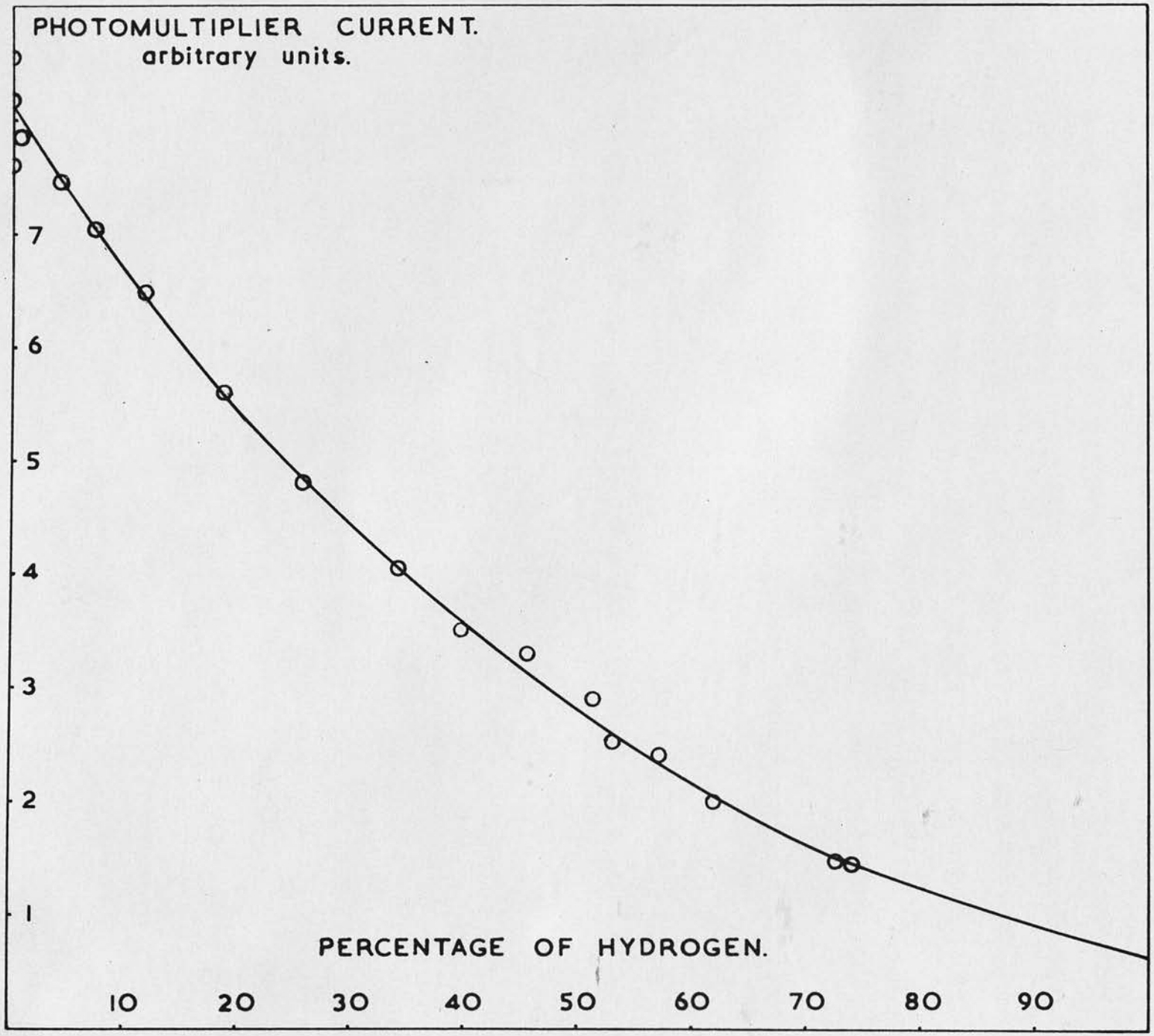

PHOTOMULTIPLIER CURRENT.
arbitrary units.
7
6
5
4
3
2
1
PERCENTAGE OF HYDROGEN.
10
20
30
40
50
60
70
80
90

FIGURE 19.

Light emission from mixtures of carbon dioxide and hydrogen in the regions where light emission was independent of pressure.

As the measurements were made in the pressure-independent regions for the light emission, k_2 is negligible compared with the other terms in the denominators

$$\therefore \quad 2(1 - a)k_3 p = k_3 p(1 - a) + k_4 ap$$

$$\therefore \quad \frac{k_3}{k_4} = \frac{a}{1 - a}$$

From Figure 19, when the light emission of the mixture is one-half of that from pure carbon dioxide,

$$\underline{a} = 0.43$$

$$\therefore \quad \frac{k_3}{k_4} = 0.754 .$$

This indicates that hydrogen is a better quencher than carbon dioxide, but it must be remembered that the collision rate for $H_2 \text{ —— } CO_2^*$ collisions will be greater than that for $CO_2 \text{ —— } CO_2^*$ collisions. The ratio of the kinetic collision rates is given by the following equation.

$$\frac{k_3'}{k_4'} = \left(\frac{2\sigma_{CO_2}}{\sigma_{H_2} + \sigma_{CO_2}}\right)^2 \left(\frac{2 M_{H_2}}{MCO_2 + MH_2}\right)^{\frac{1}{2}}$$

$$= 0.33.$$

When the greater collision rate for collisions with hydrogen is taken into account, it is found that the quenching cross-section for hydrogen is smaller than for carbon dioxide.

$$\frac{\sigma_{CO_2}^2}{\sigma_{H_2}^2} = 2.27 .$$

7.3.4. Carbon dioxide and Nitrogen.

The effect of concentrations of nitrogen of less than 10% is not detectable. If the mixture consists of 60% nitrogen the light emission is doubled, but it is then a measurement of the light emission from nitrogen quenched by carbon dioxide.

7.3.5. Carbon dioxide and Oxygen.

The light emission from mixtures of carbon dioxide and oxygen is less than that from pure carbon dioxide at all pressures. The quenching cross-section for oxygen is less than that for hydrogen

$$\frac{\sigma^2_{CO_2}}{\sigma^2_{O_2}} = 4.5.$$

7.3.6. Carbon dioxide and Argon.

The light emission rose to the same value as for pure carbon dioxide but more gradually. As with oxygen the light emission at low pressures was reduced, which was not so with nitrogen or hydrogen.

7.3.7. No ultra-violet emission from pure carbon dioxide was detected, but the low detection efficiency for it meant that an intensity equal to about half of the emission in the visible would have escaped detection.

7.3.8. Discussion

Deductions made from the light emission curves of mixtures of carbon dioxide and the luminescent gases, argon and nitrogen, may be ambiguous. In the absence of spectroscopic measurements it is impossible to isolate the separate contributions to the light emission from the two constituents. However from a qualitative examination of the curves for light emission against pressure the following deductions can be made.

1. Argon acts as a diluent, reducing both the number of carbon dioxide molecules which are excited in the "view" of the photomultiplier, and the number of quenching collisions between excited and unexcited carbon dioxide molecules. Argon does not quench carbon dioxide light, nor does it emit very much of its own light at low pressures as can be seen from Table II.

2. Oxygen acts in the same way as argon, but it quenches the carbon dioxide light.

3. Nitrogen presumably acts in the same way as argon but its higher light emission at low pressures obscures the effect.

4. Hydrogen does not appear to dilute the excitation density of the carbon dioxide as the initial slope of the light emission curves remains the same as for pure carbon dioxide. It quenches the light emission strongly. This effect could be explained if hydrogen directly excited by the alpha-particles transferred its energy to the carbon dioxide, but there is no evidence for this.

In view of the lack of spectroscopic evidence, any suggestion as to the source of the light emission from carbon dioxide irradiated by alpha-particles can only be speculative. It probably resembles that from a high voltage arc. This has been found to consist of a continuum from 2000A to 9000A on which was superposed the carbon monoxide "flame bands"[95]. There has been some speculation as to the source of these bands, both excited oxygen[96] and an excited isomer of carbon dioxide[97] having been suggested. These excited species are thought to arise from recombination reactions.

$$CO + O + M \longrightarrow CO_2^{\times} + M$$

$$CO_2^{\times} \longrightarrow CO_2 + h\nu .$$

By circulating the gas during irradiation with alpha-particles it was found that no change in the light emission occurred. Therefore the species concerned with light emission must have had a life-time less than about one-tenth of a second. If a G value of 10 is assumed for the production of the species, and with an alpha-particle flux of 2.7×10^7 per second as in these experiments, the equilibrium molecular concentration of excited species in the irradiation cell would be about 3×10^{-9}.

The absorption spectrum of carbon dioxide consists of two weak continua with maxima at 1475A and 1332A, and a strong continuum at 1121A, on which are superposed diffuse bands[98]. The latter level probably corresponds to an allowed transition. It is suggested that these continua correspond to dissociations

into ground state $CO(^1\Sigma)$ and $O(^1D)$ and $O(^1S)$. There can be no emission in the visible from these absorption levels, and a search for ultra-violet emission from carbon dioxide irradiated with alpha-particles indicated that it was no greater than the visible emission. Although both carbon monoxide, and oxygen atoms, probably occur in irradiated carbon dioxide, and their recombination probably accounts for the low chemical decomposition[99] observed, their equilibrium concentration must be small and the contribution of recombination reactions to the light emission will probably be small.

Although Grün and Schopper[52] reported no effect of an electric field on the light emission, the possibility of excited ions as the source of the light emission cannot be ruled out.

The only contribution which the present work can make to a discussion on emission from carbon dioxide is that the results are in agreement with there being a stable excited state which is responsible for the light emission in the visible. It can be de-excited by collisions with carbon dioxide, hydrogen, and oxygen. It is probably a continuum produced by a transition to a dissociation level.

7.4. Nitrogen

The fluorescence efficiency of nitrogen fell markedly with increase in pressure, indicating some self-quenching process. The light emission was also quenched by hydrogen, oxygen, carbon dioxide, and the vapours of water, alcohol and benzene. Argon in concentrations up to 10% had no effect on the light emission. Curves for light emission against pressure for pure nitrogen and mixtures of nitrogen and hydrogen are given in Figure 20. They differ only in the quenching constants from those for other quenching gases. It was found that the quenching was approximately proportional to the concentration of quencher at high pressures. However, by expanding the scales of Figure 20, which the accuracy of the measurements at low pressures allows, it was found that the light emission showed very little quenching due to the external quencher, up to pressures of about 1 mm. even when the gas mixture contained up to 20% of quencher.

The light emission curve for pure nitrogen did not correspond to a simple self-quenching curve as had been found by Grün and Schopper[78], and Ward[79], but was proportional to the square root of the pressure in agreement with the results of Audubert and Lormeau[91]. Ward found the light emission from nitrogen and air to be the same, and in discussions with him it was agreed that his nitrogen might have been impure. After a considerable number of experiments on the light emission from nitrogen it was concluded that the square root dependence was

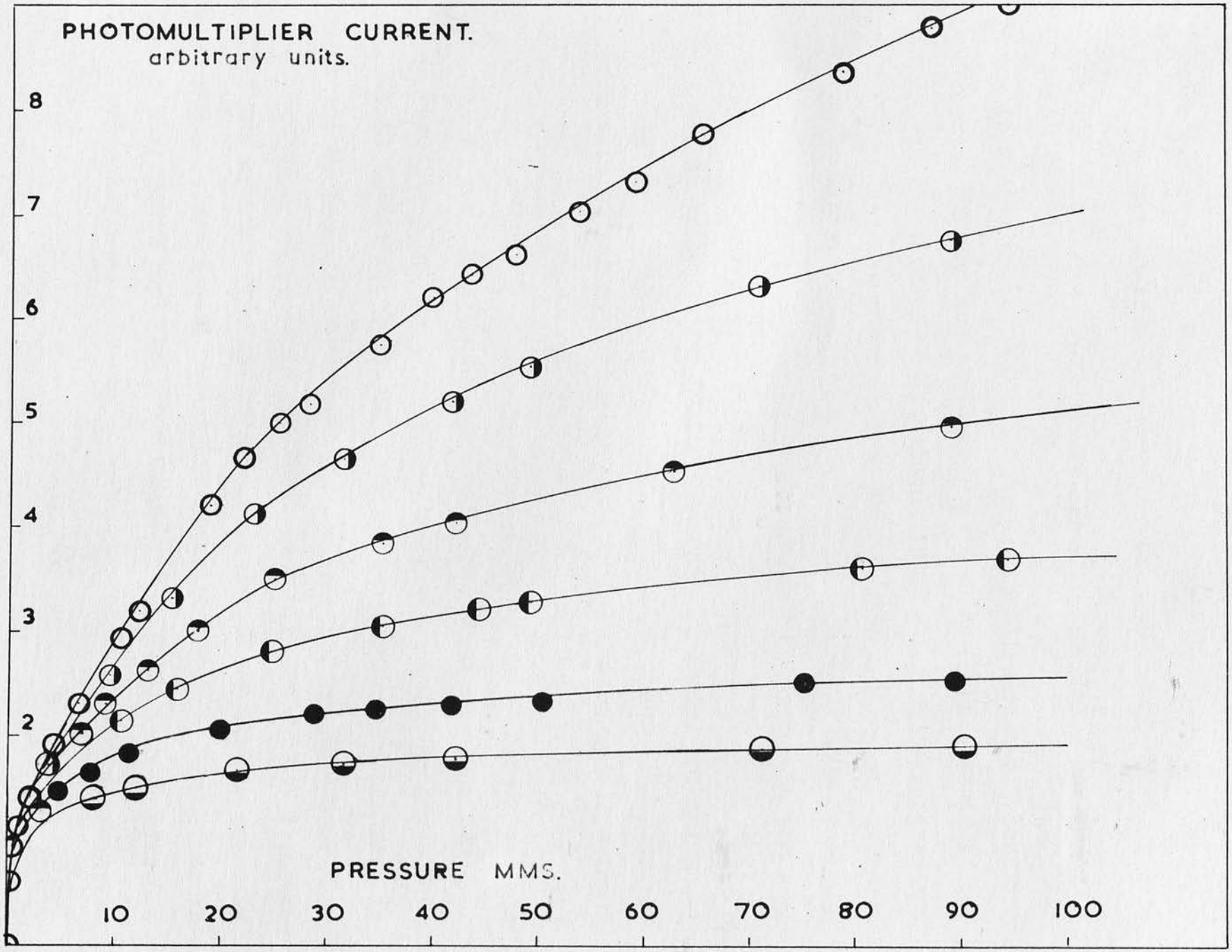

PHOTOMULTIPLIER CURRENT.
arbitrary units.
8
7
6
5
4
3
2
PRESSURE MMS.
10
20
30
40
50
60
70
80
90
100

FIGURE 20.

Light emission from pure nitrogen and mixtures of nitrogen and hydrogen.

Pure nitrogen

" " + 1.23% hydrogen

" " + 3.61% "

" " + 6.90% "

" " + 11.6% "

" " + 17.7% "

genuine. An explanation of these results lead to some difficulty, as that given by Audubert and Lormeau seemed unacceptable.

In the explanations of active nitrogen phenomena, mechanisms involving nitrogen atoms have frequently been suggested[100,101], and it is very probable that they would be present in nitrogen irradiated by alpha-particles. Suitable mechanisms can be proposed in which the concentration of excited nitrogen atoms is proportional to the square root of the nitrogen pressure. Light emission from excited nitrogen atoms would then give the square root dependence which was observed. However the light emission from nitrogen and air excited by high energy particles has been found ~~to be molecular light~~ spectroscopically to be characteristic of emission from nitrogen molecules[80, 102].

Quenching of nitrogen light by nitrogen atoms would have given a square root dependence on pressure if the nitrogen atoms were in an equilibrium with unexcited nitrogen.

$$N_2 \longleftrightarrow N + N \quad .$$

There could have been intermediate steps in the equilibrium.

$$\text{Light emission} = \frac{k_1 p}{1 + k_2 [N]} = \frac{k_1 p}{1 + k_2 \sqrt{p}} \quad .$$

It was found, as with carbon dioxide that the light emission did not vary if the gas was circulated through the irradiation cell, indicating that the light emission process

did not involve any long-lived species. Therefore any products of the irradiation could not be taking part in the reactions because their equilibrium concentrations would have been much too small to account for the light emission observed. So the above mechanism involving nitrogen atoms had to be rejected.

The quenching could have taken place in the alpha-particle track where the concentration of excited species and products of the irradiation would be much higher than in a homogeneous reaction. However the mechanism for quenching by nitrogen atoms involves an equilibrium between atoms and molecules and such an equilibrium could not have been set up in the time during which the inhomogeneity of an alpha-track persisted.

If a reaction in an alpha-track is to be invoked, it is perhaps possible that mutual quenching of two excited nitrogen molecules should occur and this would give the observed square root dependence.

If such possibilities are rejected, the only species which are in sufficient concentration to produce quenching are unexcited nitrogen molecules.

The equation for self-quenching was derived in Section 5.1.

$$\text{Light emission} = \frac{k_1 k_2 p}{k_2 + k_3 p}$$

$$= \frac{k_1 p}{1 + k_3/k_2 p}$$

$$= \frac{k_1 p}{1 + k_4 p}$$

$$= \frac{k_1 p}{1 + k_4 p}$$

where k_1 = excitation rate constant.

k_2 = luminescence rate constant.

k_3 = quenching collision rate constant.

k_4 = ratio of the probability

of de-excitation by quenching to that of luminescence.

This equation approximates to an equation of the following form, over a limited range of pressure, for any fractional value of $\underline{n}$.

Light emission = $k p^n$

For $n = \frac{1}{2}$ the approximation is valid within the experimental error of the results over about an eight-fold range of pressure. The range of pressure covered by the square root dependence found experimentally was from 0.1 mms. to 100 mms. Although at higher pressures measurements are less certain because of the increase in excitation density in the alpha-track, it would seem that the square root dependence persists up to pressures of 300 mms. A slight deviation from the square root dependence in the experimental points between 1 mm. and 10 mms. pressure had been ascribed to errors in measurement but now assumed a new significance. It was found that the sum of two self-quenching curves, with suitable constants gave a square root dependence over a considerable range, and reproduced the deviation from exact dependence which has been referred to. The sum of three

self-quenching curves was sufficient to give reasonable agreement with the experimental results over the range 0.1 mms. to 100 mms. The theoretical curve in Figure 21 was calculated from the following equation.

$$\text{Light emission} = \frac{16.7\,p}{1 + 2.8\,p} + \frac{0.7\,p}{1 + 0.025p} + \frac{0.4\,p}{1 + 0.01\,p} .$$

The first term corresponds to an emission for which the probability of excitation, and also the probability of quenching by collision is high, whether because of a high cross-section for a self-quenching collision, or because of a long life-time for emission of luminescence it cannot be said.

From this equation, the explanation follows for the very small quenching action of quenching gases at pressures below 1 mm. The species responsible for the light emission in this region is already strongly self-quenched, and any additional quenching due to oxygen or hydrogen is small in comparison. However, the self-quenching which occurs in the species emitting in the high pressure region is much less, and oxygen and hydrogen are obviously more effective quenchers for these species than is nitrogen.

The increase in light emission at high pressures when mercury vapour is present can also be explained. At low pressures the excited species would be self-quenched before transfer to mercury could occur if it was energetically possible. At high pressures the predominant excited species obviously can transfer their energy to mercury, and are not self-quenched to the same extent. The transfer of excitation takes place, giving a light

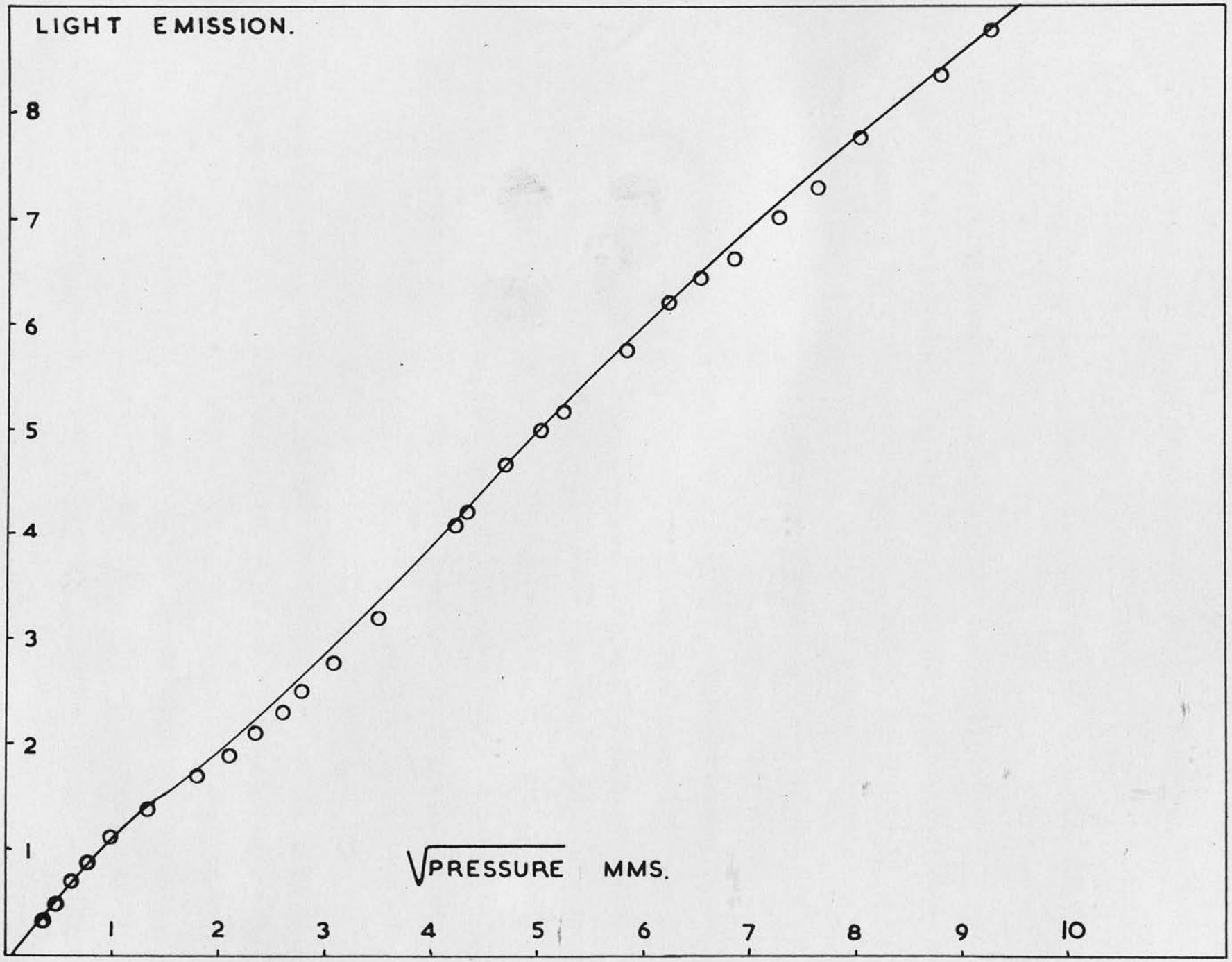

LIGHT EMISSION.
8
7
6
5
4
3
2
1
√PRESSURE MMS.
1
2
3
4
5
6
7
8
9
10

FIGURE 21.

Theoretical curve, calculated from the following equation, and experimental points for light emission from nitrogen

$$\text{Light emission} = \frac{16.7\,p}{1 + 2.8p} + \frac{0.7p}{1 + 0.025p} + \frac{0.4p}{1 + 0.01p}$$

emission proportional to the pressure instead of the self-quenching curve.

It can be seen that if the nitrogen were not pure the light emission from the excited species which emit at high pressures would be quenched and an apparently simple self-quenching curve would be obtained.

The quenching cross-sections of the gases used in the quenching experiments are difficult to measure in view of the number of emitting species which would all be quenched simultaneously but to different degrees. However in the range of pressure from 10 mms. to 100 mms. approximate values can be determined. The method used for the comparison of quenching cross-sections for excited carbon dioxide cannot be used as with nitrogen there is no region where the light emission is independent of the pressure, i.e. the luminescence decay constant cannot be neglected.

In Figure 22 have been plotted the curves for $P/_L$ against p which have been derived from Figure 20. (L = light emission, p = pressure). If the curve for light emission is subtracted, the curves of Figure 23 are obtained. The slopes of these curves are approximately proportional to the concentration of the quenchers.

For pure nitrogen,

$$L_o = \frac{k_1 p}{1 + k_4 p}$$

$$\therefore P/L_o = \frac{1}{k_1} + \frac{k_4}{k_1} p$$

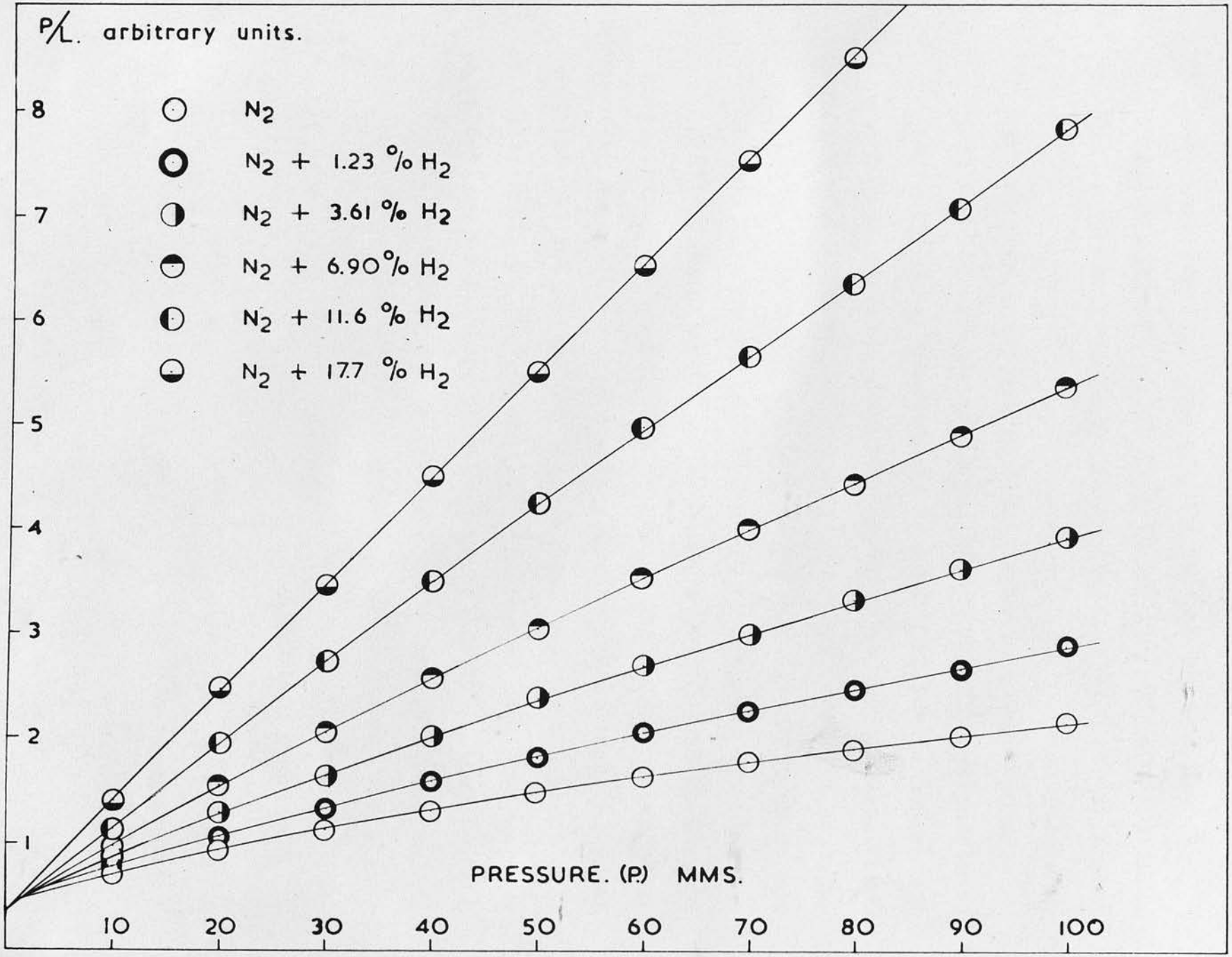

P/L. arbitrary units.
8
7
6
5
4
3
2
1
N2
N2 + 1.23 % H2
N2 + 3.61 % H2
N2 + 6.90 % H2
N2 + 11.6 % H2
N2 + 17.7 % H2
PRESSURE. (P.) MMS.
10
20
30
40
50
60
70
80
90
100

FIGURE 22.

Nitrogen P/L vs. p .

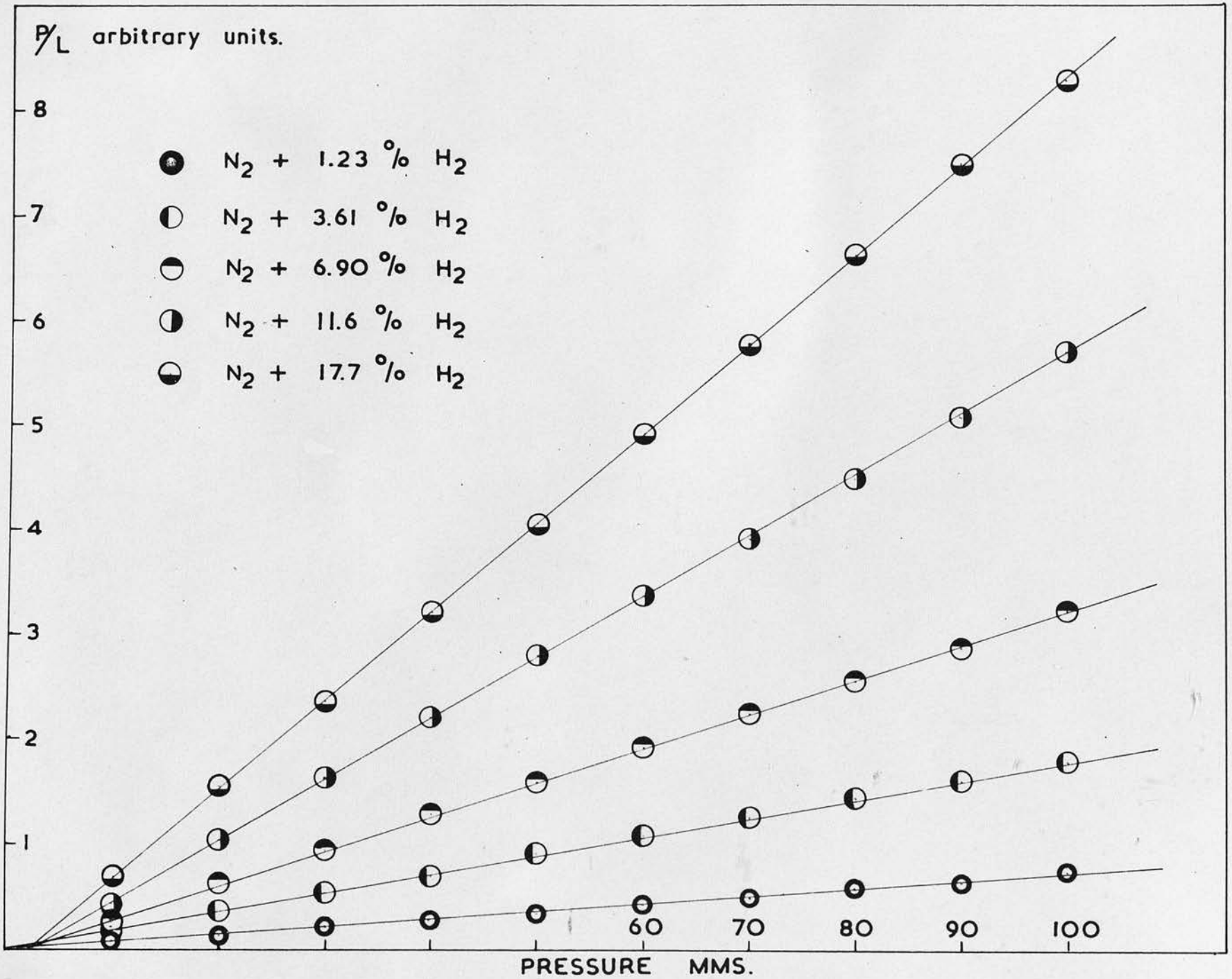

P/L arbitrary units.
8
7
6
5
4
3
2
1
N2 + 1.23 % H2
N2 + 3.61 % H2
N2 + 6.90 % H2
N2 + 11.6 % H2
N2 + 17.7 % H2
60
70
80
90
100
PRESSURE MMS.

FIGURE 23.

Nitrogen and hydrogen.

$(P/L - P/L_o)$ vs. p.

For nitrogen + quencher,

$$L = \frac{k_1 p(1 - a)}{1 + k_4 p + k_5 ap} .$$

k_5 is the ratio of the probability of collisional quenching by the quencher, to that of luminescence, and a is the fraction of quencher in the mixture.

$$P/L = \frac{1}{k_1(1 - a)} (1 + k_4 p + k_5 ap)$$

Subtract P/L_o from P/L

$$P/L - P/L_o = \frac{a}{(1 - a)k_1} (1 + k_4 p + k_5 p)$$

∴ The slope of the curve for $(P/L - P/L_o)$ plotted against p

$$= \frac{a}{(1 - a)k_1} (k_4 + k_5)$$

In the high pressure region concentrations of quencher of the order of 5% reduce the light emission to half. Therefore k_4 is of the order of 5% of k_5.

The values for the slope and for $\frac{k_4 + k_5}{k_1}$ derived from Figure 23 are given in Table III.

It is difficult to decide on a mean value for such results as there is obviously a progressive change in the values of $\frac{k_4 + k_5}{k_1}$.

TABLE III.

$a \times 10^2$	Slope (arbitrary units)	$\frac{k_4 + k_5}{k_1}$
1.23	14.5	1160
3.61	35.2	940
6.90	65.5	885
11.6	118.0	905
17.7	172.0	800

In order to compare the quenching efficiencies of a number of quenchers, the values given in Table IV, are the percentages of the quenchers in the mixture, required to reduce the light emission from nitrogen to one-half, at 80 mms. pressure.

TABLE IV.

Quencher	Half-value percentage at 80 mms. pressure.
H_2	4.9 %
O_2	6.9
CO_2	5.7
H_2O	5.4
C_2H_5OH	3.5
C_6H_6	3.1

7.5. Argon

The curves for light emission against pressure for pure argon resembled those for nitrogen. At 100 mms. pressure the light emission was about one-fifth of that from nitrogen and three times that from carbon dioxide. The measurements were less reproducible than those from other gases and variations up to 10% could be expected. Oxygen, carbon dioxide, and the vapours of water, alcohol, and benzene, quenched the light, and more effectively than they had quenched nitrogen light at similar pressures. When small percentages of the quenching gases were present the light emission increased with time. Nitrogen and hydrogen increased the light emission, and these measurements were reproducible. As a result of rather unsatisfactory measurements the following conclusions were reached.

1. The light emission did not correspond to simple self-quenching. This was not surprising as several excited levels exist in argon, and the metastable levels are sufficiently close to emitting levels for thermal collisions to produce transitions. The light emission approximated to a cube-root dependence on pressure.

2. The quenching was approximately proportional to the square of the concentration of the quencher.

3. At 70 mms. pressure hydrogen increased the light emission from argon by a factor of 2.1; nitrogen by a factor of 39.

The resonance lines for argon lie in the far ultra-violet. The visible light, if it is not due to impurities, is the result of intercombination transitions. The results shown in Figure 24 indicate that the light emission in the ultra-violet is much greater than that in the visible. If the detection efficiency for ultra-violet light is assumed to be $^1/_{15}$ of that for visible light (Section 6.3), the ratio of the ultra-violet emission to the visible emission at 70 mms. pressure is 51. Colli[103] gives a figure of 30 for this ratio in the pressure range 70 to 700 mms. It can be seen from Figure 24 that the ultra-violet emission is approximately proportional to the pressure at high pressures.

The quenching of argon resonance light would be expected to be high because of the "imprisonment" effect, which increases the effective lifetime for the emission. The studies of Molnar [104] and Phelps, and Colli indicate that the main de-excitation process in argon is by a three-body collision resulting in an excited A_2 molecule which emits at a wavelength which does not suffer resonance absorption.

In the system using alpha-particle excitation the appropriate equations for the reactions are as follows.

1. $A \xrightarrow{\alpha} A^x$ Excitation
2. $A^x \longrightarrow A + h\nu$ Resonance light
3. $A^x + A + A \longrightarrow A_2^x + A$
4. $A_2^x \longrightarrow A_2 + h\nu$

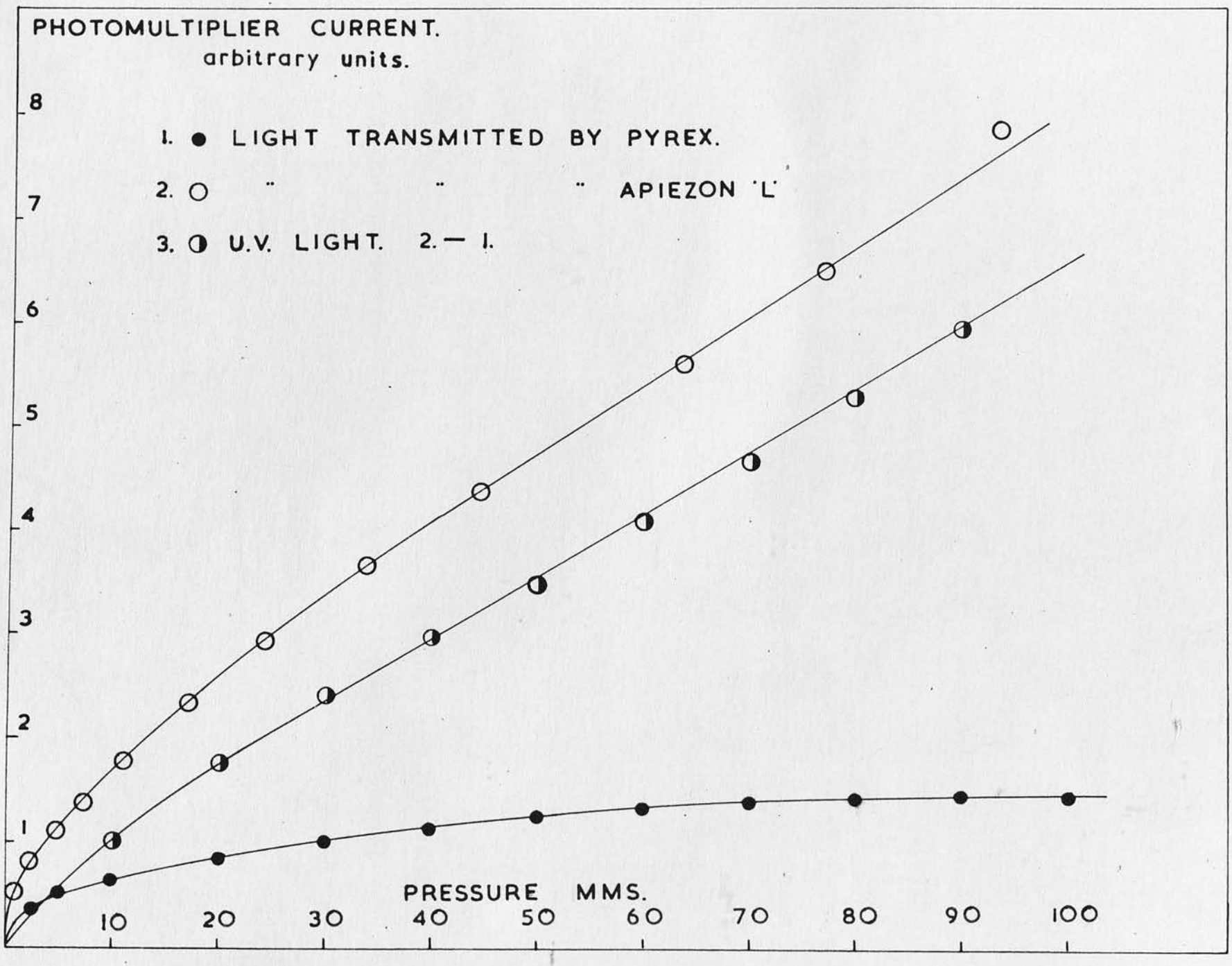

PHOTOMULTIPLIER CURRENT.
arbitrary units.
1. ● LIGHT TRANSMITTED BY PYREX.
2. ○ " " " APIEZON 'L'
3. ◑ U.V. LIGHT. 2. — 1.
8
7
6
5
4
3
2
1
PRESSURE MMS.
10
20
30
40
50
60
70
80
90
100

FIGURE 24.

Light emission from argon. The ultraviolet emission was calculated by subtracting the visible emission from the total light emission.

At steady state

$$[A^x] = \frac{k_1 p}{k_2 + k_3 p^2}$$

$$\therefore \text{ Visible light} = \frac{k_1 k_2 p}{k_2 + k_3 p^2}$$

$$k_4 [A_2^x] = k_3 [A^x][A]^2$$

$$\therefore \text{ Ultra-violet light} = \frac{k_1 k_3 p^3}{k_2 + k_3 p^2}$$

The measurements on the visible emission do not disagree with the above equation if, as is probable, a number of excited species contribute to the emission. At high pressures the ultra-violet emission would be proportional to the pressure, as has been found experimentally.

The measurements with mixtures of nitrogen and argon, and hydrogen and argon were reproducible. A selection of a large number of experimental curves is given in Figure 25. When the nitrogen concentration is increased beyond 1.4% the light emission at low pressures (less than 1 mm.) continues to increase, but falls below the curve for 1.4% nitrogen at higher pressures. On expanding the scales of Figure 25, the curves at low pressures were found to be concave upwards, as in Figure 11, for sensitized fluorescence. The light emission seems to involve a transfer of excitation from argon to nitrogen, and the nitrogen excitation is self-quenched at higher pressures. The transfer of energy would be collisional. Nitrogen is

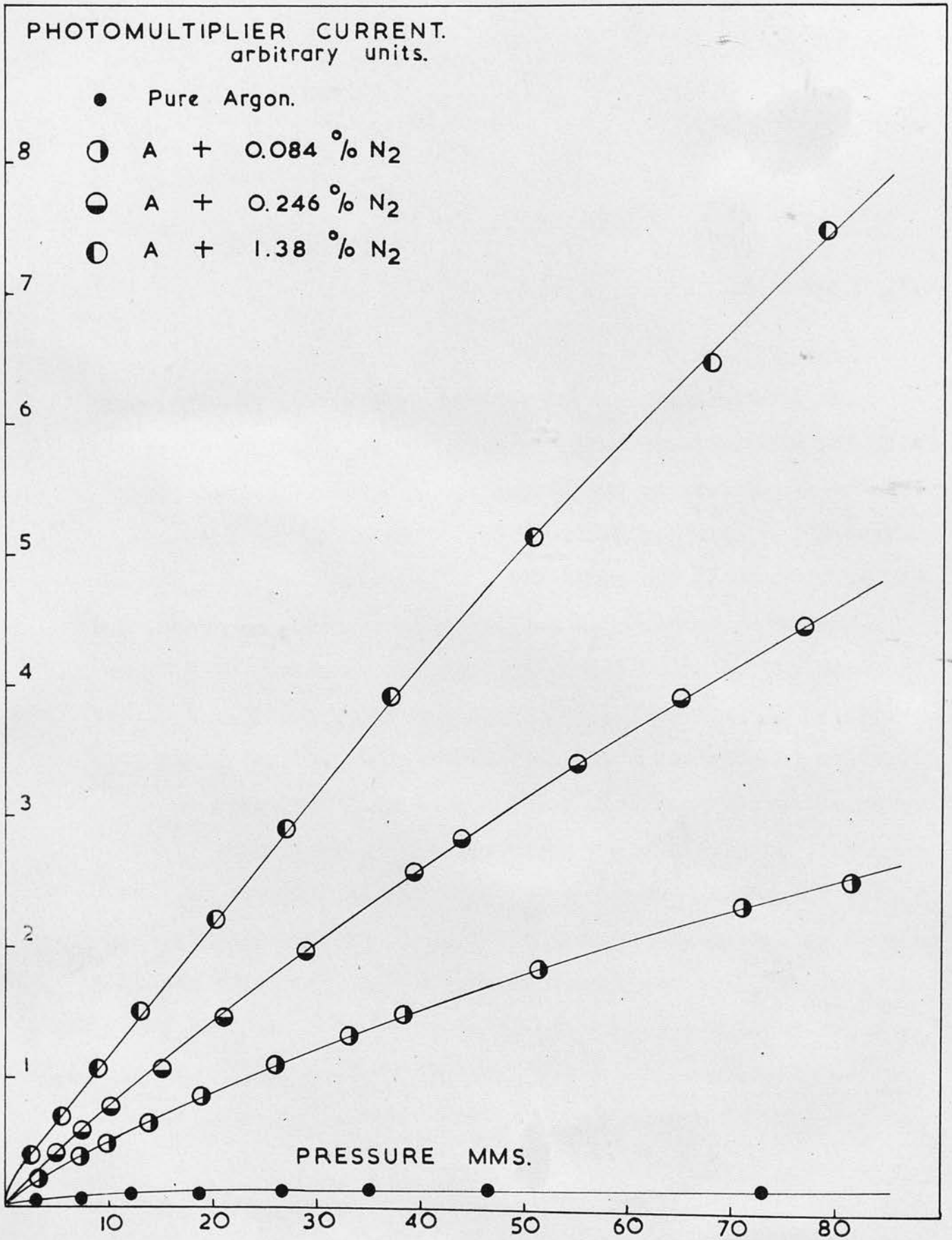

PHOTOMULTIPLIER CURRENT.
arbitrary units.
Pure Argon.
A + 0.084 % N_2
A + 0.246 % N_2
A + 1.38 % N_2
8
7
6
5
4
3
2
1
PRESSURE MMS.
10
20
30
40
50
60
70
80

FIGURE 25.

Light emission from argon and mixtures of argon and nitrogen.

transparent to ultra-violet light down to about 1000A, so a photon transfer process would be unlikely.

A cross-section of the curves of Figure 25 at a pressure of 70 mms. is shown in Figure 26. The curve is remarkably similar to those obtained from fluorescent solutions, such as terphenyl in xylene. The maximum light emission at this pressure occurs at a nitrogen concentration of 0.014. The light emission at the maximum of the curve is greater than that from argon at the same pressure by a factor of 39. The agreement with the value of 51 for the ratio of ultra-violet to visible emission at the same pressure is significant. At lower pressures the concentration of nitrogen producing maximum light emission increases.

For mixtures of argon and hydrogen, the maximum occurs for a hydrogen concentration of 0.006 at 70 mms. pressure. The light emission at the maximum is greater than that from pure argon by a factor of 2.1.

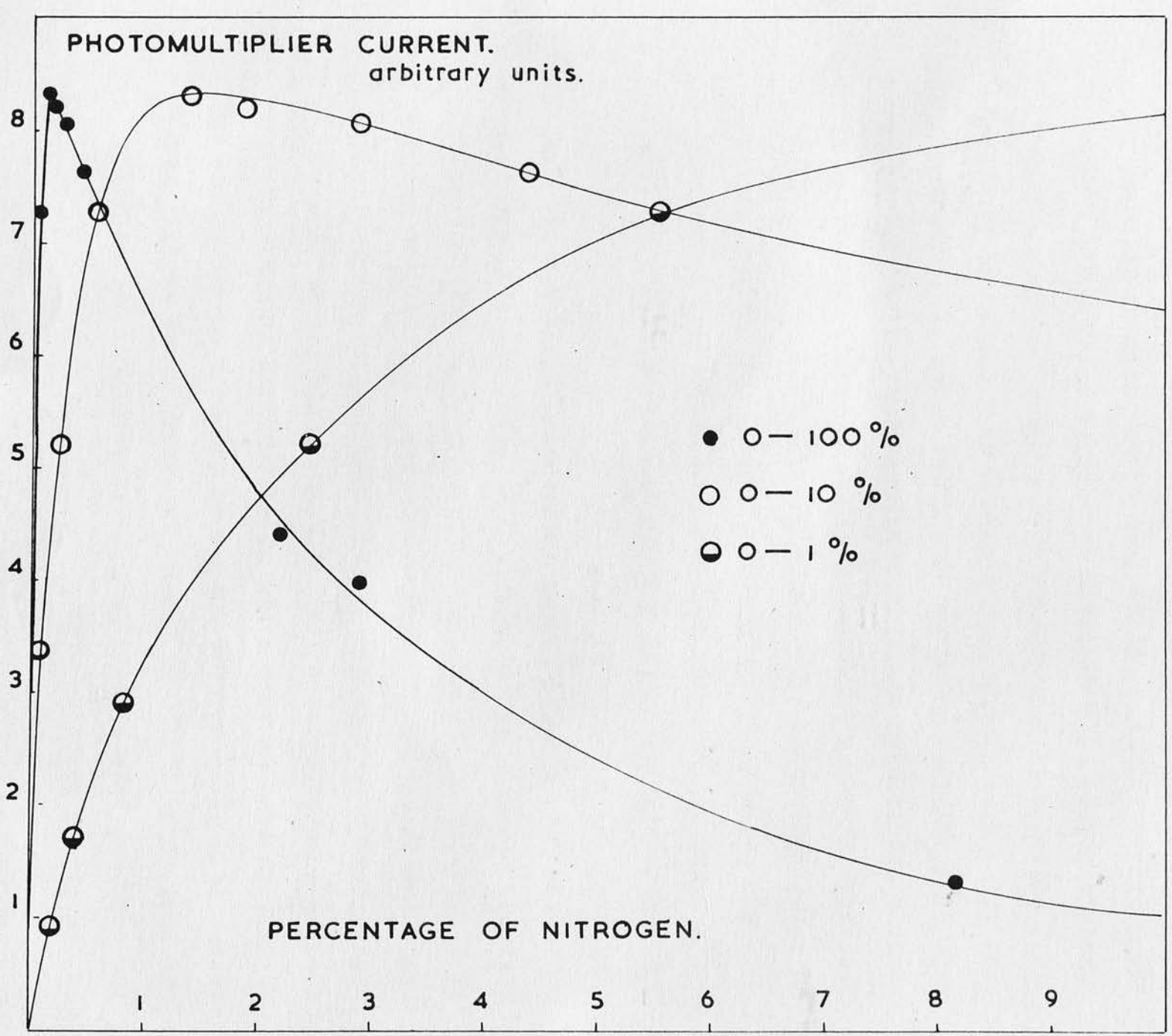
Grün and Schopper[78] have published a similar curve for mixtures of argon and nitrogen. The light emission was increased at a pressure of 585 mms. by a factor of 10. They suggest a mechanism to explain their measurements, by which the greater cross-section of nitrogen for excitation by secondary electrons, results in excitation of the nitrogen rather than the argon.

It is thought that a simple collisional transfer of energy from argon to nitrogen is more likely, particularly as the excitation levels of argon correspond approximately with the $C^3\pi$ levels of nitrogen, responsible for the emission of the second positive group.

FIGURE 26.

Light emission at 70 mms. pressure

from mixtures of argon and nitrogen.


PHOTOMULTIPLIER CURRENT.
arbitrary units.
8
7
6
5
4
3
2
1
● O — 100 %
○ O — 10 %
◒ O — 1 %
PERCENTAGE OF NITROGEN.
1
2
3
4
5
6
7
8
9

The probable mechanism for the transfer is as follows.

1.	A	$\xrightarrow{\alpha}$	A^*	Excitation
2.	A^*	$\longrightarrow$	$A + h\nu$	Luminescence of argon
3.	$A^* + N_2$	$\longrightarrow$	$A + N_2^*$	Collisional transfer
4.	N_2^*	$\longrightarrow$	$N_2 + h\nu$	Luminescence of nitrogen
5.	$N_2^* + N_2$	$\longrightarrow$	$2N_2$	Self-quenching of nitrogen

$$\therefore \text{ Nitrogen light } = \frac{k_1 k_3 [A] [N_2]}{(k_2 + k_3[N_2])(k_4 + k_5 [N_2])}$$

At low nitrogen concentrations, i.e. on the rising part of the curve in Figure 26, it is obvious that the self-quenching factor is small

$$\therefore \quad k_4 \gg k_5 [N_2]$$

$$\therefore \text{ Light emission (L) } = \frac{k_1 k_3 [A][N_2]}{(k_2 + k_3 [N_2])\, k_4}$$

$$[A] \simeq p$$

$$[N_2] = ap$$

$$\therefore \quad L = \frac{k_1 k_3 p^2 a}{k_2 k_4 + k_3 k_4 ap}$$

Plot a/L against a for the rising part of the curve for $p = 70$ mms. (Figure 26)

$$\text{Intercept} = \frac{k_2 k_4}{k_1 k_3 p^2} = 4.8 \times 10^{-5}$$

$$\text{Slope} = \frac{k_4}{k_1 p} = 2.64 \times 10^{-2}$$

$$\therefore \quad \frac{k_2 k_4}{k_1 k_3} = 0.235$$

$$\text{and} \quad \frac{k_4}{k_1} = 1.85$$

$$\therefore \quad \frac{k_2}{k_3} = 0.127$$

i.e. the ratio of the luminescence to the quenching collision constant for argon. Cf. Carbon dioxide.

On the falling part of the curve of Figure 26, the transfer of excitation from argon to nitrogen is obviously complete.

$$\therefore \quad k_2 \ll k_3 [N_2]$$

$$\therefore \quad \text{Light emission (L)} = \frac{k_1 [A]}{k_4 + k_5 [N_2]}$$

$$[A] + [N_2] = p$$

$$\therefore \quad L = \frac{k_1 (1 - a) p}{k_4 + k_5 ap}$$

Plot $\frac{1 - a}{L}$ against a after correcting for the contribution to the light emission by directly excited nitrogen

$$\text{Intercept} = \frac{k_4}{k_1 p} = 2.75 \times 10^{-2}$$

$$\text{Slope} = \frac{k_5}{k_1} = 10.5$$

$$\therefore \quad \frac{k_4}{k_1} = 1.93$$

and $$\frac{k_4}{k_5} = 0.180 \ .$$

i.e. the ratio of the luminescence to the self-quenching constants for nitrogen.

This value can be compared with the ratio of $\frac{1}{2.8}$ or 0.36 which was used in the theoretical curve for self-quenching of the most strongly quenched component of the nitrogen light (Section 7.4, Figure 21).

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