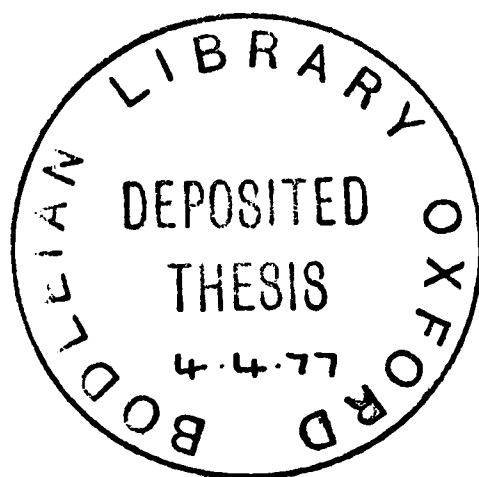


STUDIES OF REACTIONS RELEVANT TO
ATMOSPHERIC PHOTOCHEMISTRY

A thesis submitted in partial fulfillment
of the requirements of the degree of
Doctor of Philosophy

by

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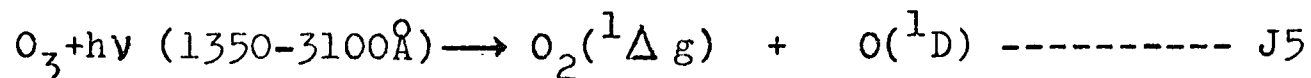
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Abstract.

I N T R O D U C T I O N.

This thesis describes the design, construction and use of a fast-flow system to study reactions of $O(^1D)$ atomic oxygen, generated by the ultraviolet photolysis of ozone.



Mass spectrometric detection of ozone and other species is employed.

$O(^1D)$ is the most important electronically excited species present in the stratosphere. It is responsible for the generation of catalytic species which to a large extent determine the atmospheric ozone concentration.

The experimental work is concerned with three problems of atmospheric significance. Chapter 5 deals with the efficiency of energy transfer from $O(^1D)$ to ground state molecular oxygen. Chapter 6 involves an investigation into the mechanism of the water catalyzed photodecomposition of ozone. Chapter 7 describes experiments done on the mechanism, products and possible stratospheric importance of the reaction of $O(^1D)$ atoms with chlorine containing halocarbons (freons).

C H A P T E R 1.

1, 1. THE ATMOSPHERE.

Ozone is an exceedingly important minor atmospheric constituent. It has played a major role in the evolution and propagation of terrestrial life on earth. By absorbing solar radiation in the $2400\text{\AA}$ - $3100\text{\AA}$ wavelength region, ozone shields the earth's surface from biologically harmful near ultra-violet light. The importance of ozone was first recognised in 1930 by Chapman, who, in the absence of precise data, identified the major sources and sinks of ozone in the atmosphere.

In this first chapter a brief introduction to the atmosphere will be presented so as to establish a context within which the particular properties of the stratosphere - the predominant ozone containing region of the atmosphere - may be examined. So as not to provide an unbalanced picture of the overall chemistry of the stratosphere by now considering in detail the backgrounds to the particular aspects of ozone photochemistry which are investigated in this thesis, these backgrounds are presented more fully in the introductions to Chapters 5, 6 and 7.

Figure 1, 1 represents the regions into which the atmosphere is normally divided. It was formerly believed that the temperature of the atmosphere fell monotonically with increasing distance from the earth's surface. The first hints that there might be a second high temperature layer (the stratosphere) were obtained from discrepancies in the density of air calculated from the slowing down of meteorites entering the upper atmosphere. Recent rocket and high level balloon measurements have confirmed that this and other regions of increasing temperature exist. The nomenclature of the atmosphere represents,

Figure 1.1 Atmosphere

Dobson, 1968

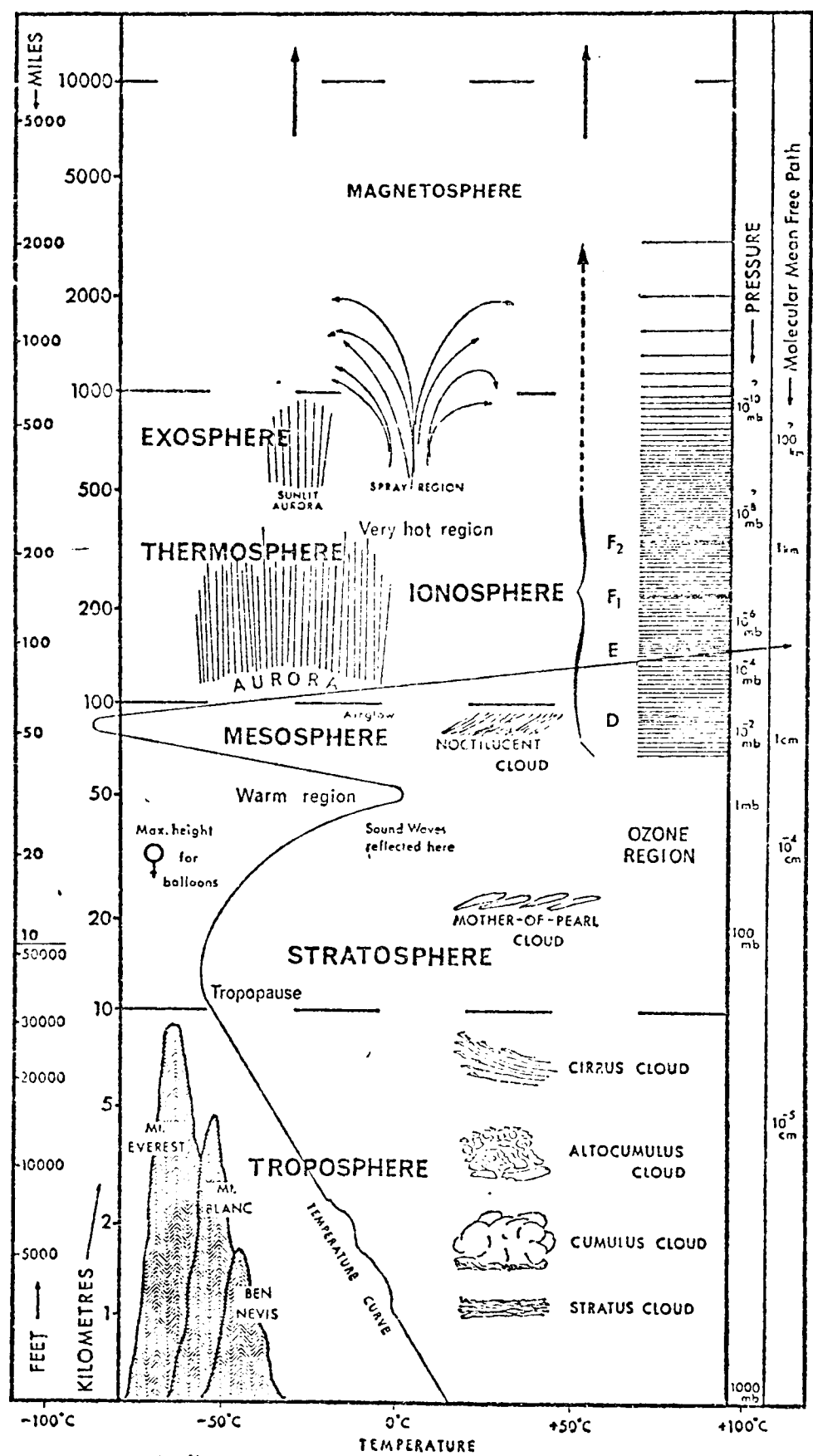


TABLE 1.1. Proportions of Gases in the Atmosphere

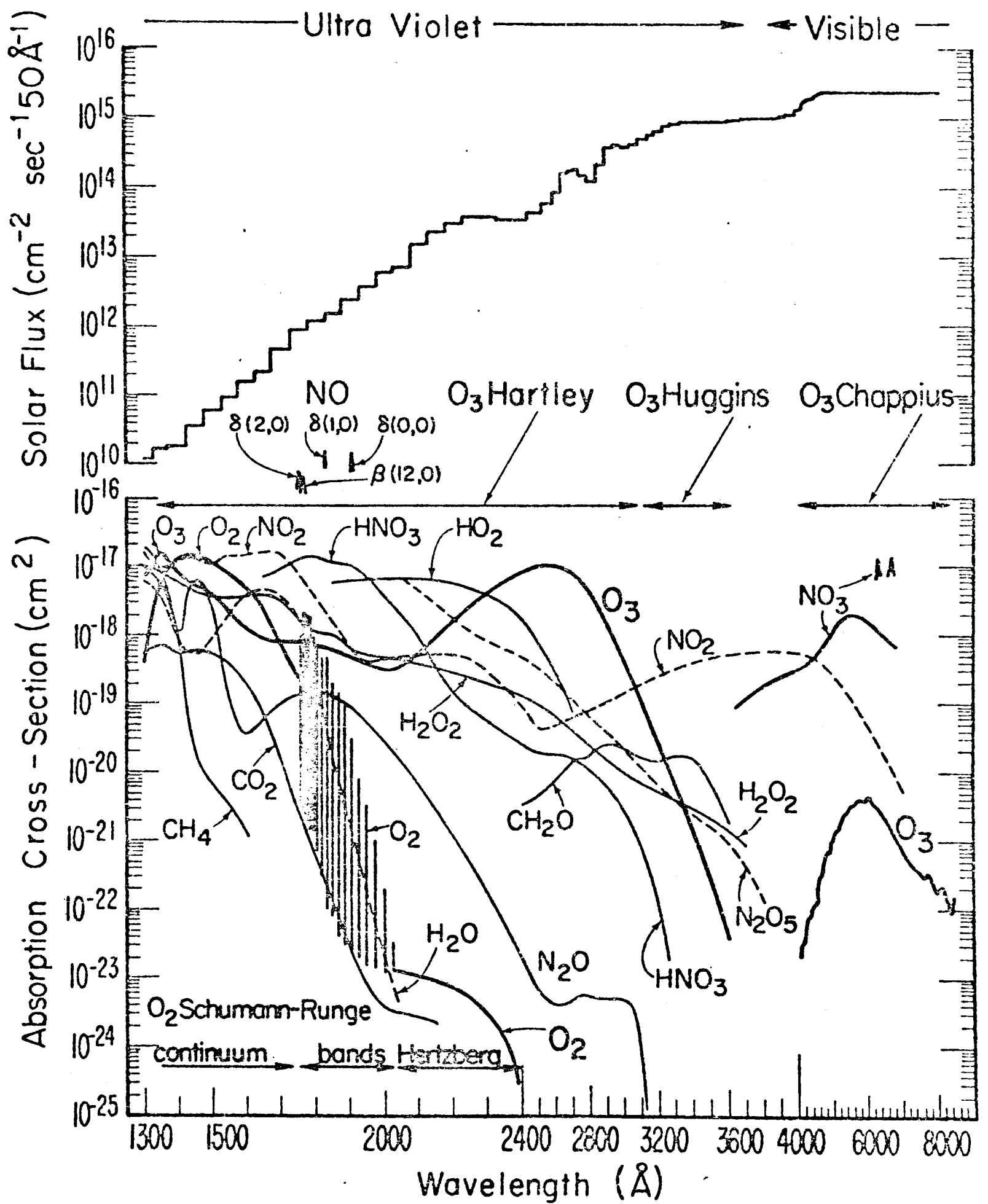
Gas	Proportion by volume		Relative thickness
Total	100	per cent	8.0 km
Nitrogen	78.1	per cent	6.25 km
Oxygen	20.9	per cent	1.68 km
Argon	0.9	per cent	74 m
Carbon dioxide	0.033	per cent	2.6 m
Neon	18	parts per million	15 cm
Helium	5	parts per million	4 cm
Methane	2	parts per million	1.6 cm
Krypton + xenon	1	part per million	8 mm
Hydrogen	0.5	part per million	4 mm
Nitrous oxide	0.5	part per million	4 mm

in part, these different temperature zones. Although the general temperature profile is qualitatively constant, the amplitude and heights of the various temperature regions vary greatly from day to day and depend strongly on the latitude, the season and the weather conditions.

Heating of the atmosphere occurs largely by the absorption of short wavelength radiation coming from the sun. Some atmospheric heating is also caused by the absorption of long wavelength radiation emitted from the earth's surface. This leads to the so-called "greenhouse effect". Figure 1,2 shows the flux of solar radiation (which has its maximum intensity in the "visible" region), that is incident on the earth's upper atmosphere. The temperature of the upper atmosphere (the exosphere) remains constant ^{with height} above around 200-300km (the top of the thermosphere) at a value which varies between about 400°C and 2000°C. The actual temperature depends not only on the season and time of day, but also on the eleven year sun-spot cycle. This demonstrates that the heating has two sources i.e. corpuscular radiation from the sun, and very short wavelength solar ultra-violet radiation.

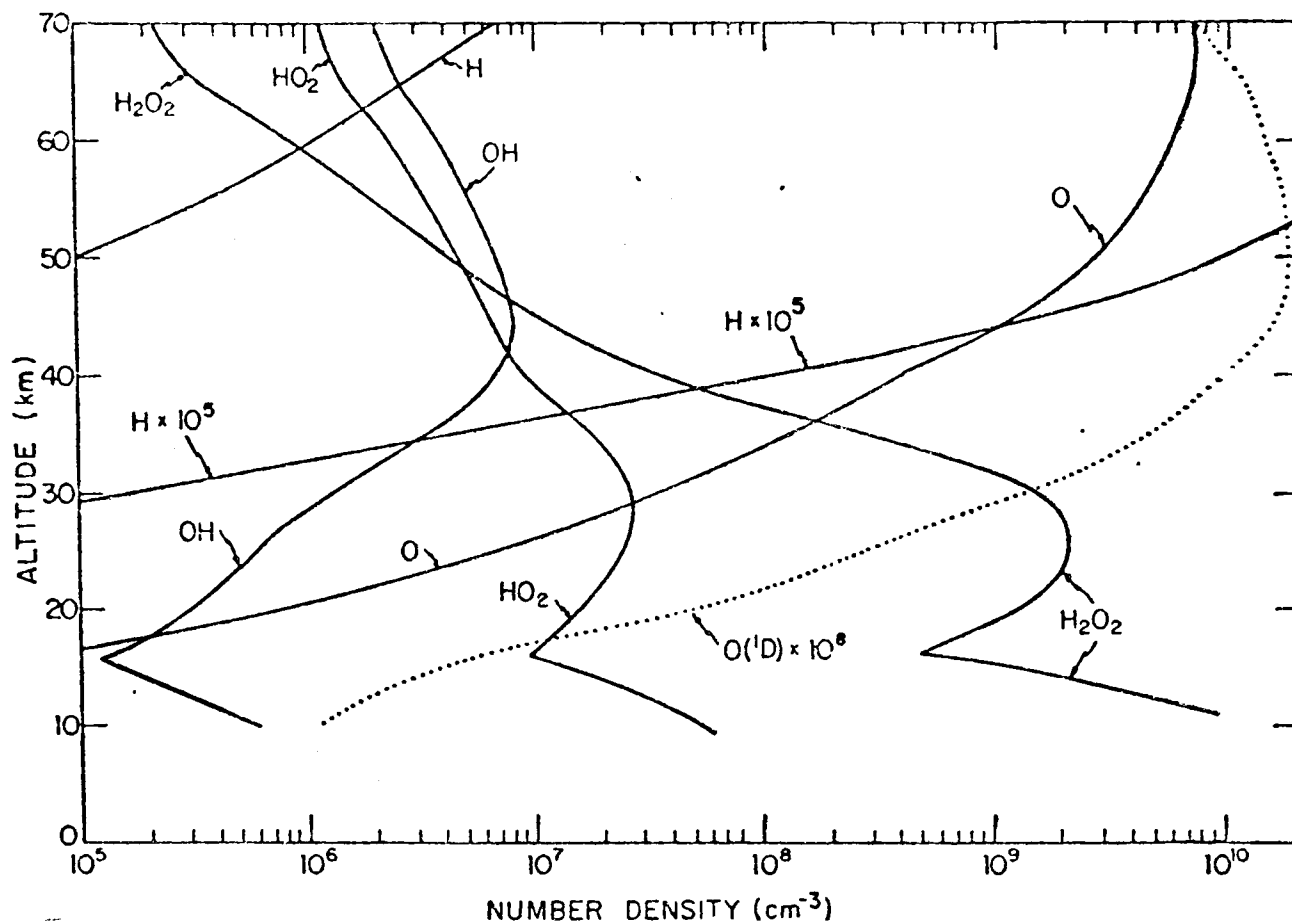
The presence of even small amounts of oxygen in the thermosphere is capable of removing all solar radiation of wavelengths less than about 1800Å by absorption in the Schumann-Runge region (as shown in the lower part of fig 1,2). Absorption in the Schumann-Runge continuum leads to the photodissociation of molecular oxygen into oxygen atoms. Atomic Oxygen is one of the predominant species in the thermosphere and the mesosphere with a calculated maximum concentration at around 70 km (according to the model of McElroy et al. 1974, shown in Fig, 1,3). This region of the

Figure 1,2

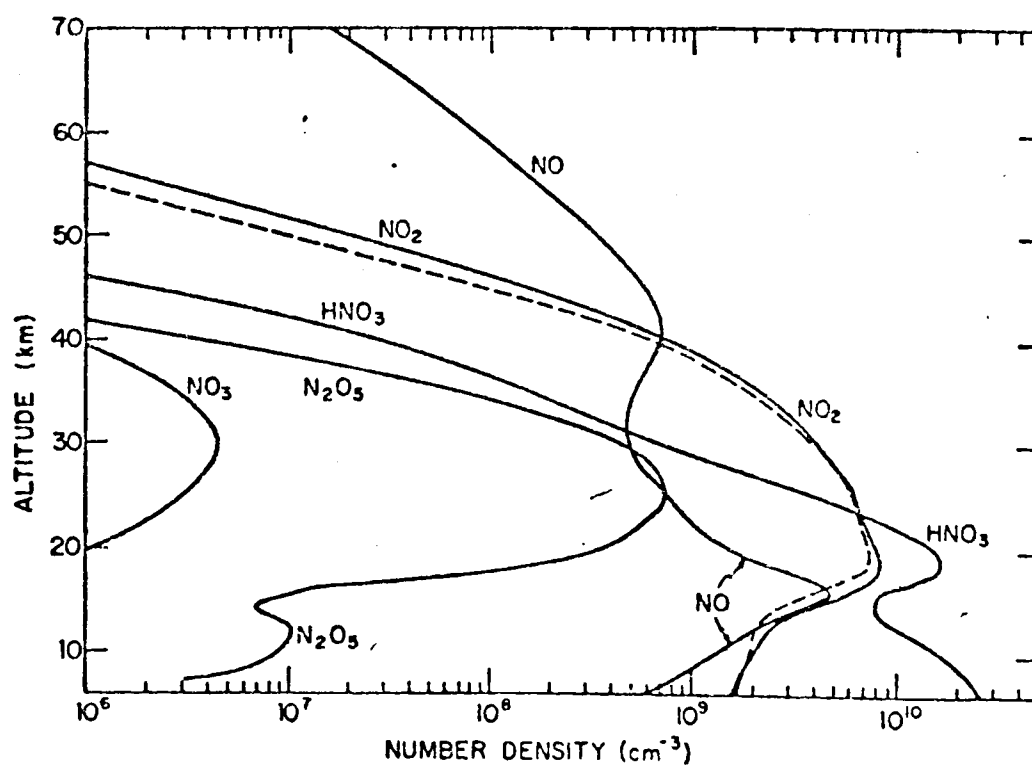


Solar radiation flux and absorption cross-section spectrum for every 50 Å.

Figure 1,3



Calculated number densities (24-hr average) for hydrogenous radicals, H_2O_2 , $\text{O}(^3\text{P})$ and $\text{O}(^1\text{D})$ for the normal atmosphere, 30N latitude, solar declination $+12^\circ$. The tropopause is at 16 km.



Calculated vertical distributions of individual NO_x constituents in the normal atmosphere, 30N latitude, solar declination $+12^\circ$. The dashed curve shows NO_2 .

atmosphere, above around 80km, is also known as the ionosphere due to the presence of ionised species. The concentration of ions and electrons is always very much smaller than the number of neutral atoms and molecules at the same level (even up to 1000 km). A plot of number of electrons per cm^3 versus height shows four maxima, with ^a daytime maximum concentrations at 300 km of around $10^5 - 10^6$ electrons cm^{-3} . In order of increasing height these are labelled the D, E, F₁ and F₂ regions. Reflection of radio waves occurs principally from the E and F regions. Because of the relatively short mean free path of electrons in the higher pressure D region medium-wave radio waves are absorbed. However, nighttime electron depletion of the D region allows them to be reflected from the E region. This is why "interference" from foreign medium-wave stations is greatest after sunset.

The region around 100km is also that at which most aurorae occur. Since aurorae occur in high latitude belts centred on the two magnetic poles they are believed to be caused by the absorption of streams of charged particles shot out from the sun, particularly during solar flares. A principal feature of auroral emission spectra is the "auroral green" line which arises from the $^1\text{S} - ^1\text{D}$ electronic transition of atomic oxygen.

A slight digression here will be useful in order to clarify the different methods of expressing the variation of concentrations of atmospheric species with height. One can, of course, express the concentration as a simple number density (molecules cm^{-3}). However, due to the exponential decrease of pressure with height it is usually more informative to use a so called mixing-ratio. The number mixing-ratio is defined as the ratio of the number of molecules of that species to the total number

of molecules present (in a small height increment) at a given height. One can also define a volume mixing-ratio in the same way. An alternative way of measuring concentrations of atmospheric constituents is to express them as the thickness of a uniform layer of the gas at STP spread over the earth's surface. This method is particularly useful for expressing the vertically integrated concentrations of most atmospheric constituents; principally those which do not show appreciable variations in mixing-ratio with height (as shown in Fig. 1,1.). Ground based measurements of ozone concentrations have been made mostly by the Dobson method which measures the overall atmospheric absorption of solar radiation at a given pair of wavelengths related to the ozone absorption. Thus most of the meteorological data on the long term and geographical variations of the ozone concentration are expressed as cm. at STP. Typical ozone thicknesses vary between 0.2 and 0.4 cm.

Oxygen in the thermosphere causes almost complete absorption of solar radiation of wavelength less than $1800\text{\AA}$. Consequently there is little solar heating^{by oxygen} in the region below the thermosphere called the mesosphere. However, absorption of radiation by oxygen in the weak Herzberg region ($2000\text{\AA}$ - $2400\text{\AA}$) yields oxygen atoms. The increasing pressure with decreasing height in the atmosphere leads to a very rapid increase in the rate of the three body reaction of O atoms with O_2 , leading to a peak production of ozone around 50km. The strong absorption by ozone in the Hartley band ($2000\text{\AA}$ - $3000\text{\AA}$) produces a second high temperature region called the stratosphere. Ozone is the only gas present in the atmosphere in large enough amounts to effectively shield the earth's surface from

biologically harmful near ultraviolet radiation. Some heating of the stratosphere may also be due to absorption by ozone of infra-red radiation in the 95,000Å region from the earth's surface.

The so-called temperature-inversion (a layer of warm air above cold air) present in the stratosphere makes it a dynamically stable region of the atmosphere. In the troposphere, however, the presence of colder air above warm air (heated from the earth's surface) leads to widespread convection currents. Hot air rises above the equator, ^{cools} and sinks towards the poles. The humidity of the stratosphere is very low and few clouds are formed there. The troposphere is a region of high humidity and as shown in Fig. 1,1 almost all cloud originates from below the tropopause. The chemistry of the troposphere is dominated by the oxidation of methane and of nitrogen oxides by OH radicals which derive largely from the reaction of O(¹D) (from the photolysis of ozone present at higher altitudes) with water vapour. Figure 1,4 shows a summary of important tropospheric reactions and some calculated number densities (H. Levy, II,1972).

1,2 THE STRATOSPHERE.

In order to explain the increased temperature of the stratosphere Chapman (1930) proposed a series of reactions to maintain a steady state ozone concentration, based on the reactions of O atoms and O₂.

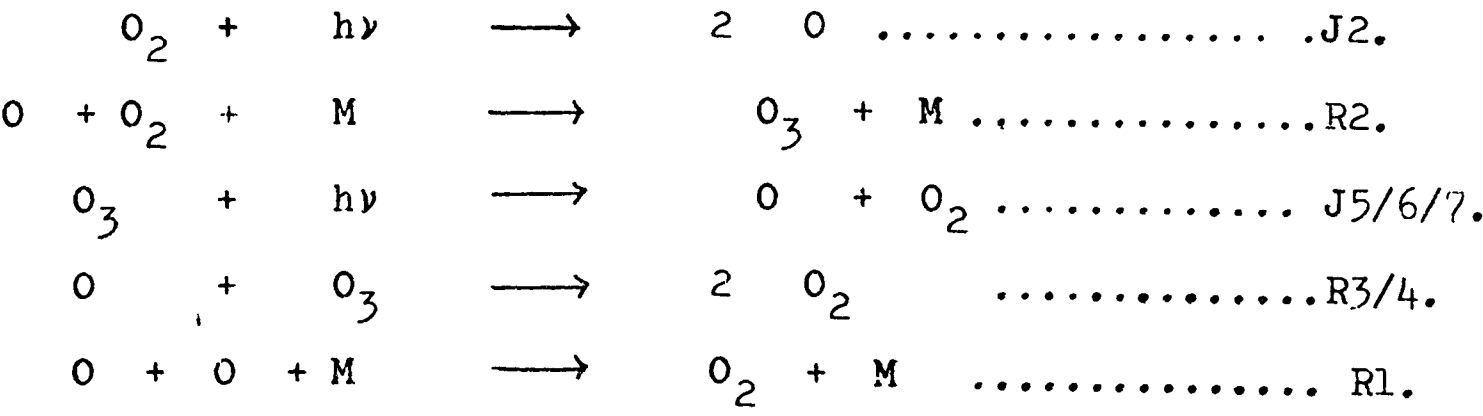
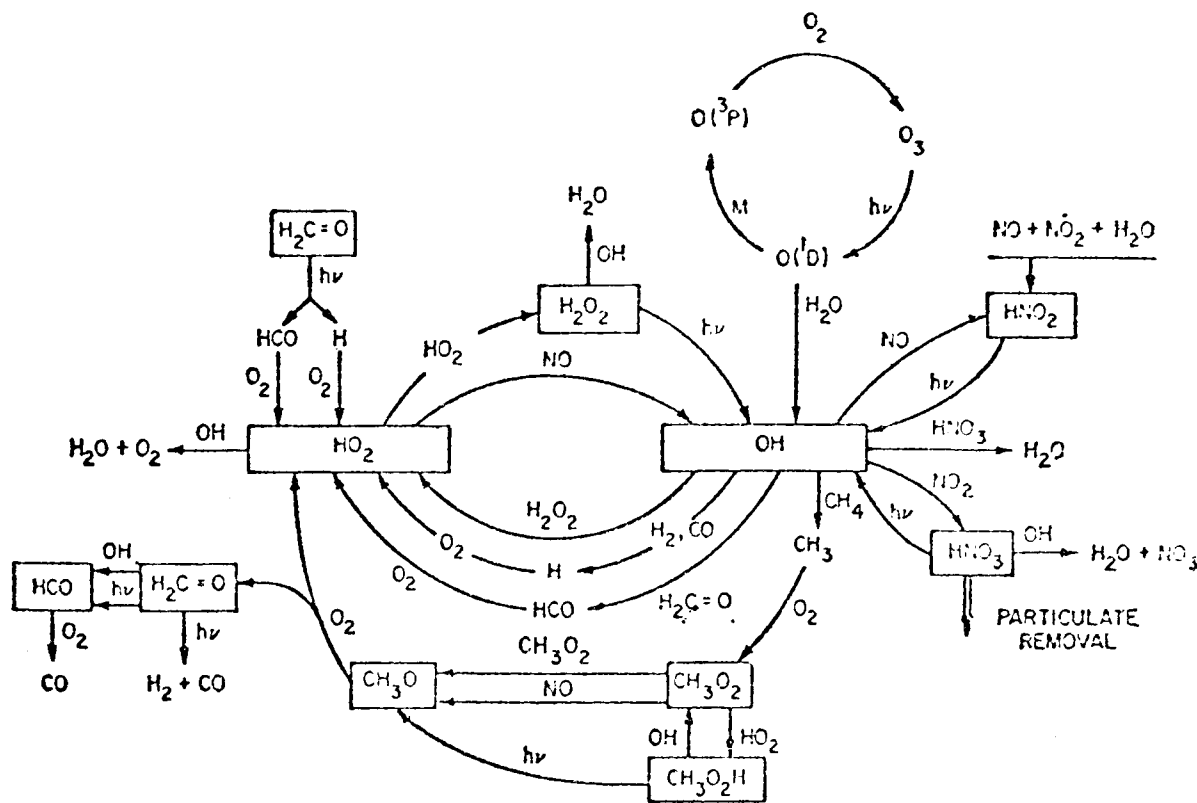


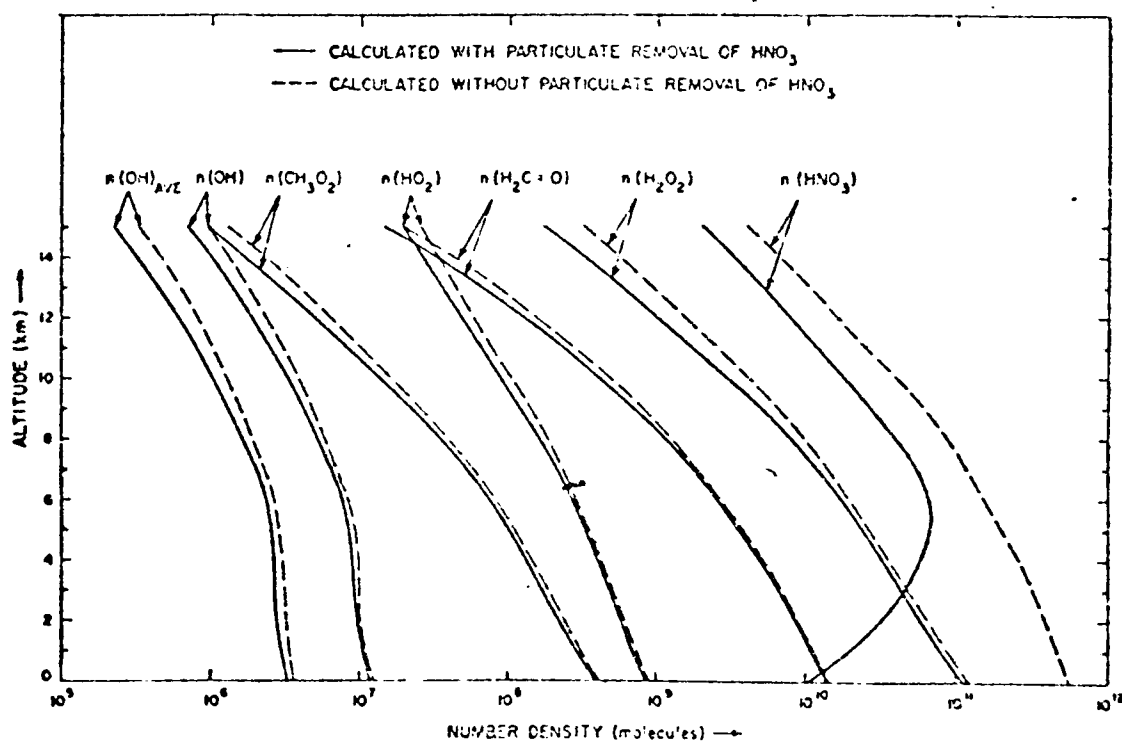
Figure 1,4 Troposphere

Levy, 1972

PHOTOCHEMISTRY OF MINOR CONSTITUENTS IN THE TROPOSPHERE



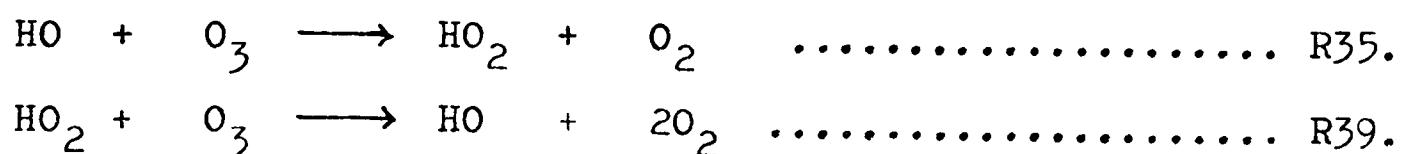
TROPOSPHERIC PHOTOCHEMISTRY.



NOONTIME ALTITUDE PROFILES OF NUMBER DENSITIES.

(Photodissociation processes and chemical reaction rates are numbered as in Tables 1 and 2. (from Shimazaki and Ogawa, 1974)). Ground based measurements of total ozone concentration have been made both at Oxford and at Arosa (47°N and 10°E) since 1926 (Goldsmith et al., 1973). Only more recently, however, has data on the relevant rate constants become available. Measurements of the rate of reaction of oxygen atoms with ozone showed that it was too slow to account for the low ozone concentrations actually observed. Additional reaction mechanisms were invoked to explain the lower than expected stratospheric ozone concentrations. All the schemes involve chain decomposition processes. Bates and Nicolet (1950) pointed out the possible importance of hydrogen-oxygen (HO_x) compounds such as H₂O, H, HO, and HO₂ in the upper stratosphere and mesosphere. Evidence that HO radicals were produced by the reaction of O(¹D) with water was obtained by McGrath and Norrish (1960) in the flash photolysis of wet ozone. It had been known since 1934 from the work of Heidt and Forbes that the addition of water caused the quantum yield for the static photolysis of ozone to rise considerably above the value of around six found for pure dry ozone.

Norrish and coworkers suggested that the chain decomposition of ozone could proceed via the reactions



The early observation by Kistiakowsky (1925) that the quantum yield for ozone decomposition by red light was unaffected by the presence of water vapour, ^{taken with} ~~the~~ later evidence, indicated that HO was generated by the reaction of O(¹D) atoms (only

Table I,1 Photodissociation processes

J1	$\text{O}_2 + h\nu$	$(1350-1750 \text{ \AA}) \rightarrow \text{O} + \text{O} (^1\text{D})$
J2	$\text{O}_2 + h\nu$	$(1750-2050 \text{ \AA}) \rightarrow \text{O} + \text{O}$
J3	$\text{O}_2 + h\nu$	$(2050-2200 \text{ \AA}) \rightarrow \text{O} + \text{O}$
J4	$\text{O}_2 + h\nu$	$(1216 \text{ \AA}) \rightarrow \text{O} + \text{O} (^1\text{D})$
J5	$\text{O}_3 + h\nu$	$(1350-3100 \text{ \AA}) \rightarrow \text{O}_2 (^1\Delta_g) + \text{O} (^1\text{D})$
J6	$\text{O}_3 + h\nu$	$(3100-3600 \text{ \AA}) \rightarrow \text{O}_2 (^1\Delta_g) + \text{O}$ $\rightarrow \text{O}_2 + \text{O} (^1\text{D})$
J7	$\text{O}_3 + h\nu$	$(4050-8500 \text{ \AA}) \rightarrow \text{O}_2 + \text{O}$
J8	$\text{H}_2\text{O} + h\nu$	$(1350-2000 \text{ \AA}) \rightarrow \text{OH} + \text{H}$
J9	$\text{H}_2\text{O} + h\nu$	$(1216 \text{ \AA}) \rightarrow \text{OH} + \text{H}$
J10	$\text{N}_2\text{O} + h\nu$	$(1350-3150 \text{ \AA}) \rightarrow \text{N}_2 + \text{O} (^1\text{D})$
J11	$\text{N}_2\text{O} + h\nu$	$(1350-2500 \text{ \AA}) \rightarrow \text{NO} + \text{N}$
J12	$\text{N}_2\text{O}_5 + h\nu$	$(2050-3800 \text{ \AA}) \rightarrow 2 \text{NO}_2 + \text{O}$ $\rightarrow \text{NO}_2 + \text{NO}_3$
J13	$\text{NO}_3 + h\nu$	$(5000-7000 \text{ \AA}) \rightarrow \text{NO} + \text{O}_2$ $(< 5760 \text{ \AA}) \rightarrow \text{NO}_2 + \text{O}$
J14	$\text{HNO}_3 + h\nu$	$(1650-2400 \text{ \AA}) \rightarrow \text{H} + \text{NO}_3$
J15	$\text{HNO}_3 + h\nu$	$(2400-3250 \text{ \AA}) \rightarrow \text{OH} + \text{NO}_2$
J16	$\text{NO} + h\nu$	$(\beta \text{ and } \delta \text{ bands}) \rightarrow \text{N} + \text{O}$
J17	$\text{NO}_2 + h\nu$	$(2450-3950 \text{ \AA}) \rightarrow \text{NO} + \text{O}$
J18	$\text{NO}_2 + h\nu$	$(1350-2450 \text{ \AA}) \rightarrow \text{NO} + \text{O} (^1\text{D})$
J19	$\text{HO}_2 + h\nu$	$(1850-2700 \text{ \AA}) \rightarrow \text{OH} + \text{O}$
J20	$\text{H}_2\text{O}_2 + h\nu$	$(1350-3700 \text{ \AA}) \rightarrow \text{OH} + \text{OH}$
J21	$\text{CH}_4 + h\nu$	$(1350-1600 \text{ \AA}) \rightarrow \text{CH}_3 + \text{H}$
J22	$\text{CH}_4 + h\nu$	$(1216 \text{ \AA}) \rightarrow \text{CH}_3 + \text{H}$
J23	$\text{CH}_2\text{O} + h\nu$	$(2400-3600 \text{ \AA}) \rightarrow \text{CHO} + \text{H}$
J24	$\text{CH}_2\text{O} + h\nu$	$(2750-3600 \text{ \AA}) \rightarrow \text{H}_2 + \text{CO}$
J25	$\text{CO}_2 + h\nu$	$(1350-2150 \text{ \AA}) \rightarrow \text{CO} + \text{O}$
J26	$\text{CO}_2 + h\nu$	$(1216 \text{ \AA}) \rightarrow \text{CO} + \text{O}$

Table 1,2 Reactions

Reactions	Rate Constant
R1 $O + O + M \rightarrow O_2 + M$	$2.8 \times 10^{-34} \exp(710/T)$
R2 $O + O_2 + M \rightarrow O_3 + M$	* $1.1 \times 10^{-34} \exp(510/T)$
R3 $O + O_3 \rightarrow 2 O_2$	* $1.9 \times 10^{-11} \exp(-2300/T)$
R4 $O(^1D) + O_3 \rightarrow 2 O_2$ $\rightarrow O_2 + 2 O$	2.5×10^{-10}
R5 $O(^1D) + N_2 \rightarrow O + N_2$	5×10^{-11}
R6 $O(^1D) + O_2 \rightarrow O + O_2$	6×10^{-11}
R7 $O_2(^1\Delta_g) + N_2 \rightarrow O_2 + N_2$	$< 1.1 \times 10^{-19}$
R8 $O_2(^1\Delta_g) + O_2 \rightarrow O_2 + O_2$	2.4×10^{-18}
R9 $O_2(^1\Delta_g) + O \rightarrow O_2 + O$	$< 1.3 \times 10^{-16}$
R10 $O_2(^1\Delta_g) + O_3 \rightarrow 2O_2 + O$	$6 \times 10^{-11} \exp(-2900/T)$
R11 $O_2(^1\Delta_g) \rightarrow O_2 + h\nu$	2.6×10^{-4}
R12 $H_2O + O(^1D) \rightarrow 2 OH$	* 3×10^{-10}
R13 $N_2O + O(^1D) \rightarrow 2 NO$	* 1.0×10^{-10}
R14 $N_2O + O(^1D) \rightarrow N_2 + O_2$	* 1.0×10^{-10}
R15 $N_2O_5 + H_2O \rightarrow 2 HNO_3$	$1 \times 10^{-12} \exp(-5000/T)$
R16 $N_2O_5 + M \rightarrow N_2O_5^*$	$2.2 \times 10^{-5} \exp(-9700/T)$
R17 $N_2O_5^* + M \rightarrow N_2O_5 + M$	1.7×10^{-10}
R18 $N_2O_5^* \rightarrow NO_2 + NO_3$	2×10^8
R19 $HNO_3 + O \rightarrow NO_3 + OH$	$< 1.3 \times 10^{-14}$
R20 $HNO_3 + OH \rightarrow NO_3 + H_2O$	* 1.3×10^{-13}
R21 $NO + O_3 \rightarrow NO_2 + O_2$	* $9 \times 10^{-13} \exp(-1200/T)$
R22 $NO + HO_2 \rightarrow NO_2 + OH$	* 2×10^{-13}
R23 $NO + O + M \rightarrow NO_2 + M$	* $4.2 \times 10^{-33} \exp(940/T)$
R24 $NO + OH + M \rightarrow HNO_2 + M$	= R29
R25 $NO + HO_2 + M \rightarrow HNO_3 + M$	= $\eta \times R29$
R26 $NO + NO_3 \rightarrow 2 NO_2$	* 8.7×10^{-12}
R27 $NO_2 + O \rightarrow O_2 + NO$	* 9.1×10^{-12}
R28 $NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.23 \times 10^{-13} \exp(-2470/T)$
R29 $NO_2 + OH + M \rightarrow HNO_3 + M$	$(0.6 - 4) \times 10^{-30}$
R30 $NO_2 + O + M \rightarrow NO_3 + M$	* 8.2×10^{-32}
R31 $NO_2 + NO_3 \rightarrow N_2O_5^*$	$3.3 \times 10^{-11} \exp(-500/T)$
R32 $H + O_3 \rightarrow OH + O_2$	* 2.6×10^{-11}
R33 $H + O_2 + M \rightarrow HO_2 + M$	* $2.1 \times 10^{-32} \exp(290/T)$
R34 $OH + O \rightarrow H + O_2$	* 4.2×10^{-11}
R35 $OH + O_3 \rightarrow HO_2 + O_2$	$1.3 \times 10^{-12} \exp(-960/T)$
R36 $OH + OH \rightarrow H_2O + O$	* $1.0 \times 10^{-11} \exp(-550/T)$
R37 $OH + OH + M \rightarrow H_2O_2 + M$	3.3×10^{-30}
R38 $HO_2 + O \rightarrow OH + O_2$	7×10^{-11}
R39 $HO_2 + O_3 \rightarrow OH + 2 O_2$	$3.3 \times 10^{-14} \exp(-1000/T)$
R40 $HO_2 + OH \rightarrow H_2O + O_2$	2×10^{-10}
R41 $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$1.7 \times 10^{-11} \exp(-500/T)$
R42 $H_2O_2 + O \rightarrow HO_2 + OH$ $\rightarrow H_2O + O_2$	* $3.6 \times 10^{-11} \exp(-2950/T)$
R43 $H_2O_2 + OH \rightarrow HO_2 + H_2O$	* $1.7 \times 10^{-11} \exp(-910/T)$
R44 $H + OH \rightarrow H_2 + O$	* $1.4 \times 10^{-14} T \exp(-3500/T)$
R45 $H + OH + M \rightarrow H_2O + M$	* $6.1 \times 10^{-26} T^{-2}$
R46 $H + HO_2 \rightarrow OH + OH$	* $4.2 \times 10^{-10} \exp(-950/T)$
R47 $H + HO_2 \rightarrow H_2 + O_2$	* $4.2 \times 10^{-11} \exp(-350/T)$

Table 1,2 (cont.)

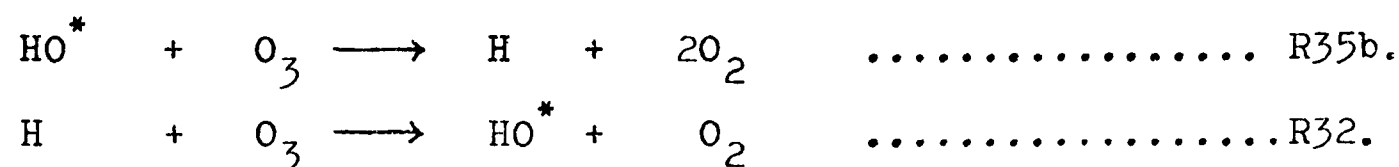
Reactions	Rate Constant
R48 $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2 + \text{HO}_2$	$* 2.8 \times 10^{-12} \exp(-1900/T)$
R49 $\text{H} + \text{NO}_2 \rightarrow \text{NO} + \text{OH}$	$* 4.8 \times 10^{-11}$
R50 $\text{H}_2 + \text{O} \rightarrow \text{H} + \text{OH}$	$1.7 \times 10^{-11} \exp(-4400/T)$
R51 $\text{H}_2 + \text{O} (^1\text{D}) \rightarrow \text{H} + \text{OH}$	$* 1.8 \times 10^{-10}$
R52 $\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}$	$6.8 \times 10^{-12} \exp(-2020/T)$
R53 $\text{CH}_4 + \text{O} \rightarrow \text{CH}_3 + \text{OH}$	$* 3.5 \times 10^{-11} \exp(-4550/T)$
R54 $\text{CH}_4 + \text{O} (^1\text{D}) \rightarrow \text{CH}_3 + \text{OH}$	$* 2.4 \times 10^{-10}$
R55 $\text{CH}_4 + \text{O} (^1\text{D}) \rightarrow \text{CH}_2\text{O} + \text{H}_2$	$* 2.0 \times 10^{-11}$
R56 $\text{CH}_4 + \text{O}_3 \rightarrow \text{CH}_3 + \text{OH} + \text{O}_2$	$2.7 \times 10^{-13} \exp(-7700/T)$
R57 $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	$* 4.7 \times 10^{-11} \exp(-2500/T)$
R58 $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2$	4.3×10^{-13}
R59 $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{OH}$	3×10^{-16}
R60 $\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$	2.6×10^{-31}
R61 $\text{CH}_3\text{O}_2 + \text{O}$	neglected
R62 $\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$	$3.3 \times 10^{-12} \exp(-500/T)$
$\quad \quad \quad \rightarrow \text{CH}_2\text{O} + \text{HNO}_2$	$6.6 \times 10^{-11} \exp(-500/T)$
$\quad \quad \quad \rightarrow \text{CH}_3\text{O}_2\text{NO}$	
R63 $\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	6.7×10^{-14}
R64 $\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{CH}_3\text{O} + \text{O}_2$	6.8×10^{-14}
$\quad \quad \quad \rightarrow \text{CH}_3\text{OOH} + \text{CH}_2\text{O}_2$	6.8×10^{-14}
R65 $\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$	$1.6 \times 10^{-13} \exp(-3300/T)$
R66 $\text{CH}_3\text{O} + \text{NO} \rightarrow \text{CH}_2\text{O} + \text{HNO}$	1.2×10^{-14}
$\quad \quad \quad \rightarrow \text{CH}_3\text{ONO}$	
R67 $\text{CH}_3\text{O} + \text{NO}_2 \rightarrow \text{CH}_2\text{O} + \text{HNO}_2$	7.0×10^{-15}
$\quad \quad \quad \rightarrow \text{CH}_3\text{ONO}_2$	
R68 $\text{CH}_2\text{O} + \text{O}_2$	neglected
R69 $\text{CH}_2\text{O} + \text{O} \rightarrow \text{CHO} + \text{OH}$	$* 1.6 \times 10^{-13}$
R70 $\text{CH}_2\text{O} + \text{OH} \rightarrow \text{CHO} + \text{H}_2\text{O}$	$* 1.4 \times 10^{-11}$
R71 $\text{CH}_2\text{O} + \text{HO}_2 \rightarrow \text{CHO} + \text{H}_2\text{O}_2$	$* 8 \times 10^{-13} \exp(-3300/T)$
R72 $\text{CHO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	1.7×10^{-13}
R73 $\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M}$	$3.8 \times 10^{-33} \exp(-2180/T)$
R74 $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$	$5.1 \times 10^{-13} \exp(-300/T)$
R75 $\text{N} + \text{O} + \text{M} \rightarrow \text{NO} + \text{M}$	$* 1.1 \times 10^{-32} \exp(273/T)^{1/2}$
R76 $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	$* 1.1 \times 10^{-14} T \exp(-3150/T)$
R77 $\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$	$3 \times 10^{-11} \exp(-1200/T)$
R78 $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$	$* 2.7 \times 10^{-11}$
R79 $\text{N} + \text{OH} \rightarrow \text{NO} + \text{H}$	6.8×10^{-11}

(* indicates preferred values in a draft of CIAP Monograph I, 1972;
unit is $\text{cm}^3\text{sec}^{-1}$ for binary reactions and $\text{cm}^6\text{sec}^{-1}$ for three body reactions)

produced in the photolysis of ozone at wavelengths less than 3080Å) with water.



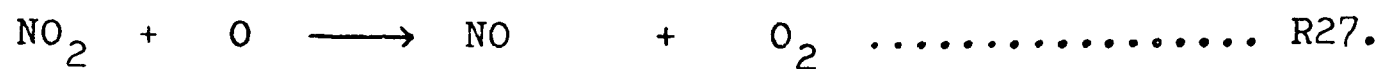
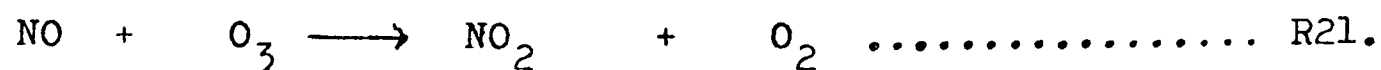
Series objections to the Norrish mechanism were raised by DeMore (1967) on the grounds that neither R35 nor R39 was fast enough to produce the long chain ^{decomposition} [observed nor to explain the low stratospheric ozone concentration. On the basis of work by Kaufman (1964) DeMore proposed a chain involving vibrationally excited HO and H atoms.



DeMore demonstrated that R32 had approximately zero activation energy by reacting H atoms with ozone in liquid argon at 87K and observing chain lengths of up to 25 molecules of ozone decomposed per H atom. The reaction of H atoms with ozone to produce HO in predominantly the ninth vibrational level, and also the increased rates of reaction of HO in various vibrational states, have been demonstrated by Coltharpe et al (1971). However, the generation of H atoms by the reaction of HO* with ozone has never been shown to occur.

It was shown by Crutzen (1969) that operation of the Norrish mechanism could not reasonably account for the low stratospheric ozone concentration found, below 30km. This was confirmed when measurements of R35 by Kaufman and Anderson (1973) and of R39 by Simonaitis and Heicklen (1973) showed the reactions to be slow.

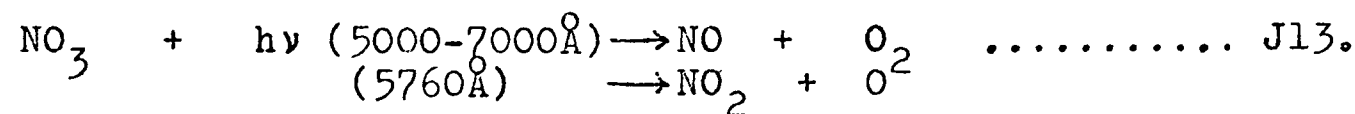
Nitrogen oxides were first suggested as catalysts for ozone decomposition by Crutzen (1970) and by Johnston (1971). NO may act as a chain propagating species.



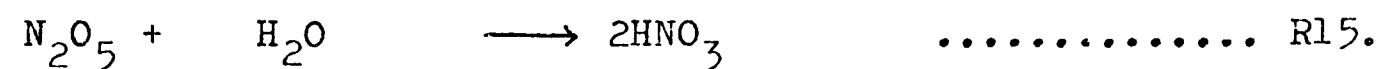
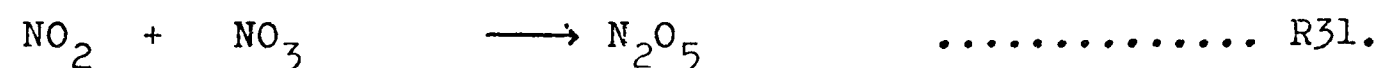
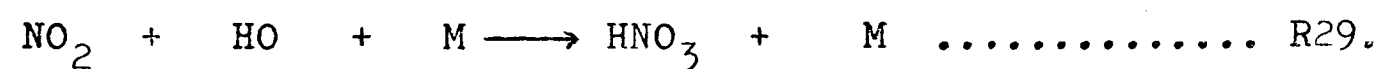
Photolysis of NO_2 also yields NO .



The reaction of ozone with NO_2 , although slower than with NO , produces NO_3 which itself photodissociates.



Nitric acid is regarded as a stable sink for the nitrogen oxides (NO_x) and work by Chapman and Wayne (1975) has shown that it only reacts very slowly with O and H atoms.



The oxidation of NH_3 and photochemical decomposition of N_2O are the dominant stratospheric sources of NO_x (see McElroy et al. 1973).

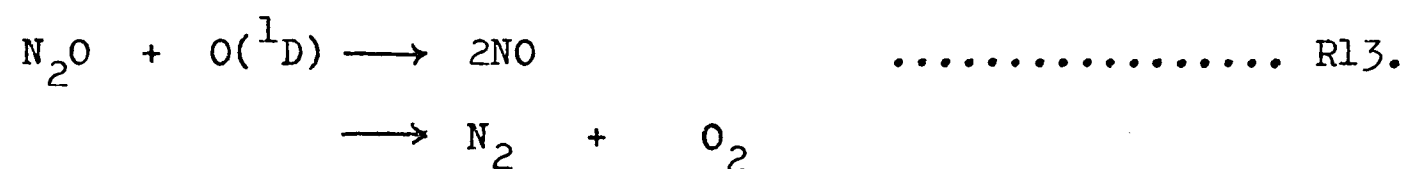
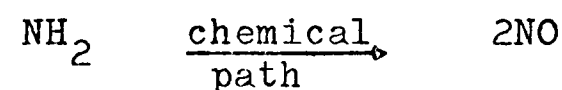
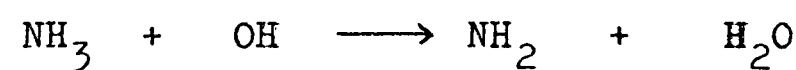
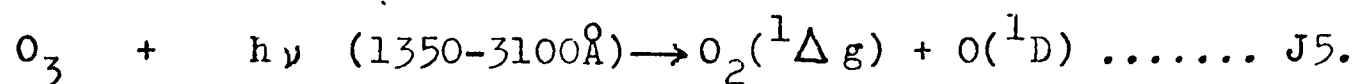
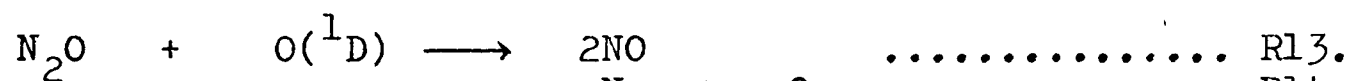
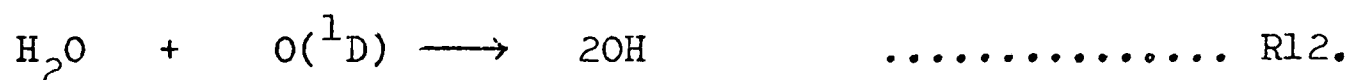


Table 1,2 shows the seventy-nine reactions of possible significance considered by Shimazaki and Ogawa (1974) in their one-dimensional model of the stratosphere. The processes involve some twenty-six minor constituents and the two major constituents (N_2 and O_2). The only electronically excited

species which appear to be important are $O(^1D)$ atomic oxygen and $O_2(^1\Delta_g)$ molecular oxygen. Both are produced in the ultraviolet photolysis of ozone (Lin and DeMore, 1973) at wavelengths less than $3100\text{\AA}$.



The fate of the majority of $O(^1D)$ is physical quenching by nitrogen (R5). As explained in Chapter 5 the quenching of $O(^1D)$ by molecular oxygen gives rise to $O_2(^1\Delta_g)$ on approximately sixty percent of reactive collisions. The small amount of reaction of $O(^1D)$ with other species (notably H_2O and N_2O) is, however, crucial as a source of the HO_x and NO_x species involved in the catalytic decomposition chain processes.



As explained in Chapter 7 the reaction of $O(^1D)$ with fluorochlorocarbon compounds (FCC's) may ultimately prove to be a source of stratospheric ClO_x .

Due to the relatively high concentrations of molecular oxygen and nitrogen, reactions involving vibrationally or translationally excited species are not generally held to be significant in the stratosphere, collisional quenching being the predominant process.

Much of the incentive for the complete understanding of the chemical and meteorological processes in the stratosphere has been due to the advent of the supersonic commercial aircraft (SST - "supersonic transport"). Designed to fly at above 17 km altitude the SST will inject large quantities of nitrogen oxides and water into the lower stratosphere. Commercial aircraft have not previously operated in the

stratosphere. As mentioned before, the temperature inversion leads to little vertical mixing in this region and (as shown in the upper part of figure 1,5) typical residence times of around two years. In order to assess the possible reduction in ozone caused by SST exhaust emission, programmes of laboratory and atmospheric measurements have been instigated in order to be able to "model" the unperturbed stratosphere. Figures 1,6; 1,7, and 1,8 show a compilation of data on NO , NO_2 , and HNO_3 concentrations. They show not only the difficulty of measuring such small quantities (mixing ratios of 10^{-8} and 10^{-10}) but also their extreme variability. Since it is well known that the ozone concentration is exceedingly variable from day to day, season to season and even over periods of several years (Goldsmith et al. 1973) it is hardly surprising that other minor constituents also show the same variability. Figure 1,9 shows observed global ozone distributions for the northern hemisphere. Maximum concentrations occur above the poles in spring. Concentrations above the equator are the lowest and show practically no seasonal variation. This is consistent with maximum production of ozone over the equator whence it is carried by convection currents towards the poles.

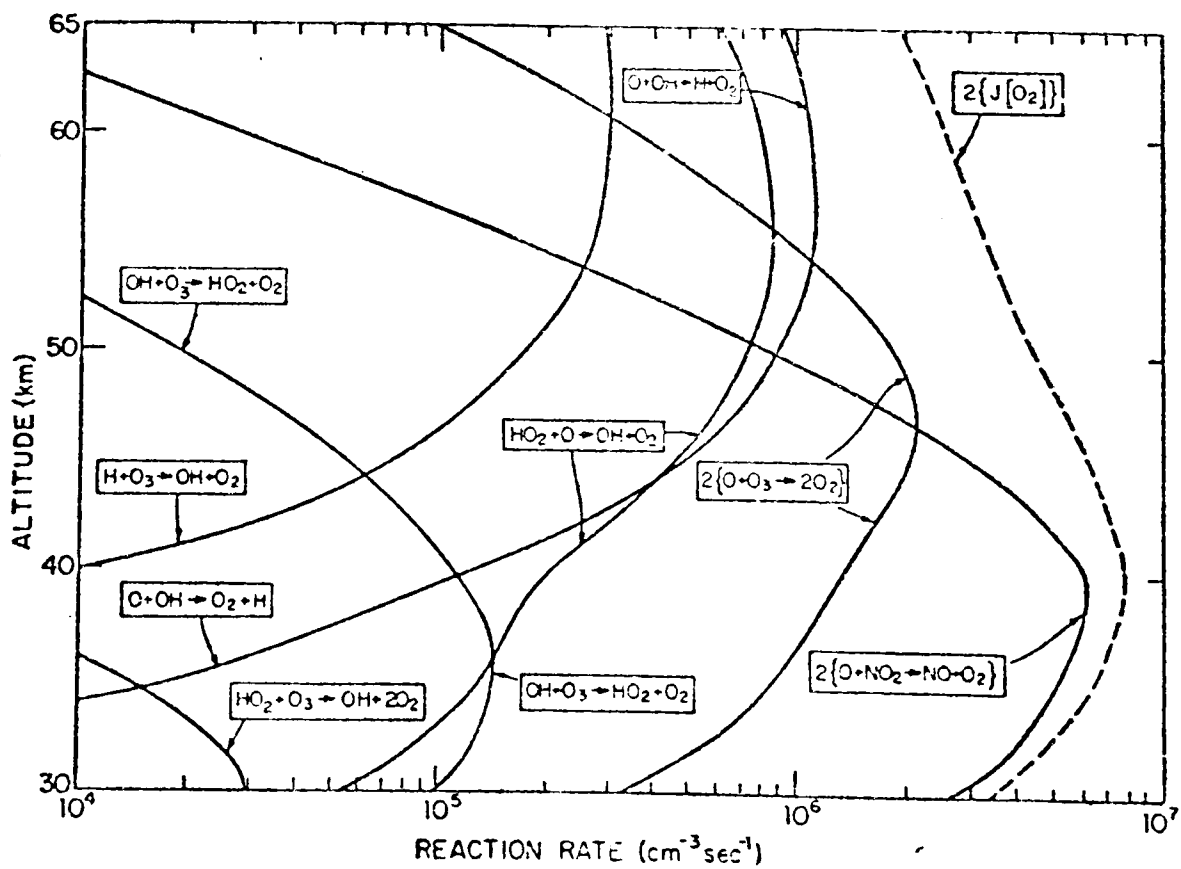
The different problems posed by the chemical processes and the transport processes have meant that models of the stratosphere have generally fallen into two categories. The first are one-dimensional models with refined chemistry, and including, in more recent models, treatment of vertical diffusion (for example, McElroy et al., 1974 Shimazaki and Ogawa, 1974). The second are three-dimensional models of the horizontal transport processes, usually using information on the chemistry deduced by the one-dimensional models (for example, Cunnold et al., 1975).

Figure 1,5 Concorde emissions

Aircraft perturbations of ozone. ^a						
Simulated aircraft fleet	Injection altitude (km)	Stratospheric source S ^b (cm ⁻² sec ⁻¹)	α (cm ² sec)	Residence time ^c (years)	Total ozone reduction (percent)	
					Fixed temperature field	Radiative equilibrium temperature field
Concorde	17	6 +7	2.78-17	2.0	3.2	2.4
Concorde	17	6 +8	2.78-17	2.0	23.7	21.3
Concorde ^d	17	6 +7	1.67-17	1.1	1.9	1.4
SST	20	4.22+7	5.55-17	3.5	4.1	3.1
SST	20	2.31+8	5.55-17	3.5	19.1	17.0
SST	20	4.2 +8	5.55-17	3.5	28.7	26.4
SST ^e	20	4.2 +8	5.55-17	3.5	28.7	26.4
SST ^d	20	4.2 +8	3.29-17	2.0	22.6	20.3
HST	25	4 +7	7.60-17	3.9	5.8	4.4
HST	25	2 +8	7.60-17	3.9	21.5	19.5
HST ^d	25	2 +8	5.15-17	2.5	18.7	16.4
1990 fleet ^e	16-21	4.3 +7	3.26-17	2.3	2.5	1.9

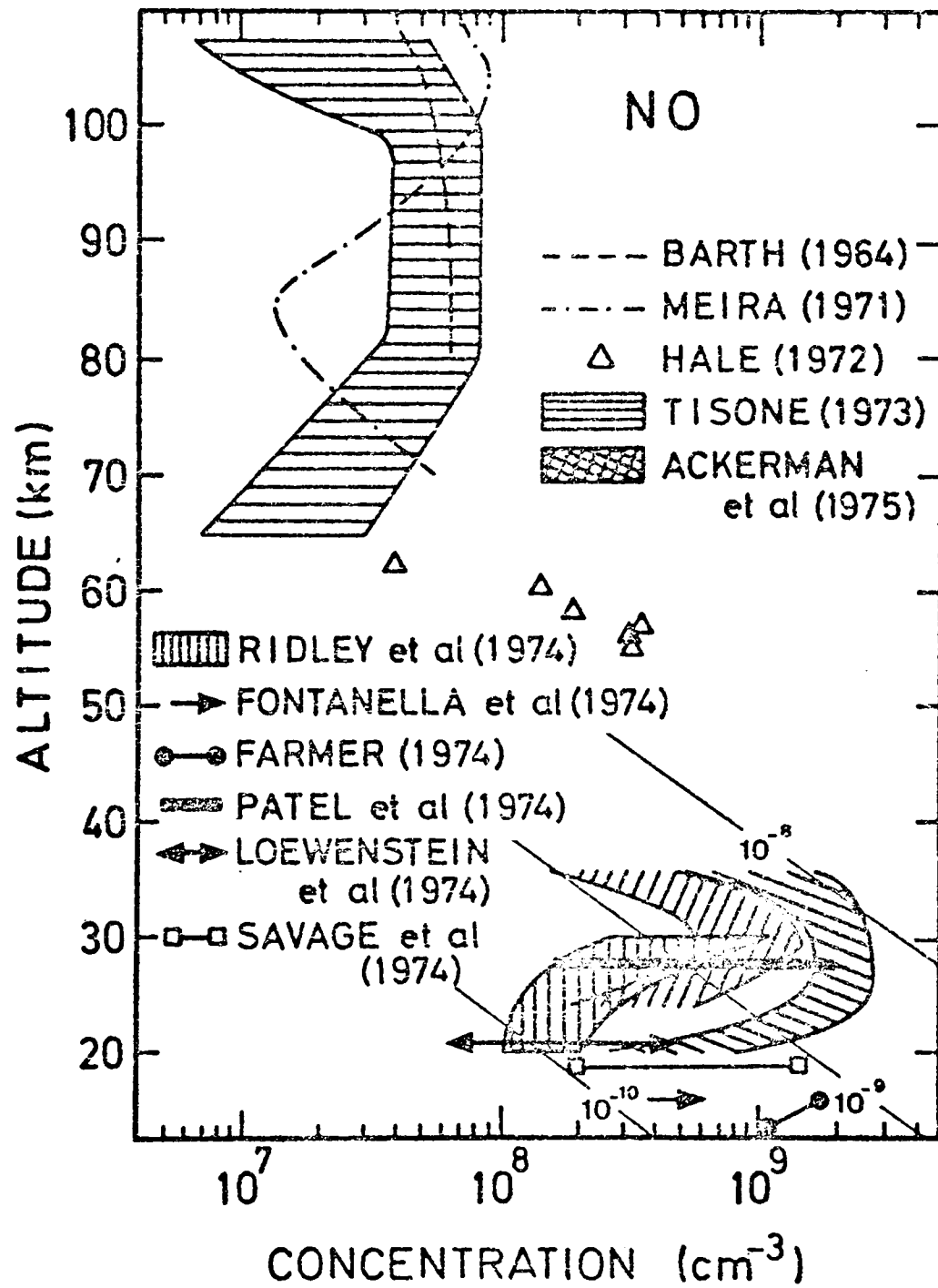
^a Plus and minus values refer to power of ten.

^d With increased eddy coefficient 16-18 km



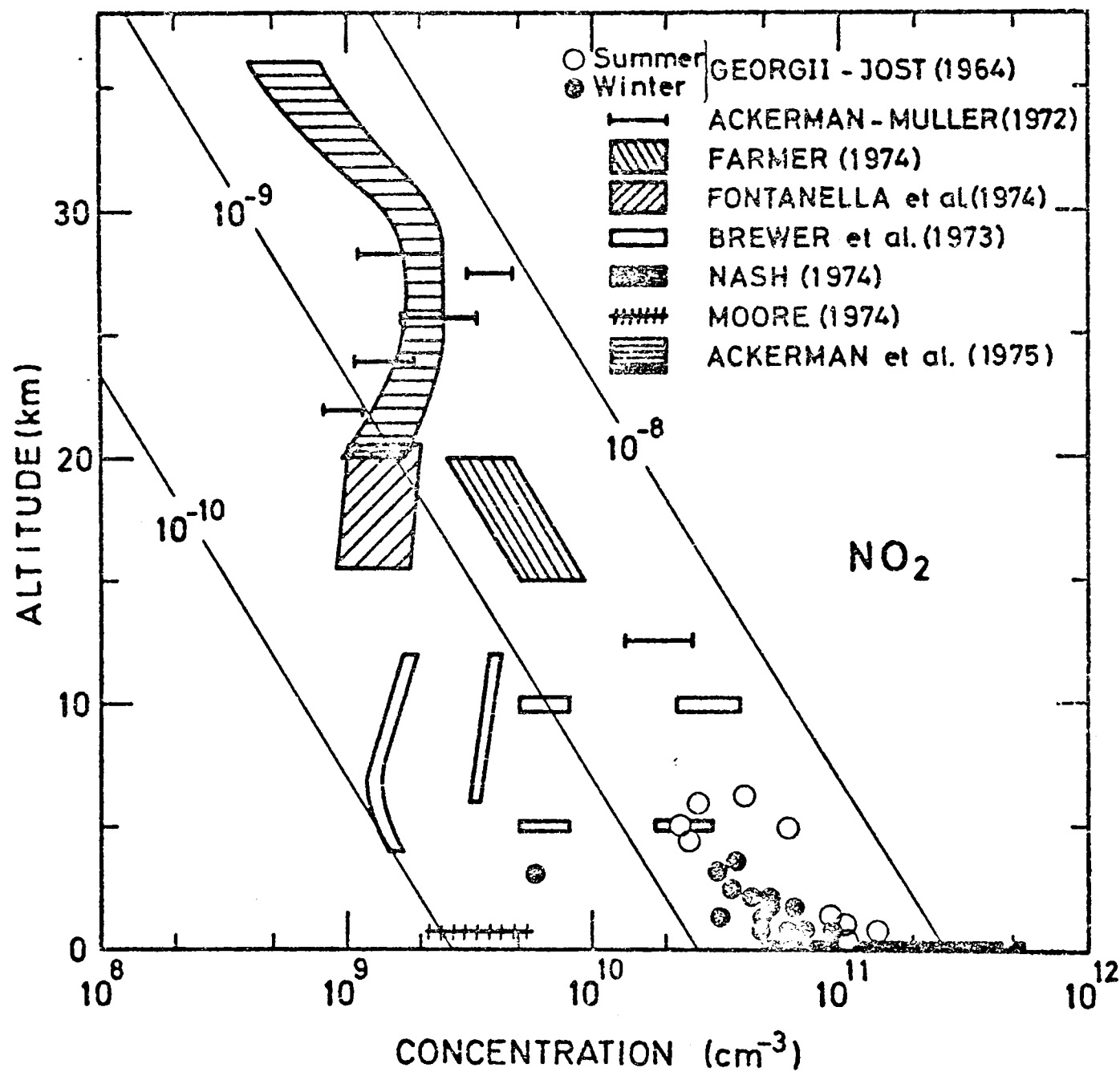
Reactions important in odd oxygen loss, and the odd oxygen production rate $2J[O_2]$ for the O_3 profile. The sum of the recombination reaction rates equals the production rate at every altitude consistent with the assumption of photochemical equilibrium followed here.

Figure 1,6 Measured [NO]



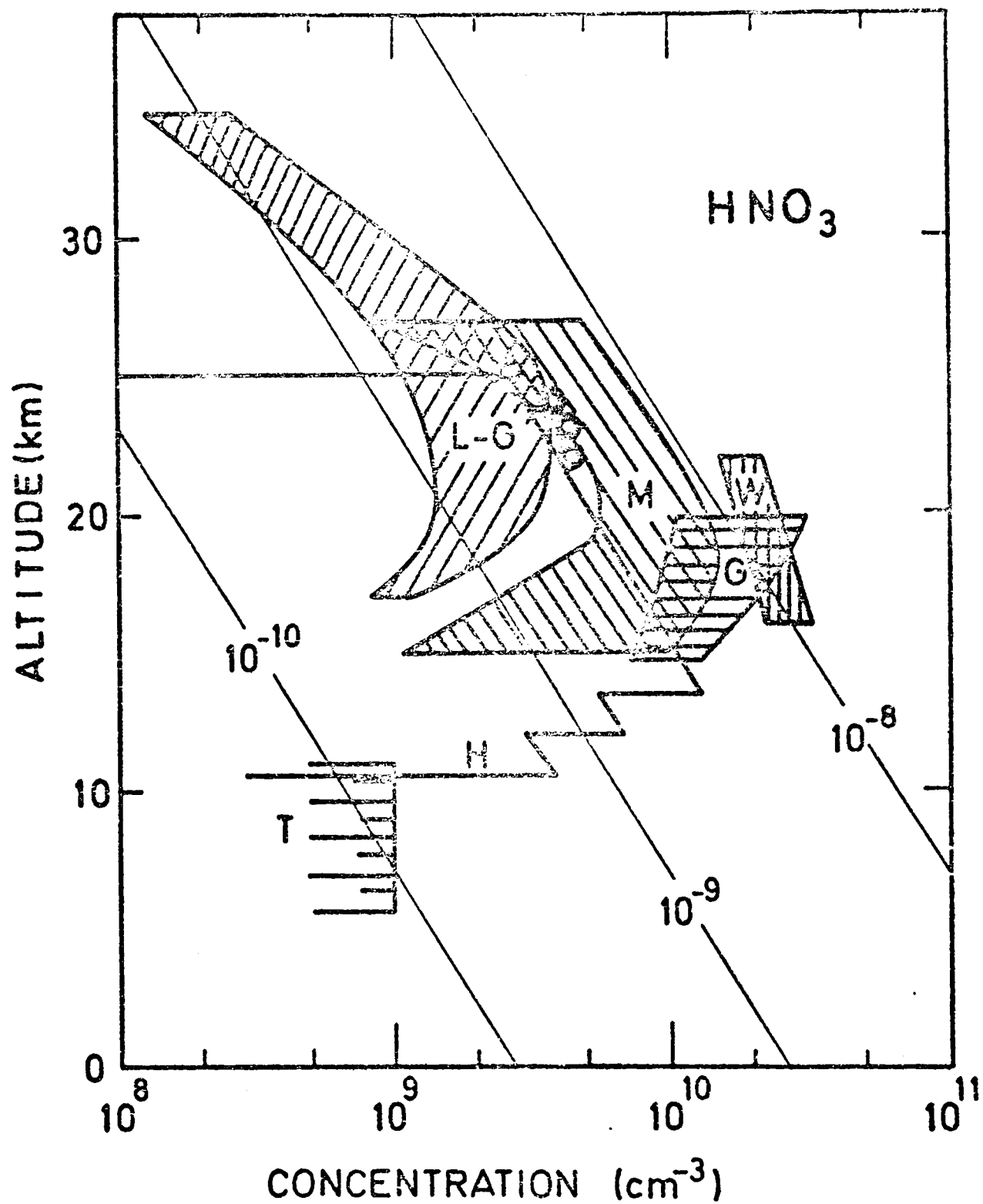
Observed nitric oxide concentrations as collected by Ackerman (1975) indicating extremely variable mixing ratios in the stratosphere. All references in Ackerman (1975). 10^{-10} , 10^{-9} and 10^{-8} lines correspond to constant mixing ratios.

Figure 1,7 Measured [NO₂]



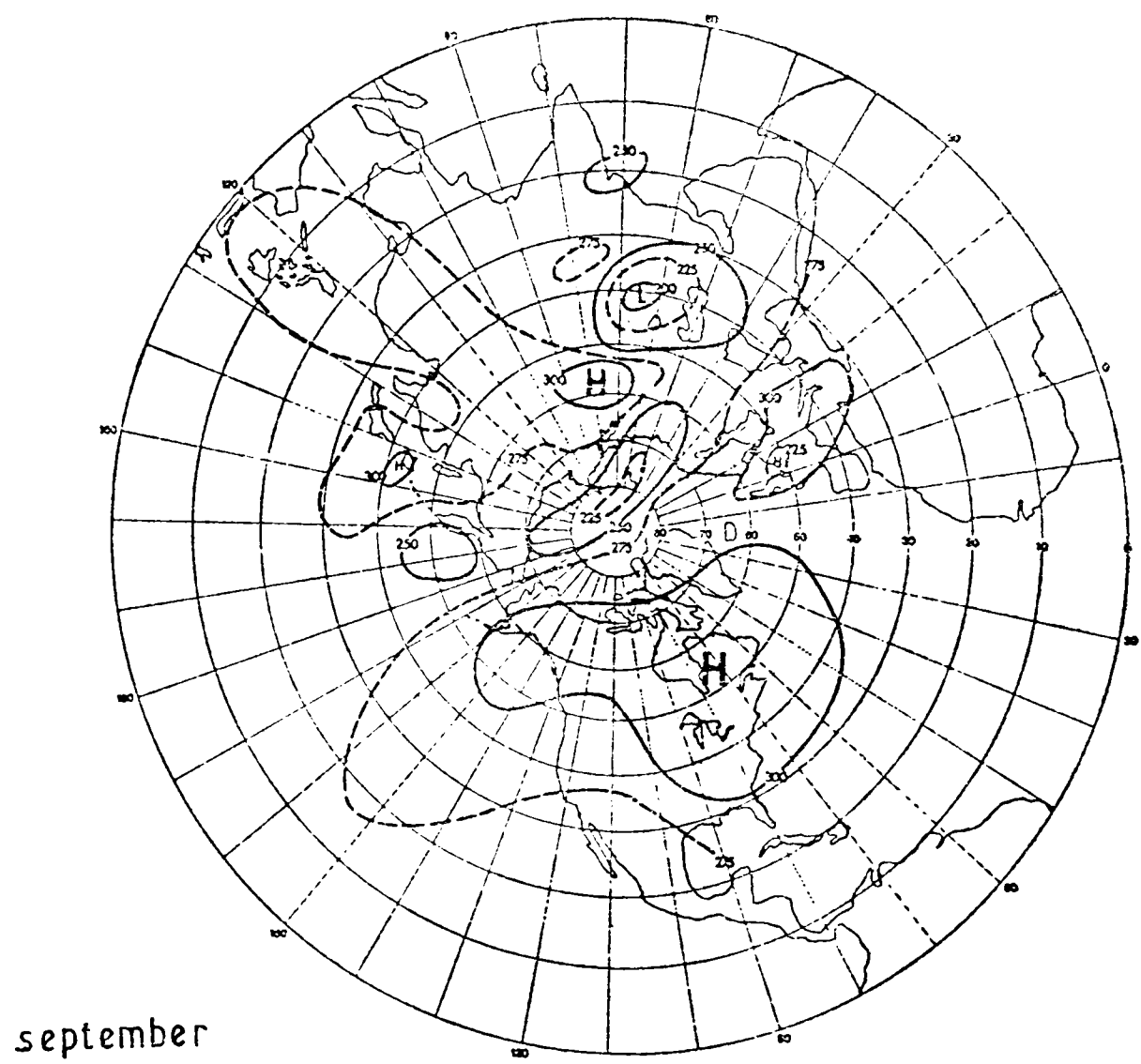
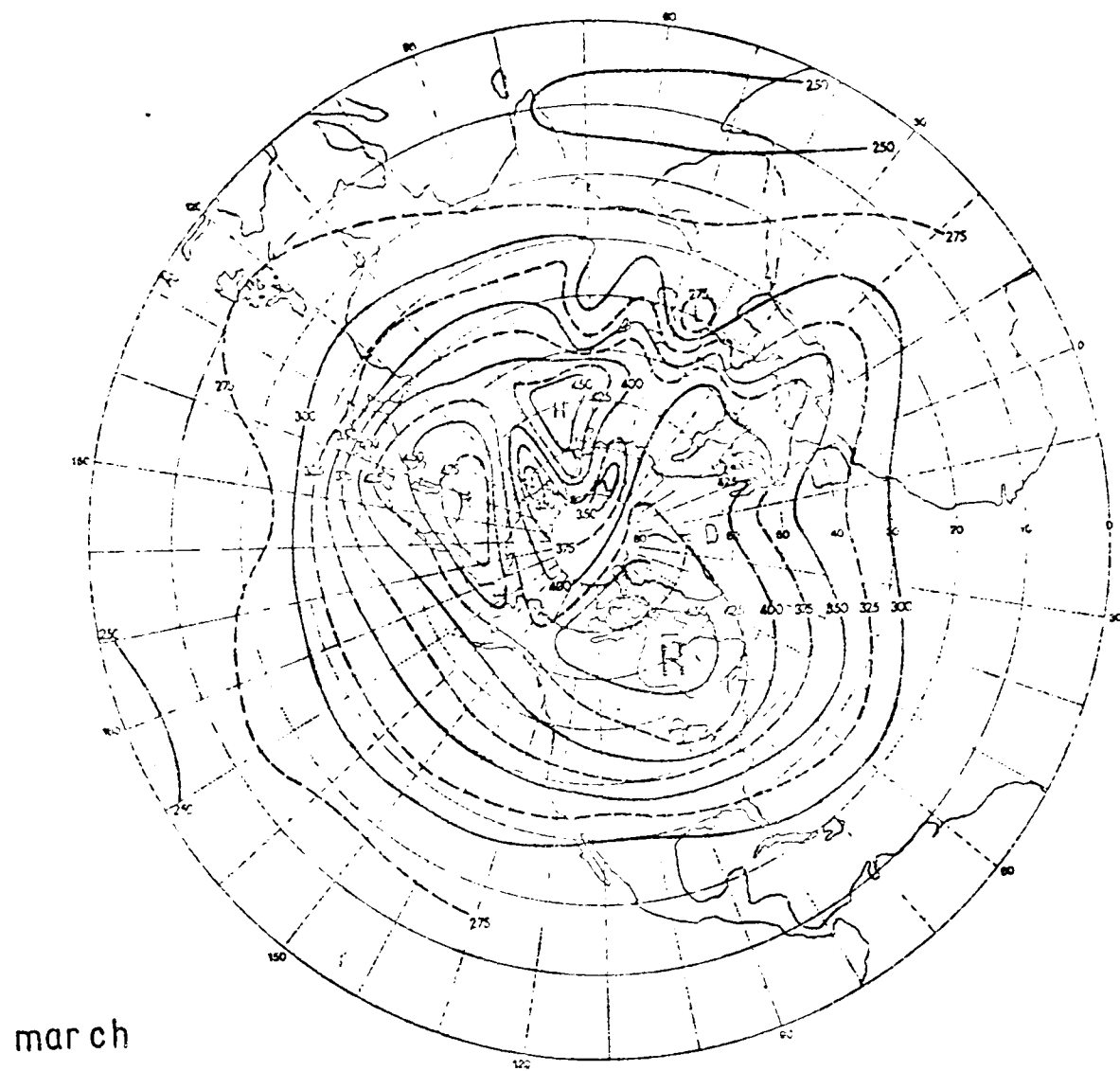
Observed nitrogen dioxide concentrations as collected by Ackerman (1975) ; 10⁻¹⁰, 10⁻⁹ and 10⁻⁸ correspond to constant mixing ratios.

Figure 1,8 Measured $[\text{HNO}_3]$



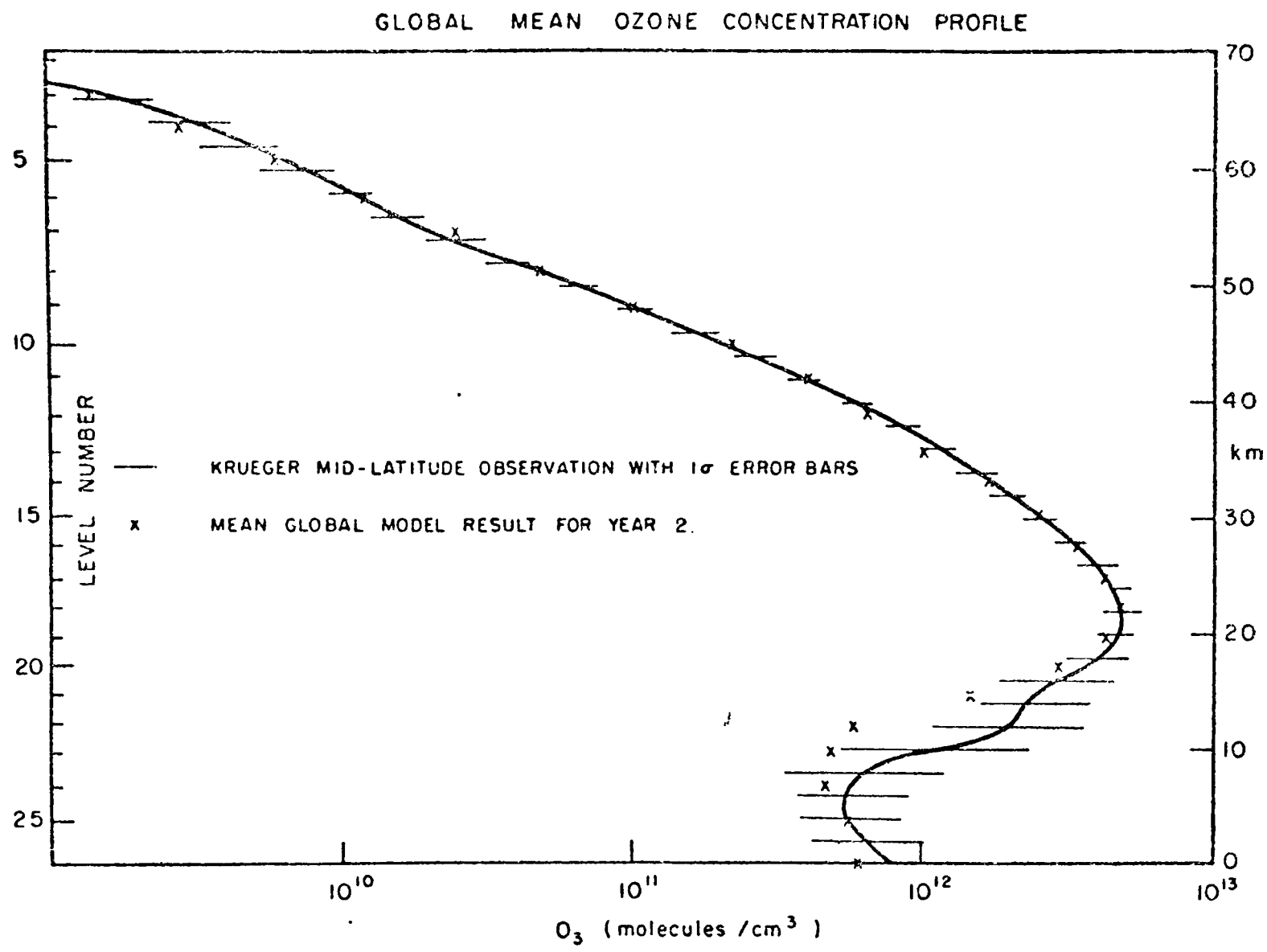
Observed nitric acid concentrations as collected by Ackerman (1975). 10^{-10} , 10^{-9} and 10^{-8} lines correspond to constant mixing ratios. L-G. Lazrus and Gandrud (1974) ; M. Murcray et al., 1974 ; G. Fontanella et al., 1974; W. Fried and Weinman (1970) and H. Harries et al. (1974). T =

Figure 1,9 Global ozone distribution



The model of Cunnold et al is remarkable in predicting fairly accurately ozone concentrations and their seasonal global variations by integrating over a three year cycle from an initially stationary atmosphere. Their resulting ozone profile is compared to the rocket data of Krueger et al. (1973) in Fig, 1,10. McElroy et al. demonstrate that the ozone concentrations above 28km can be satisfactorily estimated by a model which assumes photochemical equilibrium. Below this level the vertical mixing lifetime for ozone becomes shorter than its chemical lifetime. Any SST emissions would therefore be injected into the dynamically controlled region. It is also shown that the atmosphere is in local radiative equilibrium above about 35km. Absorption of solar UV radiation by ozone provides the major heat source. This source is balanced by IR emissions from CO_2 and, to a lesser extent, O_3 . Figure 1,3 shows some calculated concentrations of O , HO_x and HO_x species. Comparison of the NO , NO_2 and HNO_3 profiles with the experimental data in Figure 1,6 - 8 shows fair agreement within the large uncertainties of the observations. Although the McElroy model, unlike some previous ones, contains no arbitrarily "adjustable parameters" in the chemistry, there is still scope for "interpretation" in the choice of vertical diffusion coefficients. The model is, however, good enough to be able to give authoritative predictions of the percentage ozone decrease to be expected from given SST operations. The results, summarised in fig. 1.5, show that a fleet of 320 Concorde operating for 7 hr a day at 17km is predicted to lead to a 1% decrease in the column density of ozone. This ^{No emission} is equivalent to half the natural source of NO . The ambient NO concentration is, however, held to be responsible for the

Figure 1,10 Ozone vs. altitude

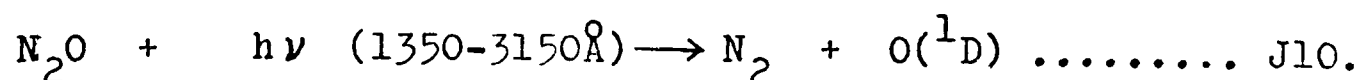


The predicted global mean ozone profile for year 2 as a function of height and its comparison with rocket data presented by Krueger and Minzner (1973).

reduction of the ozone density by a factor of two. This seems to imply that the ozone density is self compensating. That the stratospheric ozone density involved self compensatory features had already been suspected from the apparent lack of any noticeable decrease in global ozone concentrations following the massive injections of NO from H-bomb tests in 1958, 1961 and 1962. (Goldsmith et al. 1973). Nitric oxide production behind the shock wave of the 1962 explosion was said to be the equivalent of 1,047 fully operational Concorde.

There are at least three self compensating processes occurring in the stratosphere which tend to stabilise the ozone density. Consider first a decrease in $[O_3]$ caused by a local increase in HO_x . If this occurs in the region of radiative equilibrium there will be a consequent drop in atmospheric temperature. Reduction in temperature leads to an increase in the three body reaction $O + O_2 + M \longrightarrow O_3 + M$ (R2) due to its negative temperature dependence. This produces a compensatory increase in the ozone production rate.

The second effect is photochemical in origin. A local decrease in the ozone density leads to an increase in the solar UV at this level. A larger proportion of the solar UV at wavelengths less than $2440\text{\AA}$ will be absorbed by molecular oxygen, leading to an increased production rate of O atoms. This also results in an increase in R2, the ozone production reaction. A third effect concerns the atmospheric source of NO. The loss of O_3 causes an increase in the local solar UV, and a corresponding increase in the photodecomposition of N_2O . The major photolysis pathway of N_2O produces N_2 .



The N_2O concentration is reduced, leading to a reduction in

the rate of the major source reaction of NO.



The consequent reduction in NO concentration reduces the rate of catalytic recombination of odd oxygen (O, O_3) and compensates for the original ozone loss.

The apparently successful modelling of the stratosphere is a triumph for combined efforts of atmospheric physicists, laboratory chemists and the numerous modellers. However, speculation about the effects of fluorochlorocarbon compounds (FCC's) on the stratospheric ozone density imply that ClO_x catalytic destruction cycles may play an equally important (and faster growing!) role as NO_x . The introduction to Chapter 7 examines in detail the possible effect of ground level emissions of FCC's on the stratospheric ozone density.

In Chapter 6 the products of the reaction of vibrationally excited HO with ozone are investigated in a series of diagnostic experiments designed to resolve the question of whether the HO_x ozone destruction chain proposed by Norrish operates, or whether in certain circumstances (for example, when the HO has high vibrational excitation energy) the DeMore mechanism operates. The background work to this problem will be discussed in more detail in Section 6, 1.

OXYGEN SPECIES.

2,1 O; Electronic States of the Oxygen Atom.

$O(^3P)$ is the ground electronic state of the oxygen atom. There are two relatively low lying electronically-excited singlet states $O(^1D)$ and $O(^1S)$ which lie at 1.97 eV (194.5 kJ mole⁻¹) and 4.17eV(402.4 kJ mole⁻¹) respectively, above the ground state. Both singlet states are metastable with respect to radiative deactivation. The radiative lifetimes of $O(^1D)$ are 145 and 455 seconds with respect to the optically forbidden transitions which occur at 6300 and 6364⁰Å respectively (Chamberlain, 1961). These emissions occur in the atmosphere in the nightglow, and the twilight and day airglows. The emission is believed (Shepherd, 1974) to originate from $O(^1D)$ atoms produced by dissociative recombination of molecular oxygen ions in the F region of the ionosphere.



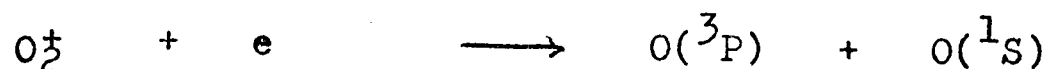
The lower part of Figure 2,1 shows satellite observation of the variation of the 6300⁰Å emission with latitude. The $O(^1D)$ atom will be of principal interest in this thesis due to certain of its very fast abstraction and energy transfer reactions. It is quenched by molecular nitrogen in a spin disallowed process on approximately one in 5 collisions (Gauthier and Snelling, 1975).



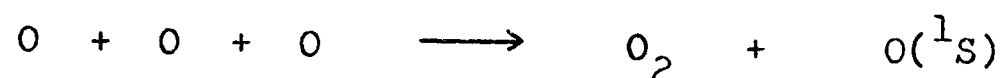
By contrast $O(^1S)$ is quenched on only one in 10⁸ collisions with nitrogen or oxygen molecules (Noxon, 1957).

The radiative lifetime of $O(^1S)$ is 0.8 and 13 seconds with respect to the spin allowed (but electric dipole L-forbidden) transition ~~and to the spin forbidden transition~~

$^1S - ^1D_0$ and to the spin forbidden transition $^1S - ^3P_1$ respectively (Correy and Williams, 1972; Chamberlain 1961). The former transition, which occurs at $5577\text{\AA}$, gives rise to the "auroral green" line, which is seen strongly during aurorae and is present in the dayglow and the nightglow. In the F region the $O(^1S)$ production is believed (Donahue, 1974) to be chiefly due to the dissociative recombination of O_2^+ .



However, emission from the E region seems to be due to the reaction (Donahue, 1974)



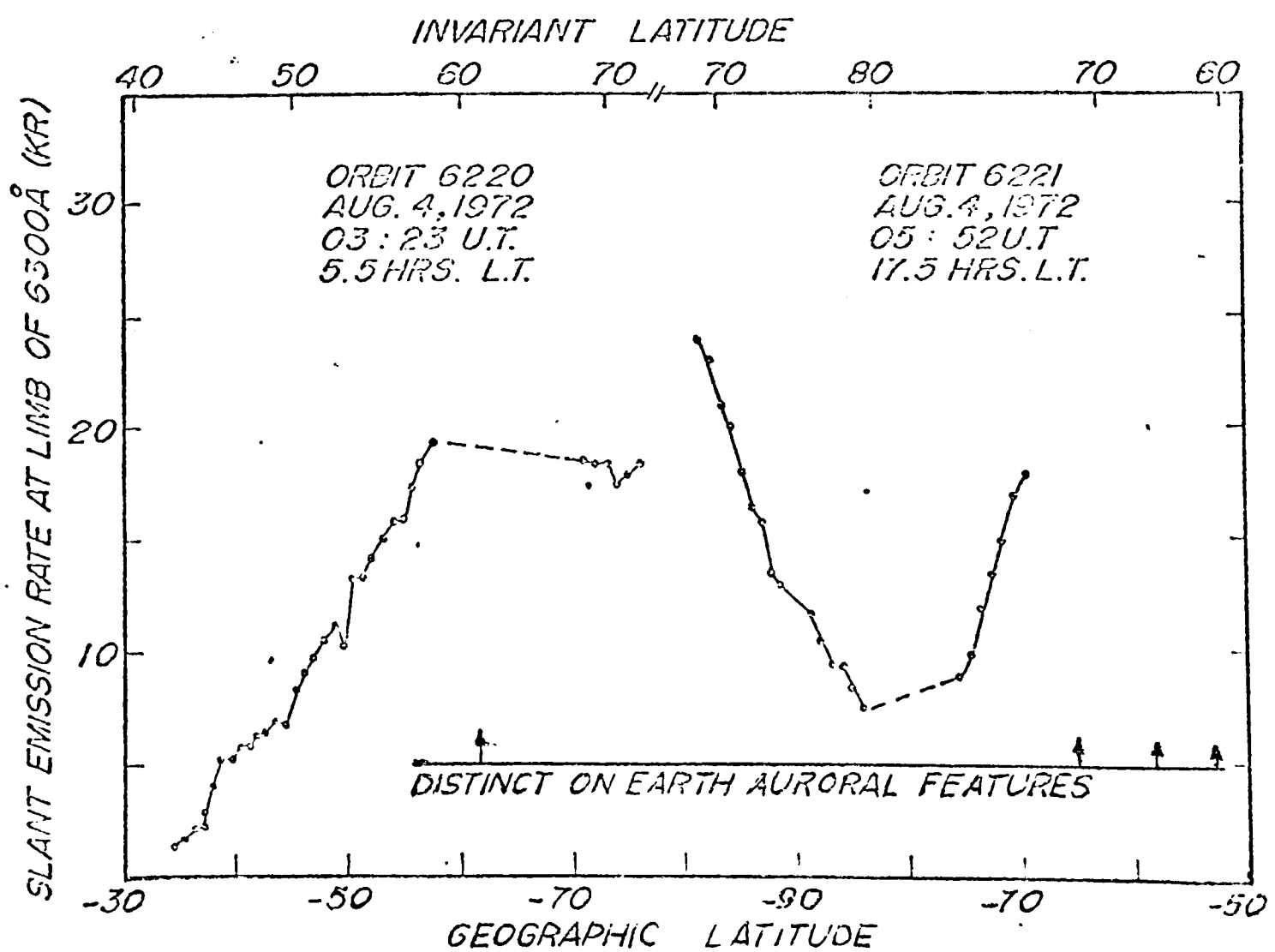
From 100-170 km altitude there appears to be a significant contribution to the $O(^1S)$ concentration from the photodissociation of O_2 (see Vallance Jones, 1974).

The spin forbidden transition at $2972\text{\AA}$ occurs only very weakly but is observed in auroral emissions.

Reference to the O atom energy level diagram in Figure 2,1 shows the existence of many other electronically excited states with energies greater than 9eV. Transitions to these states have been observed in the atmosphere. The main UV emissions are at 1302-6 and $1356\text{\AA}$, and are the $3^3S - 3P_J$ and $3^5S - 3P$ transitions, respectively.

The transitions at $4368\text{\AA}$ ($4^3P - 3^3S^0$) and $7774\text{\AA}$ ($3^5P - 3^5S^0$) are also observed. The $O(3^3S^0)$ and $O(3^5S^0)$ emissions in aurorae are believed to be due to collisional excitation of oxygen atoms by photoelectrons (Gerard, 1974).

Energy level diagram for the $2s^2 2p^3$ configuration of Nitrogen (N IV). The diagram shows energy levels in eV (0 to 15) for various configurations: $2s^2 2p^3$, $2s^2 2p^2 3s$, $2s^2 2p^2 3p$, $2s^2 2p^2 3d$, $2s^2 2p^3$, $2s^2 2p^2 3s$, $2s^2 2p^2 3p$, $2s^2 2p^2 3d$, $2s^2 2p^3$, $2s^2 2p^2 3s$, $2s^2 2p^2 3p$, $2s^2 2p^2 3d$. Key transitions are labeled with wavelengths (e.g., 1302-5-6, 1356-9, 8446 Å, 7774 Å) and oscillator strengths (e.g., 0.71, 1.108).



Shepherd, 1974

2,2 O_2 ; Electronic States of the Oxygen Molecule.

The principal absorption features of molecular oxygen at wavelengths longer than $1750\text{\AA}$ (see Figure 1,2) are the Schumann-Runge system (see Figure 2,2) between 1750 and $2050\text{\AA}$ (corresponding to the transition $B^3\Sigma_u^- - X^3\Sigma_g^-$) and the weak Herzberg continuum between 2050 and $2400\text{\AA}$ (corresponding to $A^3\Sigma_u^+ - X^3\Sigma_g^-$). As can be seen from the potential energy diagram (Figure 2,3), the O_2 B state correlates with $O(^3P) + O(^1D)$ as dissociation products for wavelengths less than $1750\text{\AA}$. The O_2 A state correlates with two $O(^3P)$ atoms for wavelengths less than $2400\text{\AA}$. Quantum yield data, however, are sparse. At $1850\text{\AA}$, the quantum yield for $O(^3P)$ formation is apparently close to two. Noxon, 1970, observed emission from $O(^1D)$ and deduced that photolysis at $1470\text{\AA}$ produces approximately equal amounts of $O(^3P)$ and $O(^1D)$. Both results are thus in accordance with expectation. Below $1330\text{\AA}$ it becomes energetically possible to produce $O(^1S) + O(^3P)$ dissociation products.

The first and second electronically excited states of molecular oxygen $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ give rise to atmosphere emission features at $7621\text{\AA}$ ($^1\Sigma_g^+ - ^3\Sigma_g^-$) and $12,687\text{\AA}$ ($^1\Delta_g - ^3\Sigma_g^-$) respectively. $O_2(^1\Delta_g)$ has a long radiative lifetime of 3876 seconds (Badger et al, 1965) and is produced by the photolysis of ozone in J5. The atmospheric (0,0) emission from $O_2(^1\Sigma_g^+)$ is not observed due to absorption by oxygen lower in the atmosphere, but Noxon, 1974, has observed enhancement of the (0,1) band at twilight.

The main production process for $O_2(^1\Sigma_g^+)$ in the atmosphere is believed to be energy transfer from $O(^1D)$

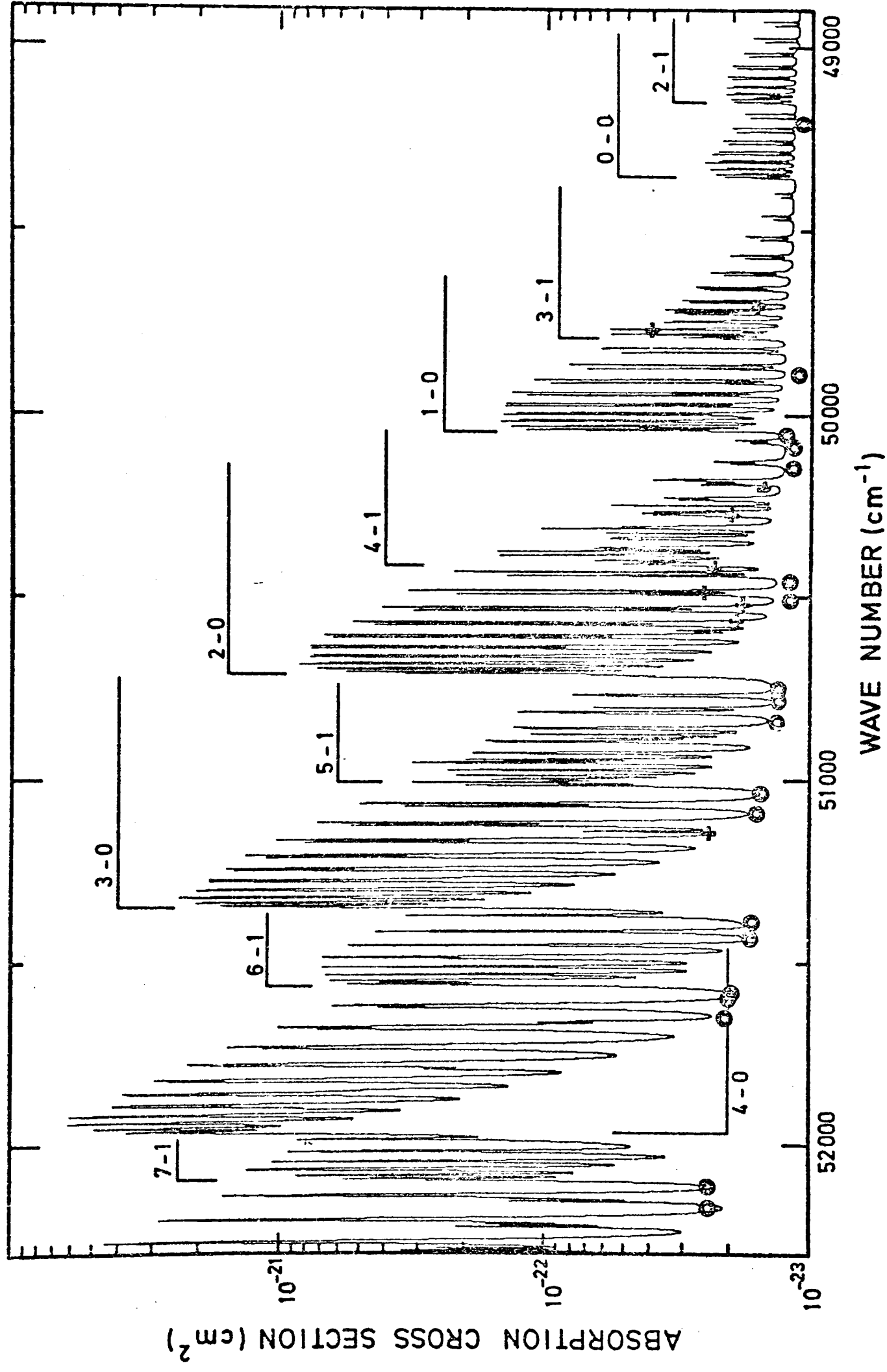
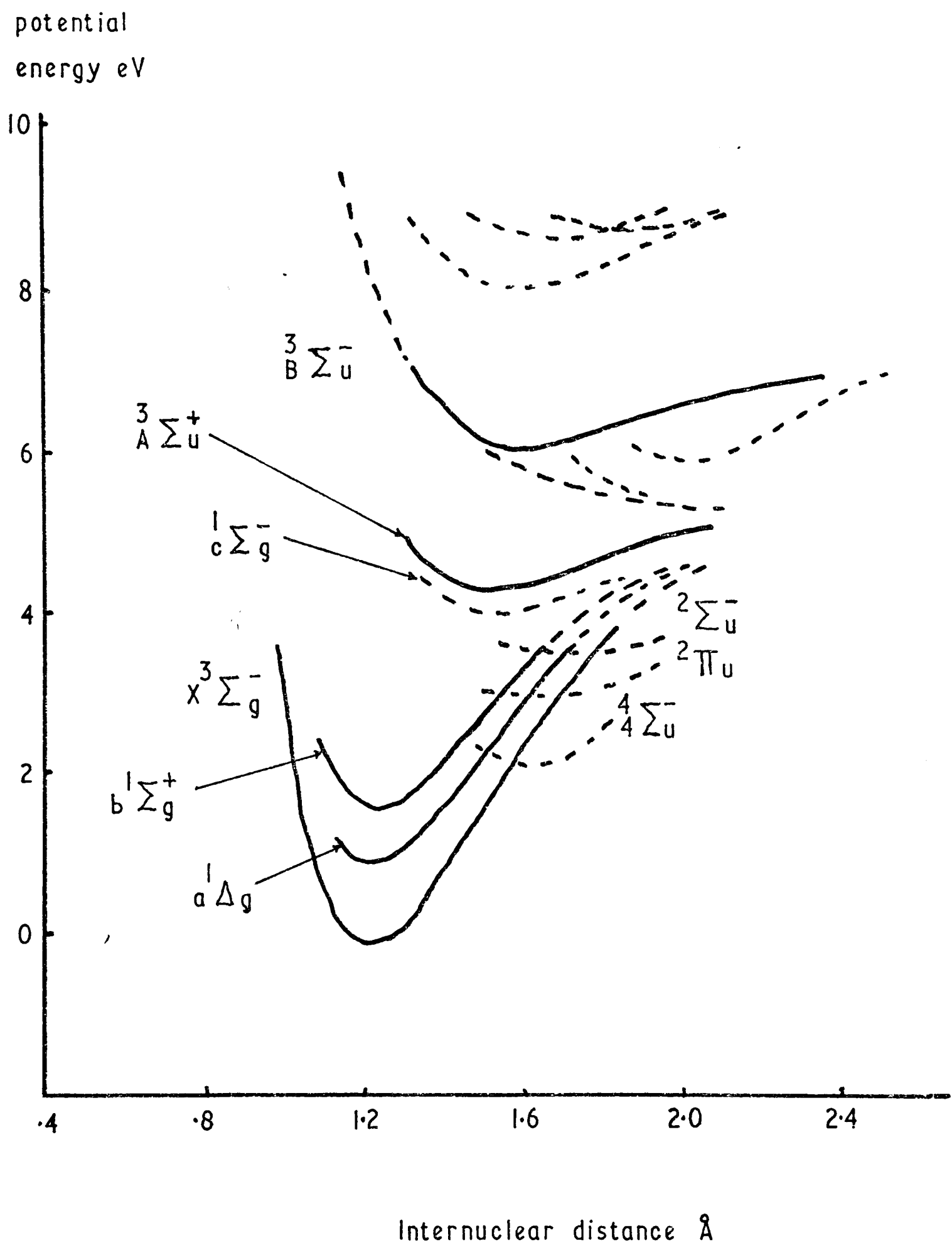


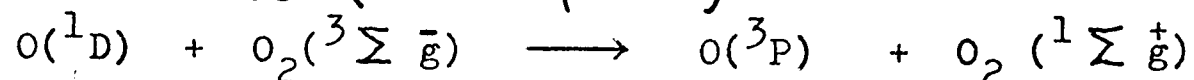
Figure 2.2

Rotational structure of the Schumann-Runge bands of O₂ at 300 K (Ackerman et al., 1970) from (0-0) to (7-1). Theoretical determination with laboratory data are indicated by crosses and with experimental continuum by Ogawa (1971) by circles. Effect of the Herzberg continuum is important for $\nu < 51000 \text{ cm}^{-1}$.

Figure 2,3 O_2 PE curves



to molecular oxygen (see Chapter 5).



$O_2(^1\Sigma_g^+)$ has radiative lifetimes of 400 and 12 seconds with respect to the transitions $b^1\Sigma_g^+ - a^1\Delta_g$ and $b^1\Sigma_g^+ - X^3\Sigma_g^-$ (Noxon, 1961; Wallace and Hunten, 1968).

2,3 O_3 : Ozone.

The ozone molecule is a slightly asymmetric prolate top (Gora, 1959) with a bond angle of $116^\circ 45'$ (microwave determination by Hughes, 1956), and bond lengths of 1.20 Å. There are three fundamental vibrational modes ν_1 (symmetric stretch, 1110 cm^{-1}), ν_2 (bend, 705 cm^{-1}) and ν_3 (antisymmetric stretch, 1043 cm^{-1}). The populations of the fundamental vibrational modes at 298K are 0.48 (1,0,0), 3.37 (0,1,0) and 0.67 (0,0,1) percent ^{of the total number of ozone molecules}, respectively (Kurylo et al., 1974).

Ozone has an unusually low dissociation energy of 1.13 eV (see Hay et al. 1973), with respect of O_2 and O. Figure 2,4 shows the UV and visible absorption spectra of ozone (Griggs, 1968).

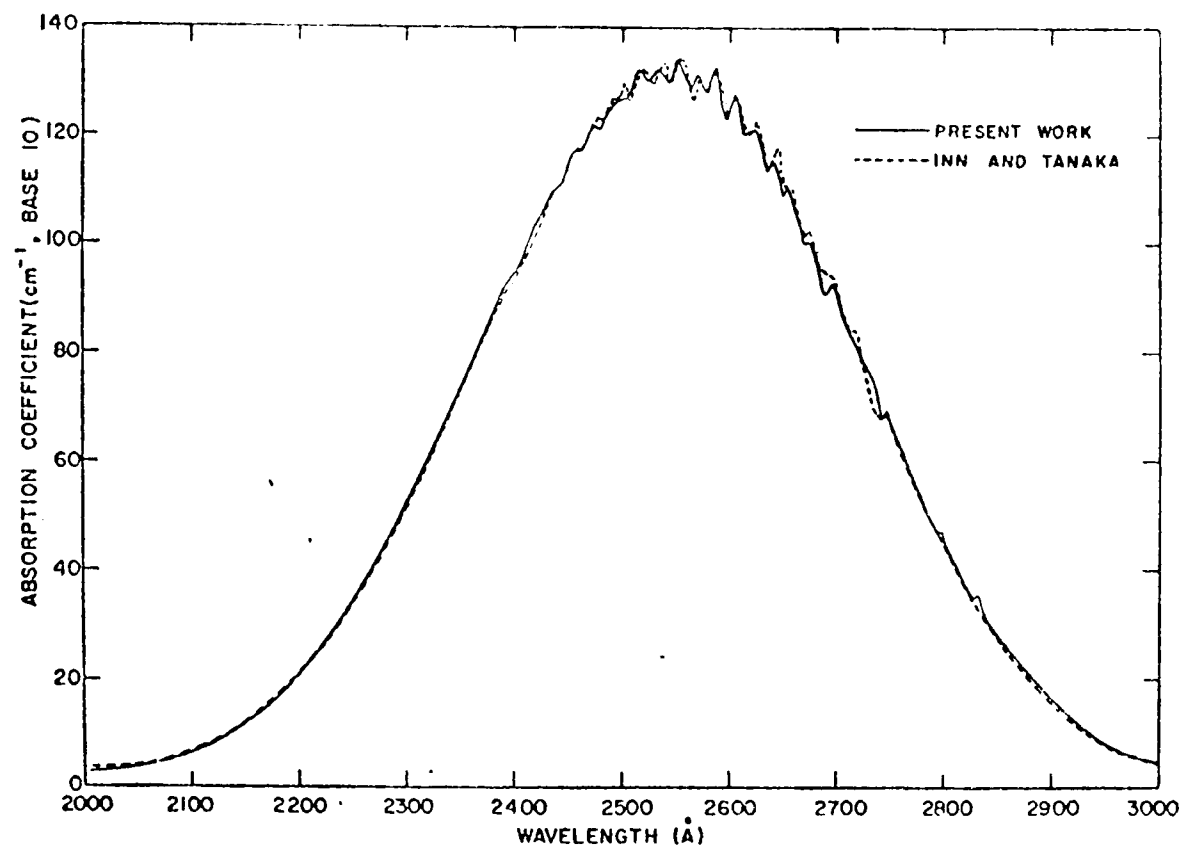
The main features are:

- 1) An intense absorption ($\epsilon = 132\text{ atm}^{-1}\text{ cm}^{-1}$, base 10) centred at 2550 Å ; the Hartley band. The tail on the low energy side is called the Huggins band.
- 11) The low intensity Chappuis band which lies in the visible region and gives rise to the blue colour of condensed ozone.
- 111) A strong absorption in the vacuum UV with maxima at 1330 Å and 1215 Å ($\epsilon = 420$ and $650\text{ atm}^{-1}\text{ cm}^{-1}$, base 10, respectively).

Figure 2,4

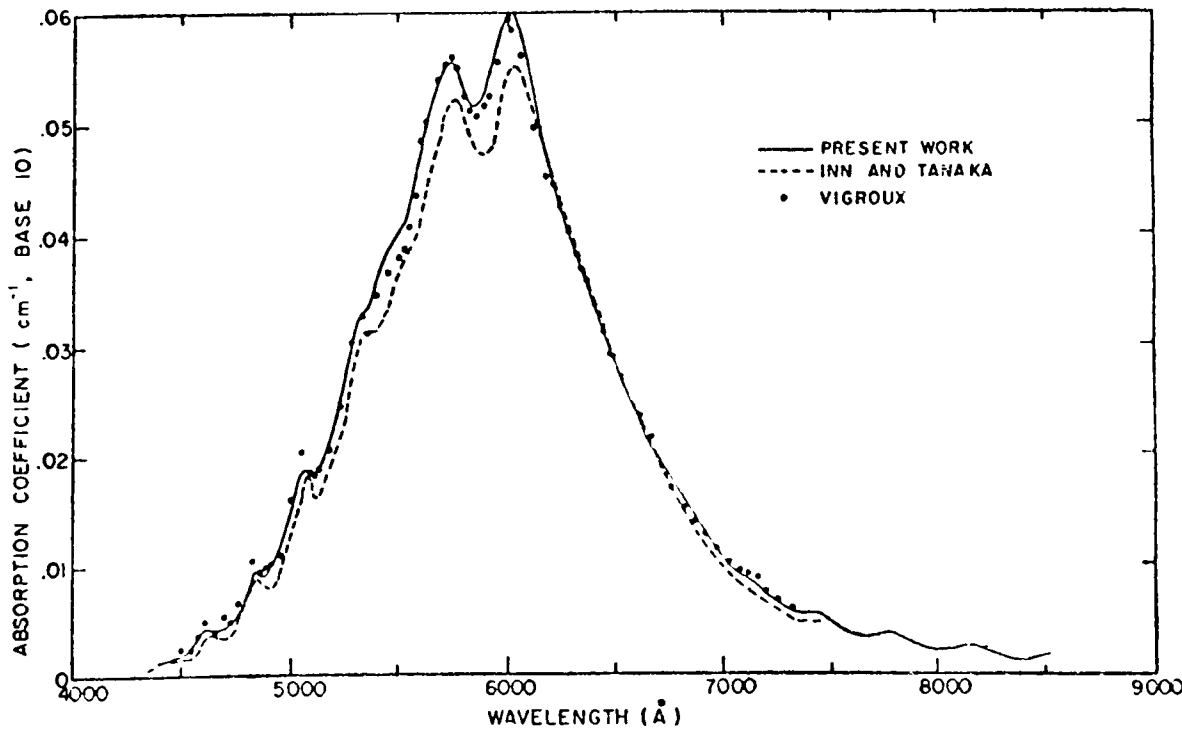
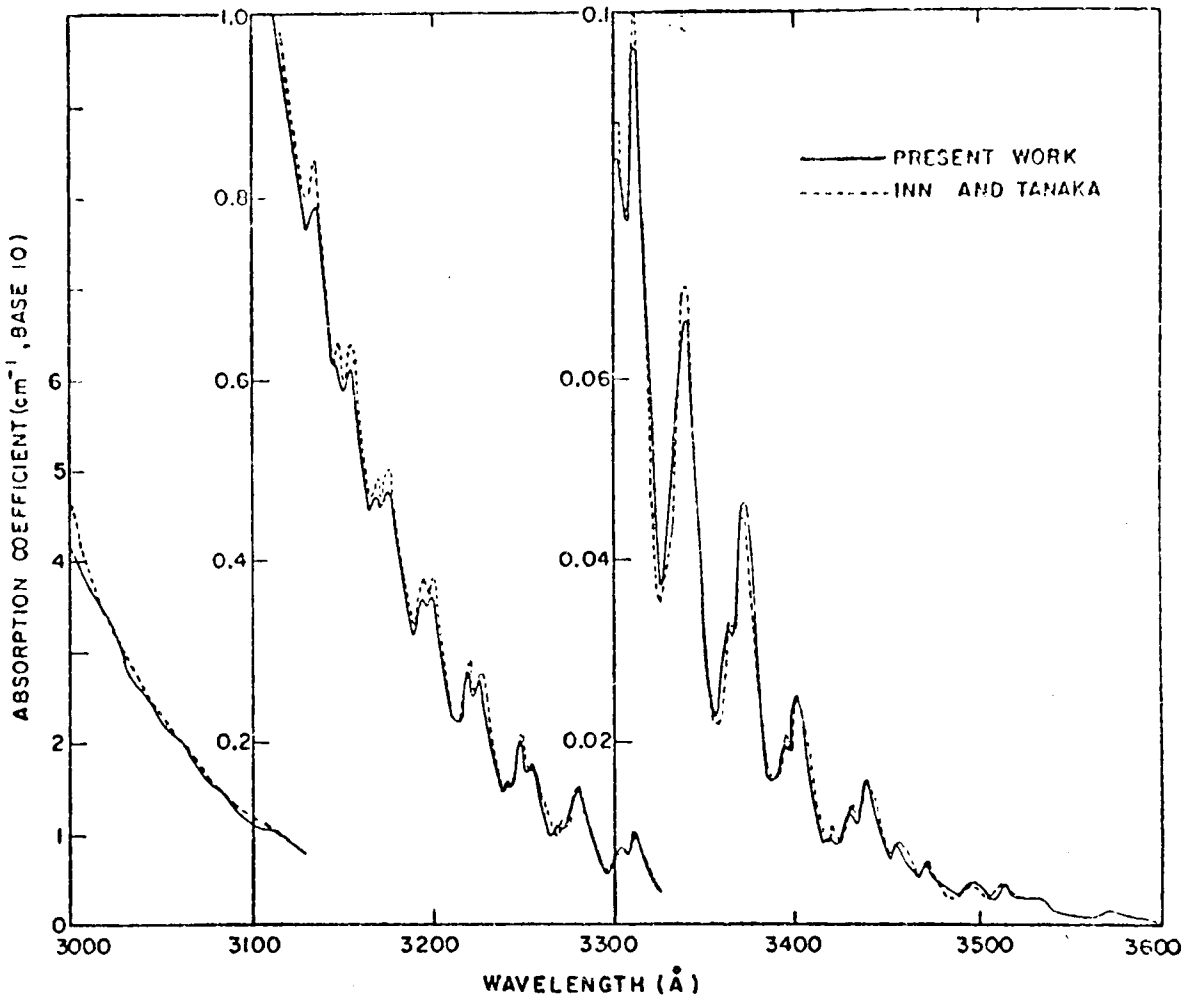
Ozone

Hartley band (2000-3000 Å)
absorption coefficients.



Griggs, 1968

Huggins band (3000-3600 Å)
absorption coefficients.



Chappius band (4400-8500 Å)
absorption coefficients.

Hay et al. have assigned the Hartley and Huggins band to the electronic transition $1^1B_2 - 1^1A_1$ and the Chappuis band to the transition $1^1B_1 - 1^1A_1$ (with possible contribution from $1^1A_2 - 1^1A_1$ also). The ground electronic level of ozone is the 1^1A_1 state. Figure 2,5 shows the results of extensive configuration interaction calculations performed on ozone by Hay et al.. using three slightly different methods. The upper portion shows the predicted potential energy curves for a constant bond length, with varying bond angle. Reference to columns 8 and 9 of the table shows that there are four bound electronic excited states with calculated adiabatic excitation energies less than 1.13 eV, the dissociation energy. Riley and Cahill observed a temporal dependence of part of the Hartley absorption band of ozone formed in the radiolysis of oxygen. They interpreted this feature as being due to a transient species that was not vibrationally excited ozone. Later work by von Rosenberg and Trainor (1974) and Bevan and Johnson, (1973) observed two time dependent absorptions at 3100Å and 2850Å in the Hartley band of ozone produced in the pulse radiolysis of oxygen. They interpreted the results in terms of three distinct species of ozone O_3^α , O_3^β and O_3 which underwent the consecutive reactions $O + O_2 + O_2 \rightarrow O_3^\alpha + O_2$, $O_3^\alpha + O_2 \rightarrow O_3^\beta + O_2$ and $O_3^\beta + O_2 \rightarrow O_3 + O_2$. The two superscripted ozone species were assumed to be vibrationally excited ozone. However, the energy separation of 0.5eV between O_3^α and O_3^β and between O_3^β and O_3 is much greater than the spacing of adjacent vibrational levels. Von Rosenberg and Trainor (1974) thus suggested that the O_3^β species might be the

O_3 ($^3B_2$) state. By the same argument O_3^α might be $o_3(^3B_1)$ at 1.09 eV above the ground state (Hay et al).

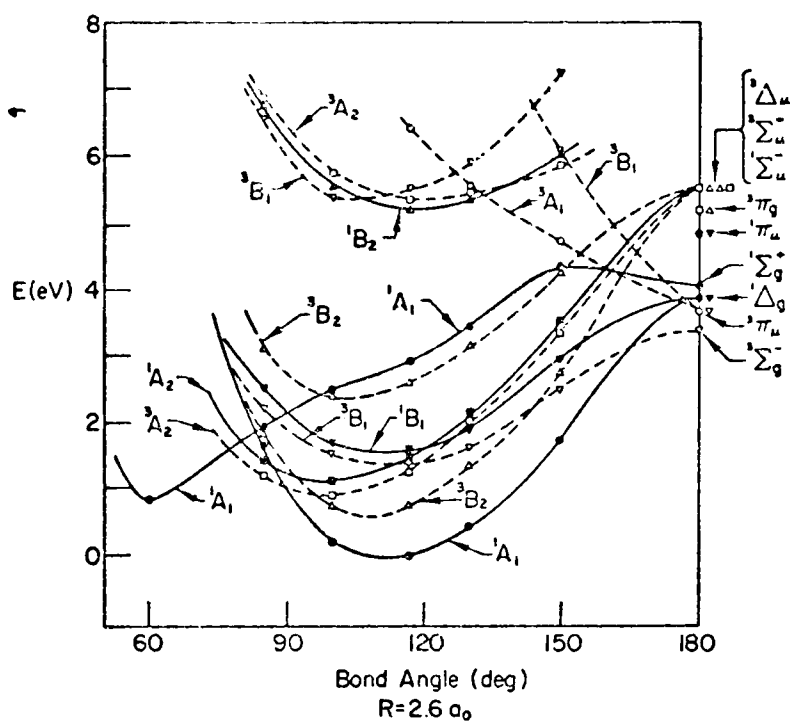
Later work by von Rosenberg and Trainor, 1974 has demonstrated that fifty percent of the recombination exothermicity appears as vibrational excitation of the ground electronic state, principally in the ν_2 bending mode. It is arguable, therefore, whether there is yet any experimental evidence for the existence of low lying electronic bound states of ozone.

The potential energy curve (figure 2,5) also shows the calculated energy of the O_3 ring configuration (2^1A_1) with a bond angle of 60 degrees. Latest results of Hay et al. (1973) included in the paper from which figure 2,5 is taken, however, show its formation from ground state O_2 and O to be energetically unfavourable.

The upper part of figure 2,6 gives the long wavelength limits for the production of various electronic O_2 and O species from the photolysis of ozone. No real evidence has been found to support the formation of any excited species other than $O_2(^1\Delta_g)$ and $O(^1D)$ (and the respective ground electronic states). After much work on the ultraviolet photolysis of ozone (for example, Jones and Wayne, 1970; Lin and DeMore, 1973) it is now accepted that photolysis in the Hartley band at wavelengths shorter than $3100\text{\AA}$ yields $O(^1D) + O_2(^1\Delta_g)$ each with unit quantum yield. Observations by Simons et al., 1973 on the Huggins band of cold ozone (195K) show that it terminates sharply at $3510\text{\AA}$. They believe that the Huggins-Hartley bands are a single system viz. $^1B_2 - ^1A_1$. The implication is therefore that

Figure 2,5 Ozone potential curves

Hay et al, 1973



Potential curves of the lower excited states of ozone.

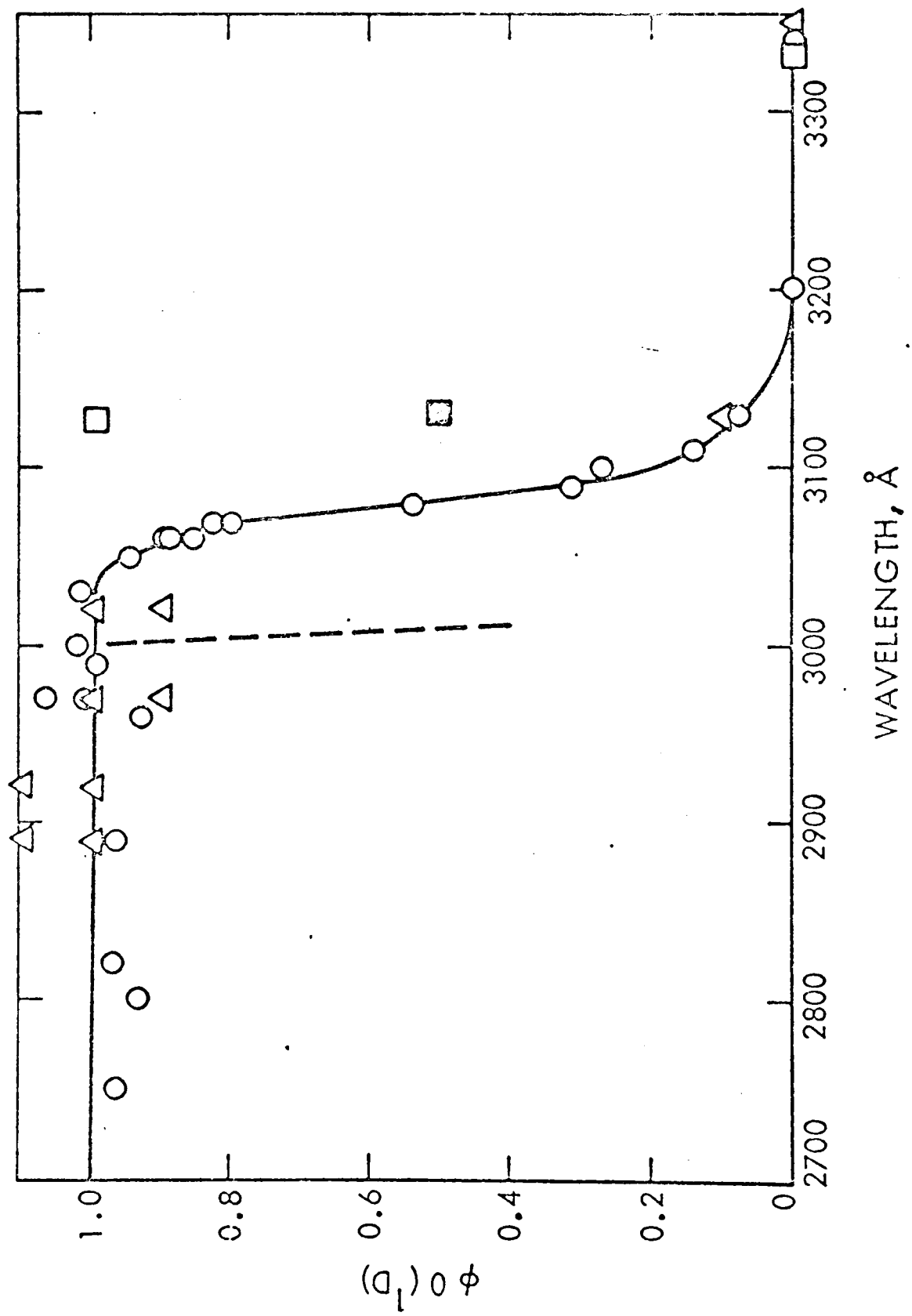
Excitation energies for ozone. All energies are in eV

		Vertical excitation energies ($R = 2.415 a_0, \theta = 116.8^\circ$)			Nonvertical excitation energies						
		CI calculations			optimum R , fixed θ (116.8°)			variable θ , fixed R ($2.6 a_0$)			
		MBS	DZ	exp.	CI calculations			CI calculations			
			GVB CI	POL CI	MBS	DZ		MBS	DZ	GVB CI exp.	
State						GVB CI	POL CI				
ionic π^4	2^3A_1	9.50	9.96			5.93 ^{d,e)}	6.59 ^{e)}				
	1^3A_1	9.02	9.23			5.18 ^{d,e)}	5.86 ^{e)}				
ionic π^5	2^1B_1	8.33	7.71	7.23		5.64	5.15	5.09			
	2^1A_2	8.12	7.56	6.93		5.64	5.33	5.06			
	2^3B_1	7.13	7.00			4.77	4.42	4.16			
	2^3A_2	7.08	6.89			4.78		4.25			
ionic π^4	3^1A_1	7.91	8.33	8.14		5.45	5.76	5.52			
	1^1B_2	6.50	6.93	5.60	4.13– 5.64	5.04	4.92	4.36	5.04	3.45	
covalent π^6	2^1A_1	4.16	4.51	4.18		2.22	2.49	2.43			
	2^3B_2	3.80	4.19	3.86		1.97	2.22	2.17	1.81		
covalent π^5	1^1B_1	2.18	2.32	2.06	2.03– 2.26	1.22	1.36	1.29	1.22	} (1.2)	
	1^1A_2	1.97	2.32	1.98		1.17	1.33	1.22	0.85		1.10
	1^3A_2	1.80	2.11	1.80		1.07	1.18	1.10	0.72		0.93
	1^3B_1	1.94	1.97	1.74		1.07	1.13	1.10	1.09		
covalent π^4	1^3B_2	1.20	1.69	1.47		0.60	0.77	0.77	0.47		
	1^1A_1	0.0	0.0	0.0		0.0	0.0	0.0	0.0	0.0	
column number		1	2	3	4	5	6	7	8	9	10

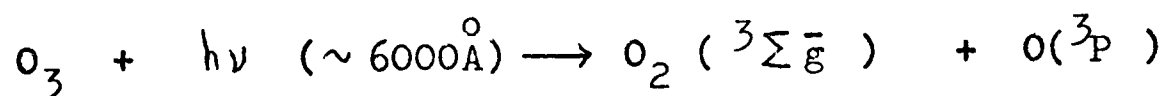
Caption: $\circ$ Lin and Demore 1973 Δ Jones and Wayne 1970 $\square$ Castellano and Schumacher 1972
 $\blacksquare$ Simonaitis et al. --- Demore and Haper 1962

Figure 2,6

$O(^1D)$ PRODUCTION in OZONE PHOTOLYSIS



transitions to the upper ${}^1B_2$ state in the Huggins band result in $O({}^3P) + O_2({}^1\Delta_g)$ by some curve crossing mechanism. Simonaitis et al. 1972, find a quantum yield of 0.5 for $O({}^1D)$ production at $3130\overset{O}{\text{\AA}}$, in disagreement with the value of about 0.1 found by Jones and Wayne, 1970, and Lin and DeMore, 1973. Clearly, however, the products in this region will depend somewhat on the vibrational temperature of the ground state. From results on the red light ($\sim 6000\overset{O}{\text{\AA}}$) decomposition of ozone in the Chappuis region (Castellano and Schumacher, 1962) it would appear that both ground state molecular and atomic oxygen are formed.



Hey et al (1973) assign the Chappius absorption as arising from the ${}^1B_1 - {}^1A_1$ transition.

C H A P T E R 3

EXPERIMENTAL TECHNIQUES.

3.1 Ozone Production and Purity Measurement.

Ozone is an endothermic compound formed from oxygen ($\Delta H_{1298}^{\circ} = 142.8 \text{ kJ mole}^{-1}$). In this case the necessary energy was provided by the passage of molecular oxygen through a 12 kV silent discharge in a conventional Siemen's ozoniser.

Oxygen from a cylinder was passed through two phosphorus pentoxide drying towers into the ozoniser, as shown in Figure 3.1. The ozoniser consists of two pairs of concentric tubes in parallel, the inner tube being filled with copper sulphate solution to form one electrode; whilst the outer tubes were surrounded by the same electrolyte to form the other electrode. The 12kV silent discharge was provided by a transformer. The oxygen stream containing several percent ozone was passed first through a cold trap (197K) to remove any unwanted oxides of nitrogen resulting from nitrogen impurity in the cylinder oxygen, and then through a silica-gel trap. Ozone is selectively absorbed onto the silica-gel (at 197K). This method of ozone collection is probably safer than trapping down liquid ozone in liquid nitrogen. Of all the flashbacks and explosions which happened none ever occurred in the silica-gel trap; although other experiments in this research group had trap explosions of considerable violence. The gas stream was then vented to the atmosphere through a second room temperature silica-gel trap whose purpose was to prevent the entry of water vapour into the system.

When the silica-gel became dark blue, indicating that it was saturated with ozone, the oxygen flow was halted and the trap isolated from the rest of the system. Excess oxygen was

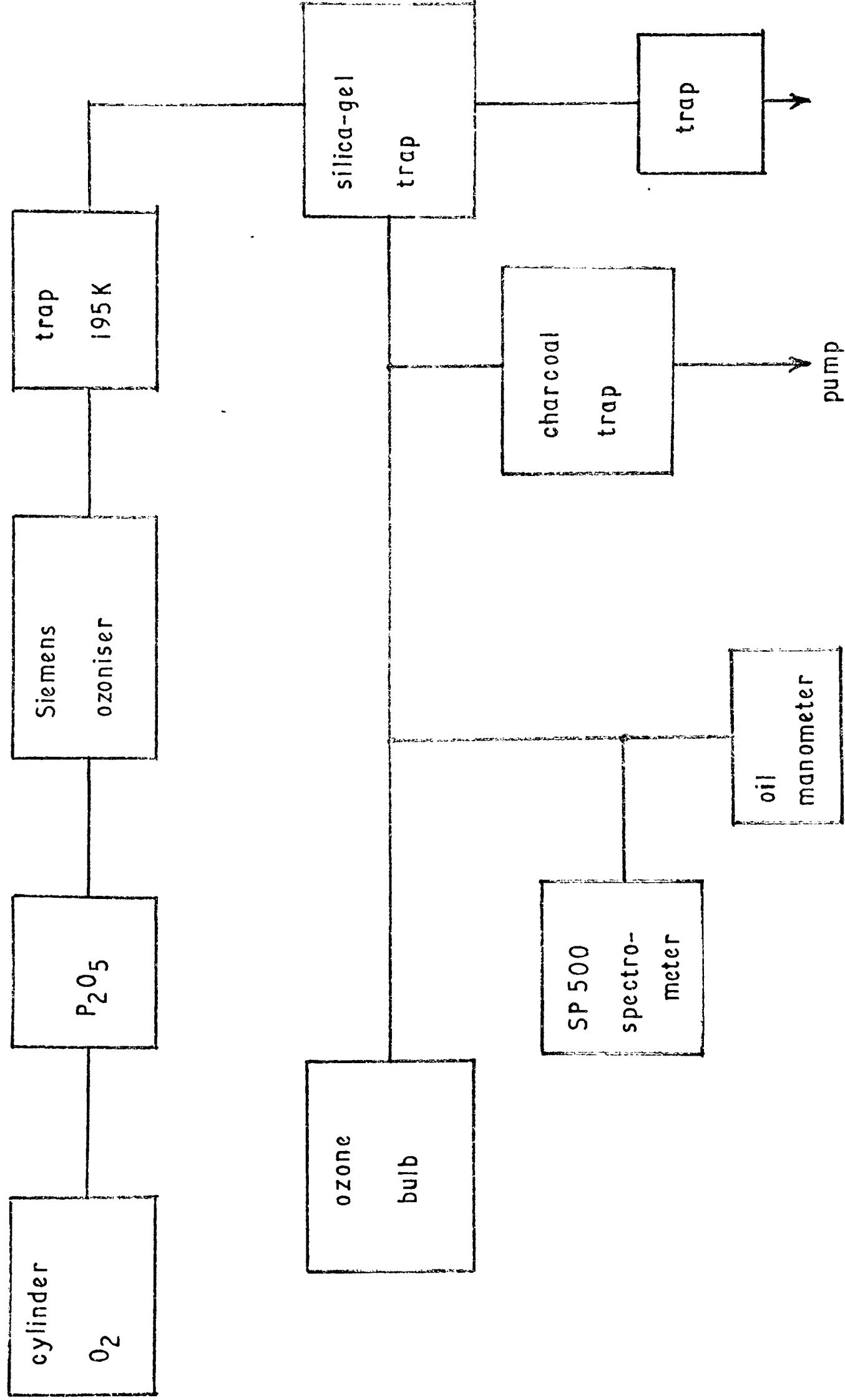


Figure 3.1 The ozoniser

removed by pumping on the trap (at 197K) for several minutes. Any ozone flushed off with the oxygen was prevented from entering the pump, by the activated charcoal trap, some of the charcoal glowing red hot. The ozone was then desorbed from the gel into a five litre pyrex storage bulb (already conditioned to ozone) as the trap was allowed to warm up to room temperature.

To measure the ozone purity a sample was admitted into a 1cm quartz cell inside the Unicam SP 500 UV spectrometer. By simultaneously measuring the optical density (at 2540Å) and the pressure of the sample on an oil manometer, percentage purity of the sample was calculated.

$$\% \text{ ozone purity} = \frac{\text{Optical density} \times 100}{0.1255 \times \text{Pressure (cm oil)}}$$

This relation employs the extinction coefficient reported by Griggs (1968) at 2540Å of $132 \text{ atm}^{-1} \text{ cm}^{-1}$ (base 10). Results consistent to one percent were obtained.

Typically, ozonising for four hours at an oxygen flow rate of five $\text{cm}^{-3} \text{ s}^{-1}$ produced 100 torr of ozone (per five litre bulb) at about 80% purity. The storage life of ozone depends greatly on how well conditioned the storage bulb is. For a well conditioned bulb the ozone might decompose by around 10% per day.

High purity gaseous ozone is notoriously unstable and liable to spontaneous detonation. The author has had two major spontaneous explosions which have destroyed two bulbs. The first involved a mixture of hydrogen and ozone, the second is more inexplicable but may have been due to ozone at a particularly high pressure, possibly containing some nitrogen oxide impurities. Consequently all storage bulbs were encased in several layers of wire mesh and packed in boxes containing a non-flammable filling. The outlet tube and tap were wired and taped to prevent flying glass. The bulbs were also kept in "explosion cabinets" beneath the apparatus.

3,2 Other Materials.

B.O.C. nitrogen, oxygen and helium were used as carrier gases. They were dried by passage through a phosphorus pentoxide tower, and then passed through a capillary spiral cold trap (77K) before entering the flow tube. Cylinder SF_6 (I.C.I.) and CF_4 (B.D.H.) were dried by passage over P_2O_5 , and CF_4 was also passed through a trap at 197K. The Freons CF_3Cl , CFCl_3 and CCl_4 (here deemed to be a Freon) were supplied by B.D.H. The liquids CFCl_3 and CCl_4 were trap-to-trap distilled and pumped on at least three times before use. Residual air (measured mass spectrometrically) was negligible. Gaseous CF_2Cl_2 and CHF_2Cl were used as supplied by B.O.C.. Cylinder Cl_2 and NO (B.D.H.) were trapped and pumped on before use. NO was used from above a cardice trap to maintain any residual higher nitrogen oxides in a condensed phase.

Oil manometers were filled with degassed di-n-butyl phthalate (B.D.H.). Apiezon N grease was used for general applications, whilst Voltalef-F was used for those applications involving ozone at high pressures; on account of resistance of Voltalef-F to attack. Greaseless taps (employing PTFE O-rings) were used in the chlorine handling line, and in the line containing the liquid freons (which are excellent solvents). Stainless steel Nupro needle valves were used to control the flow of ozone and chlorine; otherwise Edwards' needle valves were used.

3,3 Gas Handling System.

The gas handling system went through a continuous evolution during the period of the research described in this thesis. The initial arrangement is shown in figure 3,2; however, there was considerable flexibility to allow different gases to be admitted at different inlet positions down the flow tube. There are three conventional inlet trains for carrier gases, whereby their flow rates may be measured. The capillary flow meters follow the design of Melville and Gowenlock (1964) which allows for easy interchange of capillaries. The gas pressures in the inlet trains were measured initially by mercury manometers (the mercury surface being covered by a thin layer of oil). However, these manometers were replaced later on in the period of this work by oil bubblers. The latter are considerably easier to use and also remove any possibility of mercury contamination of the carrier gas (with consequent absorption of mercury resonance radiation in the photolysis zone). A special design allowed the bubblers to be evacuation and flushed. A cold trap (77K) consisting of 0.5m capillary tubing (which has a very high surface to volume ratio), was used on the helium inlet. Any residual air was monitored mass spectrometrically as N_2^+ (m/e 28) indicating that N_2 was generally less than about 4×10^{-8} mole l^{-1} . Residual water in the gas flow was generally negligible.

Since ozone oxidises mercury and di-n-butyl ^hphtalate oil, the pressure in the ozone inlet was measured with a spiral gauge. The mirror attached to the glass spiral reflects a spot of light onto a calibrated scale as the pressure inside the spiral causes the spiral to unwind. The spiral gauge was calibrated directly against a mercury manometer. Up to the maximum pressure used

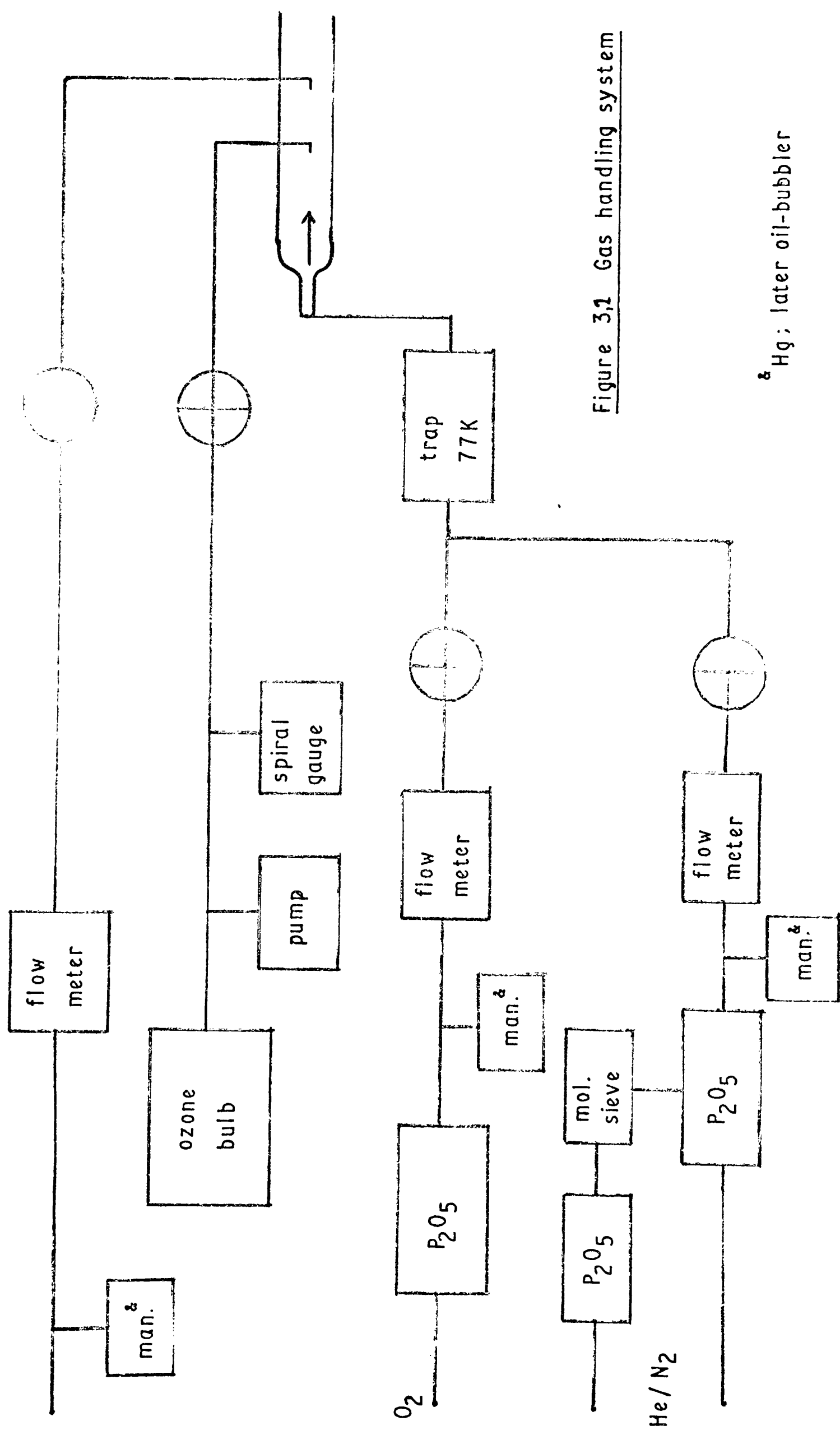


Figure 3.1 Gas handling system

& Hg; later oil-bubbler

(22cm Hg) a linear relation between spot deflection and pressure was found, as shown in figure 3,3.

$$\frac{(\text{Spiral gauge deflection on chart cm})}{(\text{Mercury manometer reading cm Hg})} = 2.725$$

The concentrations in the flow tube of added gases, including ozone, were not measured by using flow meters. As will be dealt with in section 3,7 their concentrations were measured by monitoring a characteristic calibrated peak in their mass spectra. During the work on freons the NO and Cl₂ inlet systems were added. The NO inlet into the flow tube allows nitric oxide to be admitted downstream of the lamp zone via a narrow nylon tube (of variable length) which runs inside the main flow tube. The advantage of this arrangement is that the photolysis lamp is still free to be moved along the quartz flow tube, unimpeded by the presence of inlet jets.

3.4 Capillary Calibration

The flow of gases through a capillary is treated here initially in terms of Poiseuille's equation. This equation is approximately applicable provided the diameter of the capillary is greater than the gas mean free path, but small enough for friction to be significant. The Poiseuille formula for isothermal flow (neglecting the end correction) is:

$$F = \frac{\pi r^4}{16 \eta l} (P_2^2 - P_1^2)$$

where F = flow rate (mole s⁻¹)

p₁ = back pressure (dyne cm⁻²)

p₂ = forward pressure (dyne cm⁻²)

l = length of capillary (cm)

η = viscosity (poise ≡ g cm⁻¹ s⁻¹)

R = gas constant (erg K⁻¹ mole⁻¹)

T = temperature (K)

This formula assumes no slip on the walls, which may be remedied in a correction of the form (1 + 4g/r) where g is the slip

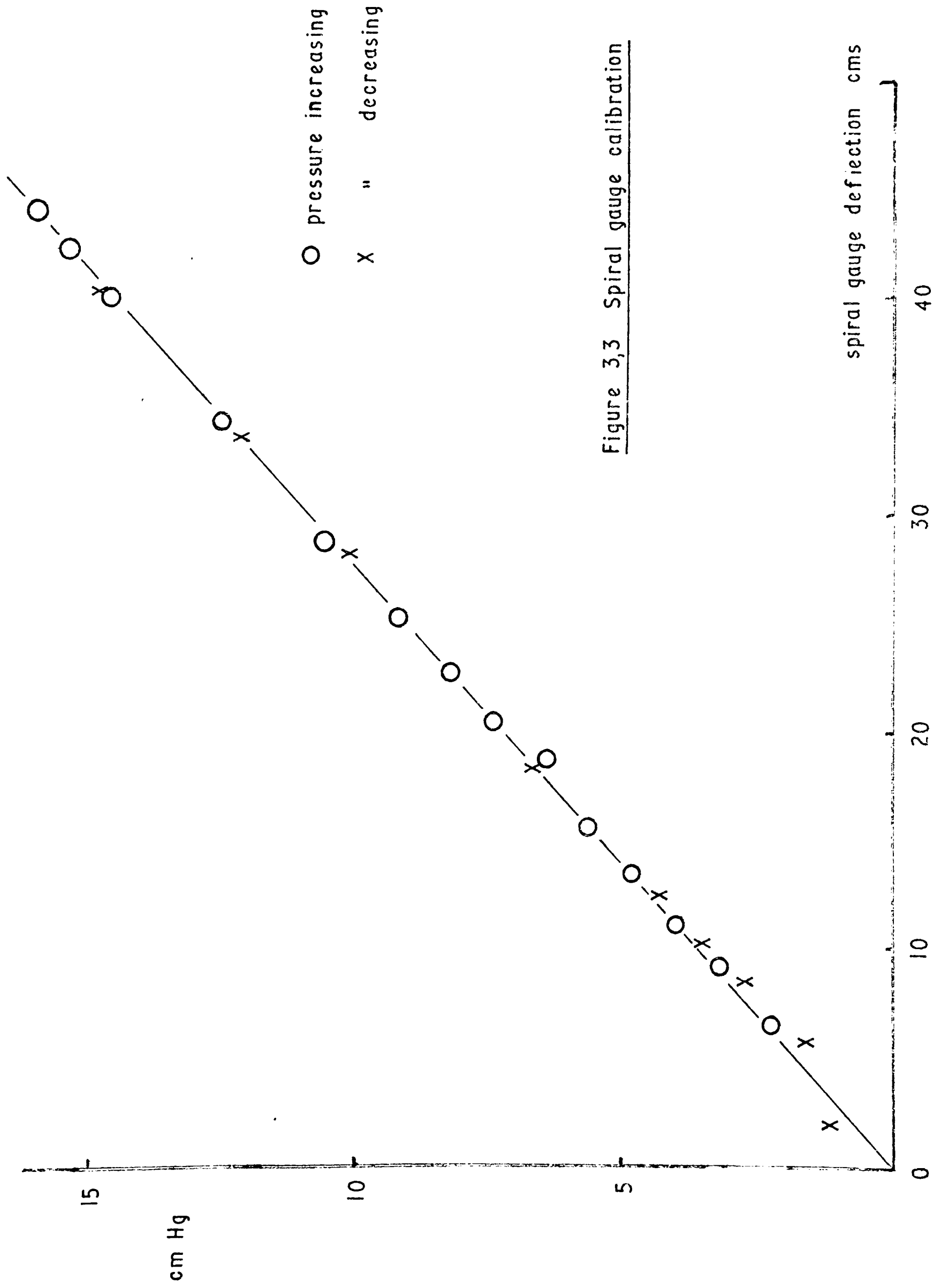


Figure 3,3 Spiral gauge calibration

coefficient and is inversely proportional to the density. In our experiments p_1 and p_2 are close to atmospheric pressure and $(p_2 - p_1)$ is generally less than ten centimetres oil pressure (7.6 torr).

To a fair approximation we can then let

$$(p_1 + p_2) = 2P \quad (\text{where } P \equiv p_1)$$

$$(p_2 - p_1) = \Delta P$$

The formula then reduces to

$$F = \frac{\pi R^4}{813RT} P \Delta P$$

which may be used empirically in the form

$$F = kP \Delta P$$

The "capillary constant" k is then measured for each capillary, by observing the product $P\Delta P$ for given flow rates.

Figure 3,4 shows a block diagram of the equipment used to calibrate capillaries. Gas from a cylinder was pumped through the capillary flow meter, which registers the pressure drop ΔP across the capillary. The outlet of the conventional rotary vacuum pump was connected (via a glass wool trap to remove any traces of oil vapour) to a 50 ml burette containing a small amount of soap solution. The flow rate was measured by noting the time taken for the soap film to travel a given distance up the tube. It is necessary to saturate the pump oil with the gas being used by running for a few minutes before taking measurements. This apparently crude method, in fact, worked well, giving much better precision (better than 1%) than the method wherein a bulb of known volume is pumped out (about 10%). A correction of around 2 percent may be made for the vapour pressure of water in the soap solution. The former method also has the advantage of measuring k at a fixed value of P and ΔP . Figure 3,5 shows values of k at various $P\Delta P$ for He, N_2 , O_2 and SF_6 .

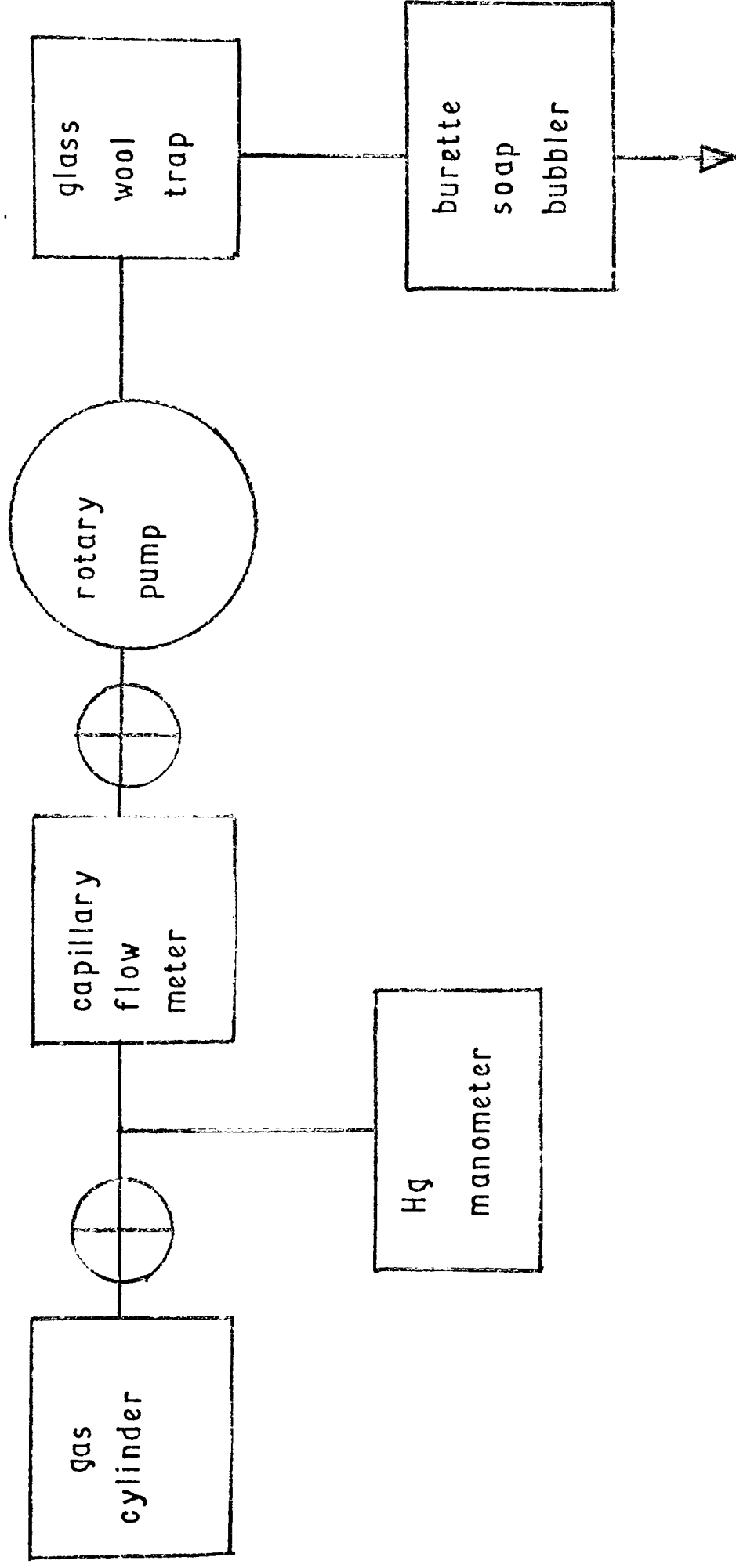


Figure 3.4 Capillary calibration apparatus

Poiseuille's equation predicts that k should be a constant independent of P and ΔP . Figure 3,5 shows that this is indeed the case for helium. N_2 and O_2 show slight variations, but the value for SF_6 is strongly dependent on $P\Delta P$. The effect of using a wider and shorter capillary (to accommodate higher gas flows) is shown in Figure 3,6. Only k_{He} is invariant.

To account for this dependence of k on the molecular weight of the gas and the dimensions of the capillary, we must consider a more detailed equation for viscous flow. The Bernoulli equation

shows that

$$F = \frac{4\pi r^4}{W} \left(\left[1 + \frac{r^4 W P \Delta P}{16 RT l^3} \right] - 1 \right)$$

where W is the molecular weight of the gas. If the term in square brackets is small we can expand as $(1 + x)^{\frac{1}{2}}$ and take the first two terms,

$$F = \frac{4\pi r^4}{W} \left(1 + \frac{r^4 W P \Delta P}{32 RT l^3} - 1 \right)$$

$$= \frac{\pi r^4}{81 \cdot 3 RT} P \Delta P$$

which is Poiseuille's equation. In the event of a high molecular weight gas, or a wide or a short capillary, the expansion is no longer valid and k is not a constant. However, it is still convenient to treat k as a conversion factor as exemplified by figures 3,5 and 3,6. For SF_6 , and the approximate dimensions of the capillary in figure 3,6, (which was used for almost all the experiments described) the flow rate calculated from the Poiseuille equation is larger than the actual flow rate calculated by the Bernoulli equation by a factor of about 1.7.

Figure 3,5 Calibration capillary I

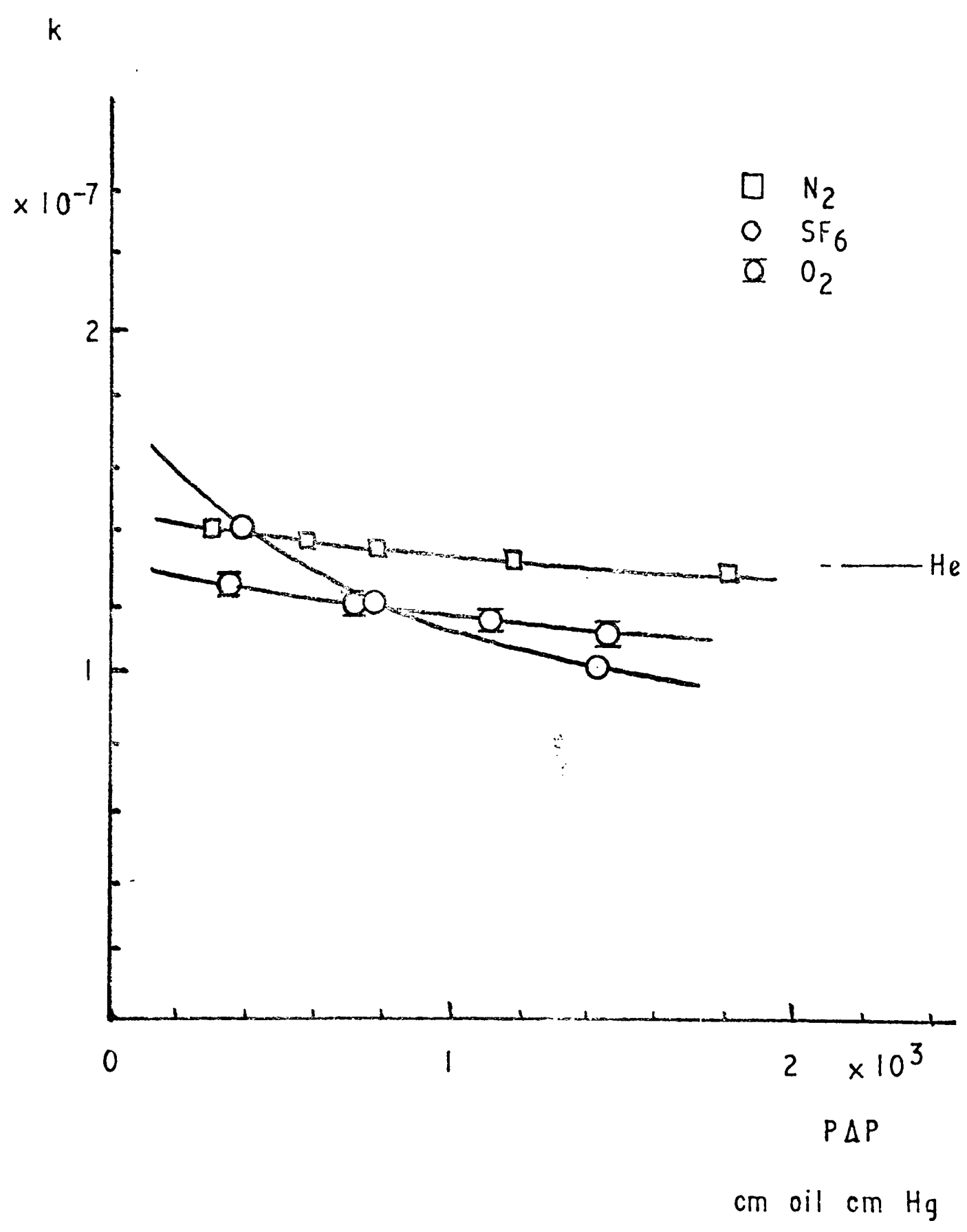
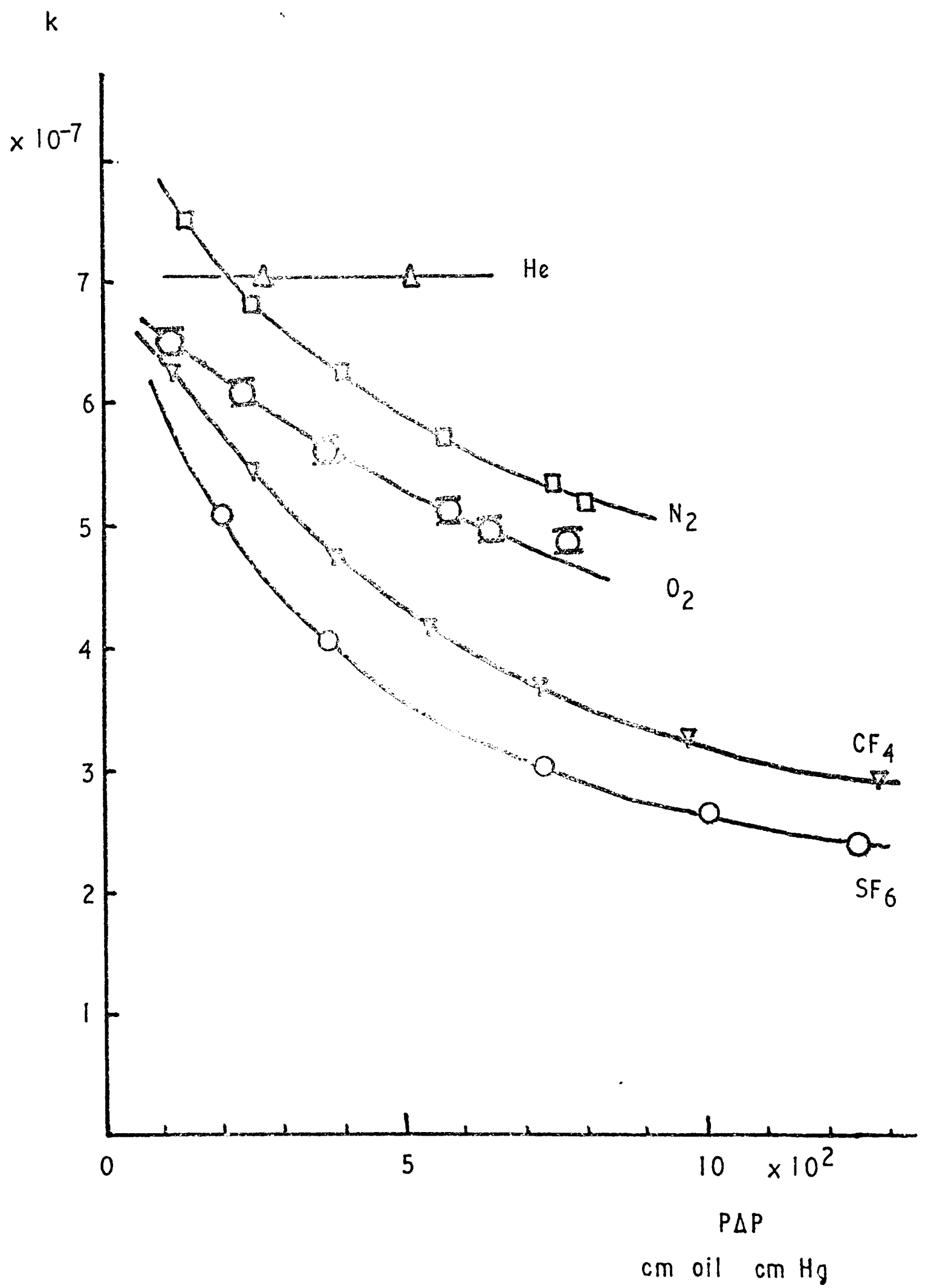


Figure 3,6 Calibration capillary II



3.5 Flow System.

The glass flow system is shown schematically in figure 3.7. Carrier gases entered via their own inlet trains and reactants could be added either at the inlet manifold or through three other jets, as shown. The system was designed to be easily demountable. To transmit the 2537⁰Å mercury photolysing radiation a one metre section of the flow tube was made of quartz.

The flow rate of carrier gas into the flow tube was controlled by Edwards' needle valves. The pressure in the flow tube (and consequently the flow velocity) could be finely controlled by bleeding air into the pump downstream of the sampling region. If we assume plug flow then the flow velocity is given by

$$F = \frac{CVA}{10}$$

where F = flow rate (mole s⁻¹)
 C = concentration (mole l⁻¹)
 V = velocity (m s⁻¹)
 A = cross sectional area of tube (cm²)

The cross sectional area of the quartz section of the flow tube was 2.54 cm². Since the flow rate is that measured by the capillary flow meter, the flow velocity

$$V = \frac{10k P \Delta P}{CA}$$

As a check, an experiment was performed to actually measure the flow velocities. The passage of an air-afterglow chemiluminescent front was timed electronically by two photomultipliers placed 54cm apart along the flow tube. The experimental arrangement is illustrated in figure 3.8. The first photomultiplier provides a signal which sends the μ 709 integrated circuit (which has a response time of around 10 microseconds), arranged with

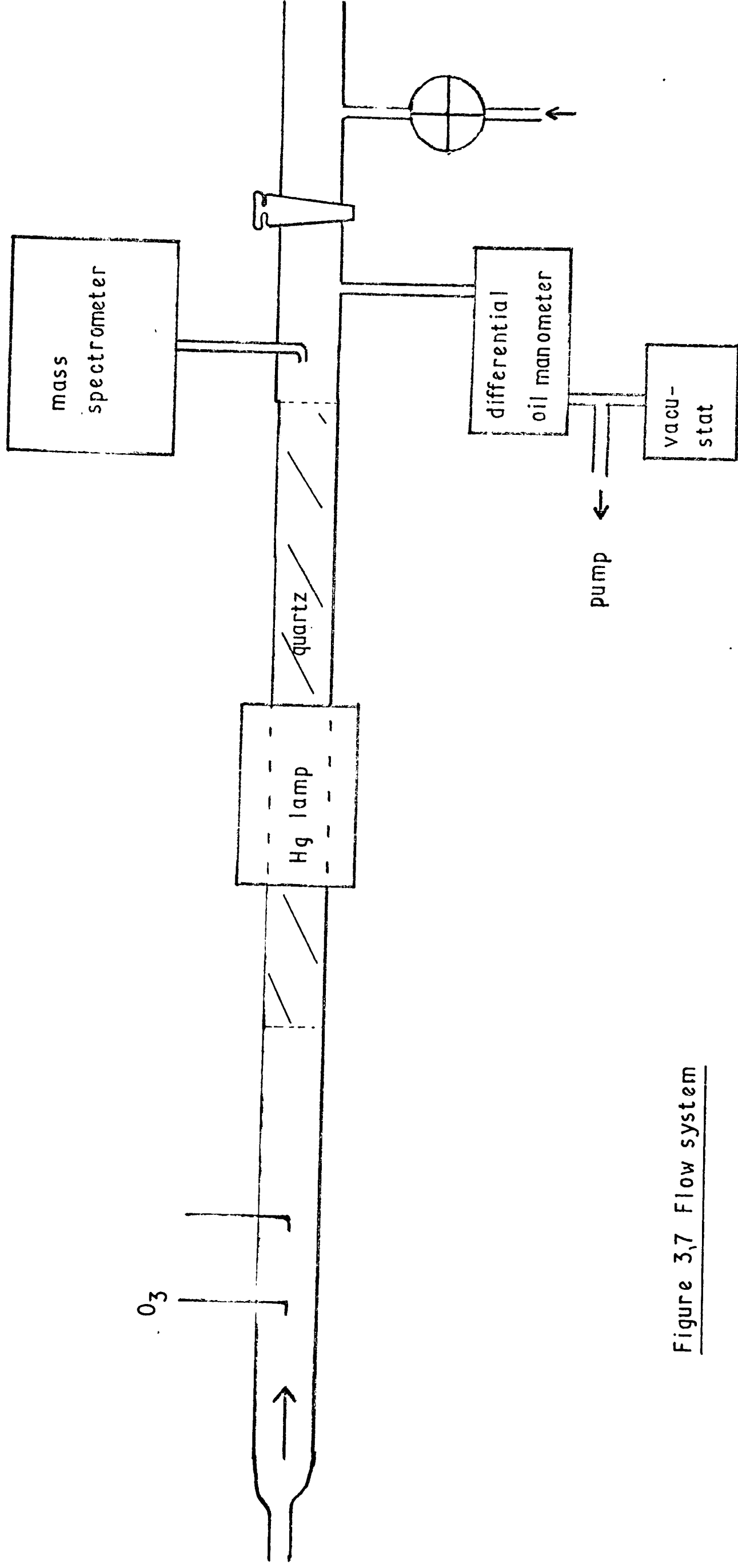


Figure 3,7 Flow system

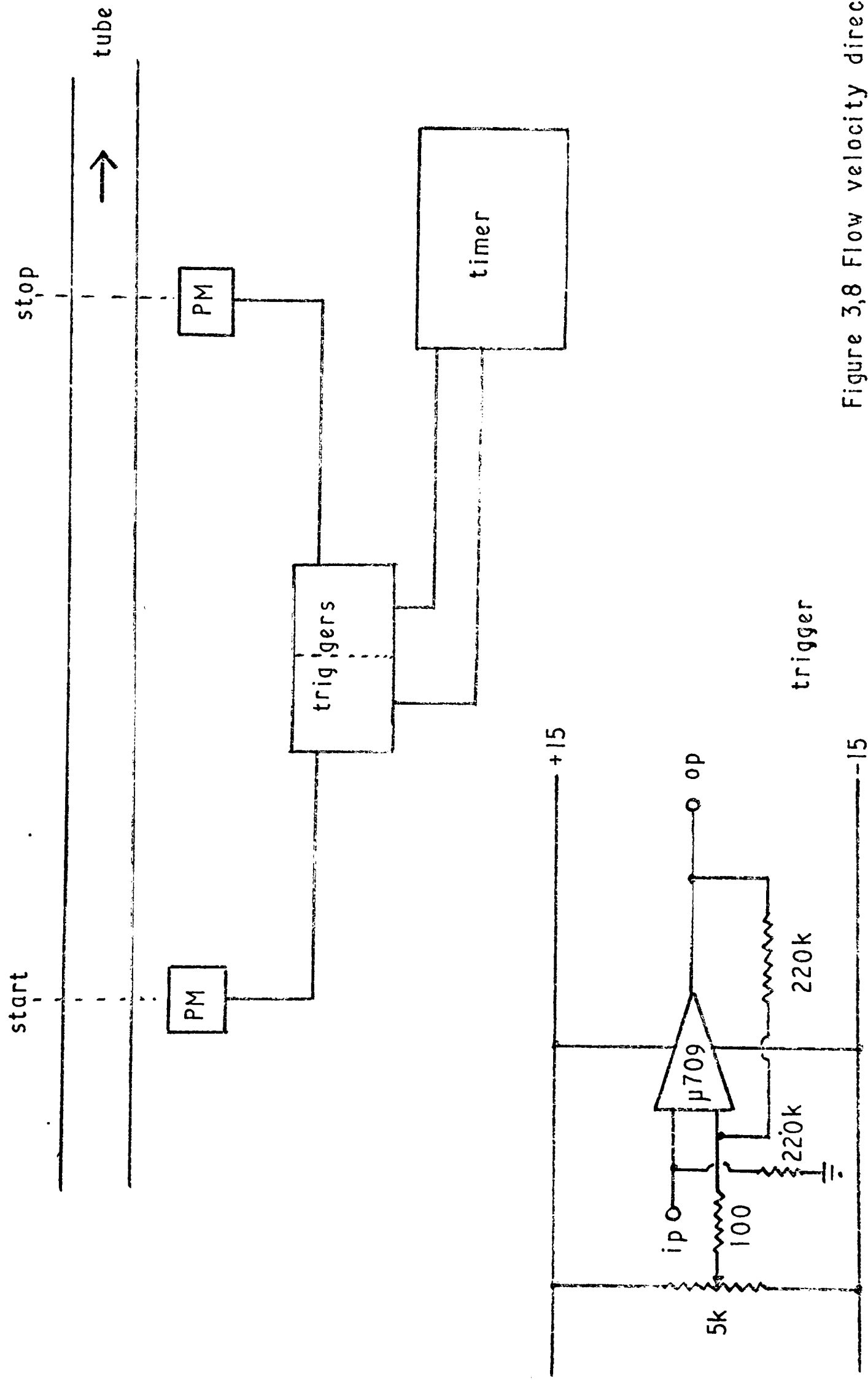


Figure 3,8 Flow velocity direct

measurement

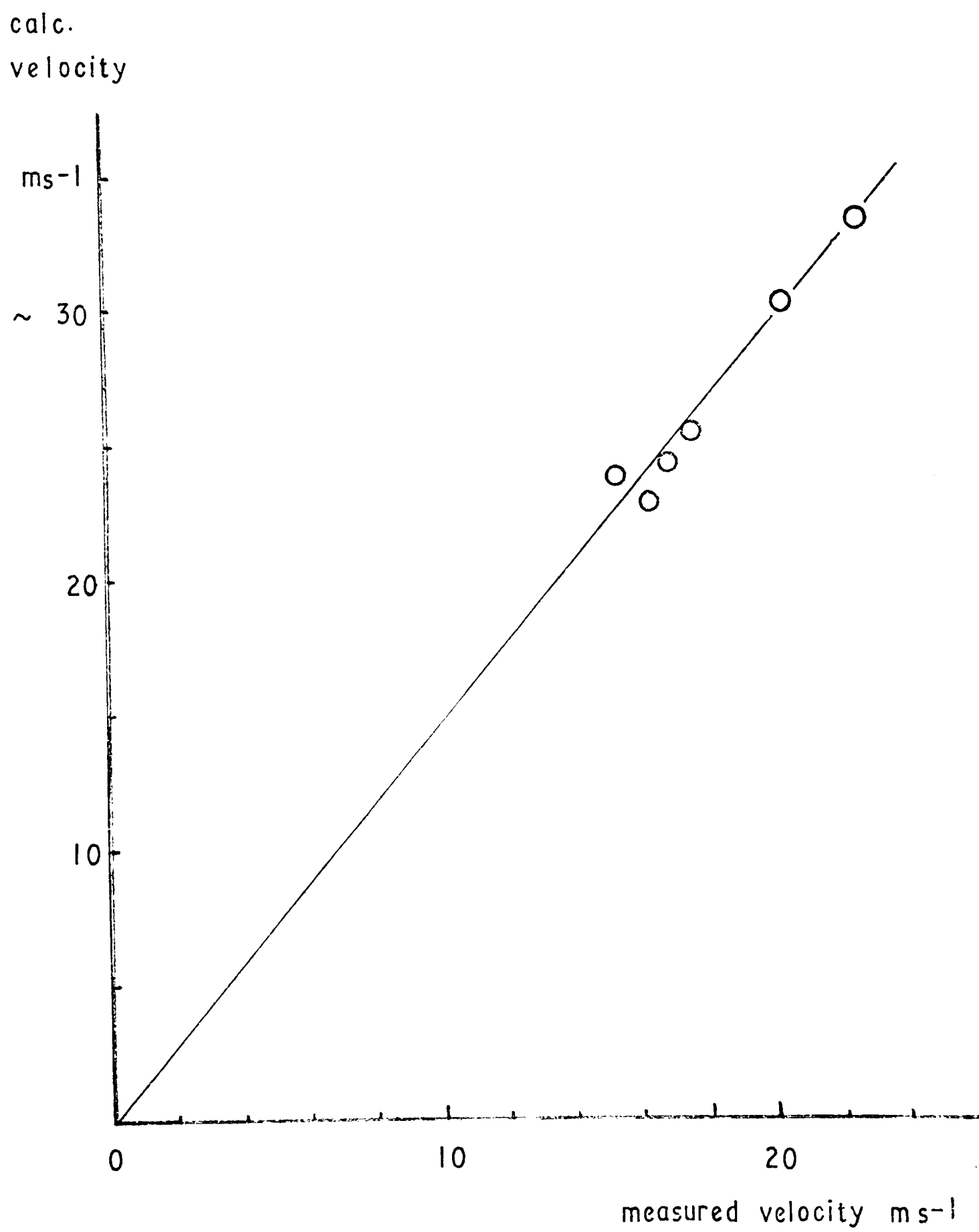
positive feedback, upto the rail voltage. This provides the necessary fast negative-going edge (at least three volts) to start a digital timer. The second photomultiplier provides the stop signal. Figure 3,9 shows the results obtained for helium which appear to justify the plug flow assumption. Reynold's numbers for helium and nitrogen under typical experimental conditions were about 2 and 14 respectively. This means that at a flow velocity of 10 m s^{-1} the regime is most likely that of slip-flow (i.e. slip at the walls - see Estermann pl33) rather than full laminar-flow. Appendix 2 contains a simple treatment of the effect of a laminar-flow type régime on the amount of photolysis radiation absorbed by gas in the flow tube viz à viz the amount absorbed in a plug-flow régime.

The pressure in the flow tube was measured at a point close to the mass spectrometer inlet with a differential oil manometer. One side of the manometer was continuously pumped by a rotary pump and the backing pressure measured absolutely on an Edwards Vacustat gauge. The head of oil was measured using a travelling vernier microscope.

3, 6 Photolysis Region.

The $2537\text{\AA}$ radiation emitted from an intense low pressure mercury lamp was used to photodissociate ozone and generate $\text{O}(^1\text{D})$ atoms. The helical mercury lamp was powered by two stray-field transformers in series (figure 3,10) About 1 kV was required to start the lamp because of the large distance between the electrodes. Stray field transformers limit the amount of current that may be drawn by the lamp as it heats up. The electrical resistance of a mercury lamp falls with increasing temperature as more mercury is vapourised. An AC voltage was used as experience has shown that DC leads to variable and unstable light output. The lamp

Figure 3,9 Calc. vs measured velocity



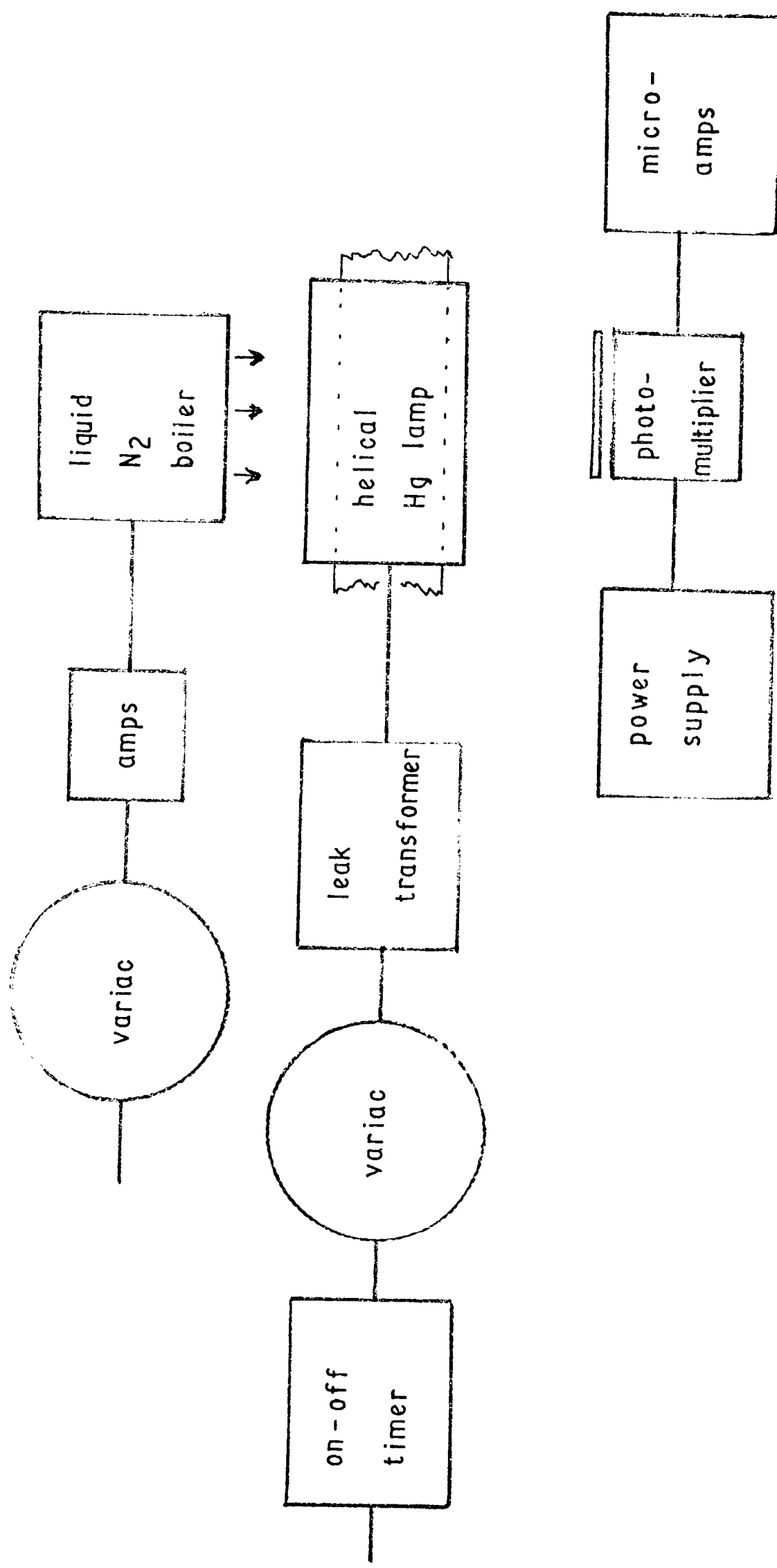


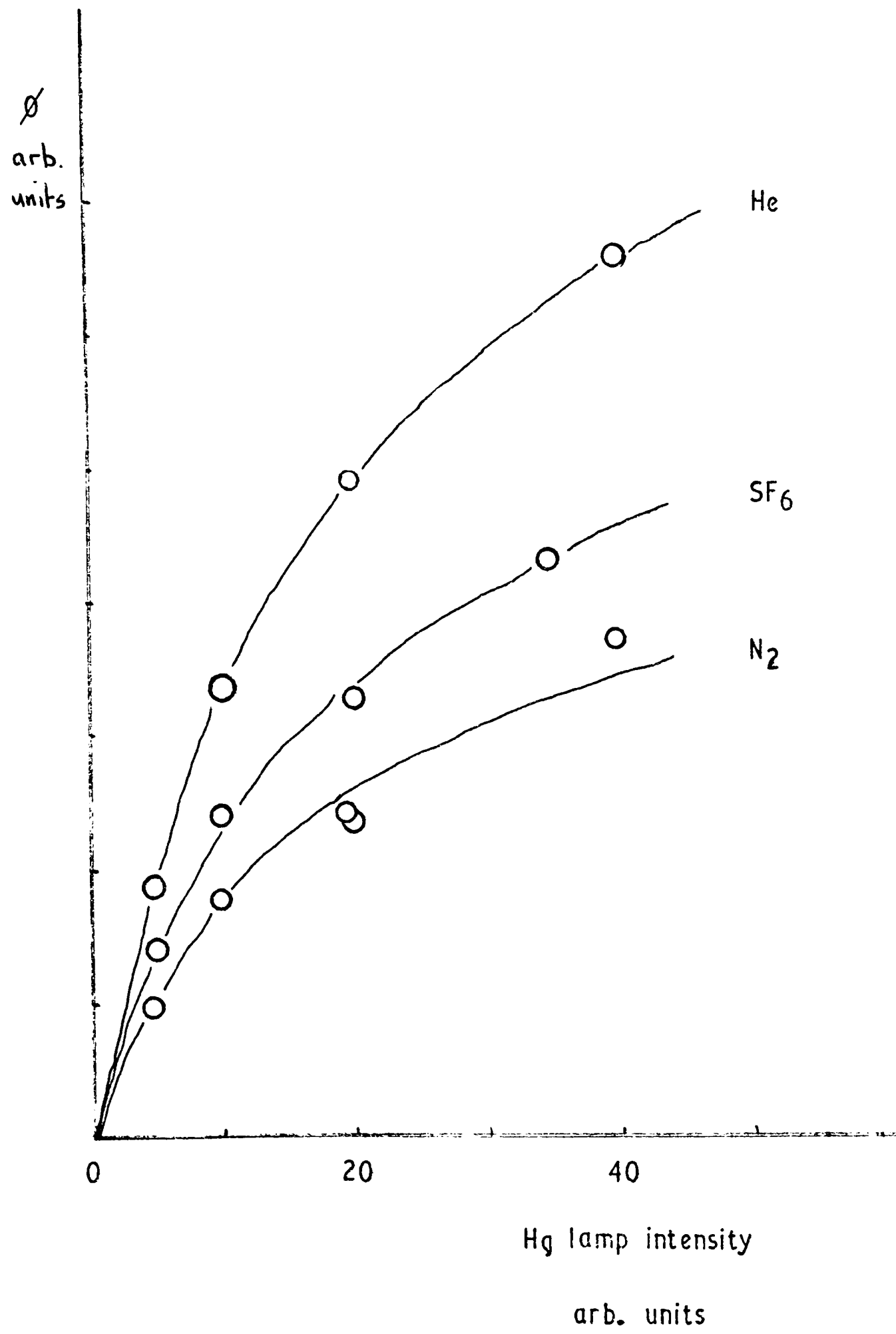
Figure 3,10 Photolysis lamp

was contained within a cylindrical metal can which acted as a reflector and defined the photolysis region (normal length 20 cm). The lamp was free to be moved up or down the metre long quartz section of the flow tube, to obtain time resolution.

The lamp intensity was monitored by a photomultiplier (Mazda 27M3 Quartz) mounted outside the lamp housing. The photomultiplier was used with four dynodes operational and run at 200V from a stabilised power supply. The lamp was viewed through a $2545\text{\AA}$ interference filter which had 8-10% peak transmission and a bandwidth of $143\text{\AA}$ (FWHH). The lamp intensity was controlled by blowing cold nitrogen (produced by boiling liquid nitrogen) through it. The flow was arranged, by varying the heater current, to keep the lamp at the optimum temperature for maximum emission of $2500\text{\AA}$ radiation. Flushing with nitrogen also prevented the formation of profuse quantities of ozone around the lamp. The lamp intensity could also be controlled by a Variac in the primary circuit of the stray field transformers. Figure 3,11 shows the variation of quantum yield for ozone loss in nitrogen (when $-\phi\{O_3\}$ is unity) and in helium (when $-\phi\{O_3\}$ is two) at various lamp intensities.

The spectrum of the lamp viewed with an EMI 9558Q ^{au} photomultiplier/Bösch and Lomb monochromator arrangement showed an intense peak at around $2500\text{\AA}$ which fell to about five percent at $3000\text{\AA}$ and to zero at $2300\text{\AA}$. A second weak peak was also seen around $4300\text{\AA}$. In order to verify that the quartz flow tube transmitted uniformly along its length (since ground quartz joints had been glass-blown on at either end) a photodiode on the end of a long lead was passed down the centre of the flow tube. The photodiode viewed the photolysis lamp, which was moved to different positions along the tube, through an OX7 filter. The transmission of the quartz monitored in this way showed no noticeable variation along

Figure 3,11 ϕ vs lamp intensity



the tube.

To obtain alternate measurements of the ozone concentration $[O_3]$ and the change in ozone concentration due to photolysis ΔO_3 , the lamp was pulsed at approximately twelve second intervals. A motor and cam switched a microswitch controlling a relay connected into the lamp primary circuit.

3.7 Mass Spectrometer and Calibrations.

The detection facility used in these experiments was a 180° sector magnetic mass spectrometer (AEL. Type MS10). The mass range nominally covers m/e values 2,3,4, 12 to 45 and 36 to 200. Ionisation is by electron impact (from a hot filament) at energies upto 100eV and trap currents of upto 300 microamps. The ion current produced is measured by an electrometer. The electrometer head contains a 10^{11} ohms input resistance and a valve preamplifier stage. The limiting sensitivity is nominally 10^{-12} amps for full scale deflection of the output meter. Long term stability was found to be improved by installing a fan to cool the electronics (which uses valves). An effective back-off control was installed by connecting a simple battery/potential-divider into the negative feedback loop of the amplifier section. This control became essential in order to back-off significant backgrounds usually caused by fragmentation of one of the reactants. The problem was particularly troublesome when observing the ozone peak (m/e 48) in the presence of freons (which may give rise to fragments at the following m/e values; CCl^+ 47.5, CF_2^+ 50). The diffusion pump was filled with Santovac 5 polyphenyl-ether diffusion pump oil which has a good stability to oxidation. The chamber could be pumped down to 10^{-8} torr.

The inlet to the ionisation chamber was via a pinhole in the end of a narrow pyrex probe which extended into the centre of the flow tube. This system was effective but had the disadvantage

that the chamber pressure was controlled by the size of the pinhole and by the pressure in the flow tube. Since the sensitivity of the mass spectrometer varied according to the chamber pressure, it was necessary to calibrate the mass spectrometer response to given concentrations of reactants in the flow tube, at various carrier gas pressures. Figure 3,12 shows the mass spectrometer response to various pressures of oxygen in the flow tube. The size of the pinhole was a compromise between allowing in a large amount of gas in order to obtain the maximum signal, and between not allowing the chamber pressure to rise above 10^{-4} torr (which would seriously reduce the filament life). The pinhole finally used (about 0.2mm) was produced by carefully collapsing a small hole in a heated glass tube. A better arrangement would have a second differentially pumped chamber to isolate the ion chamber from the flow tube.

The main objective in using mass spectrometric detection was to be able to monitor concentrations of ozone that were too small to be measured by conventional absorption spectroscopy, even using some elegant techniques (see Horner, 1973). For kinetic reasons (see Chapter 4) it was necessary to be able to work with total ozone concentrations of between 1×10^{-8} and 1×10^{-7} mole l^{-1} . Since it is necessary to measure changes in the total ozone concentration at low conversions (typically less than ten percent), the equipment had to be able to reliably measure ozone concentrations down to 1×10^{-9} mole l^{-1} . The various experimental parameters were, therefore, optimised for maximum sensitivity to ozone. The ultimate sensitivity to ozone attained (measured as O_3^+ at m/e 48) was about 5×10^{-10} mole l^{-1} (signal-to-noise

Figure 3,12 MS sensitivity vs chamber pressure

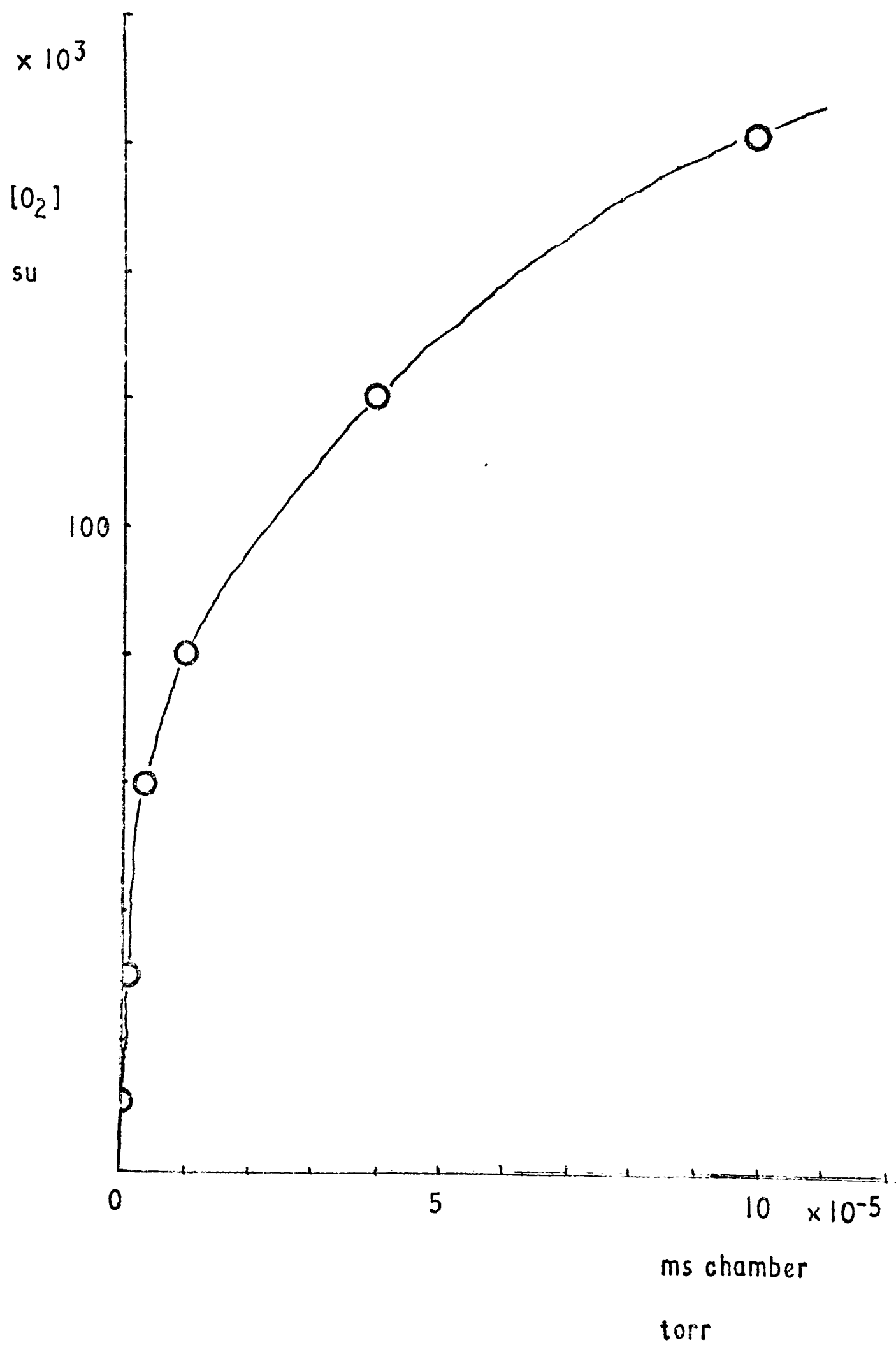
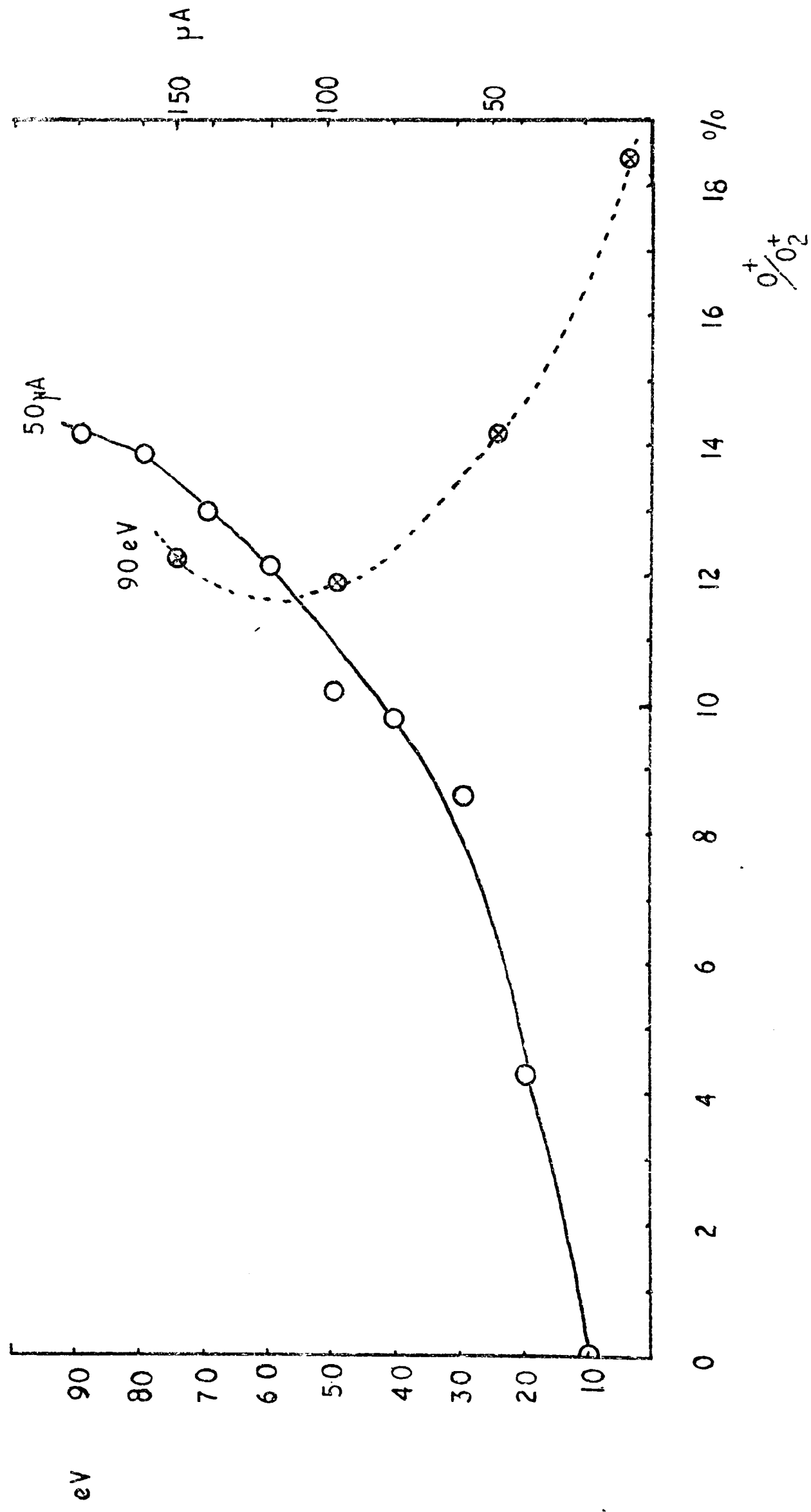


Figure 3,13 Fragmentation O_2^+



ratio of unity). Rough estimates indicate that about 7 percent of all ozone interacting with the electron beam appears as O_3^+ at the collector.

Figure 3,14 and 3,15 show the variation of the O_3^+ ion current as a function of electron beam energy and electron beam current, respectively. (The electron beam energy was not measured and the values quoted are the nominal scale values). Since the appearance potential of ozone is 12.9eV the scale appears to read eight electron volts low!) Figure 3,15 shows the behaviour of ozone at varying electron currents. The electron beam was consequently operated at maximum energy (90eV) and a "trap current" of 150 microamps.

Measurements of the concentrations of species were made by tuning into, and "sitting on", the appropriate previously calibrated peak. This method had the advantage (in relation to scanning through the peak) that any background at that particular mass number was easily allowed for by switching on and off the flow of the species. The concentration was then simply proportional to the difference in readings. The ion current is, strictly speaking, proportional to the area under the peak. Therefore, to use the method described it was necessary to establish that the peak height was proportional to the peak area. Figure 3,16 shows that there is a linear relationship between peak height and peak area for various ozone concentrations in both helium and nitrogen carrier gases.

The mass spectrometer was calibrated to measure absolute concentrations of species as follows. A complete mass spectrum (m/e 12-200) was taken to establish which peaks appeared. Appendix 4 shows the fragmentation patterns (at 90eV and 150 A) of reactants used. The freons, for example, do not show detectable parent peaks. A suitable calibration peak was then chosen, usually on the basis of

Figure 3,14 Appearance potential O_3^+

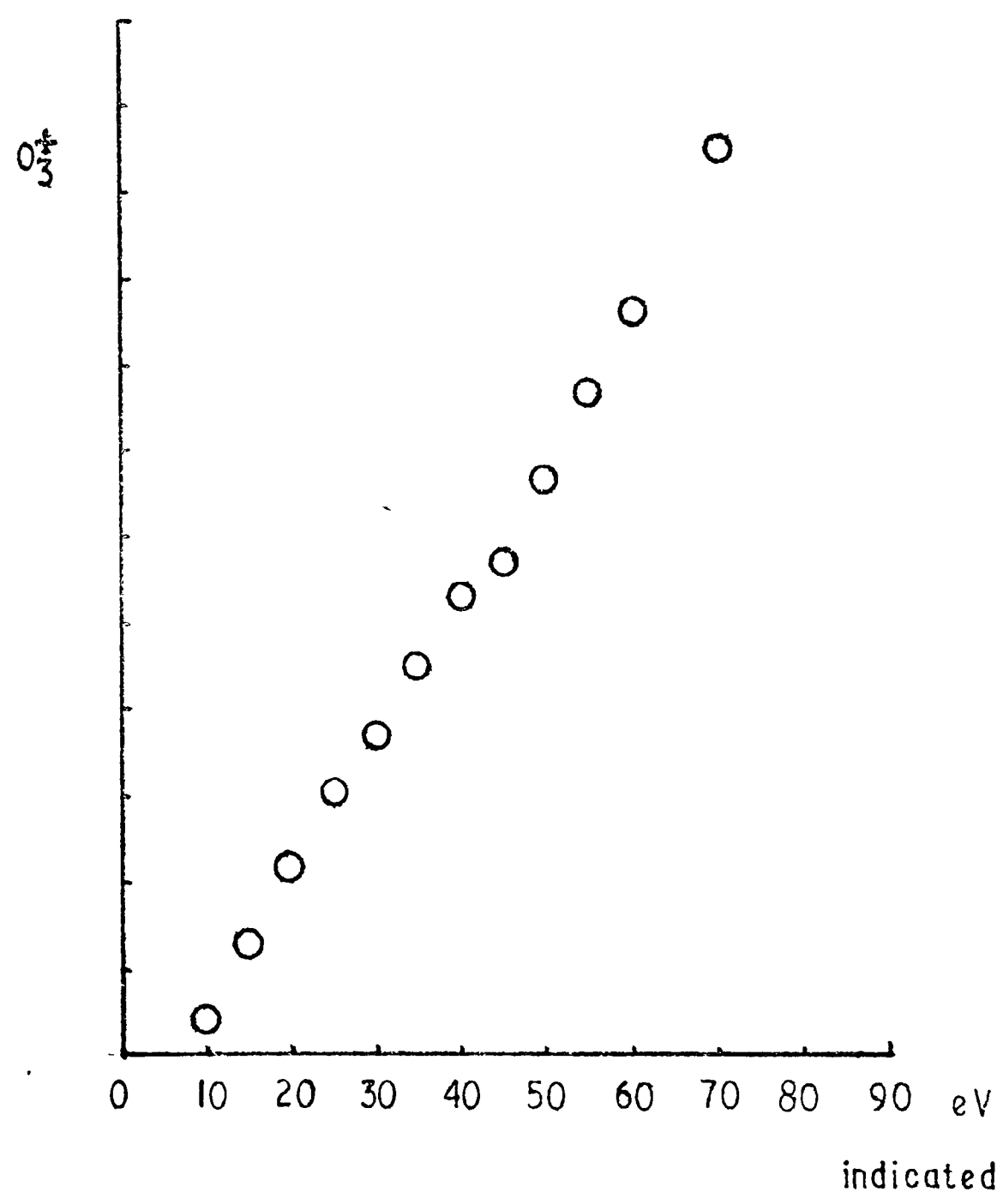


Figure 3.15 O_3^+ vs trap current

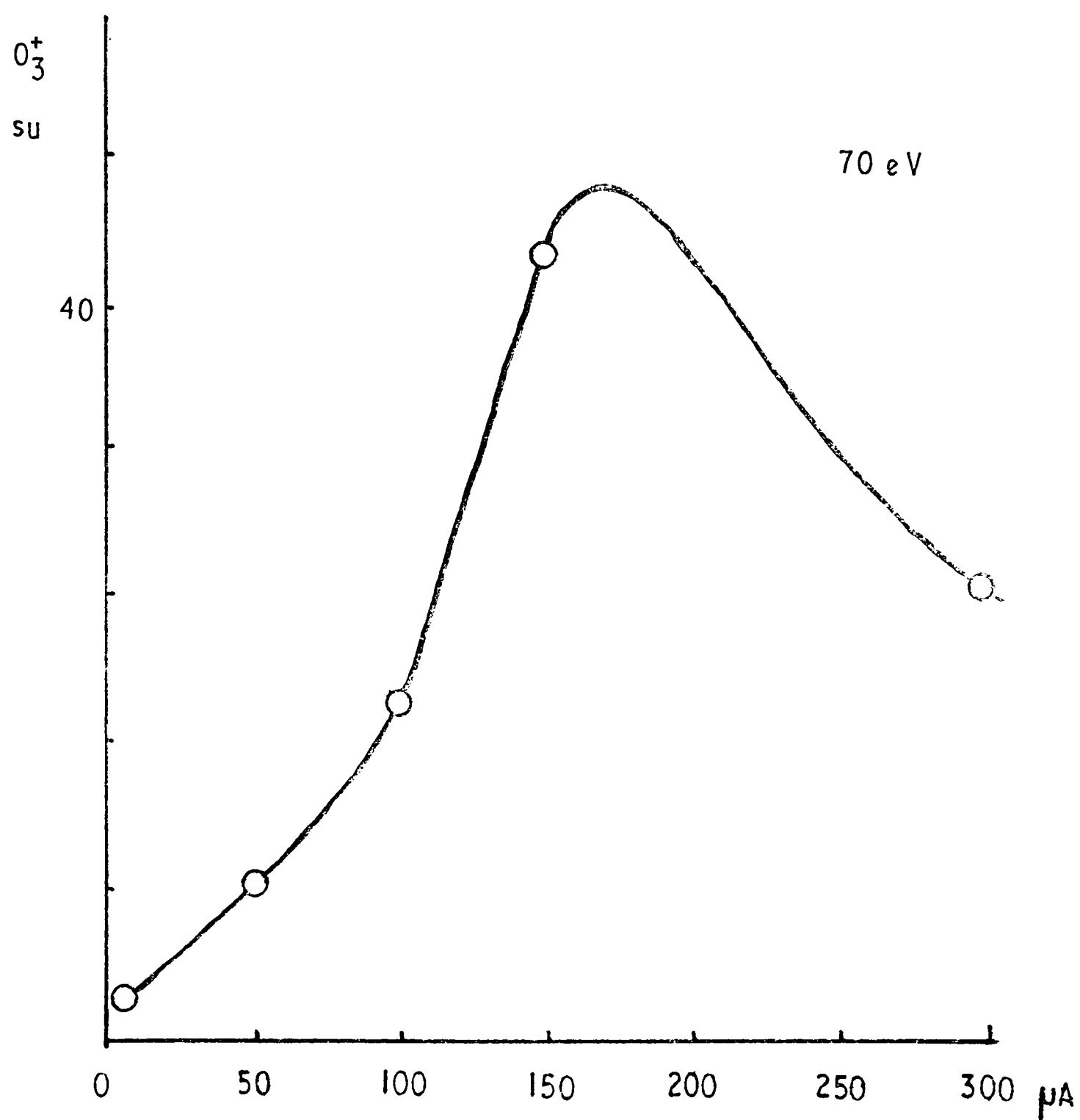
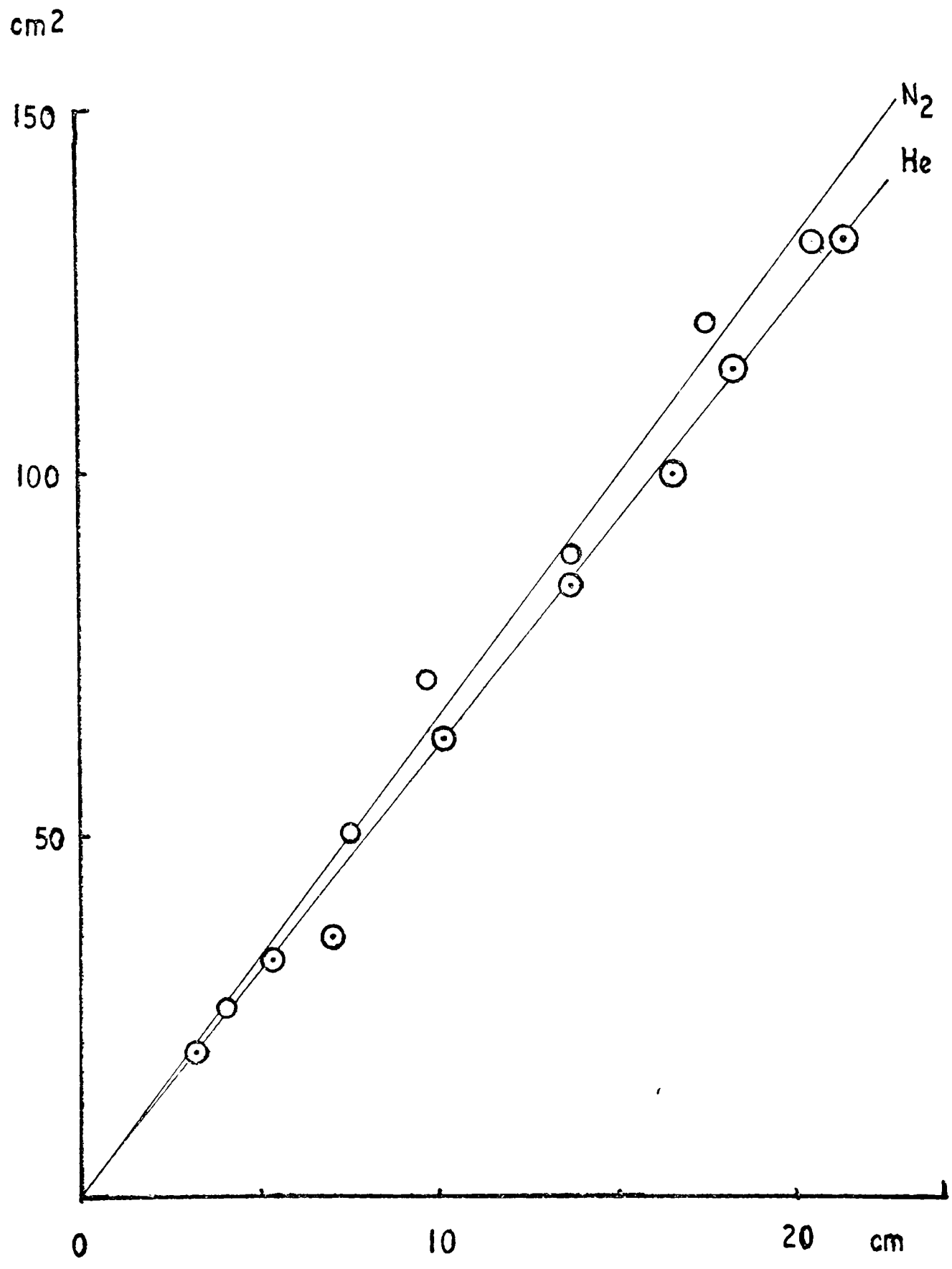


Figure 3,16 O₃ Peak area vs height



being the highest molecular weight fragment consistent with reasonable sensitivity. In the case of NO it was necessary to calibrate the strong $m/e=30$ peak at 30eV rather than 90eV.

Flows of helium carrier gas, of between 1 and 1.5 torr, were set up. The pressures of small amounts of added reactant (so as not to perturb the flow conditions) were measured by the vernier microscope ^(see page 30). Plots of mass spectrometer ^{ion current} ~~response~~ (in arbitrary "scale units") against reactant concentration were made at various carrier gas pressures. A calibration factor F (at each pressure) was defined as

$$\text{concentration (mole l}^{-1}\text{)} = \text{concentration (scale units)} \times F.$$

F is thus the inverse of the gradient of the calibration plot.

The concentration in "scale units" is arbitrarily defined as

$$\text{concentration (scale units)} = \text{peak height (cm)} \times \text{range multiplier.}$$

The range switch provided ranges of from one to one thousand times.

Figures 17 to 24 inclusive show mass spectrometer calibrations for O_3 , NO, CF_4 , CHF_2Cl , CF_2Cl_2 , $CFCl_3$ and CCl_4 ^(calibrated from peaks are marked with an asterisk in Appendix 4)

The O peak m/e 16 was calibrated in relation to the concentration of O atoms in the flow tube. Oxygen atoms were generated by the reaction of N atoms, produced by passing a few percent N_2 in helium through a microwave discharge, with NO.



The N atoms were titrated out by monitoring the appearance of excess NO at m/e 30. The O atom peak at m/e 16 was noted. The discharge was switched off and the NO concentration measured. The O atom concentration is then equal to the measured NO concentration. As can be seen from figure 3,24 the mass spectrometer is only slightly less sensitive to O atoms than to O_3 . (For the purpose required, no attempt was made to allow for wall recombination of O atoms down the tube.)

Figure 3,17 MS calibration O_3

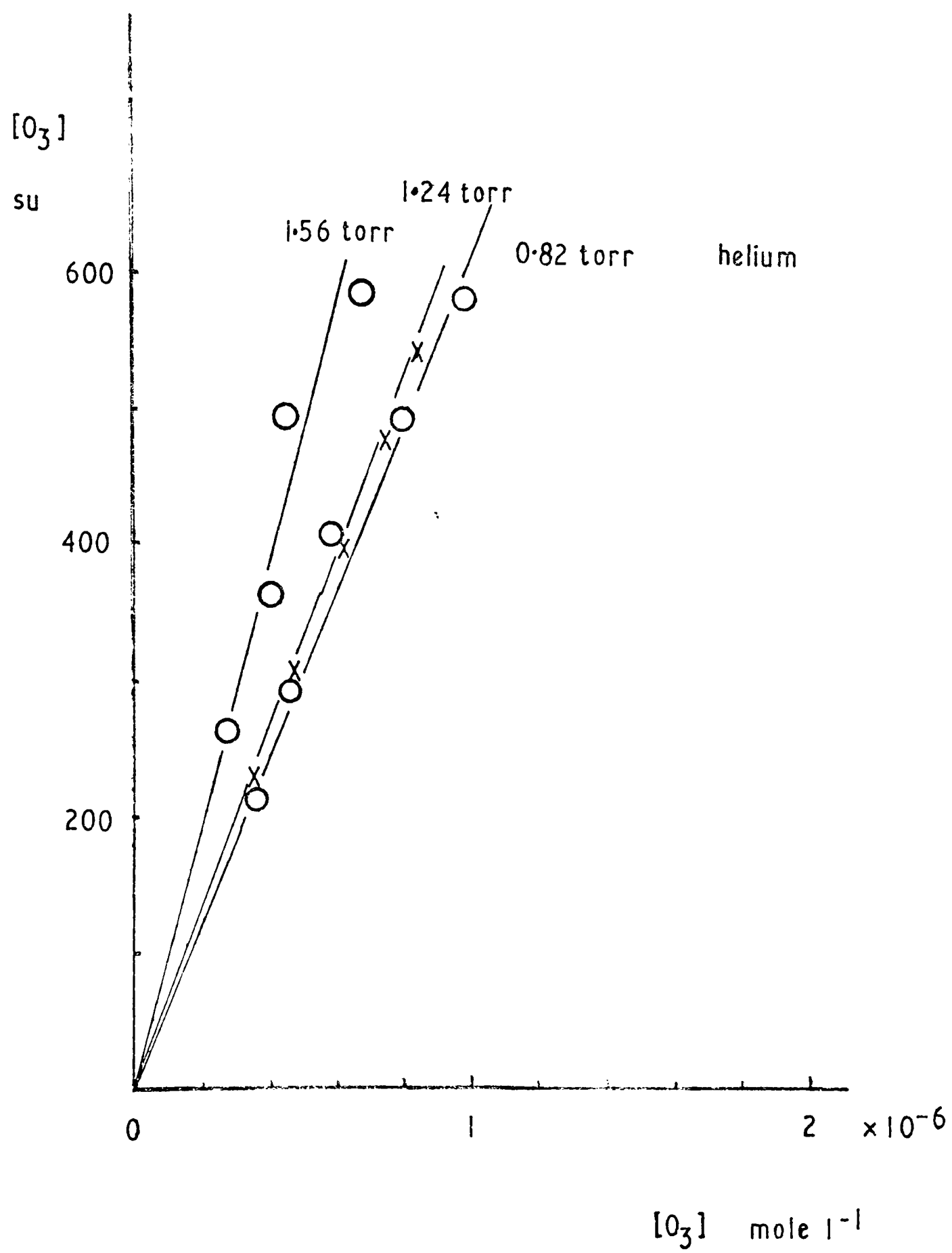


Figure 3,18 Variation O_3^+ response vs pressure

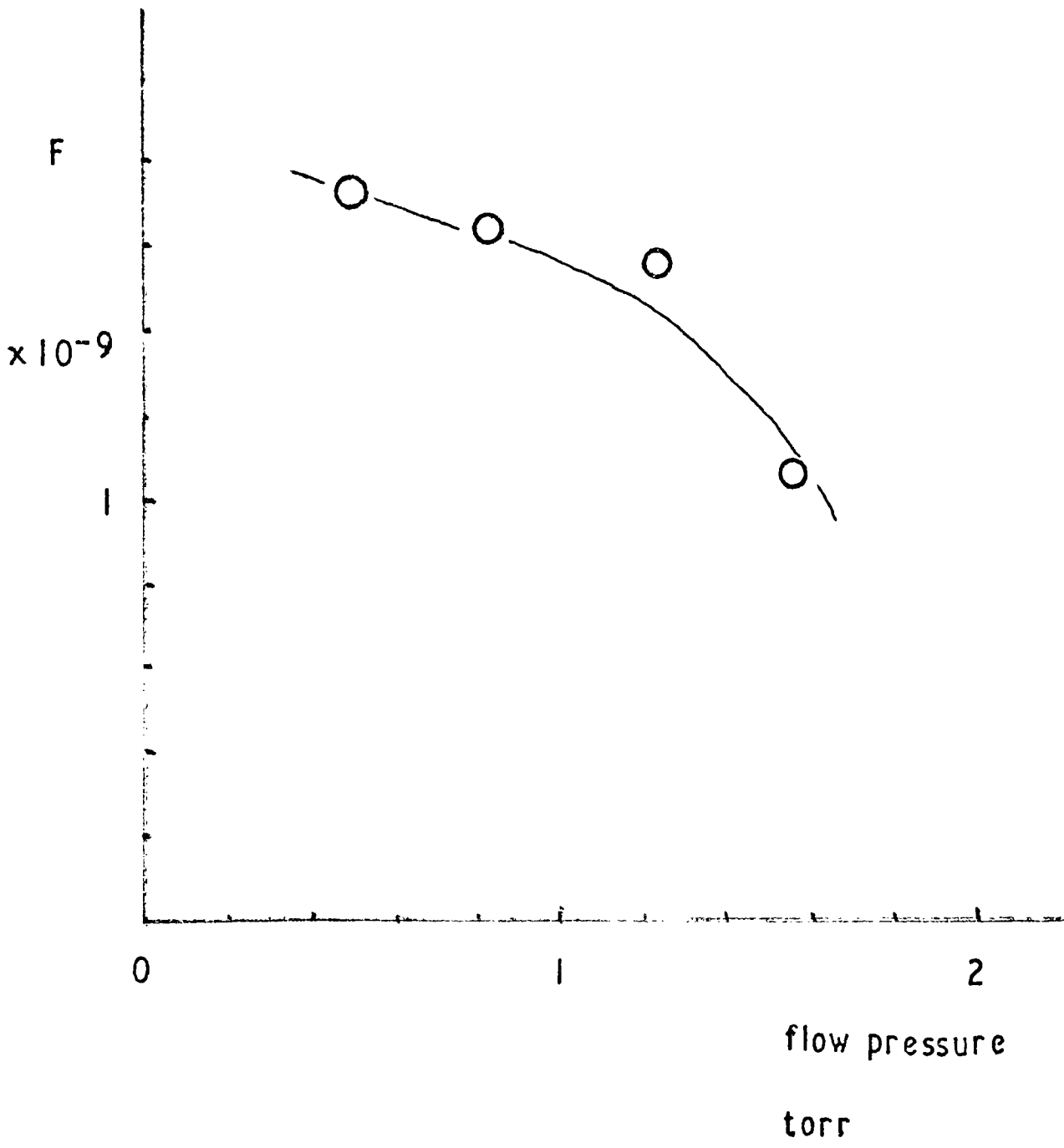


Figure 3,19 MS calibration NO

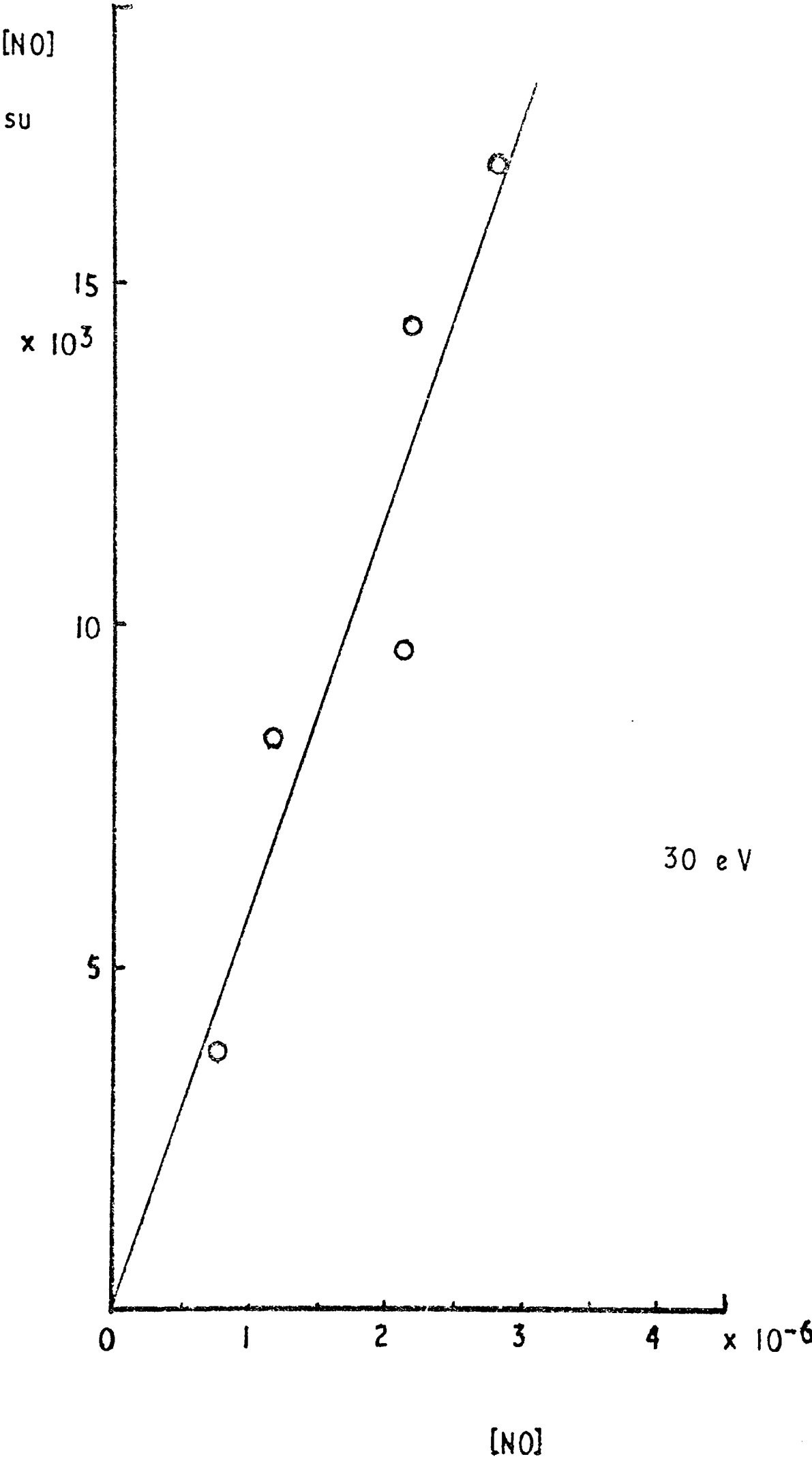


Figure 3,20 MS calibration CF_4

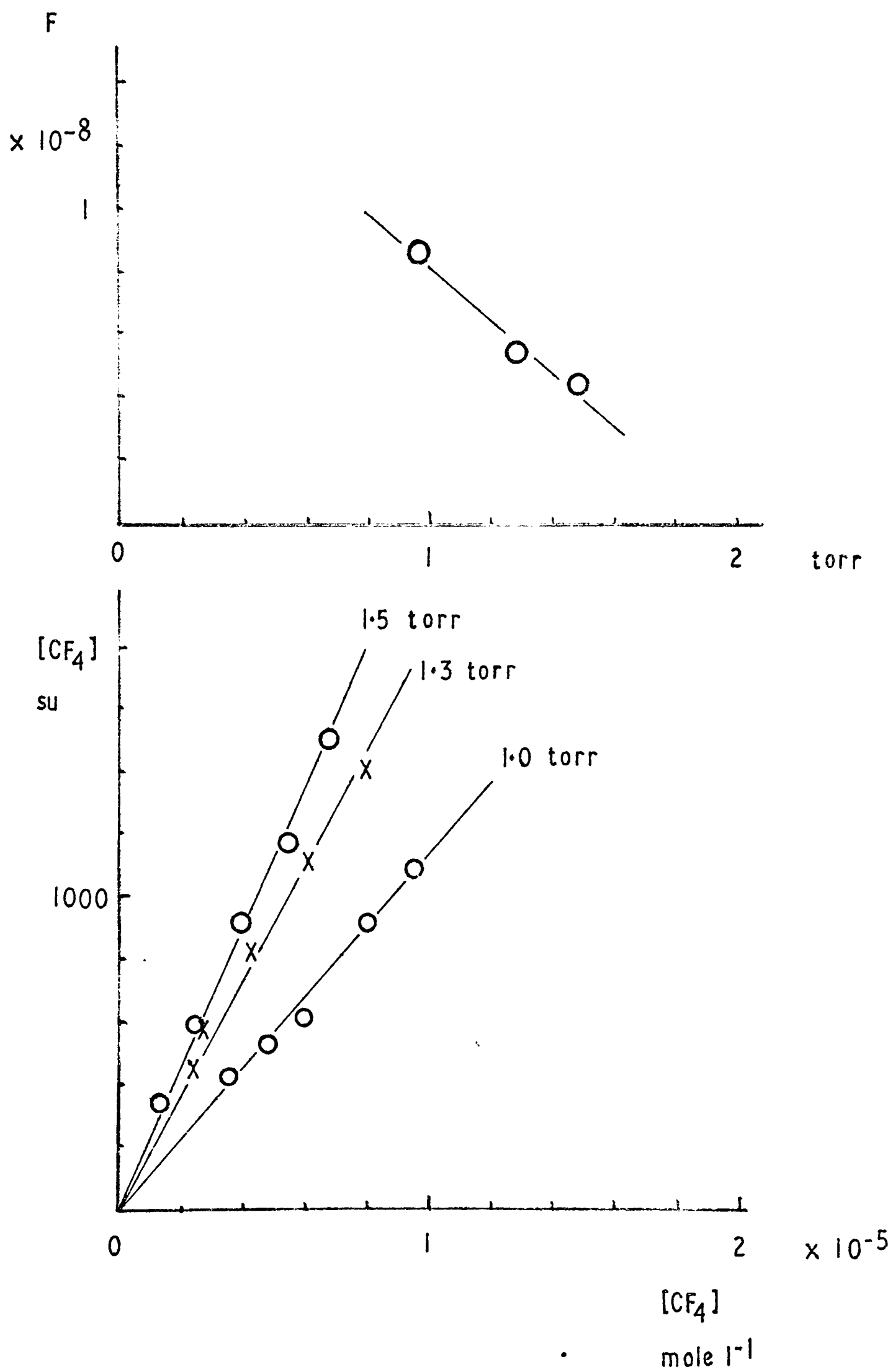


Figure 3.21 MS calibration CHF_2Cl

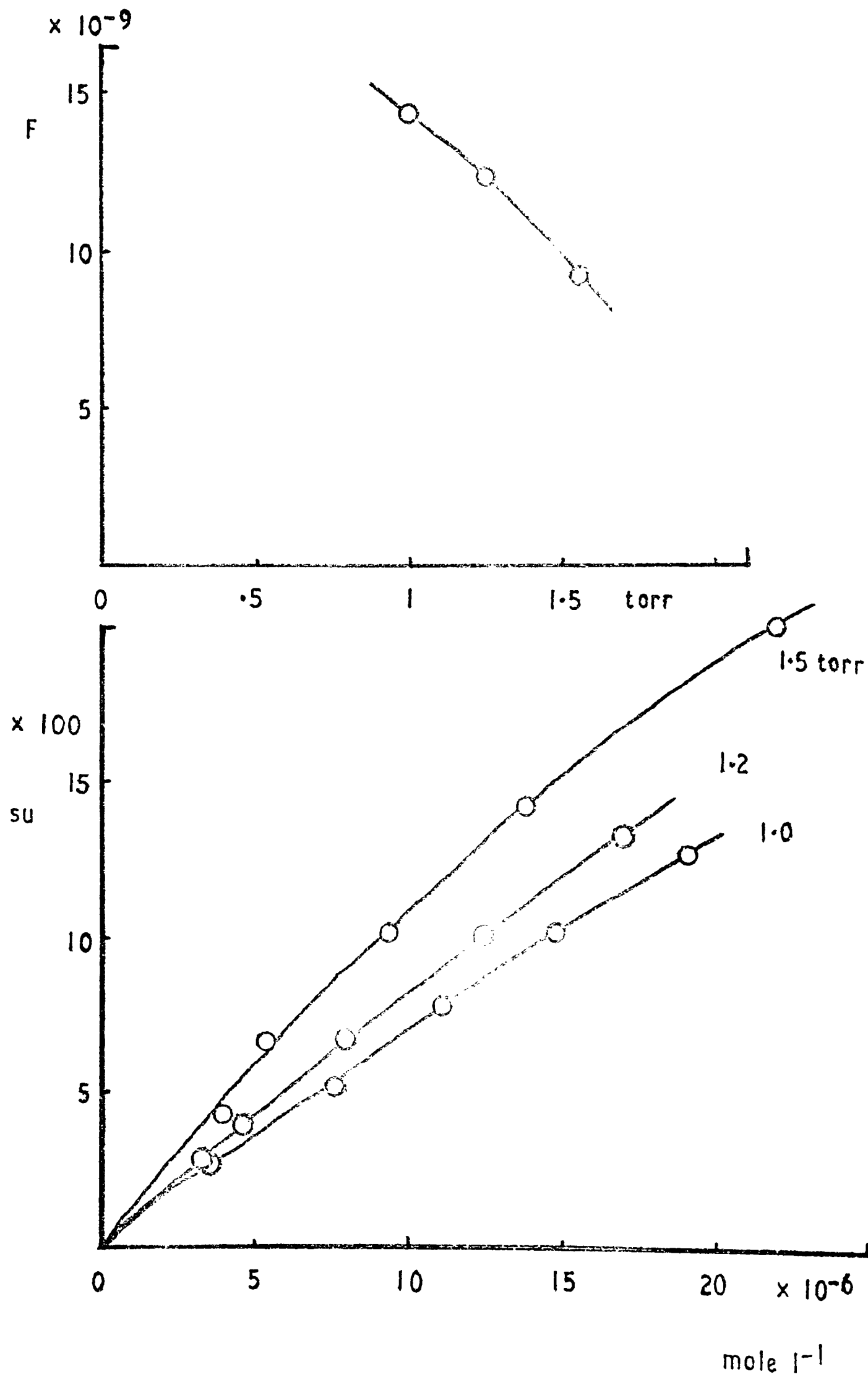


Figure 3.22 MS calibration CF_2Cl_2

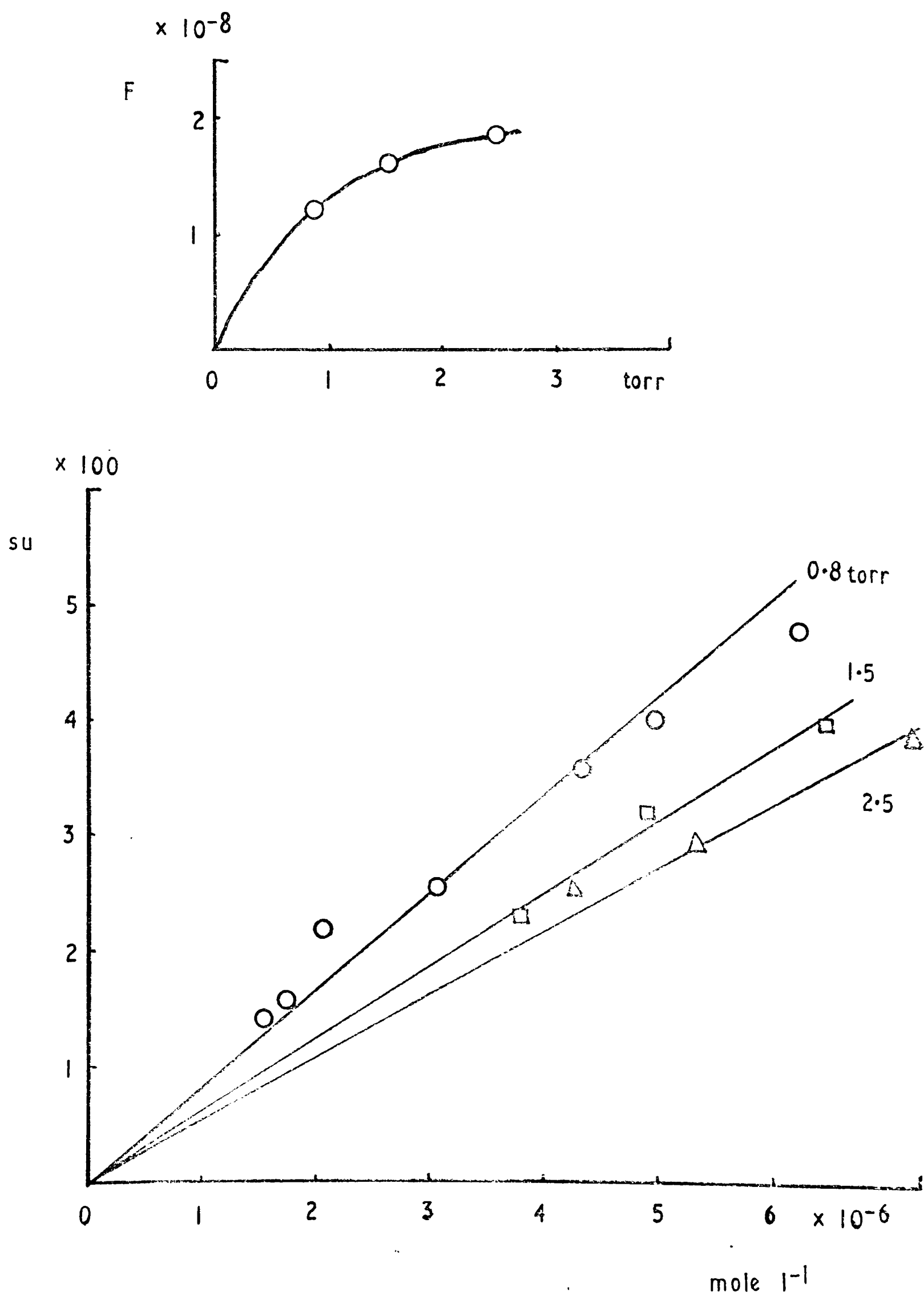


Figure 3,23 MS calibration CFCl_3

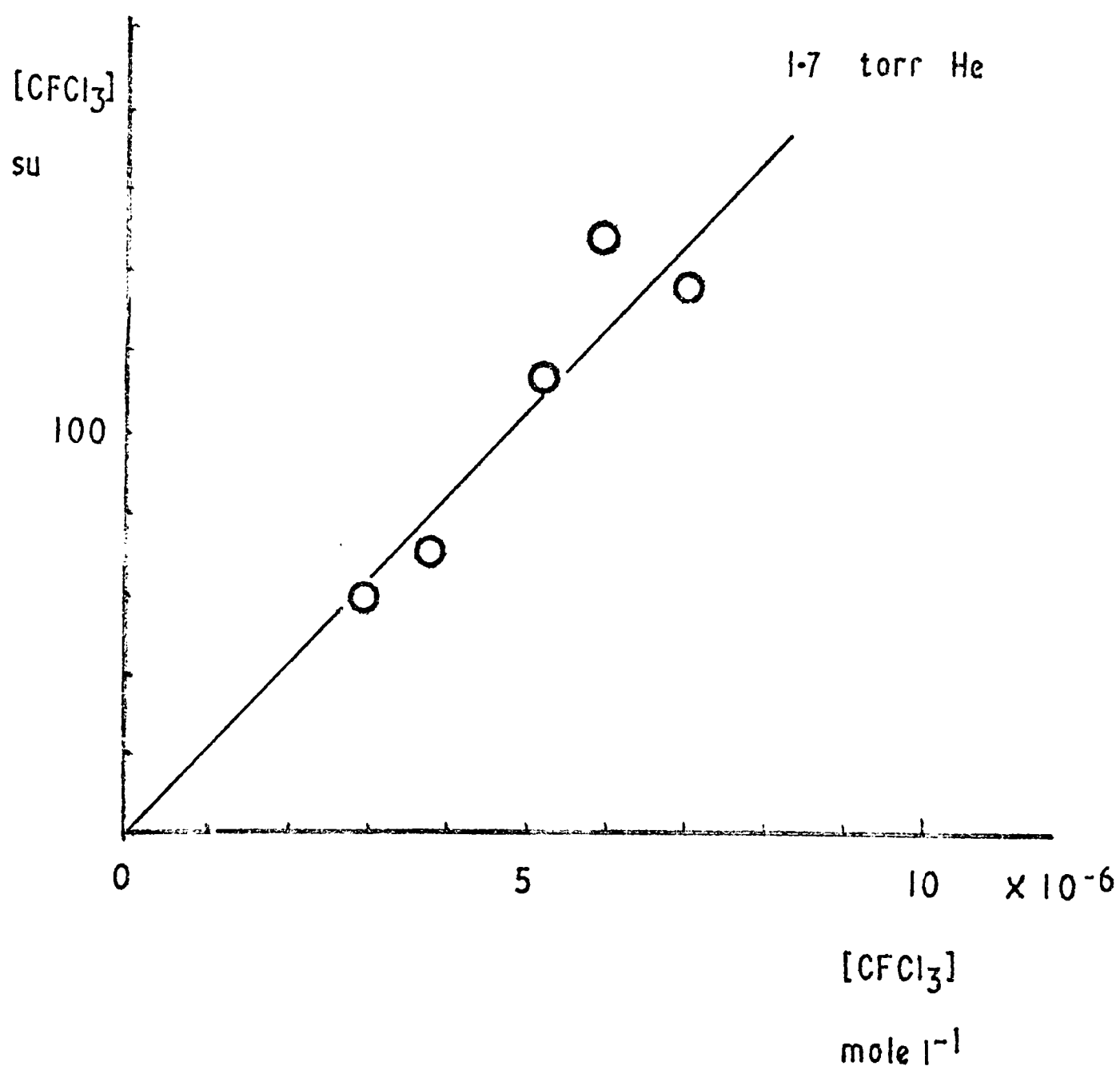


Figure 3,24 MS calibration CCl_4

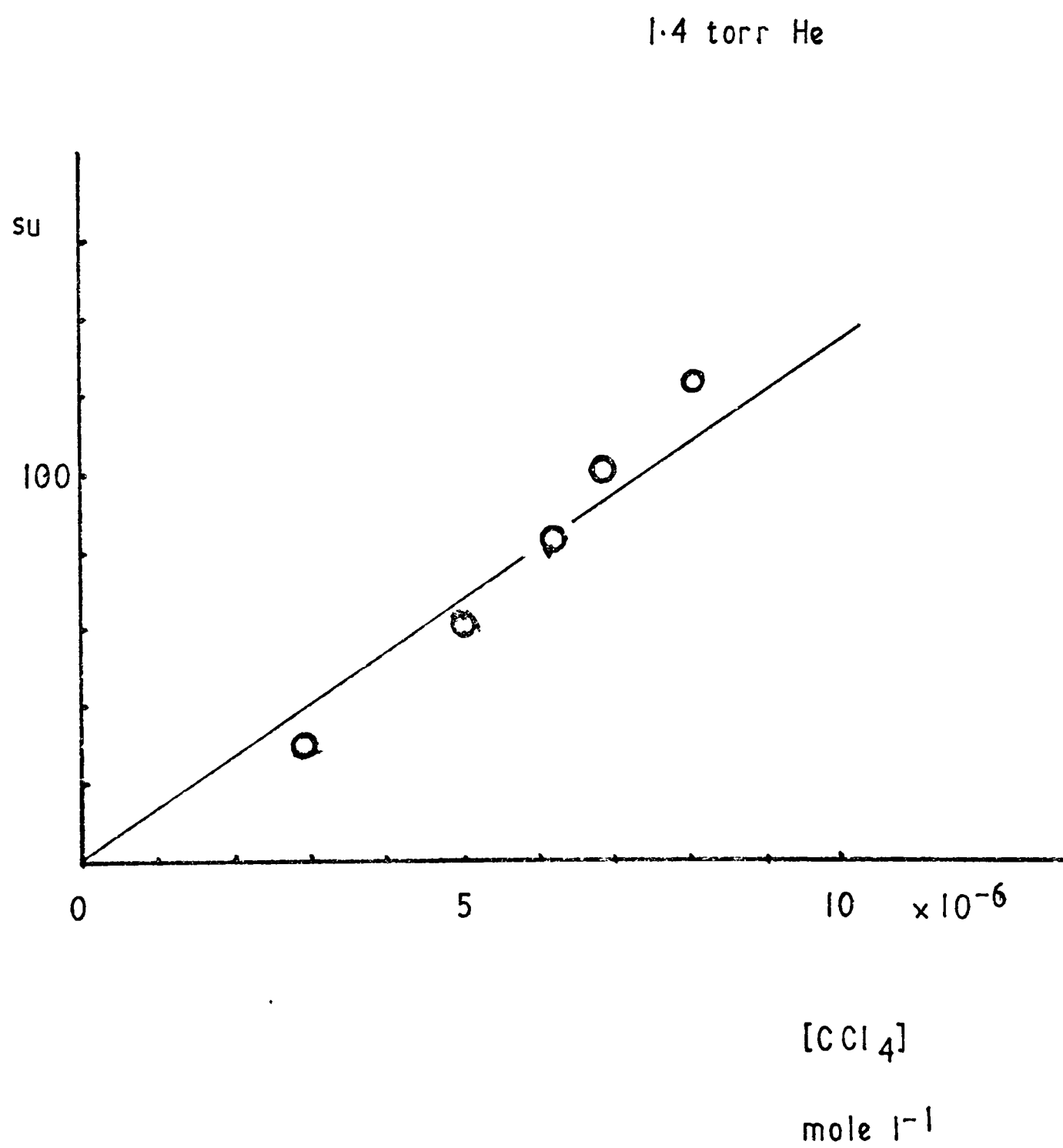


Figure 3,25 MS calibration 0 atoms

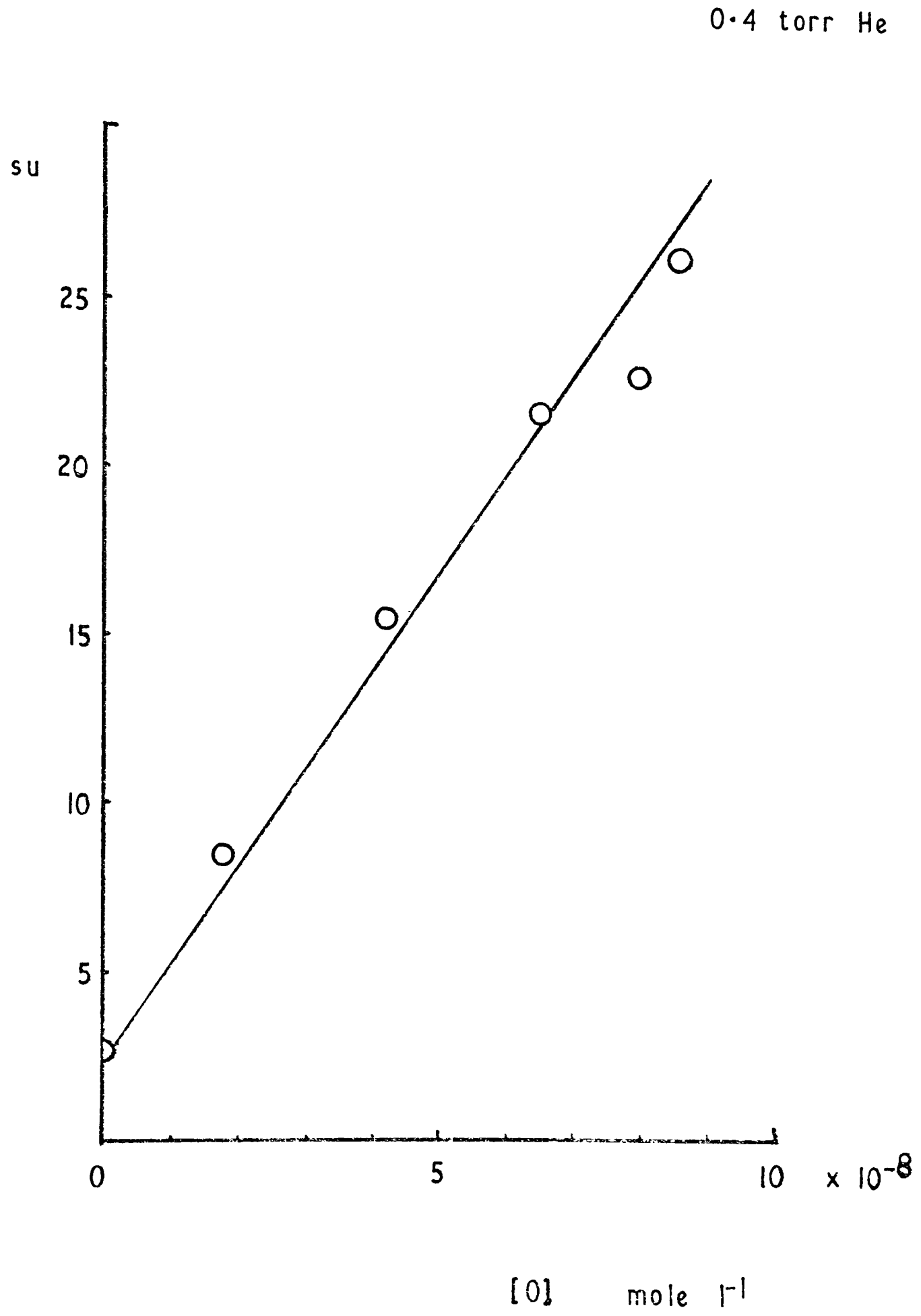
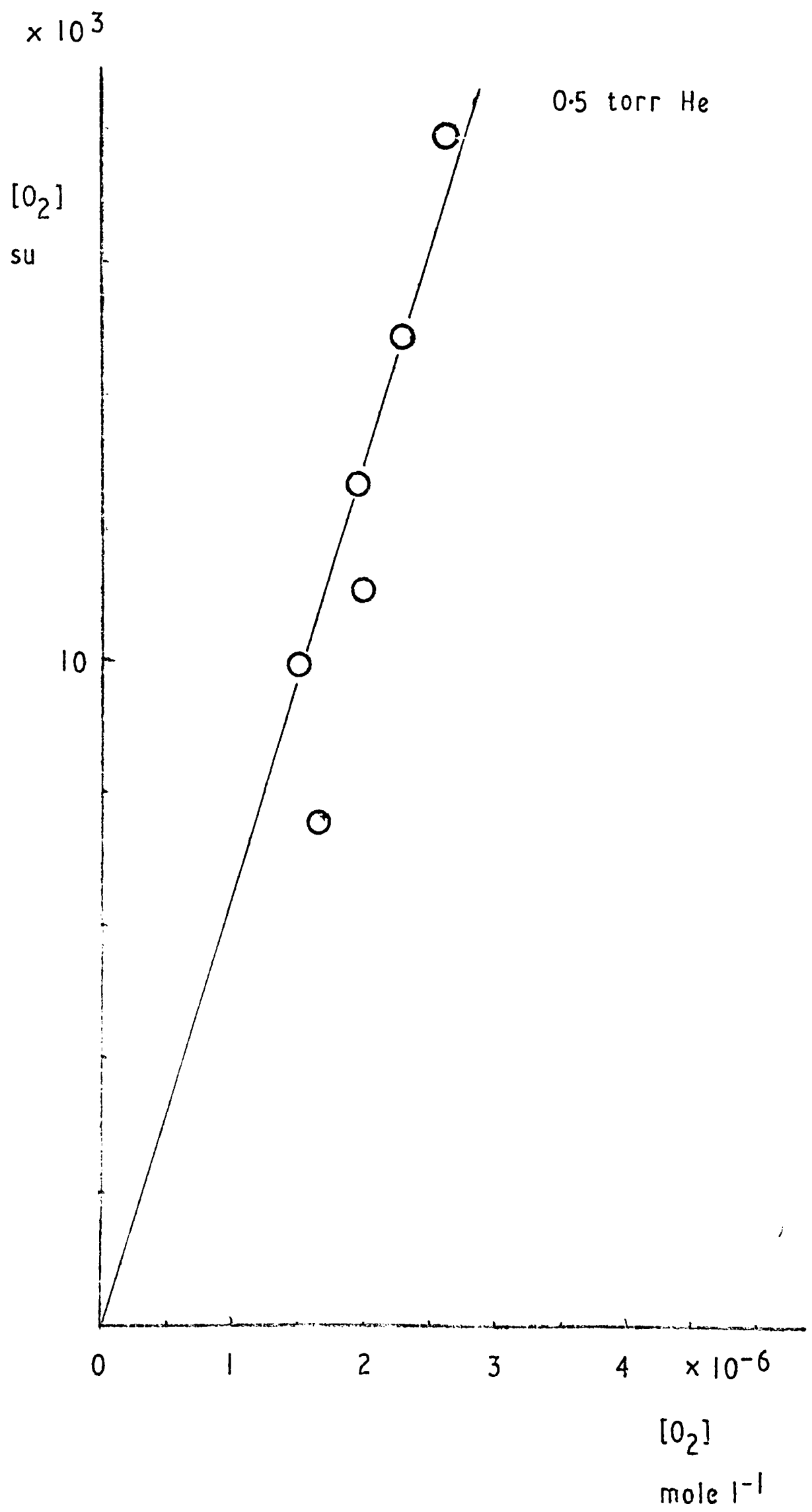


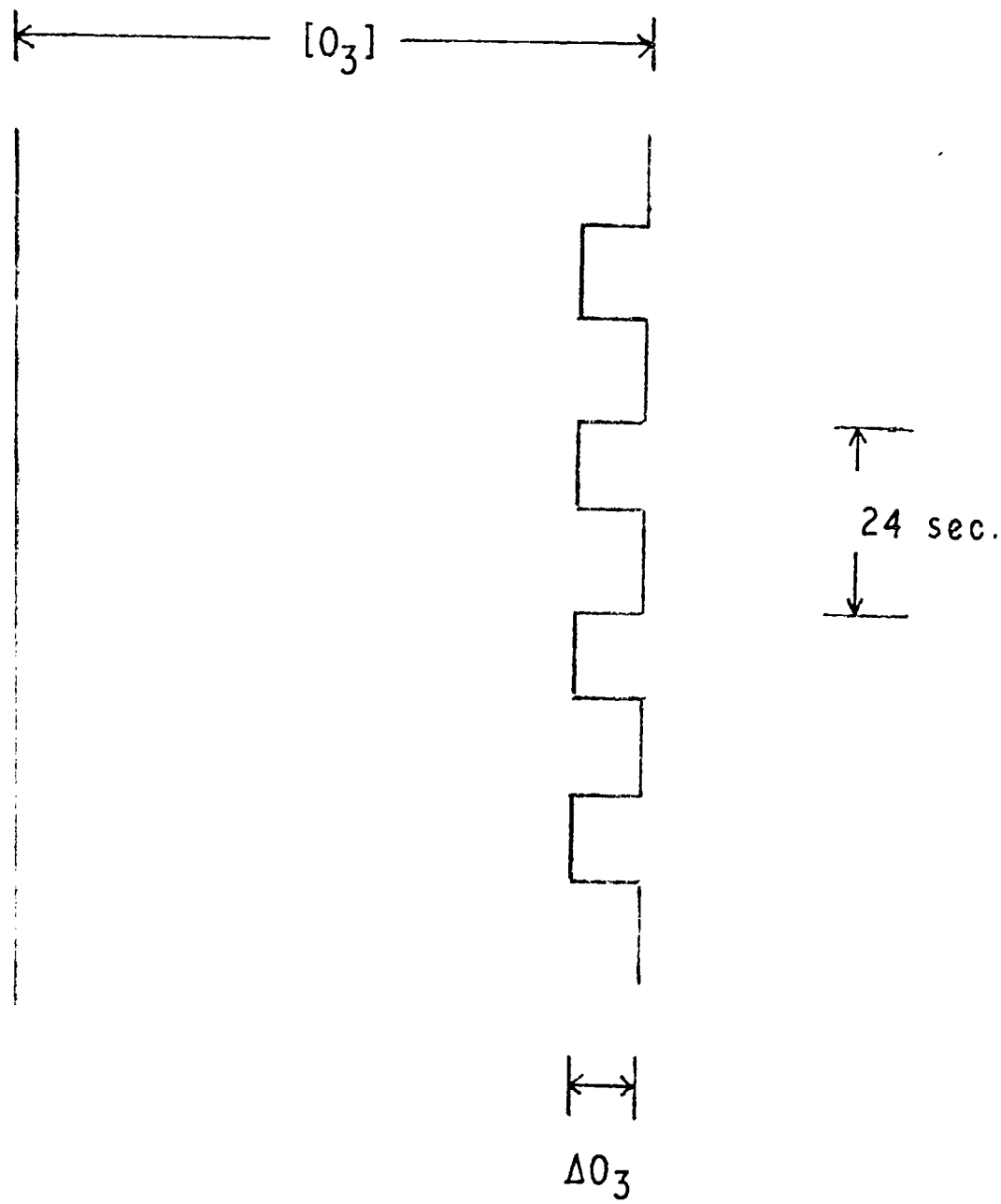
Figure 3,26 MS calibration O_2



3.8 Experimental Procedure.

For most experiments helium was used as carrier gas. A flow tube pressure of 1.0 - 1.5 torr at a flow velocity of around 12 m s^{-1} was set up. The nitrogen impurity was monitored until it had fallen to negligible concentrations. Small amounts of reactant gases were added so as not to appreciably perturb the carrier gas flow. Ozone concentrations of between 2×10^{-8} and $1 \times 10^{-7} \text{ mole l}^{-1}$ were normally used. The pulsed photolysis lamp was switched on. Quantum yields for ozone loss due to photolysis at low conversions were calculated from the fractional changes produced in the ozone concentrations (see figure 3.27). Typically twenty to thirty measurements were taken for each experimental point.

Figure 3,27 MS chart trace



C H A P T E R 4.

METHOD OF RELATIVE QUANTUM YIELDS.

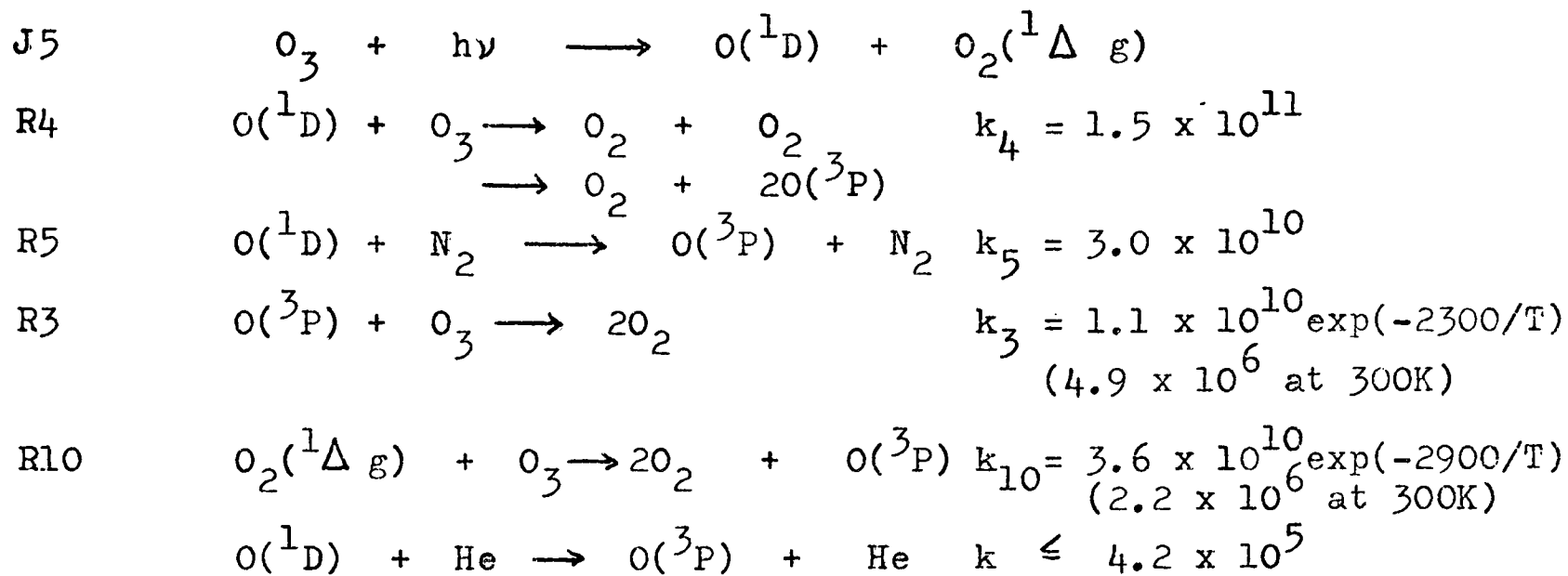
The method compares the amount of ozone lost by photolysis and subsequent reaction to that amount which is lost in the primary photolysis process. The relative quantum yield for decomposition of ozone is thus defined in this work as:

$$-\phi \{O_3\} = \frac{(\text{number of molecules of ozone photodissociated})}{(\text{total number of ozone molecules decomposed})}$$

The relative quantum yield may be measured for a reaction, or series of reactions, which have gone "to completion". (Heicklen and co-workers have used this method to determine relative quantum yields in "static" photolysis experiments using ozone and other gases). Alternatively, one can measure the relative quantum yield at some meaningful time intermediate in the overall scheme of reaction steps. This second method has been used previously by Giachardi and Wayne (1972) who used optical absorption to monitor the ozone concentration in a fast flow system. It turns out that in the pure ozone photolysis system it is possible to separate the reactions which occur into those which are "fast" (i.e. those which produce reaction on almost every collision) and those which are "slow" (i.e. those which lead to reaction at room temperature on only about one in 10 collisions). It is thus convenient (and meaningful!) to work in an experimental régime wherein the fast reactions go to completion and in which the slow reactions occur to a negligible extent. Biedenkapp and Bair (1970) call this an "intermediate quantum yield"; we shall simply refer to it as a relative quantum yield since we shall never be considering the overall quantum yield for the static ozone photolysis.

4, 1 Kinetic Scheme.

We shall list the reactions which may occur following the ultraviolet photolysis of ozone in either helium or nitrogen carrier gas. They appear in order of decreasing bimolecular rate constant (units: $l \text{ mole}^{-1} \text{ s}^{-1}$)



The upper limit for the quenching of $\text{O}({}^1\text{D})$ by helium is from Heidner and Husain (1974); references for other reactions are given in Table 1,2 . From consideration of the bimolecular rate constants it is clear that the reactions of $\text{O}({}^1\text{D})$, R4 and R5, are "fast" whilst the other reactions of $\text{O}({}^3\text{P})$ and $\text{O}_2({}^1\Delta_g)$ are "slow". Table 4,1 shows the reactive lifetimes of the species in helium and nitrogen carrier gases, calculated for typical experimental conditions. After a time 3τ a reaction is 99% complete, whilst after a time $\tau/3$ only 5% of a decaying reactant has been consumed (see Appendix 3). The reaction time in ~~these~~^{our} experiments could be varied between 1×10^{-3} and 100×10^{-3} seconds. Reference to Table 4,1 shows that under these conditions the fast reactions have gone to completion whilst the slow reactions have occurred to a completely negligible extent. It was one of the objects of this work to devise and construct a fast flow system capable of working with overall

ozone concentrations of less than 1.0×10^{-7} mole l^{-1} so that no corrections (which rely necessarily on experimental rate data) need be made for contributions to the relative quantum yield from the slow reactions.

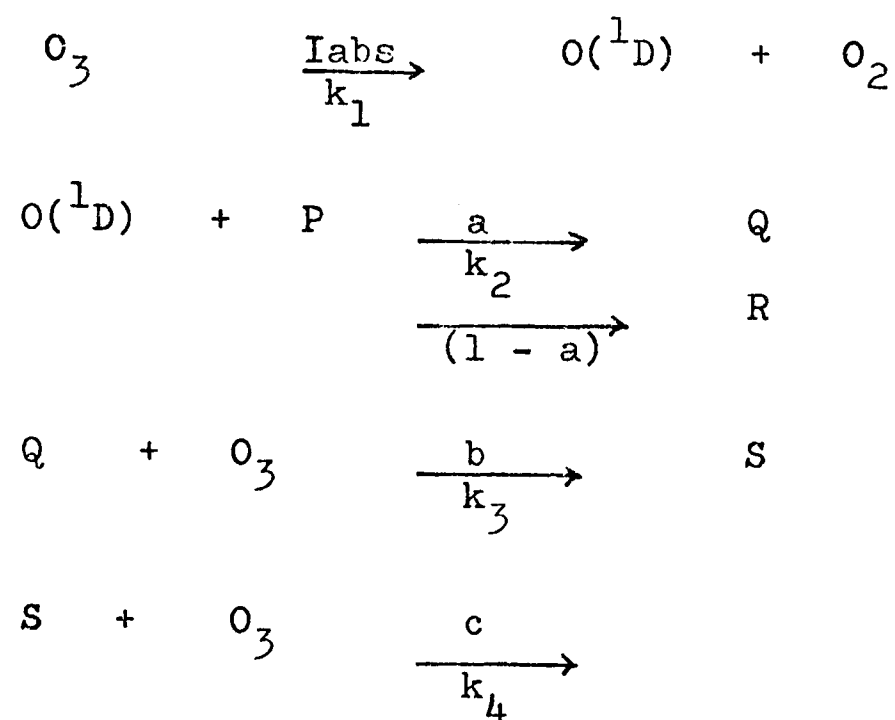
The photolysis of ozone in helium carrier gas (the He/O₃ system of table 4,1) proceeds via reactions J5, R4, R3 and R10 (the quenching of O(¹D) by He is negligible). In our ozone-contact time regime R3 and R10 make no contribution to the ozone loss. For small percentage photolysis of ozone the relative quantum yield is thus 2.0. In the presence of nitrogen as carrier gas the O(¹D) is completely quenched in R5 and makes no addition to the ozone loss. The relative quantum yield in the N₂/O₃ system is thus 1.0.

All reactions of O(¹D) atoms with simple molecules occur at close to gas kinetic frequency (see for example Gauthier and Snelling, 1975). Almost all those studied to date are H-abstraction reactions. In view of these fast reaction rates it is possible to study the reactions of O(¹D) with a variety of reaction partners (in place of O₃ in R4) and yet retain the convenient separation into the fast and slow reactions. Chapters 5,6 and 7 involve the fast reactions of O(¹D) with O₂, H₂ and various freons respectively.

4.1 Treatment of Data.

The number of molecules of ozone photodissociated in the flow tube is equal to the number of radiation quanta absorbed (since the primary quantum efficiency is known to be unity at the wavelengths employed here (Lin and DeMore, 1973)). The lamp intensity is controlled to be constant, and therefore our only variable parameter is the "contact time" i.e. the mean time (t) for which an ozone molecule remains in the photolysis region.

Let us consider a generalised reaction scheme which involves the photolysis of ozone followed by several reactive pathways (each of which results in the loss of ozone) of efficiencies (with respect to formation of the products) a,b,c



The loss equations are:

$$-\frac{d[\text{O}_3]}{dt} = k_1 I_{\text{abs}} + k_3 [\text{Q}][\text{O}_3] + k_4 [\text{S}][\text{O}_3]$$

$$-\frac{d[\text{O}({}^1\text{D})]}{dt} = k_2 [\text{P}][\text{O}({}^1\text{D})] - k_1 I_{\text{abs}}$$

$$-\frac{d[\text{Q}]}{dt} = k_3 [\text{Q}][\text{O}_3] - a k_2 [\text{P}][\text{O}({}^1\text{D})]$$

$$-\frac{d[\text{S}]}{dt} = k_4 [\text{S}][\text{O}_3] - b k_3 [\text{Q}][\text{O}_3]$$

Applying the steady state approximation to the rates of formation of $\text{O}({}^1\text{D})$, Q and S yields.

$$[\text{O}({}^1\text{D})] = k_1 I_{\text{abs}} / k_2 [\text{P}]$$

$$[\text{Q}] = a k_2 [\text{P}][\text{O}({}^1\text{D})] / k_3 [\text{O}_3]$$

$$[\text{S}] = b k_3 [\text{Q}] / k_4$$

The ozone loss rate is then given by

$$- \frac{d[O_3]}{dt} = k_1 I_{abs} (1 + a + ab)$$

This equation may be generalised to a series of n consecutive ozone loss reactions each of efficiency e_n

$$- \frac{d[O_3]}{dt} = k_1 I_{abs} (1 + \sum_n e_n \cdot e_{n-1} \dots \dots \dots e_1)$$

The absorbed light intensity I_{abs} is given by the Beer-Lambert law

$$I_{abs} = I_0 (1 - \exp /- E [O_3] d))$$

where E = extinction coeff. ozone ($\lambda = 2537\text{\AA}$) $\text{cm}^2 \text{mole}^{-1}$
 $[O_3]$ = ozone concentration mole l^{-1}
 d = thickness of sample cm
 I_0 = incident light intensity

The ozone loss rate can then be expressed as

$$- \frac{d[O_3]}{dt} = k_1 I_0 (1 + \sum_n) (1 - \exp (- E d [O_3]))$$

where $\sum_n$ signifies $\sum_n e_n \cdot e_{n-1} \dots \dots \dots e_1$

The equation may now be integrated to obtain the dependence of the ozone concentration on the time (t) in the photolysis region.

$$k_1 I_0 (1 + \sum_n) \int_0^t dt = - \int_{[O_3]_0}^{[O_3]_t} \frac{d[O_3]}{(1 - \exp(-Ed [O_3]))}$$

$$k_1 I_0 (1 + \sum_n) t = - \left[[O_3] + \frac{1}{Ed} \ln (1 - \exp (-Ed [O_3])) \right]_{[O_3]_0}^{[O_3]_t}$$

$$= [O_3]_0 - [O_3]_t + \frac{1}{Ed} \ln \left(\frac{1 - \exp(-Ed [O_3]_0)}{1 - \exp(-Ed [O_3]_t)} \right)$$

In our experimental regime the values of the optical densities $\text{Ed } [O_3]_0$ and $\text{Ed } [O_3]_t$ are in the region 10^{-4} (and therefore very much smaller than unity) Thus, the relation simplifies to:

$$\text{Ed } k_1 I_0 (1 + \sum_n) t - \text{Ed } ([O_3]_0 - [O_3]_t) = \ln \frac{[O_3]_0}{[O_3]_t}$$

Further approximation may be carried out. The first term on the left hand side of the equation has a value of around 5×10^{-2} under typical experimental conditions. The second term, which has a typical value of 3×10^{-5} , may therefore be neglected in relation to it. To a good approximation,

$$\ln \frac{[O_3]_0}{[O_3]_t} = \text{Ed } k_1 I_0 (1 + \sum_n) t$$

Let us introduce a constant β such that $\beta = \text{Ed } k_1 I_0$ (seconds⁻¹).

The loss of ozone after time t is given by ΔO_3 where

$$\Delta O_3 = [O_3]_0 - [O_3]_t$$

The relationship of the ozone concentration to the time then becomes

$$\frac{[O_3]_0}{[O_3]_t} = \exp ((1 + \sum_n) \beta t)$$

$$\frac{\Delta O_3}{[O_3]_0} = 1 - \exp (- (1 + \sum_n) \beta t)$$

Expressing β (which is a constant dependent on the ozone extinction coefficient, the cell geometry and the lamp intensity) in relation to the measured quantities ΔO_3 , $[O_3]_0$ and t gives

$$(1 + \sum_n) \beta = - \frac{1}{t} \ln \left(1 - \frac{\Delta O_3}{[O_3]_0} \right)$$

To calculate β the photolysis of ozone is performed in nitrogen carrier gas, as previously described in Section 4,1. In the nitrogen-ozone experiment there are no subsequent ozone loss reactions so that $n = 0$ and $\sum_n = 0$. The quantity β is then given by

$$\beta = - \frac{1}{t} \ln \left(1 - \frac{\Delta O_3}{[O_3]_0} \right)$$

In the case of the photolysis of ozone in helium carrier gas, one subsequent ozone loss reaction (R4) occurs. In the absence of any quenching of $O(^1D)$ atoms R4 proceeds with unit efficiency. Thus $\sum_n$ is equal to unity in the helium-ozone experiment. For convenience we have used the quantity $\Delta O_3^{cor} / [O_3]$ which is defined by the relation

$$\frac{\Delta O_3^{cor}}{[O_3]} = - \ln \left(1 - \frac{\Delta O_3}{[O_3]_0} \right)$$

where ΔO_3^{cor} signifies the value of ΔO_3 "corrected" to zero fractional conversion of ozone

$[O_3]$ is equivalent to $[O_3]_0$ used previously

In the helium-ozone experiment

$$- \frac{1}{t} \ln \left(1 - \frac{\Delta O_3}{[O_3]_0} \right) = 2\beta$$

$$\frac{\Delta O_3^{cor}}{[O_3]_t} = 2\beta$$

The values of $\Delta O_3^{cor} / [O_3]_t$ in the N_2/O_3 and He/O_3

experiments are β and 2β , respectively. The values of the relative quantum yields ϕ_{N_2} and ϕ_{He} in these flow gases are therefore (subject to the ideal kinetic conditions as defined in section 4,1) predicted to be 1.0 and 2.0. respectively.

It has also been demonstrated that the simple linear relationship between $\Delta O_3^{cor} / [O_3] t$ and the relative quantum yield also holds for sequences of ozone loss reactions which may have efficiencies of less than unity. The relative quantum yield for an "unknown" system is, therefore, given by

$$\phi = \Delta O_3^{cor} / [O_3] t \beta$$

where ϕ is the shorthand abbreviation which will be used to denote $-\phi\{O_3\}$ - the relative quantum yield for the loss of ozone.

Values of $\Delta O_3^{cor} / [O_3] t$ determined experimentally in nitrogen and helium carrier gases are shown in Tables 4,2 and 4,3, respectively. The results are discussed in detail in section 4,3.

The relation of ΔO_3 to the other parameters, which has been derived above, gives the same result as would have been obtained by simply treating the system as being "optically thin". It may seem somewhat contradictory to have a system which is optically thin (O.D. of around 10^{-4} in these experiments) and yet which undergoes significant photolysis (up to 30% in extreme cases).

The optical density of a system tells us nothing about the rate at which light quanta are being absorbed. It simply says that the light intensity across the tube is approximately constant, and consequently that ozone photodissociation occurs isotropically across any flow tube cross section. However,

the axis of the flow tube represents a time coordinate and along this coordinate there is significant exponential decay of ozone concentration with distance.

Whilst it may be argued that this method of measuring the quantum yield smacks of empiricism it nevertheless has several strong advantages over a more "fundamental" approach. Beta (β) is a function of the intensity of the photolysis lamp, the ozone extinction coefficient and the flow tube radius. In principle, it is possible to measure these quantities; the extinction coefficient is in fact well known (Griggs, 1968). Measurement of the lamp intensity presents several problems. The first is to ensure an optically thin system to allow for multiple reflections inside the cylindrical lamp reflector - many actinometry systems rely on complete absorption of radiation. A second problem is that considerable skill is often required to obtain even relatively poor accuracy. The results in the following section show that β may be measured by the relative quantum yield method to a precision greater than 2% (Table 4,5). The flow tube radius can be easily measured (although the tube has by no means a perfectly uniform bore). However, whether this measurement represents a true path-length is doubtful. (The lamp is a non-focussed helix with an empty annulus of several centimetres thickness between itself and the flow tube). The principal advantage of the relative quantum yield method lies, however, in the fact that calibration is performed under very similar conditions to those under ^{which} the subsequent experiments are carried out.

4.3 Results and Discussion.

Even after the apparatus had been built a long time elapsed before usable results could be obtained. Two major problems existed. The first was that the measured quantum yields

were irreproducible. The second was that the quantum yields for ozone loss in the helium and nitrogen carrier gas experiments did not lie in the expected ratio of two to one (a ratio of less than one and a half to one was common).

The major experimental parameters were as follows: Photolysis lamp intensity and position, ozone concentration, flow velocity, flow tube pressure, and mass spectrometer conditions. As well as being irreproducible from run to run, the quantum yields obtained under the same conditions tended to increase very sharply at low ozone concentrations.

The precautions taken to ensure that the photolysis lamp emitted $2537\overset{\circ}{\text{Å}}$ radiation of constant intensity have been described already in section 3,6. A spectrum of the lamp was taken to ensure that the $2537\overset{\circ}{\text{Å}}$ line was not strongly reversed, a situation which occurs in medium pressure mercury lamps, and that the principal light output occurred in this line. The lamp house was flushed with cold nitrogen to prevent build-up of ozone. The quartz flow tube was checked for uniform UV transmission.

The variations of the quantum yield with ozone concentration pointed, given that we were in the ideal kinetic regime described in Section 4,1, to non-linear response of the detection system with respect to ozone concentrations in the flow tube. On all occasions plots of m/e 48 signal versus ozone concentration were linear to within experimental uncertainty (see figure 3,18). To ensure that there were no water or nitrogen oxide impurities in the ozone an experiment was performed in which ozone from the storage bulb was passed through a trap at 197K before entering the flow tube. The presence of the trap, however, did not appear to affect the quantum yields obtained.

One of the principal difficulties initially encountered in investigating the irreproducibility of the measured quantum yields was the day to day variability of the flow conditions. The flow velocity increased strongly with increasing flow tube pressure. The efficiency of the flow pump also varied from day to day. A variable air bleed was added downstream of the mass spectrometer inlet so that the flow tube pressure and the flow velocity could be controlled independently (as described in section 3,5). The obvious parameter which might lead to the low measured quantum yield ratio in helium and nitrogen carrier gases is incorrect calculation of t , the time in the photolysis zone (which would result from incorrect capillary calibrations). The dependence of the capillary "constant" on the molecular weight of the gas (as demonstrated in figures 3,5 and 3,6) was first appreciated when using SF_6 as a carrier gas. The capillaries were therefore carefully recalibrated by the method described in section 3,4. To ensure that some non-linear light absorption process was not arising from a possible breakdown of the plug-flow assumption, baffles were inserted inside the photolysis region. The object of the teflon coated gauze baffles was to promote a turbulent flow situation (which for the purposes of light absorption approximates to the plug-flow situation in that there are no net velocity gradients across the flow tube). The result of this exercise was simply to quench all the $\text{O}(^1\text{D})$ atoms and bring the helium and nitrogen relative quantum yields down to the same value!

In considering the effects of the various experimental parameters on the measured values of $\Delta \text{O}_3^{\text{cor}} / [\text{O}_3]t$, it had been tacitly assumed that ΔO_3 was a linear function of $[\text{O}_3]$ and of t . In order to verify that this was indeed the case

the data were replotted to show ΔO_3 as a function of $[O_3]$. Further experiments were performed also to show the dependence of ΔO_3 on t .

Figure 4,1 shows the plot of ΔO_3 versus $[O_3]$ (at constant t and flow tube pressure) and the dependence of ΔO_3 on t (at constant $[O_3]$ and flow tube pressure). The plot ΔO_3 versus t goes through the origin. The plot of ΔO_3 versus $[O_3]$, however, shows a significant positive intercept on the ΔO_3 axis. The same intercept is also observed on ΔO_3 versus $[O_3]$ plots in helium (figure 4,3) and oxygen (figure 4,4) carrier gas. The physical significance of the intercept, which implies a change in ozone at zero ozone concentration, was obscure. In addition, moreover, the value of the intercept appeared to change with flow tube pressure. Figures 4,2 and 4,4 show ΔO_3 plotted versus $(f.t.press)^{-1}$. Extrapolation to infinite pressure gives approximately constant values for $\Delta O_3/[O_3]t$ implying that the intercept becomes zero at infinite pressure. Comparison of figures 4,2 and 4,4 shows that the gradients of the ΔO_3 versus $(flow\ tube\ pressure)^{-1}$ are identical (for various values of $[O_3]$ and t) in both nitrogen and oxygen, respectively. (The data for helium, shown in the lower part of figure 4,3, is too scattered to enable a representative gradient to be drawn). For nitrogen and oxygen, therefore, the intercept found on the plots of ΔO_3 versus $[O_3]$ could be expressed as a function of the flow tube pressure by the relationship:

$$\text{Intercept} = 0.3 (\text{flow tube pressure})^{-1}$$

A multiple linear regression fit of the complete data* gave the following empirical formula:

*footnote. This was performed using a version of the University Computer (ICL 1906) Stat 15 program which had been modified to run on the Elliot 903 computer available in the Physical Chemistry Laboratory.

Figure 4.1 Photolysis N_2/O_3

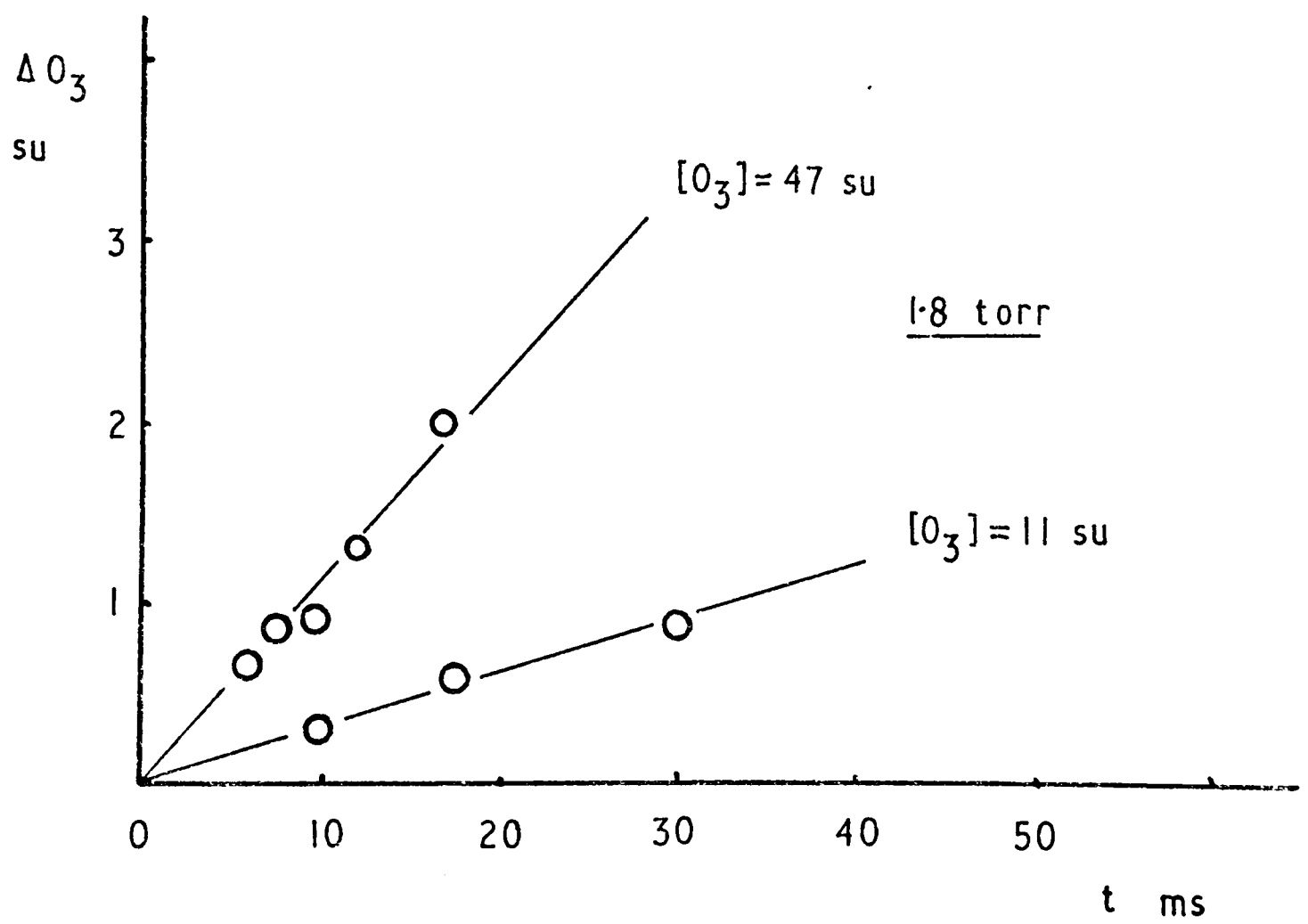
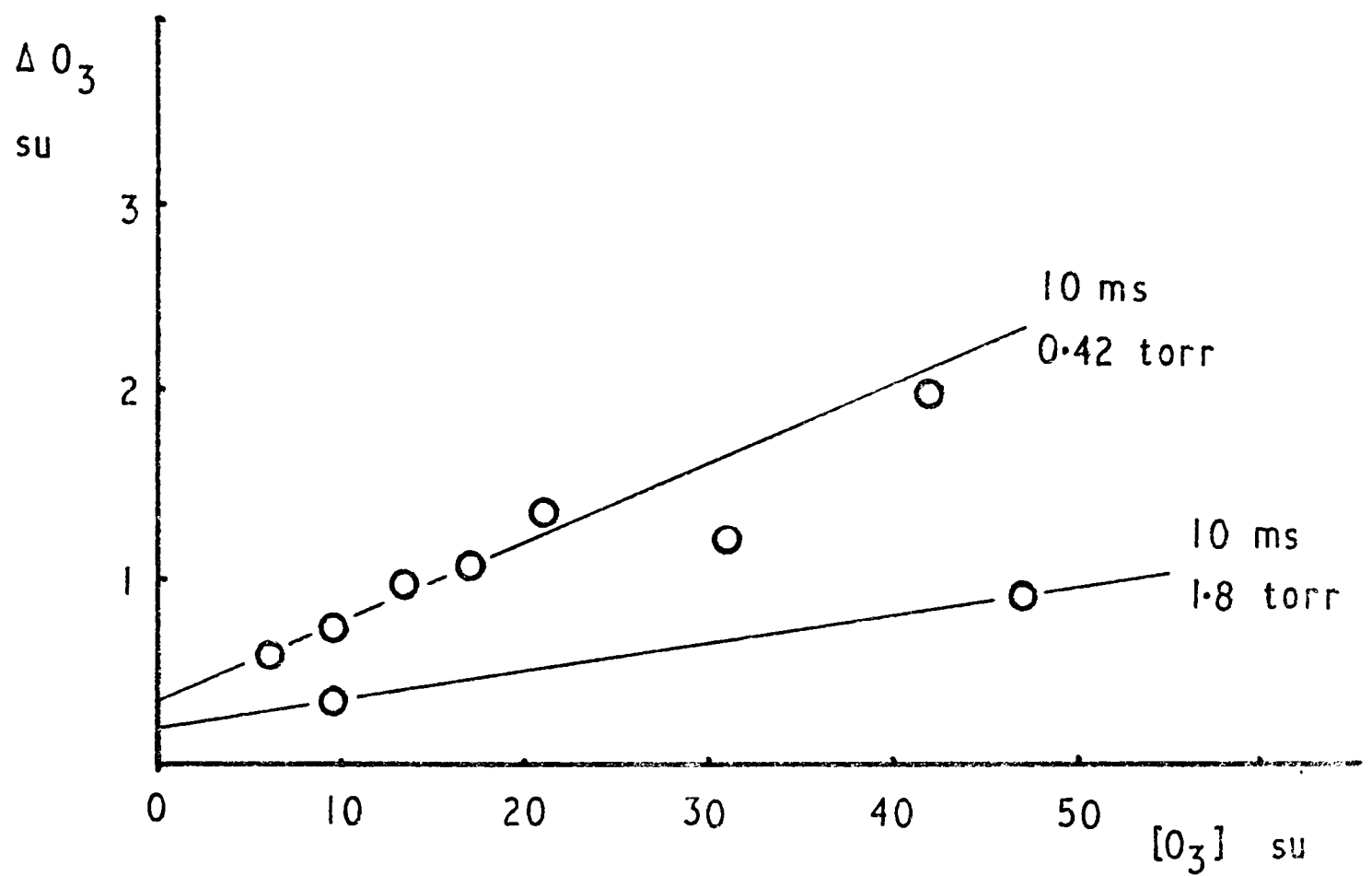


Figure 4,2 N_2/O_3

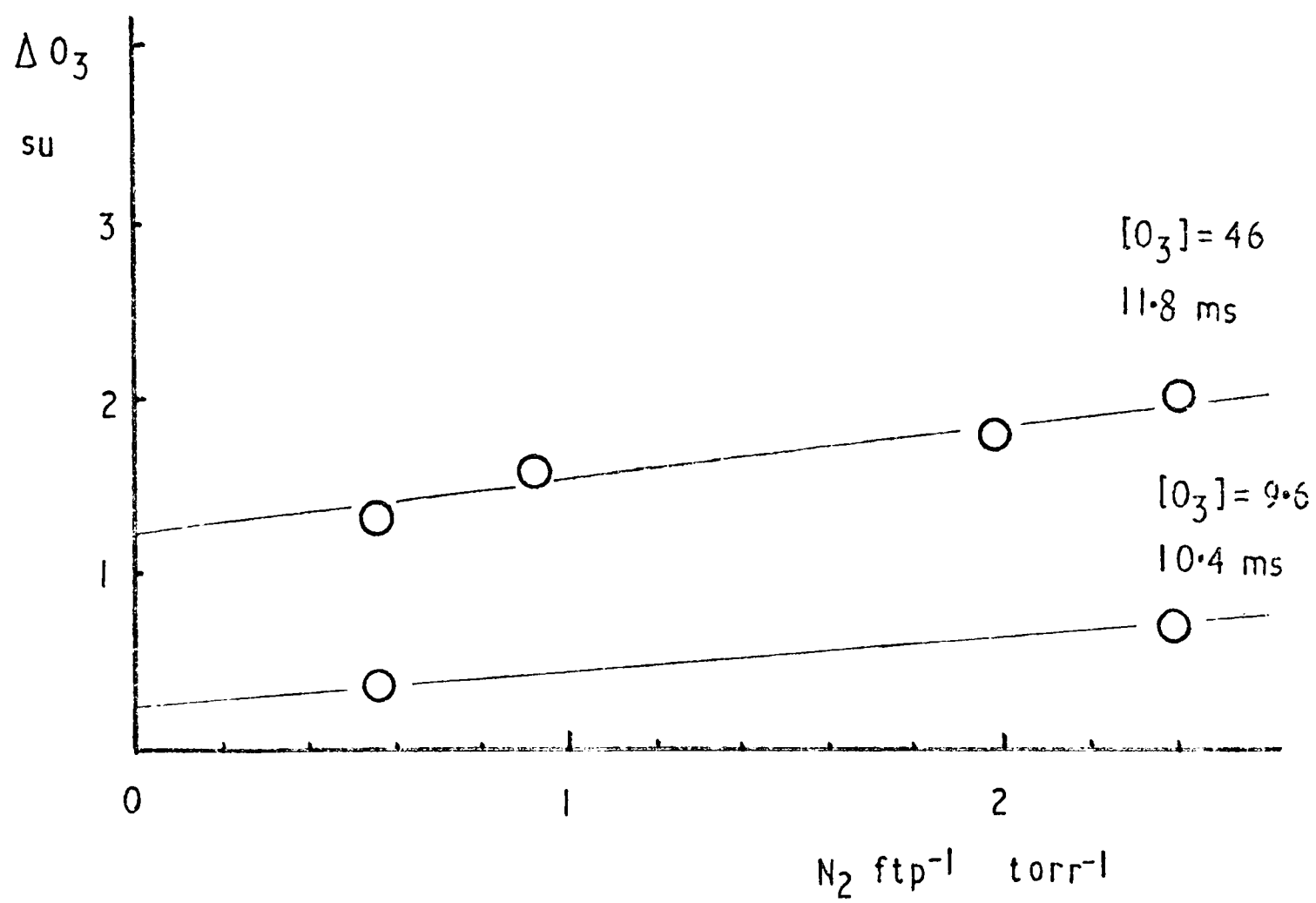


Figure 4,3 Photolysis He/O₃

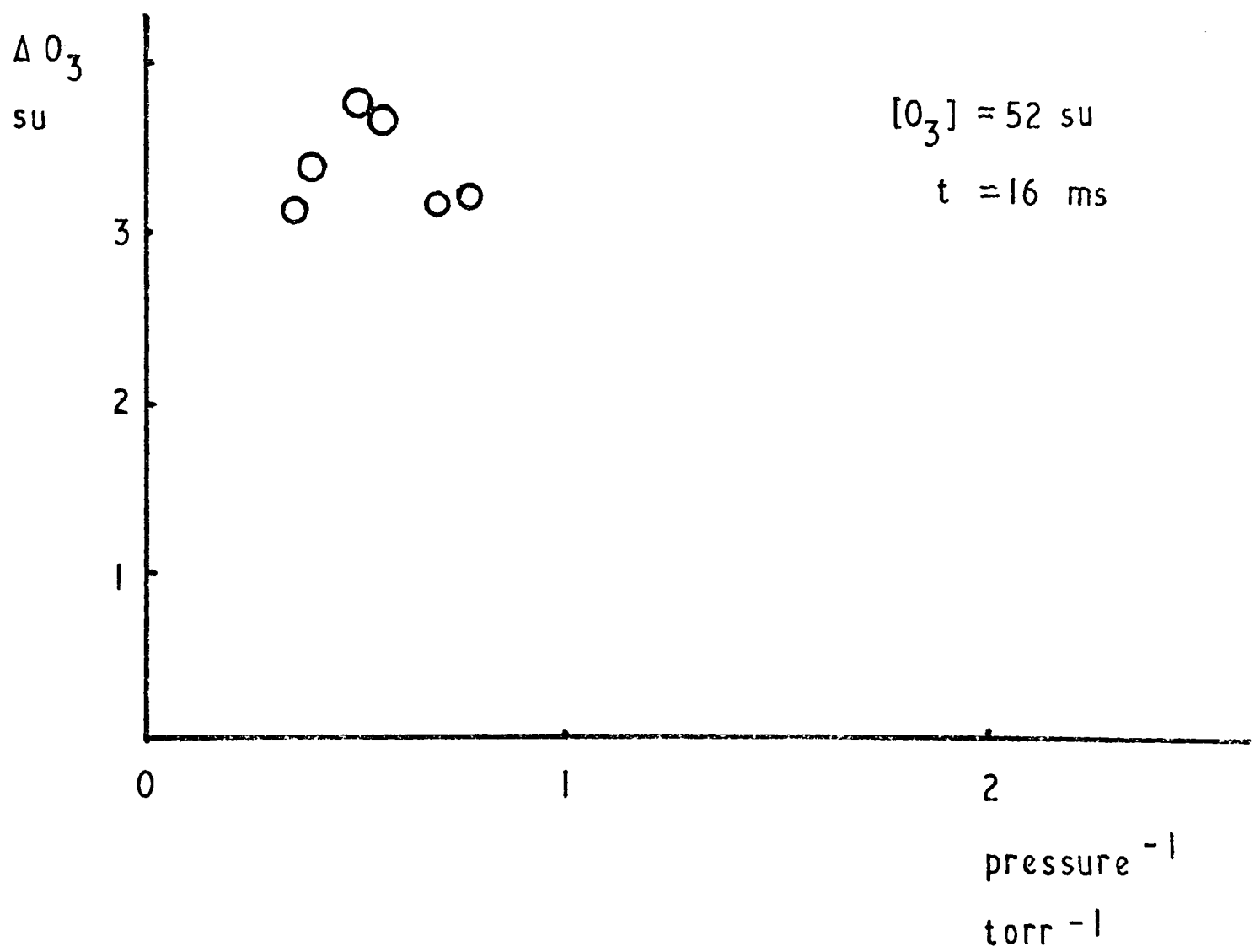
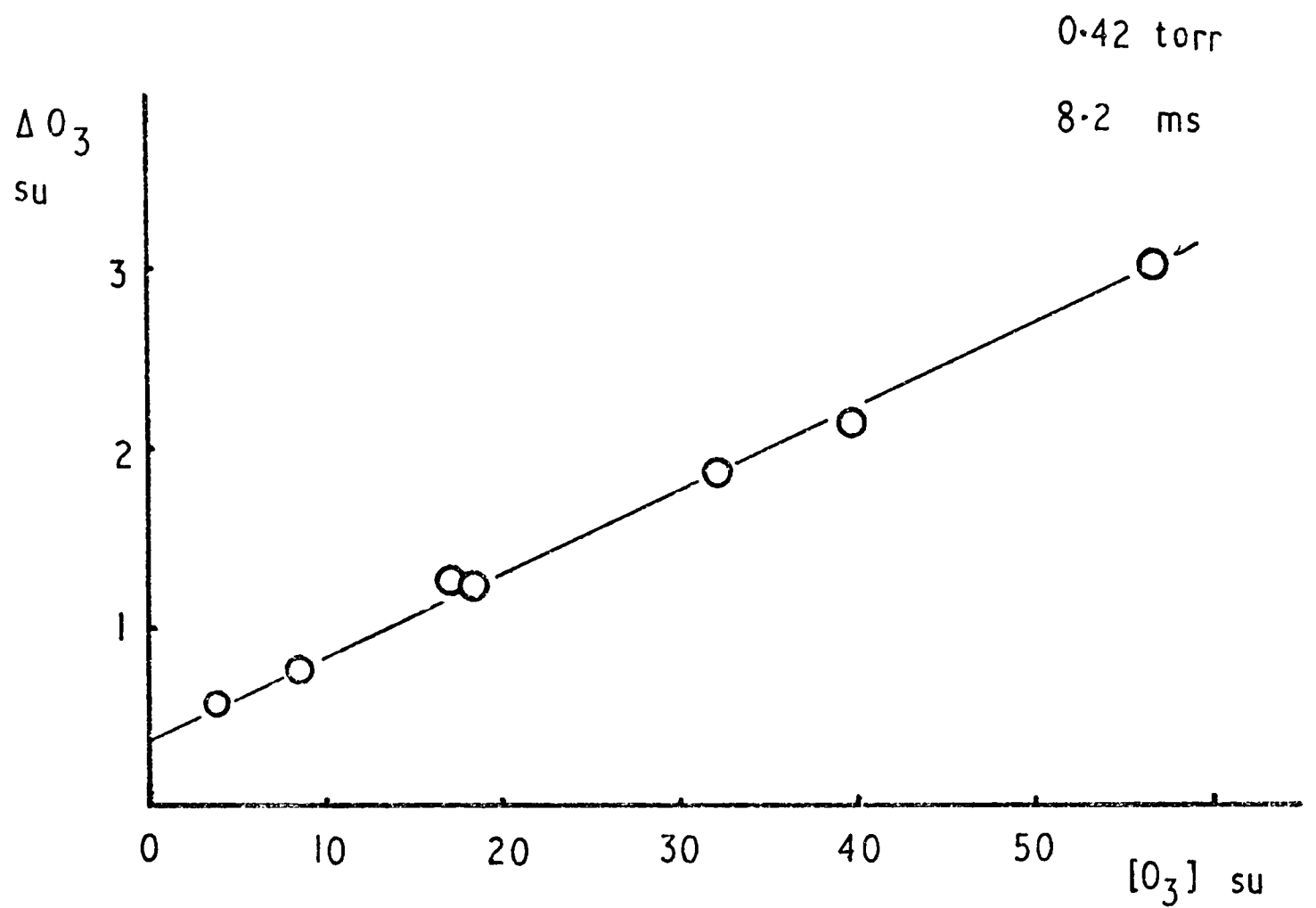
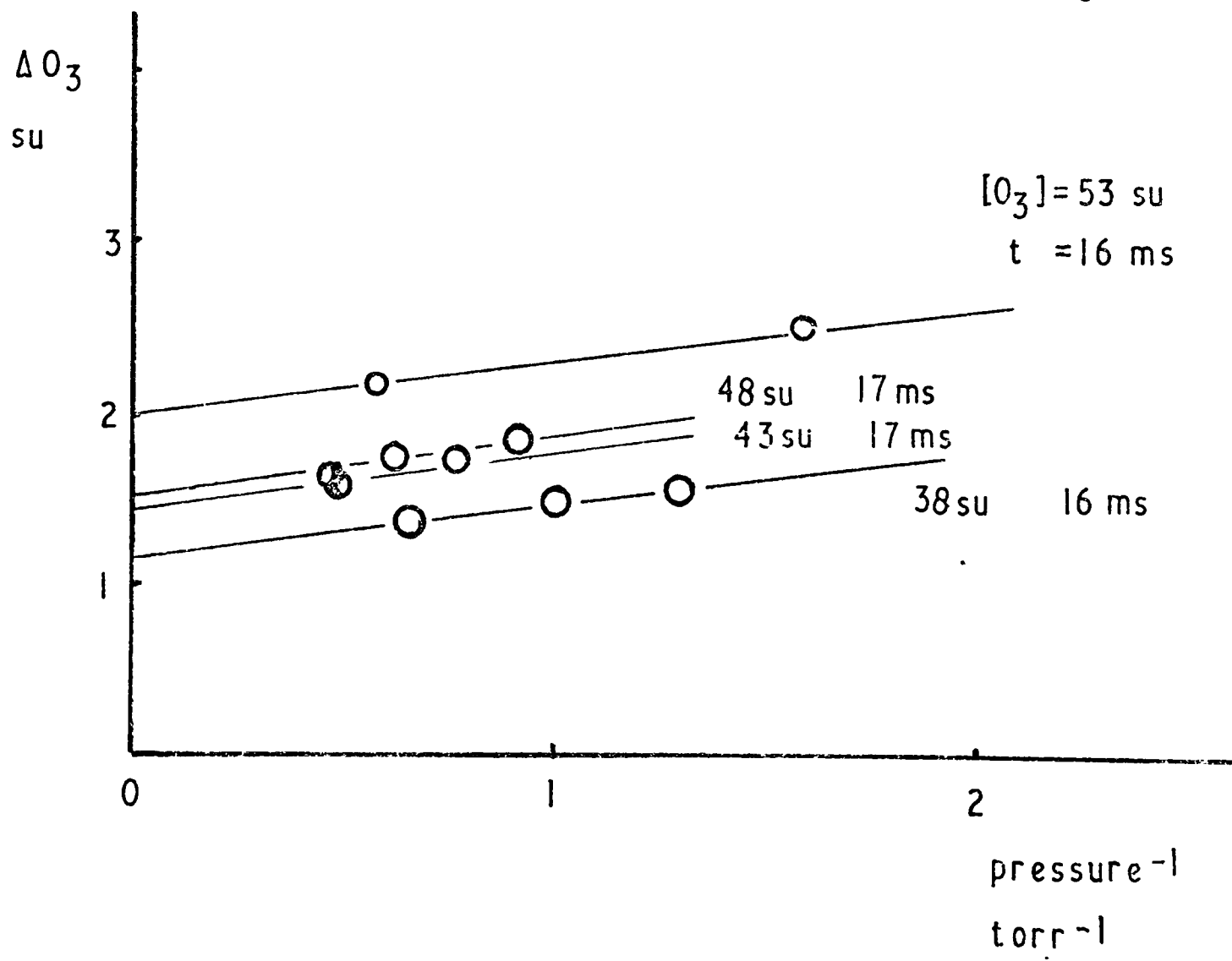
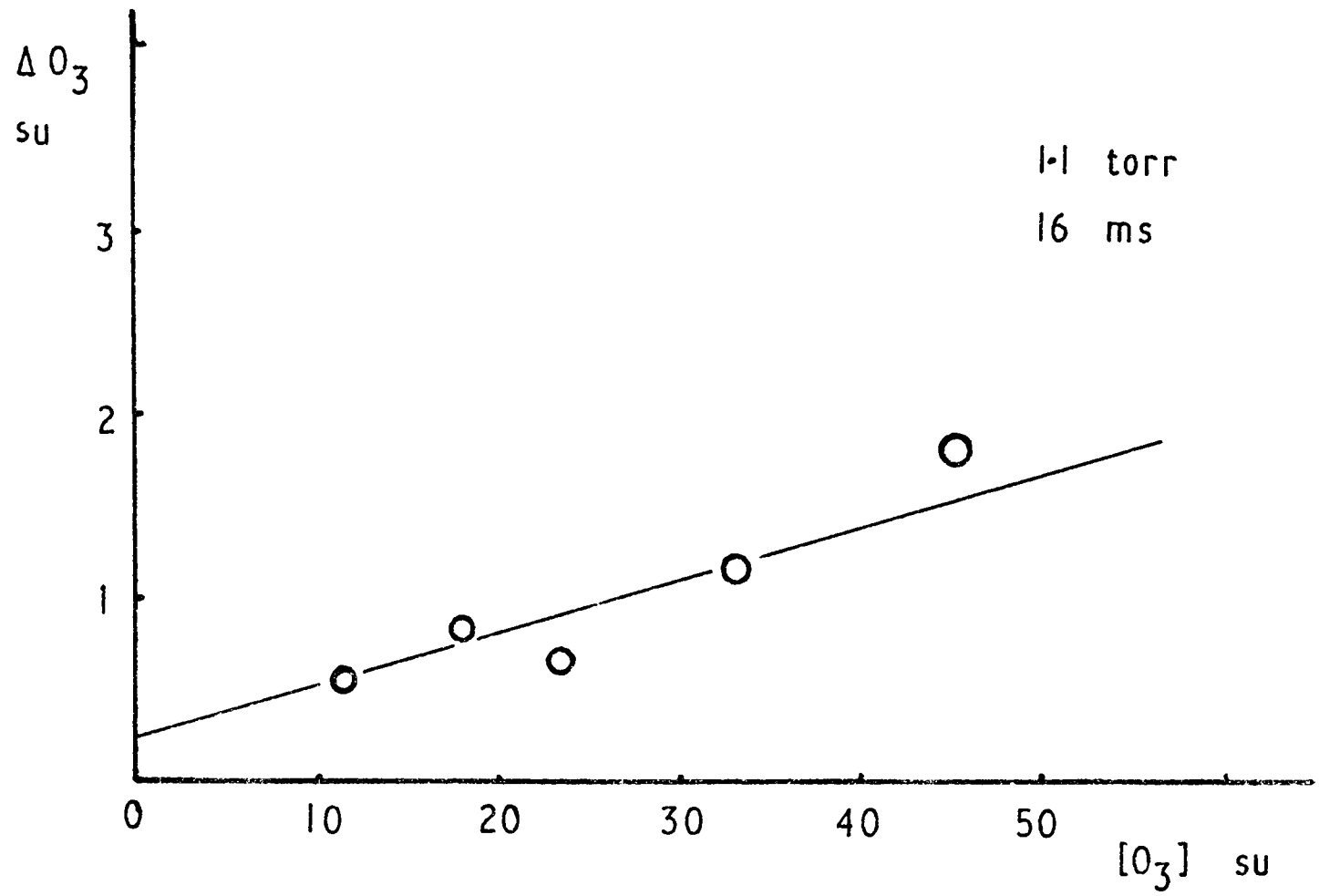


Figure 4,4 Photolysis O_2/O_3



$$\text{Intercept} = 0.6 \times 10^{-4} [\text{O}_3] \cdot 1.3t + 0.23 (\text{ftp})^{-1} - 0.11$$

where ftp = flow tube pressure

t = time in photolysis zone.

This formula shows fair agreement with the value of the $(\text{ftp})^{-1}$ coefficient derived from the ΔO_3 versus $(\text{ftp})^{-1}$ plots, and reinforced the impression that the intercept did not depend significantly on $[\text{O}_3]$ or t . (Since t is generally around 10^{-2} the dependence on t is negligible; and as we deal generally with $[\text{O}_3] \leq 50$ scale units (equivalent to approx 1×10^{-7} mole l^{-1}) the dependence on ozone concentration is also negligible).

Correction using this relation for the intercept (or use of higher pressures to make it negligible) largely overcame the irreproducibility and brought the relative quantum yield ratio near to two.

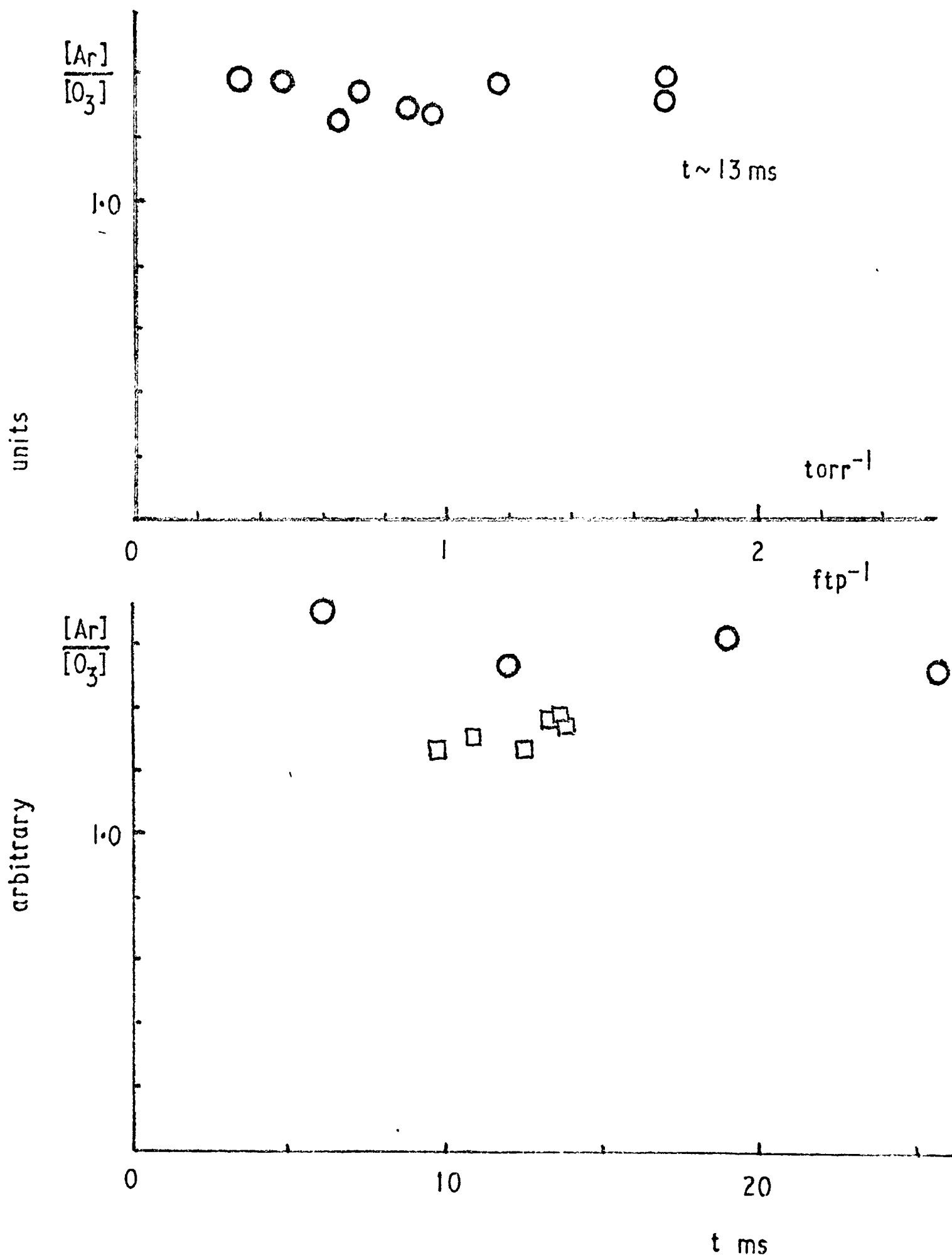
As mentioned before, the physical significance of the intercept was not obvious. Electrical interference from the flashing photolysis lamp was ruled out as there was a negligibly small effect on the baseline in the absence of ozone. By passing a mixture of argon (peak convenient to observe at m/e 40) and ozone with various pressures of helium carrier gas down the flow tube, it was hoped to observe any effects of preferential diffusion through the pinhole. Figure 4,5 shows the results.

Within experimental uncertainty the ratio of the ion currents at m/e 40 and m/e 48 does not depend on the helium pressure.

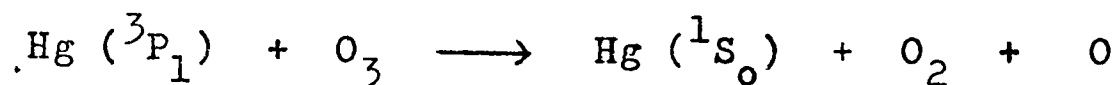
The intercept on the ΔO_3 versus $[\text{O}_3]$ plots is believed to be due to the presence of tiny amounts of mercury carried over from the mercury manometer in the gas handling line. This apparently entered the system despite the layer of oil on the mercury surface and despite the liquid nitrogen trap on the flow line. The intercept could possibly be caused by mercury photosensitised decomposition of ozone. Absorption of

Figure 4,5 Test for preferential diffusion

through pinhole



resonance radiation excites mercury atoms into the $^3P_1$ excited state which energy transfers to ozone on collision.



The observation that the intercepts at a given pressure are the same for oxygen, nitrogen and helium indicates that the Oxygen atom may be produced in the ground electronic state. The production of an electronically excited O atom might be expected to yield twice the intercept in helium as in nitrogen, due to subsequent reaction with ozone.

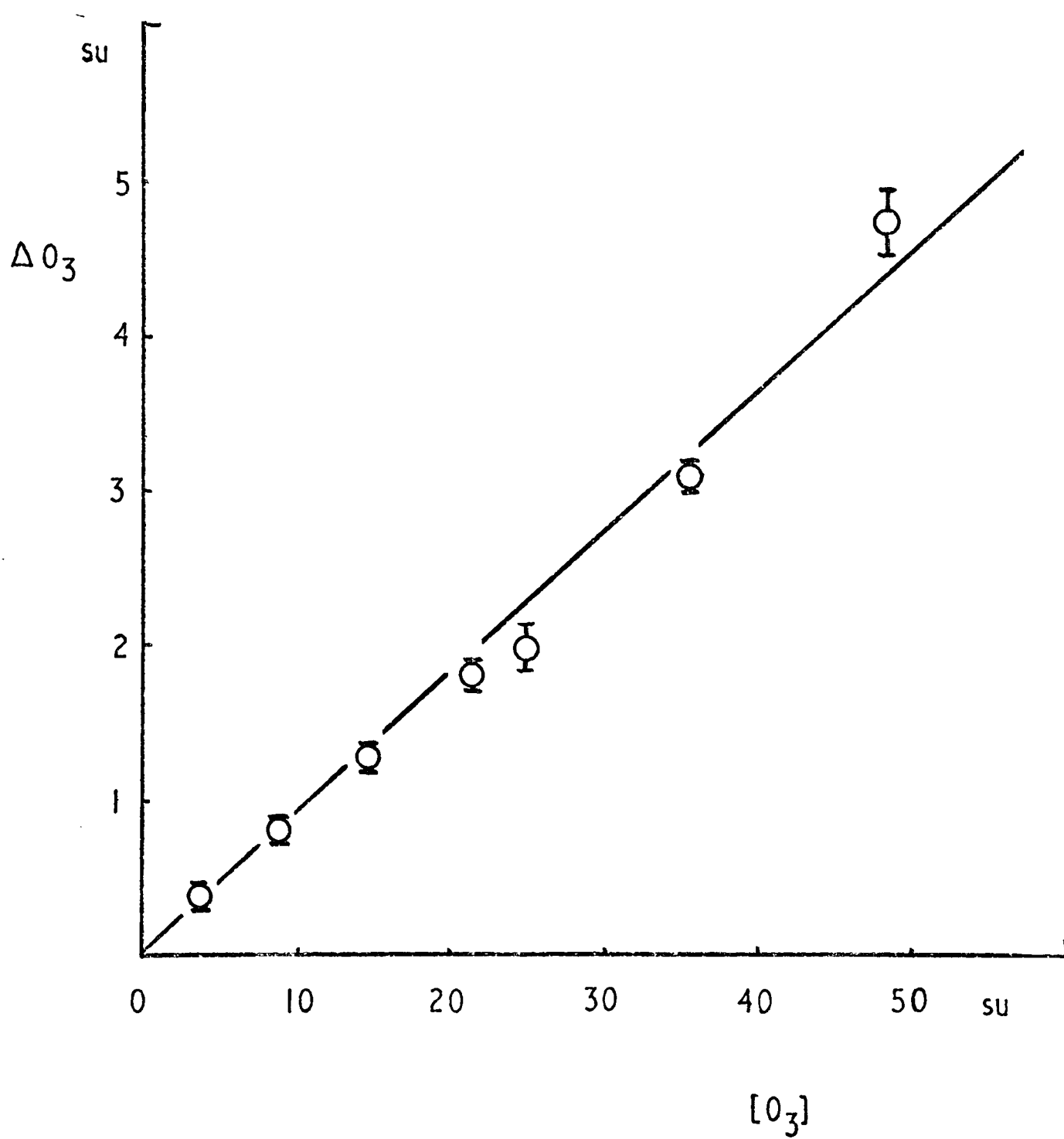
It might be proposed that the pressure dependence of the intercept might be due to collisional quenching of the excited mercury by the carrier gas competing with energy transfer to ozone. This must be discounted on two counts. The first is that, at a given pressure, the intercept would depend on the ozone concentration, which it does not appear to do. The second is that the ΔO_3 versus $(\text{ftp})^{-1}$ plots for oxygen and for nitrogen have the same slopes, which indicates that they are equally efficient quenchers of the excited mercury. This is believed not to be the case (Calleja and McGurk (1973); Doeche et al. (1971)). The dependence of the intercept on the reciprocal of the flow tube pressure is analogous to the pressure dependence of diffusion coefficients. A possible explanation as to the origin of the intercept might involve diffusion controlled desorption (oxygen and nitrogen have similar self-diffusion coefficients) of mercury from the walls of the flow tube. Absorption of mercury onto the walls inside the photolysis zone might occur during the lamp-off period followed by desorption, due perhaps to the heat of the lamp, during the on period.

Whatever the precise origin of the intercept, it

disappeared after the inlet system was carefully cleaned and the mercury manometer replaced by an oil bubbler (as described in Section 3,3). Figure 4,6 shows a ΔO_3 versus $[O_3]$ plot for nitrogen in the absence of any possible sources of mercury contamination. The error bars represent one estimated standard deviation on either side of the mean value of ΔO_3 . The plot shown was obtained from an experiment at a typical flow tube pressure (1.3 torr). Plots of ΔO_3 versus $[O_3]$ at other pressures are shown in Figure 4,7. The line drawn through the points is the linear least squares fit (see computer programs, Appendix 1) of all the data from which the points shown are derived. An average of twenty sets of ΔO_3 and $[O_3]$ measurements are embodied in each weighted point shown. Table 4,2 tabulates the complete (i.e. in the absence of any traces of mercury) N_2/O_3 quantum yield data at various pressures. Table 4,4 shows the standard errors of the linear least squares fits. The fitted values of $\Delta O_3 / O_3$ are then corrected for finite fractional decomposition of ozone according to the relation derived in Section 4,2. Values of β (equivalent to $\Delta O_3^{cor} / [O_3]^t$) are plotted in figure 4,8 for N_2/O_3 (flow tube pressure 1.36 torr). They are very similar to previously obtained values of β when using the mercury manometer.

Figure 4,8 also shows values of $\Delta O_3^{cor} / [O_3]^t$ for He/O_3 . It can be seen that they lie very close to the line which represents a relative quantum yield of 2.0 with respect to the mean nitrogen value. The linear least squares fit (summarised in Table 4,4) of the He/O_3 data (100 points) which go to make up the points shown in figure 4,8 is drawn in figure 4,9. The error bars again represent $\pm$ one standard deviation. The fitted line lies within two standard deviations (95% reliability) of the mean values of the points shown.

Figure 4,6 Photolysis N_2



FTP = 1.36 torr
 $t = 43.3$ ms

Figure 4,7 N_2/O_3

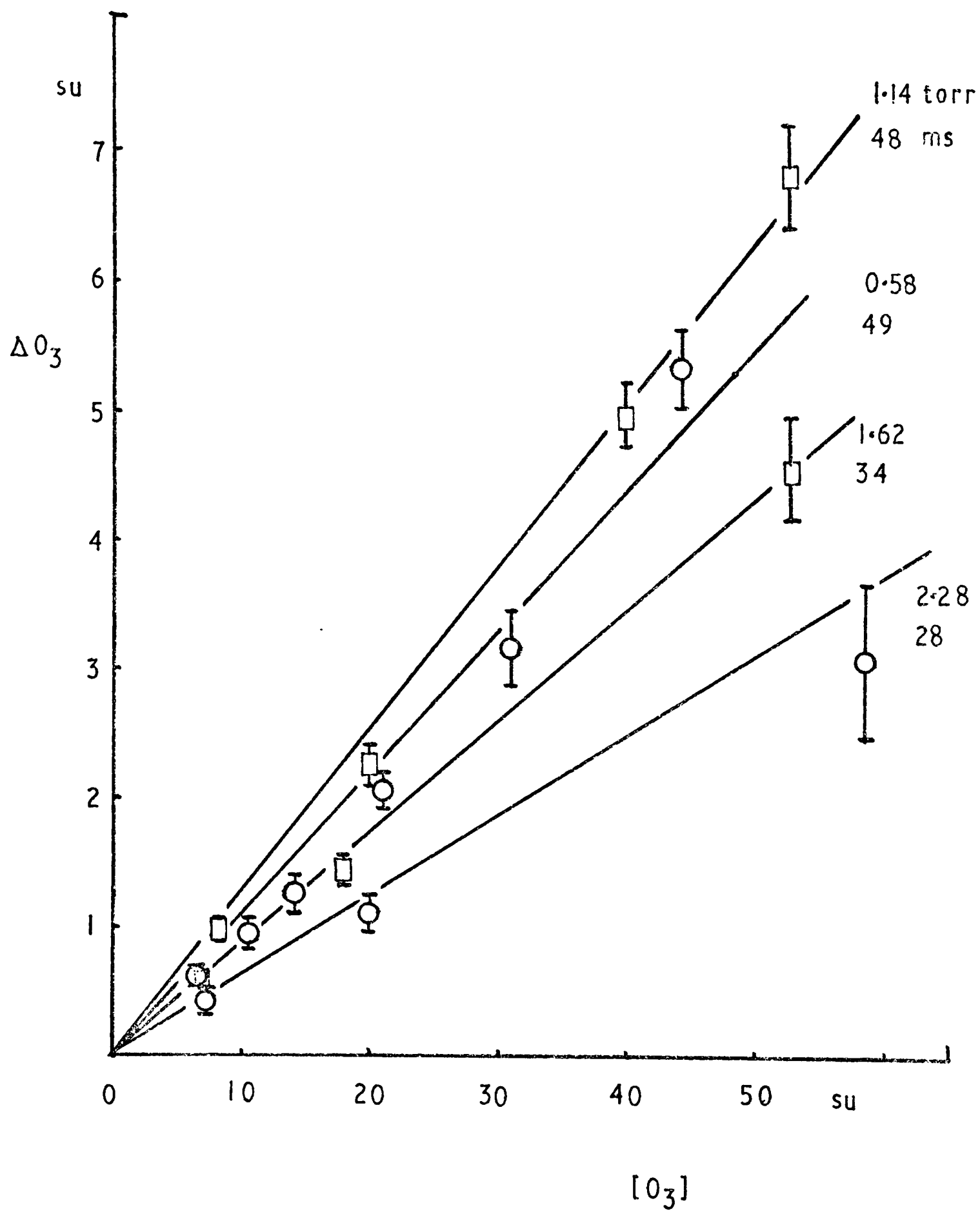


Figure 4,8 He /O₃ , N₂/O₃ relative quantum yields

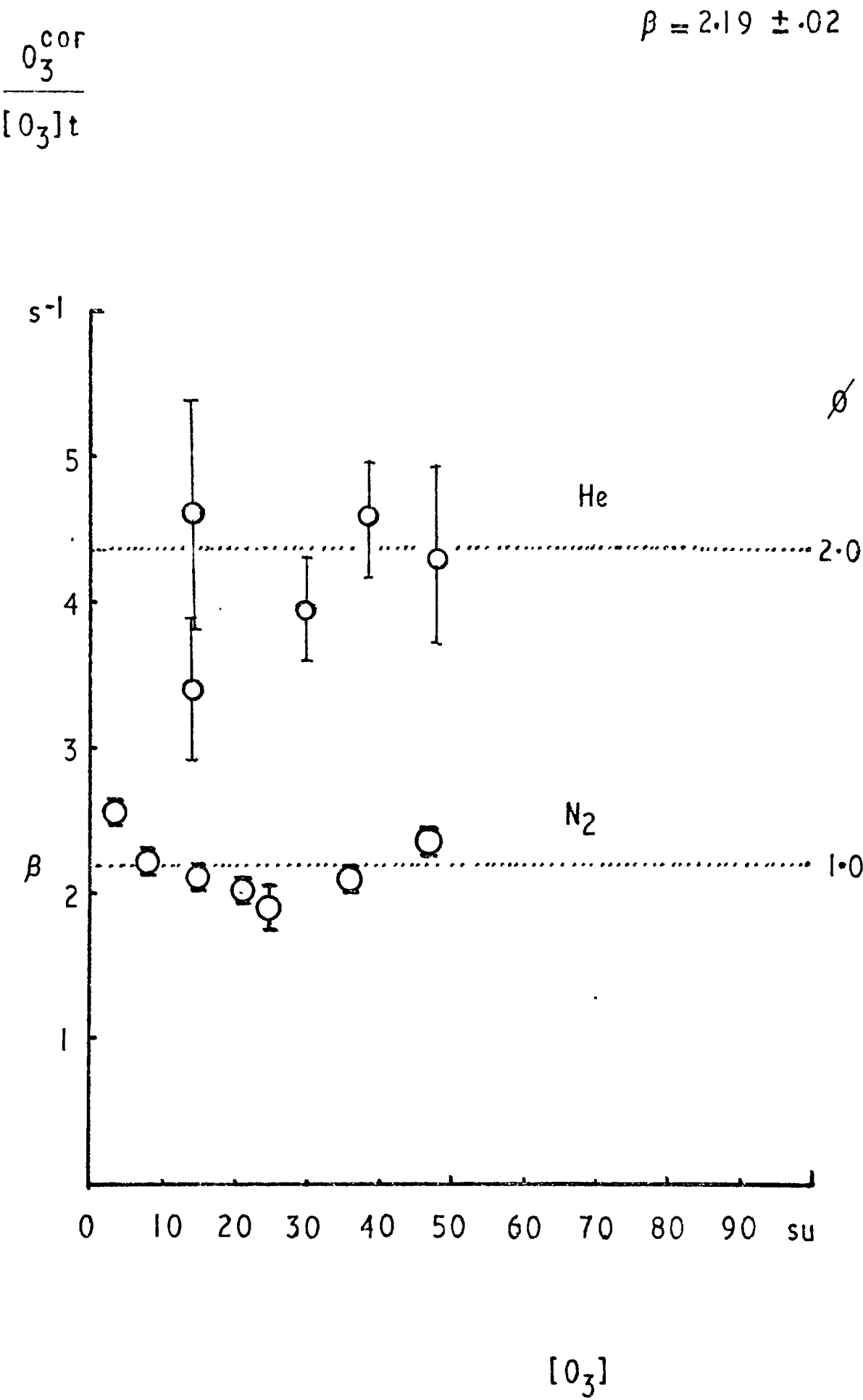


Figure 4,9 Photolysis He/O₃

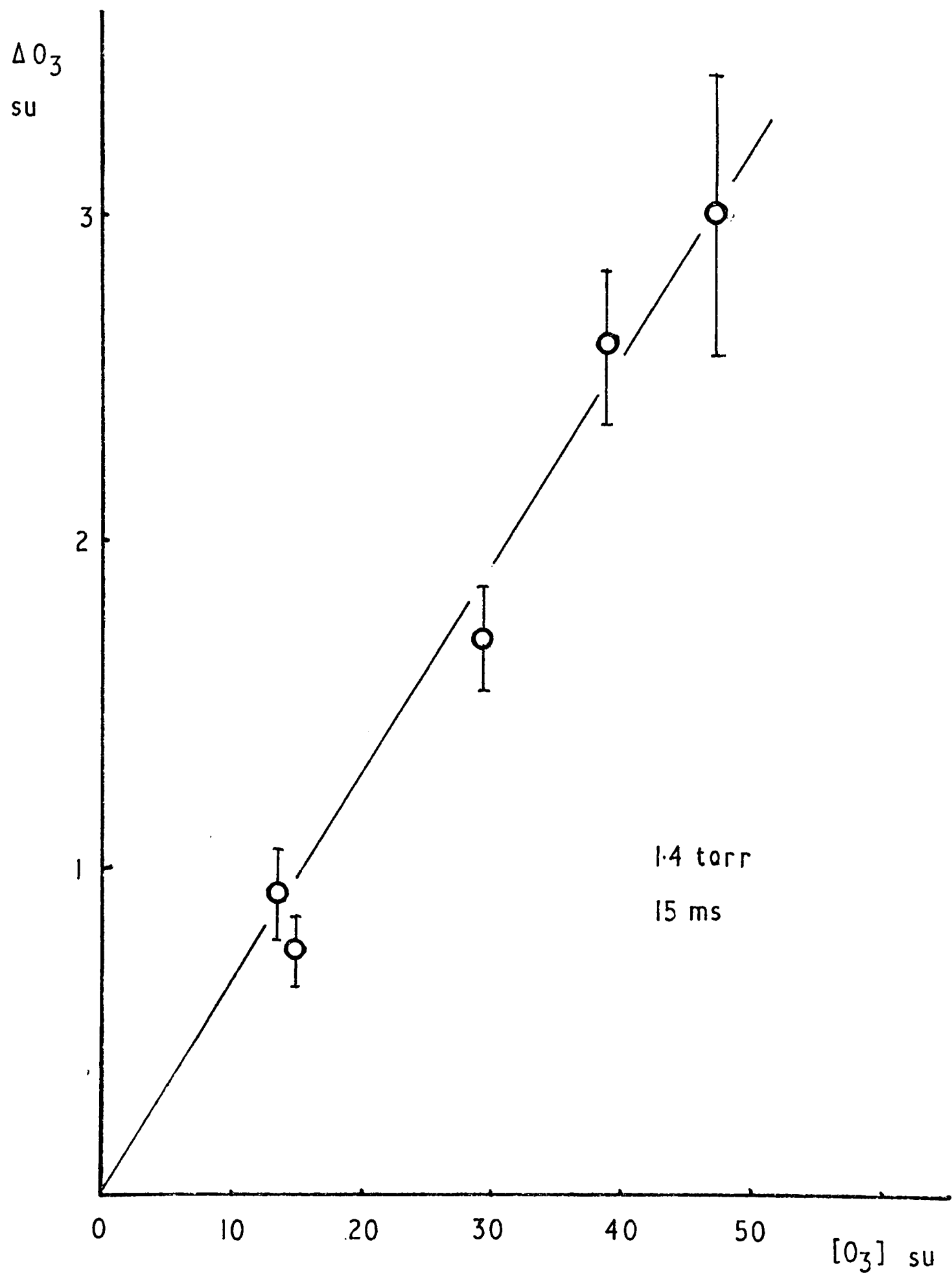


Table 4,5 compares the values of $\Delta O_3^{cor}/[O_3]^t$ obtained for the photolysis of ozone in nitrogen and in helium carrier gases, subject to the kinetic conditions defined in Section 4,1. The value of β found was $2.187 \pm 0.016 \text{ s}^{-1}$. The measured relative quantum yield for the photolysis of ozone in helium was 1.99 ± 0.04 which compares very well with the predicted value of 2.00.

It is clear from figure 4,8 that the error bars drawn, which represent the standard deviation of the ΔO_3 measurements making up any point, do not fully represent the error in the overall relative quantum yield (see footnote). The error is calculated on the assumption that t (time in the photolysis zone) is known precisely. The greatest error involved in the determination of t (if we accept that t is a relative measurement in this case, between the various flow gases) is measurement of ΔP . At small deflections, ΔP read from the capillary flow meter is probably accurate to $\pm 5\%$. An estimate of the overall precision of t would be $\pm 10\%$. Inclusion of the error in t into the error bars drawn in figure 4,8 (if we assume that it is a random error) brings the helium and nitrogen results all to within one standard deviation of the relative quantum yields of two and one, respectively.

In calculating the estimated standard deviations and confidence limits we have assumed a Normal Distribution. This is a fair approximation since each point generally consists of more than twenty pairs of measurements. For this number of measurements the confidence limits calculated on the basis of Students t -Distribution are almost identical to those from the Gaussian Distribution.

We have used a linear least squares analysis on the individual data measurements. Such a treatment assumes that the error on each measurement is potentially the same. In our case the noise on ΔO_3 measurements is proportional to $[O_3]$. (In comparison, $[O_3]$ measurements are very precise). This arises because we are taking the small difference between two large $[O_3]$ signals, the noise on which is of fairly similar absolute intensity.

Footnote: The standard deviation of ΔO_3 is almost always greater than the standard deviation of the relative quantum yield for each set of measurements. This is because the value of $[O_3]$ tended to fall slightly during a run as the storage bulb was pumped out. Consequently the values of ΔO_3 also tended to fall slightly during a run. The error bars based on the scatter present in the ΔO_3 values, therefore, often grossly overestimate the scatter actual present on the values of the relative quantum yield, $\Delta O_3^{cor}/[O_3]t$.

In this chapter we have described the relative quantum yield method and have shown that the results give good agreement with expectation. We have also demonstrated the worth of having two independent measurements of a phenomenon; in this case the quantity β , which was measured both in the N_2/O_3 and He/O_3 experimental regimes.

TABLE 4,1

Lifetimes of Certain Reactive Species in Ozone Photolytic System.

System	Carrier gas Concentration.	$O(^1D)_s$	$O(^3P)_s$	$O_2(^1\Delta g)_s$
He/ O_3	mole l^{-1} 6.0×10^{-5}	$6.7 \times 10^{-5}(R4)$	2.0 (R3)	4.5. (R10)
N_2/O_3	6.0×10^{-5}	$5.6 \times 10^{-7}(R5)$	2.0 (R3)	4.5. (R10)

The lifetime is defined here as the reciprocal of the pseudo-first order loss rate of the species concerned. The bracketed reaction numbers refer to the principal loss process in that system for the species concerned.

Calculated for $[O_3] = 1.0 \times 10^{-7}$ mole l^{-1}

TABLE 4,2

Loss of Ozone in Nitrogen Carrier Gas

Flow pressure torr	mean ΔO_3 su	mean [O_3] su	t ms	Number of points*	T ms	$\frac{\Delta O_3}{[O_3]_t}$ s ⁻¹	standard deviation s ⁻¹
2.288	3.063	48.67	28.0	24	37.8	2.321	0.434
	1.118	19.95	28.0	22	37.8	2.061	0.221
	0.449	7.24	28.0	20	37.8	2.287	0.422
1.620	4.540	52.90	34.4	20	46.4	2.608	0.185
	1.424	18.90	34.4	22	46.4	2.384	0.183
	0.637	7.24	34.4	20	46.4	2.679	0.324
1.360	4.727	48.27	43.3	18	58.4	2.380	0.110
	3.098	35.75	43.3	20	58.4	2.093	0.079
1.360	1.982	25.00	43.3	20	58.4	1.908	0.162
	1.813	21.45	43.3	28	58.4	2.039	0.082
	1.272	14.66	43.3	24	58.4	2.096	0.132
	0.816	8.87	43.3	22	58.4	2.230	0.161
	0.382	3.62	43.3	20	58.4	2.575	0.487
1.144	6.782	52.64	48.4	24	65.4	2.849	0.125
	4.950	39.90	48.4	20	65.4	2.737	0.121
	2.301	20.00	48.4	18	65.4	2.530	0.124
	0.943	8.56	48.4	16	65.4	2.412	0.218
0.587	5.335	44.31	49.1	22	66.2	2.612	0.148
	3.160	31.09	49.1	32	66.2	2.183	0.213
	1.245	13.98	49.1	20	66.2	1.899	0.219
	0.962	10.52	49.1	20	66.2	1.953	0.259
	0.612	6.583	49.1	24	66.2	1.990	0.234
	2.045	20.96	49.1	20	66.2	2.090	0.166

* Number of sets of ΔO_3 and [O_3] measurements.

TABLE 4,3

Loss of Ozone in Helium Carrier Gas.

Flow pressure torr	mean ΔO_3 su	mean [O ₃] su	t , ms	number of points ^r	T ms	$\frac{\Delta O_3}{[O_3] t}$ s ⁻¹	standard deviation s ⁻¹
1.395	2.603	38.77	15.13	20	56.0	4.594	0.428
	1.704	29.52	15.13	18	56.0	3.929	0.371
	0.751	14.96	15.13	16	56.0	3.404	0.469
	2.991	47.35	15.13	28	56.0	4.312	0.624
	0.922	13.72	15.13	18	56.0	4.598	0.874

* Number of sets of ΔO_3 and [O₃] measurements.

TABLE 4.4

Least Squares Fit of ΔO_3 versus $[O_3]$ data

	Flow pressure torr	$\frac{\Delta O_3}{[O_3]}$ $\times 10^2$	standard deviation $\times 10^2$	$\frac{\Delta O_3}{[O_3]_t}$ s^{-1}	standard deviation s^{-1}
N_2/O_3	2.288	6.208	0.136	2.288	0.049
	1.620	8.511	0.078	2.586	0.023
	1.360	9.036	0.067	<u>2.187</u>	0.016
	1.144	12.63	0.076	2.789	0.017
	0.587	10.93	0.116	2.358	0.025
He/O_3	1.395	6.364	0.092	4.346	0.063

Values of $\Delta O_3/[O_3]$ were obtained by performing a linear least squares regression of ΔO_3 on $[O_3]$. Individual sets of ΔO_3 and $[O_3]$ measurements (e.g. a total of 100 sets in the He/O_3 case) were treated as having equal statistical weights, independent of $[O_3]$.

TABLE 4.5

Comparison of the Relative Quantum Yields for Ozone Loss in Nitrogen and Helium Carrier Gases.

	N ₂	He
$\Delta O_3 / [O_3]t$	2.187	4.346
standard deviation	0.016	0.063
ϕ	1.00	1.99 ± 0.04

flow tube pressure N₂ = 1.360 torr

flow tube pressure He = 1.395 torr

Contact time T in N₂ = 58.4 ms

Contact time T in He = 56.0 ms

$$\underline{\beta = 2.187 \pm 0.016 \quad s^{-1}}$$

C H A P T E R 5
THE REACTION $O(^1D) + O_2$

5. 1 Introduction.

This chapter relates to measurement of the efficiency of production of electronically excited molecular oxygen in the $O_2 (^1 \Sigma_g^+)$ state when electronically excited atomic oxygen in the $O(^1D)$ state energy transfers to ground electronic state molecular oxygen. The work of previous authors, which will be examined in detail later in this section, has demonstrated the possible production of both $O_2 (^1 \Sigma_g^+)$ electronically excited oxygen and vibrationally excited ground state molecular oxygen as products of this reaction.

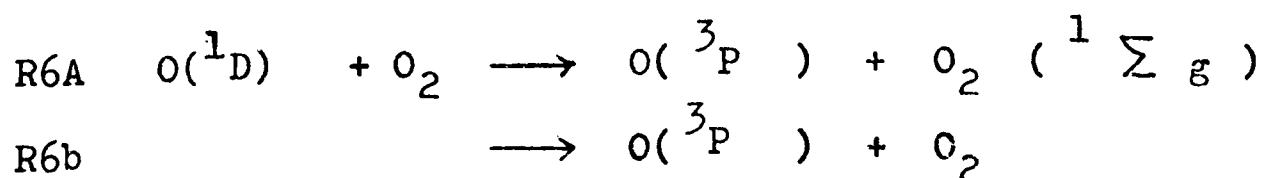
As pointed out in Chapter 1, $O(^1D)$ is produced in the earth's atmosphere by the vacuum - ultraviolet photolysis of molecular oxygen and by the ultraviolet photolysis of ozone. In aurorae, $O(^1D)$ is produced in certain reactions involving ions. The 6300Å emission characteristic of $O(^1D)$ has been observed many times in the dayglow and in auroral spectra (see for example Shephard, Liege, 1974). Most, though not all, reactions of $O(^1D)$ occur at close to gas-kinetic frequency. In particular, the reactions of $O(^1D)$ with molecular oxygen and nitrogen and with ozone are very fast. Therefore, since $O(^1D)$ has a long radiative lifetime of the order of 100 seconds, the principal fate of $O(^1D)$ produced in the atmosphere by the photolysis of oxygen or ozone will be collisional deactivation rather than radiative loss.

Most, if not all, of the $O_2 (^1 \Sigma_g^+)$ present in the atmosphere is believed to be produced by the reaction of $O(^1D)$ with molecular oxygen (see Noxon, 1970).

The rate of production of $O(^1D)$ in the atmosphere may be inferred from observation of the $O_2(^1\Sigma_g^+)$ emission at $7618\text{\AA}$, given a knowledge of the oxygen concentration and the rate of production of $O_2(^1\Sigma_g^+)$ from the reaction of $O(^1D)$ with oxygen. This, in turn, may be inferred from a knowledge of the efficiency of $O_2(^1\Sigma_g^+)$ production and of the overall rate of $O(^1D)$ reaction with oxygen.

Whilst it is energetically possible to produce $O_2(^1\Sigma_g^+)$ from the photolysis of ozone at wavelengths shorter than $2660\text{\AA}$ (see Table 2,1), early suggestions by Izod and Wayne (1968a), and Jones, Kaczmar and Wayne (1970) that $O_2(^1\Sigma_g^+)$ is in fact one of the products have not been substantiated. Gilpin, Schiff and Welge (1967) have put an upper limit of 0.05 on the primary quantum yield for $O_2(^1\Sigma_g^+)$ production. Further work by Jones and Wayne (1971) has shown $O_2(^1\Delta_g)$ to be the principal molecular oxygen fragment formed in the photolysis of ozone at $\lambda = 2537\text{\AA}$.

The rate constant recommended by Cvetanovic (1974) for the reaction $O(^1D) + O_2$ is about $(4.5 \pm 0.9) \times 10^{10} \text{ l mole}^{-1} \text{ s}^{-1}$. Reference to Table 5,2 shows that this value adequately summarises the work to date. The gas kinetic collision frequency was calculated by Gauthier and Snelling (1975), using collision diameters of $2.54\text{\AA}$ and $3.56\text{\AA}$ for $O(^1D)$ and O_2 respectively, to be $2.2 \times 10^{11} \text{ l mole}^{-1} \text{ s}^{-1}$. Therefore, an $O(^1D)$ atom will survive on average one collision in three with molecular oxygen before it is quenched. Many laboratory studies have demonstrated the formation of $O_2(^1\Sigma_g^+)$ by energy transfer in this reaction and we can write the pathways as:



(Where a species is written without bracketed suffixes, the species indicated is in its ground electronic state).

The ratio $k_{6a} / (k_{6a} + k_{6b})$, which is the fractional efficiency for $O_2(^1\Sigma_g)$ formation per $O(^1D)$ deactivation, is referred to below as α . The energy transfer process is almost exactly resonant if the $O_2(^1\Sigma_g)$ is formed in its second vibrational level. Reaction R6 is spin-allowed, however, the rate of deactivation of $O(^1D)$ by a variety of gases, including, for example; Cl_2 , N_2 and H_2 , occurs at a similar rate and yet is spin - forbidden. Heidner and Husain (1974) investigated the rate of $O(^1D)$ deactivation by the Rare Gases Xe, Kr, Ar, Ne, and He and found that the number of collisions required for quenching by these gases (which all have singlet ground electronic states) varied from 2.5 (for Xe) to greater than 5×10^5 collisions (for He). It may be that spin conservations arguments are, therefore, not necessarily applicable to this system.

Laboratory investigations of reaction R6 may be very generally classified into those in which $O(^1D)$ has been generated either by the vacuum ultraviolet photolysis of oxygen to yield $O(^1D) + O(^3P)$ or by the ultraviolet photolysis of ozone/oxygen mixtures yielding $O(^1D)$ and $O_2(^1\Delta_g)$. The $O_2(^1\Sigma_g)$ generated by energy transfer of $O(^1D)$ to molecular oxygen has been detected by its emission at $7618\text{\AA}$; alternatively, its presence has been deduced from its subsequent reactions. One group of workers have monitored the vibrationally excited oxygen produced in reaction R6b and thereby deduced a value of α . The present work generates $O(^1D)$ by the photolysis of ozone in oxygen and deduces the fractional efficiency of $O_2(^1\Sigma_g)$ production by means of subsequent reaction with ozone.

The deactivation of $O(^1D)$ has commanded much attention and a recent review by Cvetanovic (1974), only, will be mentioned. Gauthier and Snelling (1975) have undertaken an exhaustive and definitive experimental investigation into the relative rates of $O(^1D)$ deactivation by seventeen gases of possible relevance to studies of the atmosphere. A brief discussion of experiments relevant to the present study will now be presented.

In an early study of reaction R6, Young and Black (1967) photolysed O_2 with $1470\text{\AA}$ radiation from a Xenon lamp. They were unable to observe the $6300\text{\AA}$ emission from $O(^1D)$ but were able to monitor the $7618\text{\AA}$ emission from $O_2(^1\Sigma_g)$ as a function of oxygen and added gas pressure in a small cell. Unfortunately, their analysis was carried out in the absence of almost any knowledge of the rates of quenching of $O(^1D)$ and $O_2(^1\Sigma_g)$. The added gas was assumed only to quench $O_2(^1\Sigma_g)$, whereas in fact quenching of $O(^1D)$ would have been the dominant process, and consequently rates of deactivation of $O_2(^1\Sigma_g)$ are approximately two orders of magnitude higher than currently accepted values. The complex analysis also postulated a collision induced emission process for $O_2(^1\Sigma_g)$, a feature which has not been independently substantiated. Ultimately their value of α depends on the calculation of a "reasonable" diffusion coefficient for $O_2(^1\Sigma_g)$ in helium and therefore it is difficult to evaluate their assertion that α is near unity; given these caveats.

Snelling and Bair (1968) report a flash photolysis experiment involving mixtures of ozone with helium, oxygen and nitrogen. Unfortunately, the body of the analysis is based on the assumption that molecular oxygen simply quenches $O(^1D)$. In a note added in proof the authors acknowledge the possibility that $O_2(^1\Sigma_g)$ is a product of energy transfer from $O(^1D)$

to O_2 . Reanalysing their data in this light yields a value of α equal to around 1.5; an impossibly high value for a single step process, in which α cannot be greater than unity. The authors, however, believe that the result may be due to "experimental fluctuation".

Izod and Wayne (1968 a and b) generated $O(^1D)$ by the photolysis of molecular oxygen in a similar experimental system to that of Young and Black (1967). However, Izod and Wayne monitored $O_2(^1\Sigma_g^-)$ and $O(^3P)$ concentrations in a time resolved flow system, and as a function of added pressure of O_2 , N_2 or Ar. They measured $O_2(^1\Sigma_g^-)$ as a function of time and calculated the initial concentration by extrapolation back to the production region. Clark (1970) has subsequently shown that this treatment is open to criticism on the grounds that vortex formation in the production region led to a much faster rate of wall deactivation, therein, than in the main flow section. This led him to suppose that Izod and Wayne's conclusion that only one $O(^1D)$ deactivation in 180 leads to production of $O_2(^1\Sigma_g^-)$ might be too low by a factor of approximately fifty. This would tend to increase Izod and Wayne's value of α to 0.3, with large error limits.

The vacuum ultra-violet photolysis of oxygen in a static system was also performed by Noxon (1970). He succeeded in detecting $O(^1D)$, for the first time by optical emission at 6300Å. $O_2(^1\Sigma_g^-)$ was monitored by the 7618Å emission and from a complicated consideration of reaction rates and diffusive loss processes Noxon deduced that values of α close to unity were consistent with his observations. The treatment leads to an anomalously high rate of diffusion of $O(^1D)$ through helium. Noxon postulated that this might be due to the effects of excess

kinetic energy of the newly formed $O(^1D)$, but a reanalysis in the light of further experimental data by Clark and Noxon (1972) did not reproduce this observation. Noxon's value of $\alpha \approx 1.0$ may, therefore, be regarded as a qualitative observation.

Biedenkapp and Bair (1970) were the first to study reaction R6 following the production of $O(^1D)$ by the ultraviolet photolysis of ozone. They pioneered the method of relative quantum yields (which they referred to as the "intermediate quantum yield method") which has already been fully described in Chapter 4. Thus by careful choice of concentration-time régime it was possible to avoid the complication which would otherwise arise from the contributions of the reactions of $O(^3P)$ and $O_2(^1\Delta_g)$ with ozone to the overall quantum yield.

Biedenkapp and Bair repetitively flash-photolysed ozone in the presence of thousand-fold excesses of nitrogen, oxygen and of helium. Ozone concentration was monitored by optical absorption as a function of time, typically up to 100 microseconds, after the flash. They obtained an intermediate quantum yield of 1.5 in excess oxygen; however, it is clear they expected that the quantum yield should have been closer to 2.0 (which would have been consistent with the efficiency $\alpha = 1.0$), and they sought reasons to correct their experimental value of α . The efficiency for R6a was quoted as $1.0 \gg \alpha \gg 0.6$ on the basis that the experimentally determined value of 0.5 was a lower limit. They argued that the recombination reaction $O + O_2 + O_2 \longrightarrow O_3 + O_2$ would lead to significant regeneration of ozone and hence a low quantum yield. Since they used 20 torr of O_2 , and the rate constant for reaction R2 is of the order $2.3 \times 10^8 \text{ l}^2 \text{ mole}^{-2} \text{ s}^{-1}$ (Stuhl and Niki, 1971), the first order loss rate for O atoms by this reaction in their system will be

about 275 s^{-1} . The half life for this process is therefore 3.6×10^{-3} seconds, and its effect would be insignificant on a 100 microsecond time scale. It was also suggested that atomic oxygen might be a highly efficient quencher of $\text{O}_2(^1\Sigma_g)$, a conclusion which has not been substantiated by subsequent workers. Their analysis also leads them to conclude that the rate constant for the quenching of $\text{O}_2(^1\Sigma_g)$ by ground state molecular oxygen is $2 \times 10^6 \text{ l mole}^{-1} \text{ s}^{-1}$ whereas more direct measurements have shown it to be $2.8 \times 10^4 \text{ l mole}^{-1} \text{ s}^{-1}$ (Thomas and Thrush). Finally, their method of fitting the predicted ozone concentration - time curve to the experimental data by varying the rate constants in the model is insensitive to the value of α , which could apparently be fitted equally satisfactorily by any values between 0.5 and 1.0. We therefore conclude that their work is consistent with $1.0 \gg \alpha \gg 0.5$.

Langley and McGrath (1971) performed an essentially similar experiment to that of Biedenkapp and Bair. They photolysed O_3/Ar , $\text{O}_3/\text{O}_2/\text{Ar}$ and $\text{O}_3/\text{N}_2/\text{Ar}$ mixtures, measured the time dependent quantum yield for ozone decomposition and extrapolated the observed concentrations back to the time immediately after the flash to obtain the intermediate quantum yield. Their relative quantum yields were in the ratio 0.32: 0.22: 0.16 for Ar , O_2/Ar and N_2/Ar respectively and they therefore concluded that $\alpha = 0.37$ with error limits ± 0.1 .

The work has been subjected to lengthy criticism by Snelling (1974), since Snelling's work, which was performed in an experimental system very similar to that of Langley and McGrath, arrives at a significantly higher value for α . Snelling makes three broad criticisms. The first makes the point that, in an optically thin system with a significant amount of photolysis,

the expected 2:1 ratio in the O_3/Ar and $O_3/Ar/N_2$ cases will not be applicable unless one allows (for example, in the manner described in Chapter 4) for the decrease in the ozone concentration, below its initial value, as a result of the subsequent reaction of $O(^1D)$ with ozone, in the O_3/Ar case. One would have expected this effect to be quite marked in Langley and McGrath's experiment as they report up to 32% overall ozone losses. A further point, not made by Snelling, is that in the O_3/Ar case quenching of $O(^1D)$ by argon would account for approximately 12% of the $O(^1D)$. The quenching of $O(^1D)$ by argon would not be significant in the $O_3/Ar/N_2$ and $O_3/Ar/O_2$ systems owing to the presence of large excesses of N_2 and O_2 respectively. In view of these criticisms Langley and McGrath might be expected to have obtained basic experimental data of approximate ratio 1.7 : 1 in the O_3/Ar and $O_3/Ar/N_2$ regimes, respectively, rather than the observed 2.0 : 1 ratio.

Snelling's second criticism is of Langley and McGrath's work is that the temperature rise in their system must have been of the order $50 - 100^\circ$, which would increase the importance of the $O + O_3$ and $O_2(^1\Delta_g) + O_3$ reactions. However, in the absence of detailed experimental data it is difficult to assess the increase in contribution from these two reactions to the overall quantum yield for ozone loss which might be expected at the higher temperature. The third criticism is that use of more recent values for the ratio of the rate constants for the reactions $O(^1D) + O_2$ and $O(^1D) + O_3$ would lead to a higher value of α . In view of these various observations and their own error limits, one could estimate that the results of Langley and McGrath are consistent with $0.3 \leq \alpha \leq 0.7$.

In another paper from the same group McCullough and McGrath (1971) describe the observation of vibrationally excited

ground state molecular oxygen in the $v = 13$ and 14 levels in the $O_3/O_2/He$ flash-photolysis system. They attribute the enhancement of the $(0,13)$ and $(0,14)$ bands of the Schumann-Runge system of O_2 , which attends the addition of extra oxygen, to the production of vibrationally excited oxygen from the $O(^1D) + O_2$ reaction. It was also observed that no increase in the $(0,15)$ band occurred. They deduced that the efficiency for production of $O_2(v = 13,14)$ was ≥ 0.3 , which implies, in the absence of any other pathways for R6, a value of $\alpha \leq 0.7$.

McCullough and McGrath were not able to observe the $(0,12)$ band and their estimate of the amount of vibrationally excited O_2 produced appears to have been made by summing only the observed $O_2(v = 13)$ and $O_2(v = 14)$ enhancement intensities. Whilst it has been shown by Polanyi and Sloan (1975) in the case of the $H + O_3$ reaction, that initial excitation may be predominantly into a single vibrational level, this argument is not applicable to these authors' experiments where several thousand collisions of vibrationally excited O_2 with ground state O_2 will have occurred before observation of the $(0,13)$ and $(0,14)$ emission bands is made. It is therefore to be expected that the highest vibrational levels would have been rapidly lost by $V - V$ transfer, long before they could be observed in this experiment. In addition the production of $O_2(v = 14)$ is 10 kcal endothermic in the $O(^1D) + O_2$ reaction. This would require each $O(^1D)$ atom to have at least 10 kcal of translational energy. It seems unlikely that such translationally hot atoms could exist for a sufficiently long time in the presence of the experimental pressure of 215 torr of helium.

In addition, there would appear to be more possible sources of vibrationally excited O_2 than are recognised by

McCullough and McGrath. The reaction $O(^1D) + O_3$ is capable of producing vibrationally excited O_2 up to the dissociation limit. It may be possible therefore that the enhancement of the addition of oxygen results, in some undefined way, from an increased rate of V-V transfer from excited to ground state molecular oxygen. In addition it is possible that the reaction of $O_2(^1\Sigma_g) + O_3$ may also produce $O_2(v = 13, 14)$ directly or indirectly. A new analysis of the data of these workers including treatment of the effects of V - V transfer appears necessary before coming to any final conclusions about their deduced value of α .

Snelling and co-workers have studied the ozone-oxygen photolysis system using both constant-illumination flow systems and flash photolysis. In an earlier paper Gauthier and Snelling (1971) showed that in the O_3/O_2 system the $O_2(^1\Sigma_g)$ produced was formed by the energy transfer $O(^1D) + O_2$ rather than as a primary product of the photolysis of ozone at 2537Å. In the same paper these authors cite unpublished work in their own laboratory which indicated $\alpha \geq 0.6$, although their neglect to correct for the loss of ozone by the reaction $O_2(^1\Sigma_g) + O_3$ is an omission which would lead to this value of α being an underestimate. From measurements of $O_2(^1\Sigma_g)$ and $O_2(^1\Delta_g)$ (monitored by optical emission) and $[O_3]$ (monitored by optical absorption) in a system where O_3/O_2 mixtures were UV photolysed, Snelling and Gauthier (1971) concluded that $\alpha = 0.85 \pm 0.15$. (This value is quoted in the abstract of the paper, consideration of the text leads one to believe that $\alpha = 0.85 \pm 0.33$ which is surprising since $\alpha \leq 1$). In a recent paper Snelling (1974) has revised this value of α to take into account uncertainties in the rate of the reaction $O_2(^1\Sigma_g) + O_3$ as well as, uncertainties in the Einstein A factors for the $O_2(^1\Sigma_g)$

and $O_2(^1\Delta_g)$ emissions. He therefore concludes that a more reasonable value would be $\alpha \geq 0.5$.

Snelling (1974) reports the results of flash photolysis experiments on O_3/N_2 , $O_3/N_2/O_2$ and O_3/N_2 mixtures, in which ozone is monitored by UV absorption as a function of time after the flash. Fitting the relevant rate parameters to the O_3 decomposition curves results in a "best fit" value of $\alpha = 0.85 \pm 0.10$. Snelling finally reports $\alpha \geq 0.75$ on the grounds that since his observations do not fit the numerically integrated decay curves over the whole range of observation times there must be some residual uncertainty as to the completeness of the reaction scheme used.

There have been various studies of reaction R6 by Wayne and coworkers. These have all been flow system studies and the present work is the most recent study and, arguably, the one least prone to systematic error. Jone, Kaczmar and Wayne (1970) measured the overall (rather than intermediate) quantum yield in the UV photolysis of O_3/O_2 mixtures and obtained quantum yields near 4. This is consistent with $\alpha = 0$, but they state that "It is not possible, on the basis of our data, to make a meaningful choice between $\alpha = 0$ and $\alpha = 0.3$ ". The predicted quantum yields show a weak dependence on α ; the same being true of similar work by Jones and Wayne (1971) who concluded that $\alpha \sim 0.3$.

Giachardi and Wayne (1972) used the intermediate quantum yield technique to obtain values of $1.89 (\pm 0.03) : 1.16 (\pm 0.02) : 1.00$ for the intermediate quantum yields resulting from the photolysis of O_3/He , O_3/O_2 and O_3/N_2 mixtures, respectively. They photolysed ozone using 2537Å mercury resonance radiation in a fast flow system and monitored its concentration by optical absorption. In a second experiment Giachardi and co-author

monitored by resonance fluorescence the ground state O atoms produced as a result of the consecutive reactions $O(^1D) + O_2 \rightarrow O + O_2 (^3\Sigma_g \text{ and } ^1\Sigma_g)$ and $O_2(^1\Sigma_g) + O_3 \rightarrow 2O_2 + O$. The resonance fluorescence data showed that 1.50 ± 0.11 O atoms are produced for every O_3 molecule photodissociated. These results are consistent with $0.5 \leq \alpha \leq 0.6$. It was not possible, for reasons of detector sensitivity, for the experiments of Giachardi to fulfil the concentration-time requirements of the intermediate quantum yield method. In addition it has been argued by Snelling (1974) that insufficient nitrogen was present in the O_3/N_2 mixtures to completely suppress the $O(^1D) + O_3$ reaction. Giachardi (1975) has undertaken a detailed reanalysis of the experimental data and now proposes $0.53 \leq \alpha \leq 0.62$.

Table 5,9 summarises the literature values of α .

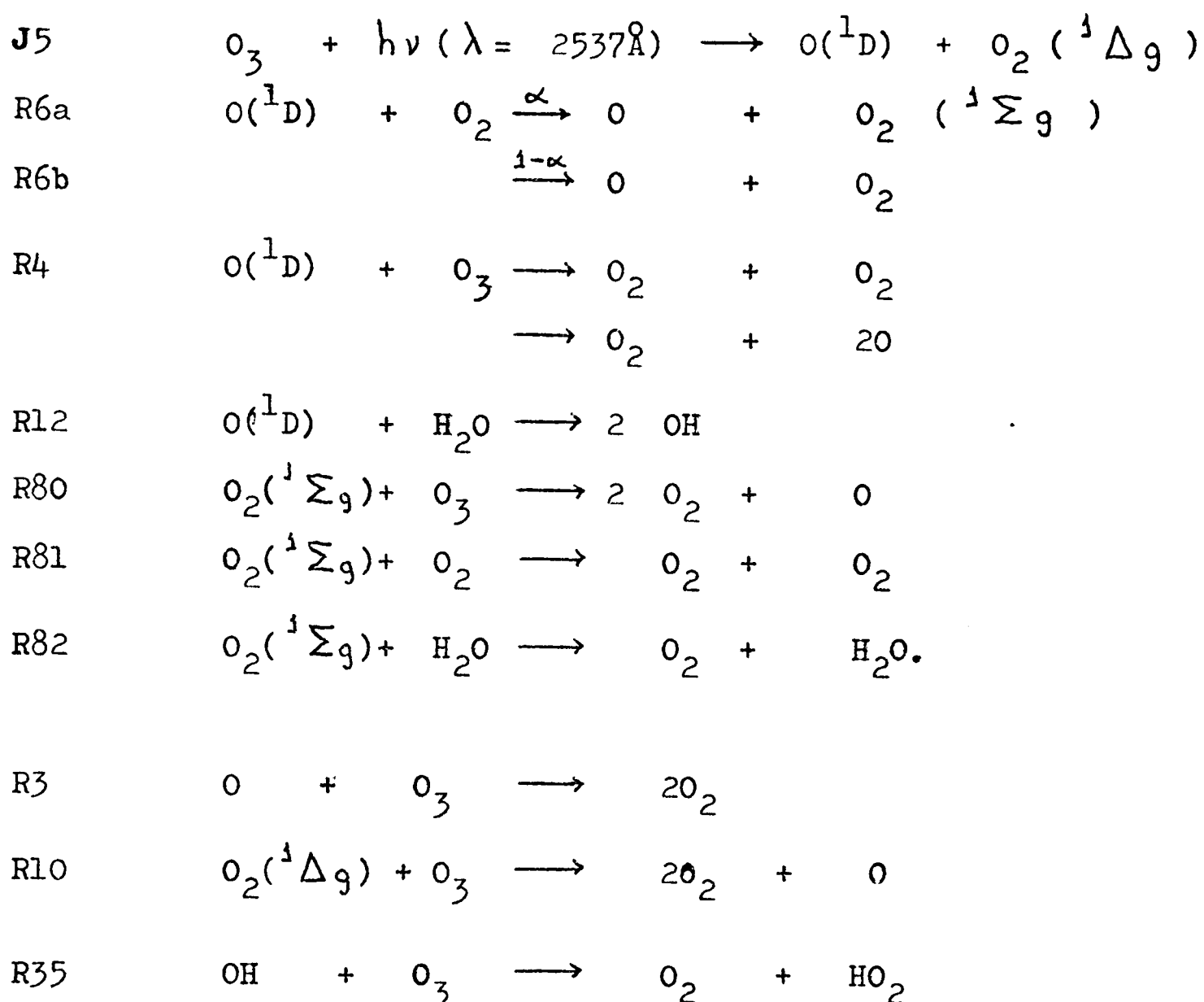
The present work aims to overcome the experimental shortcomings of Giachardi and Wayne (1972), and in addition to remove any systematic errors which may result from use of the different flow gases in the O_3/He , O_3/O_2 and O_3/N_2 experiments. The present study compares the relative (i.e. intermediate) quantum yields obtained in the O_3/O_2 and $O_3/O_2/H_2O$ photolytic systems. The H_2O present in the latter system is designed to completely quench any $O_2(^1\Sigma_g)$ produced (and to partially quench the $O(^1D)$ produced by the primary photolysis of ozone). Ozone decomposition was monitored mass spectrometrically at variable contact time in a fast photolysis flow system.

5,2 Kinetic Scheme.

The two basic principles upon which the experiments in this chapter are based have been fully described in the previous chapter which deals with the method of relative quantum yields. These principles are (a) that the "fast" and "slow" reactions are differentiated by use of the correct concentration-time conditions; (b) that at least two parallel experiments are carried out; in the first the unknown quantum yield is measured relative to a quantity β (which constant includes the ozone extinction coefficient, the lamp intensity and the cell geometry), in the second experiment β is determined by use of a "control" experiment in which the quantum yield (measured in terms of β) is known. In previous work by Giachardi and Wayne (1972), Biedenkapp and Bair (1970) and others, O_2/O_3 and N_2/O_3 mixtures have been photolysed; the constant β being determined from the N_2/O_3 "control" system. This approach suffers from the disadvantage that it depends critically on accurate knowledge of the absolute flow velocities of each of the two different carrier gases, O_2 and N_2 . In our experiments measurement of the flow velocities relies ultimately on precise calibration of the capillary flowmeter for each of the carrier gases. We have eliminated this possibly serious source of systematic error by using an oxygen carrier gas in both the "unknown" and the "control" experiments.

This chapter describes the photolysis of O_2/O_3 and $O_2/O_3/H_2O$ mixtures. The quantity β was determined in the $O_2/O_3/H_2O$ photolytic system, sufficient water being present to successfully quench all the $O_2(^1\Sigma_g)$ generated.

The reaction sequence which we shall consider in order to describe the $O_2/O_3/H_2O$ system is as follows, (the relevant rate constants are recited in Table 5,2):



Reaction R12, R82 and R35 are omitted in consideration of the O_2/O_3 system.

It was an object of the experiments to choose concentration-time conditions such that the "fast" reactions R6, R4, R12, R80, R81 and R82 had gone essentially to completion; whilst the "slow" reactions R3, R10 and R35 had occurred to a negligible extent. It can be shown (see Appendix 3) that in a pseudo first order reaction 95% loss of the minor reactant has occurred after 3τ ; whereas, 5% loss has occurred after 0.05τ . The relaxation time τ is time taken for the concentration of the minor reactant to fall to $1/e$ of its initial value and is equal to the reciprocal of the pseudo first order rate constant. In the experiments described here the photodecomposition of ozone (J5) occurs typically to an extent of 5%, so that the concentrations of the minor reactants $\text{O}({}^1\text{D})$, $\text{O}_2({}^1\Sigma_g)$, $\text{O}_2({}^1\Delta_g)$, O and OH never exceed about 5% of the ozone concentration (and an even

lower percentage of the other major reactants; O_2 and H_2O). Thus for the object of establishing the experimental concentration-time regime it is a useful approximation to take $\tau = 1 / (k[\text{major reactant}])$.

If we take as arbitrary requirements that, at the time T of observation, the "fast" reactions shall be 95% complete whilst the combined "slow" reactions are only 5% complete, then we may write for the O_2/O_3 system.

$$3 \tau_{80} < T < 0.05 / (k_3 [O_3] + k_{10} [O_3])$$

For the purposes of simplification we have neglected the contribution of R6 to the overall relaxation time of $O_2(^1\Sigma_g)$ in reaction R80. Under our experimental conditions τ_6 is, in any case, smaller than τ_{80} by a factor of at least one hundred. The inequality may then be written

$$2.0 \times 10^{-10} < T [O_3] < 5.9 \times 10^{-9} \text{ s mole l}^{-1}$$

The sensitivity of our ozone detection system and the time resolution available is such that we are able to (and do) vary the concentration-time régime (i.e. the product $T[O_3]$) to any value within these limits. Consequently we are able to avoid the need to make any corrections for the contribution of the "slow" reactions to the overall quantum yield.

A similar inequality may be set-up for the $O_2/O_3/H_2O$ system in the presence of sufficient water for reaction R82 to dominate reaction R80.

$$3 \tau_{82} < T < 0.05 / (k_3 [O_3] + k_{10} [O_3] + k_{35} [O_3])$$

If we allow τ_{82} to be smaller than τ_{80} by a factor of at least ten, in order for R82 to dominate R80, then

$$2.0 \times 10^{-11} < T [O_3] < 1.3 \times 10^{-9} \text{ s mole l}^{-1}$$

Again, concentration-time régimes within this range are easily attainable in these experiments.

Wall loss of the reactive species $O(^1D)$ and $O_2(^1\Sigma_g)$ has been neglected in the kinetic analysis, since it is unlikely that, at the pressures used, wall quenching could not be complete even if quenching occurred on every collision with the wall. A rough estimate of the maximum first order wall loss rate constant is 3000 s^{-1} (see Chapter 6), whilst the pseudo first order homogenous loss rates of $O(^1D)$ and $O_2(^1\Sigma_g)$ are about $2 \times 10^6\text{ s}^{-1}$ and $1 \times 10^3\text{ s}^{-1}$ respectively. Whilst it is conceivable that $O(^1D)$ might be quenched on every collision, it is generally accepted that γ for $O_2(^1\Sigma_g)$ is around 10^{-4} which would lead to a first order wall loss rate constant of about 10^2 s^{-1} in our system. It is therefore unlikely that wall loss contributes significantly to the loss rates of $O(^1D)$ or $O_2(^1\Sigma_g)$.

The generalised reaction scheme for the production of $O(^1D)$ from the photodecomposition of ozone, its reaction, and the subsequent reaction of the products with ozone has already been dealt with in Chapter 4. We shall therefore present only a cursory treatment of the kinetics in order to derive expressions from which α and β may be obtained. The quantity α it will be remembered is the efficiency for the production of $O_2(^1\Sigma_g)$ in the reaction $O(^1D) + O_2$; whilst β is an experimental constant embodying the ozone extinction coefficient, the lamp intensity and a term dependant on the geometry of the irradiation zone.

$$\begin{aligned} \text{In the } O_2/O_3 \text{ system the relevant rate equations are} \\ - \frac{d[O_3]}{dt} &= J_5 I_{\text{abs}} + k_4 [O(^1D)][O_3] + k_{80} [^1\Sigma][O_3] \\ - \frac{d[O(^1D)]}{dt} &= k_4 [O(^1D)][O_3] - J_5 I_{\text{abs}} \\ - \frac{d[^1\Sigma]}{dt} &= k_{80} [^1\Sigma][O_3] - \alpha k_6 [O(^1D)][O_2] \end{aligned}$$

where $[^1\Sigma]$ denotes the concentration of $O_2(^1\Sigma_g)$

By working under experimental conditions such that the O_2 concentration greatly exceeds the O_3 concentration it is possible to neglect R4, to a good approximation, and to regard all the $O(^1D)$ as reacting with O_2 , in reaction R6. In these experiments it was customary to work with at least a five hundred fold excess of O_2 over ozone. Notwithstanding the excess oxygen and owing to the very slow rate ($2.8 \times 10^4 \text{ l mole}^{-1} \text{ s}^{-1}$; Thomas and Thrush) of quenching of $O_2(^1\Sigma_g)$ by O_2 in reaction R81, under the concentration régime employed, reaction R81 may be neglected in this analysis.

The requirements for the attainment of an approximate "steady state" concentration of an intermediate species are derived in Appendix 6. For $[O(^1D)]$ to have reached within 1% of the steady state concentration $\tau \gg 1 \times 10^{-10} / [O_2]$ seconds; at an oxygen pressure of about 1 torr $\tau \gg 2 \times 10^{-6}$ seconds. Similarly, the time required for $[^1\Sigma]$ to reach a steady state value, at an average ozone concentration of $5 \times 10^{-8} \text{ mole l}^{-1}$, is $\gg 6 \times 10^{-3}$ seconds. Typical experimental values of contact time are in the range 20 to 80 milliseconds, which is therefore sufficient time for establishment of steady states in $[O(^1D)]$ and $[^1\Sigma]$. These are given by

$$[O(^1D)]_{ss} = J5 I_{abs} / k6 [O_2]$$

$$[^1\Sigma]_{ss} = k6 [O_2] [O(^1D)] / k80 [O_3]$$

The rate of ozone loss is then given by

$$- \frac{d[O_3]}{dt} = J5 I_{abs} (1 + \alpha)$$

Integration and substitution into this equation, in a way exactly analogous to the working carried out in Chapter 4 shows that

$$\frac{\Delta O_3}{[O_3]_0} = 1 - \exp (- (1 + \alpha) \beta t)$$

where ΔO_3 is the observed resultant change in ozone concentration

$[O_3]_0$ is the initial ozone concentration

t is the average time in the irradiation zone

The quantities ΔO_3 , $[O_3]$ and t are determined experimentally.

The quantity β is determined in a separate experiment on the $O_2/O_3/H_2O$ system.

In the $O_2/O_3/H_2O$ system we aim to work under conditions where all the $O_2(^1\Sigma_g)$ produced in the $O(^1D) + O_2$ reaction is quenched by H_2O in reaction R82, and does not destroy the further increment α of ozone concentration. As an added bonus the water also quenches $O(^1D)$ and so is also partially effective in preventing the formation of $O_2(^1\Sigma_g)$. The work of Gauthier and Snelling (1975) confirms that water is one of the most efficient quenches of $O_2(^1\Sigma_g)$ and they quote the rate constant ratio R82/R80 as 0.22. In our experiments an approximate 250 times excess of water over ozone was used, and this results in over 96% quenching of $O_2(^1\Sigma_g)$ by water (see values of Y in Table 5,5). In addition the fast rate of quenching of $O(^1D)$ by water compared to the rate of quenching by oxygen (Gauthier and Snelling, 1975, give R6/R12 as 0.20) means that up to 50% of the $O(^1D)$ produced may be quenched by the water, so that the rate of formation of $O_2(^1\Sigma_g)$ will be halved, with respect to the rate in the O_2/O_3 system.

In view of the above we may to a good approximation neglect the reactions $O(^1D) + O_3$ (R4) and $O_2(^1\Sigma_g) + O_3$ (R80) due to the presence of excess O_2 , and an H_2O concentration as described above; in the $O_2/O_3/H_2O$ system. The ozone loss processes are therefore limited to the photolysis step J5.

Thus, this system, in which the relative quantum yield is known to be unity, may be used to evaluate β .

By analogy to Chapter 4 and the entirety analogous treatment of the O_2/O_3 system in this chapter we show that for the $O_2/O_3/H_2O$ system.

$$\frac{\Delta O_3}{[O_3]_0} = 1 - \exp(-\beta t)$$

where the symbols have the same meaning as above.

By measuring ΔO_3 and $[O_3]$ at known t in both the O_2/O_3 and $O_2/O_3/H_2O$ experimental régimes, as defined above, we are able to obtain values for the quantities α and β .

This method possesses the great advantages of

- 1) not being dependant on calibrated flow meters
- 11) not depending directly on values of measured rate constants .

We therefore believe the method to be capable of providing the most independent determination of α to date.

5, 3 Results and Discussion.

It was an unfortunate fact of these experiments that they were performed under the experimental conditions already discussed in detail in Chapter four, wherein plots of ΔO_3 versus $[O_3]$ at constant time showed an intercept which was inversely dependent on the flow tube pressure. When the way to eliminate this intercept was discovered, insufficient time remained in which to repeat these experiments. However, in view of the fact that the gradients of the ΔO_3 versus $[O_3]$ plots seemed, within experimental uncertainty, to be unaffected by the presence or otherwise of the intercept, we believe that the results are valid. One important consequence of fitting the ΔO_3 versus $[O_3]$ plots to the form $y = mx + c$, is that the error on the slope produced by linear least squares regression fitting is worse than which would result from fitting to the form $y = mx$. This is clearly true since in the latter case the zero point is paired with each data point, producing in effect twice the number of observations, and consequently a lower standard error. Thus, the errors quoted for α may be somewhat conservative.

Tables 5,4 and 5,5 contain the experimental data on the photolysis of O_2/O_3 and $O_2/O_3/H_2O$ mixtures. Each mean value of ΔO_3 and $[O_3]$ is the average of between twenty and thirty individual measurements. The standard deviation of ΔO_3 is the standard deviation of the individual measurements; however, this standard deviation is an over estimate since it was rarely possible to prevent $[O_3]$ from varying somewhat during the "run" of individual measurements. Thus the standard deviation of ΔO_3 (represented by the error bars in figures 5,1 and 5,3, and tabulated in Tables 5,4 and 5,5,) includes

a contribution due to drift in the $[O_3]$ values during a run.

In order to calculate the best value for $\Delta O_3^{cor} / [O_3] t$ for the O_2/O_3 system experiments, in which $[O_3]$ was varied at various flow tube pressures, were performed. This enabled plots of ΔO_3 versus $[O_3]$ and ΔO_3 versus $(\text{pressure})^{-1}$ to be constructed; at constant values of the other two parameters. Figures 5,1 and 5,2 respectively show the experimental plots. The data could then be treated in two independent ways and the results compared.

The first was to fit the data shown in figure 5,1 (at constant t and pressure) to an equation of the form $\Delta O_3 = O_3 + \text{intercept}$. The results are shown in Table 5,6. The linear fit is the linear least squares fit of the points in figure 5,1 giving each point an equal weight; the weighted least squares fit fits the line according to the weight of each point (taken as $1/(\text{variance})$ of the individual measurements). In addition the weighted least squares fit is constrained to pass through the intercept $\Delta O_3 = 0.3 \text{ su}$. This was the intercept found to occur, at the flow tube pressure used in these particular runs, in the N_2/O_3 and He/O_3 systems at similar pressures, as described in chapter 4. This weighted least squares fitted line is the one drawn in figure 5,1 and lies within the error-bars on the points. The linear least squares fitted line passes through the y axis close to zero, however, we believe this fit, through five points, to be unduly affected by the one very low point.

The second approach to the calculation of $\Delta O_3^{cor} / [O_3] t$ for the O_2/O_3 system was to plot ΔO_3 versus $1/(\text{Pressure})$ and eliminate the intercept by extrapolation to infinite pressure (zero reciprocal pressure). However, the data at constant $[O_3]$ were experimentally difficult to obtain and each line

Figures 5,1 and 5,2 Photolysis O_2/O_3

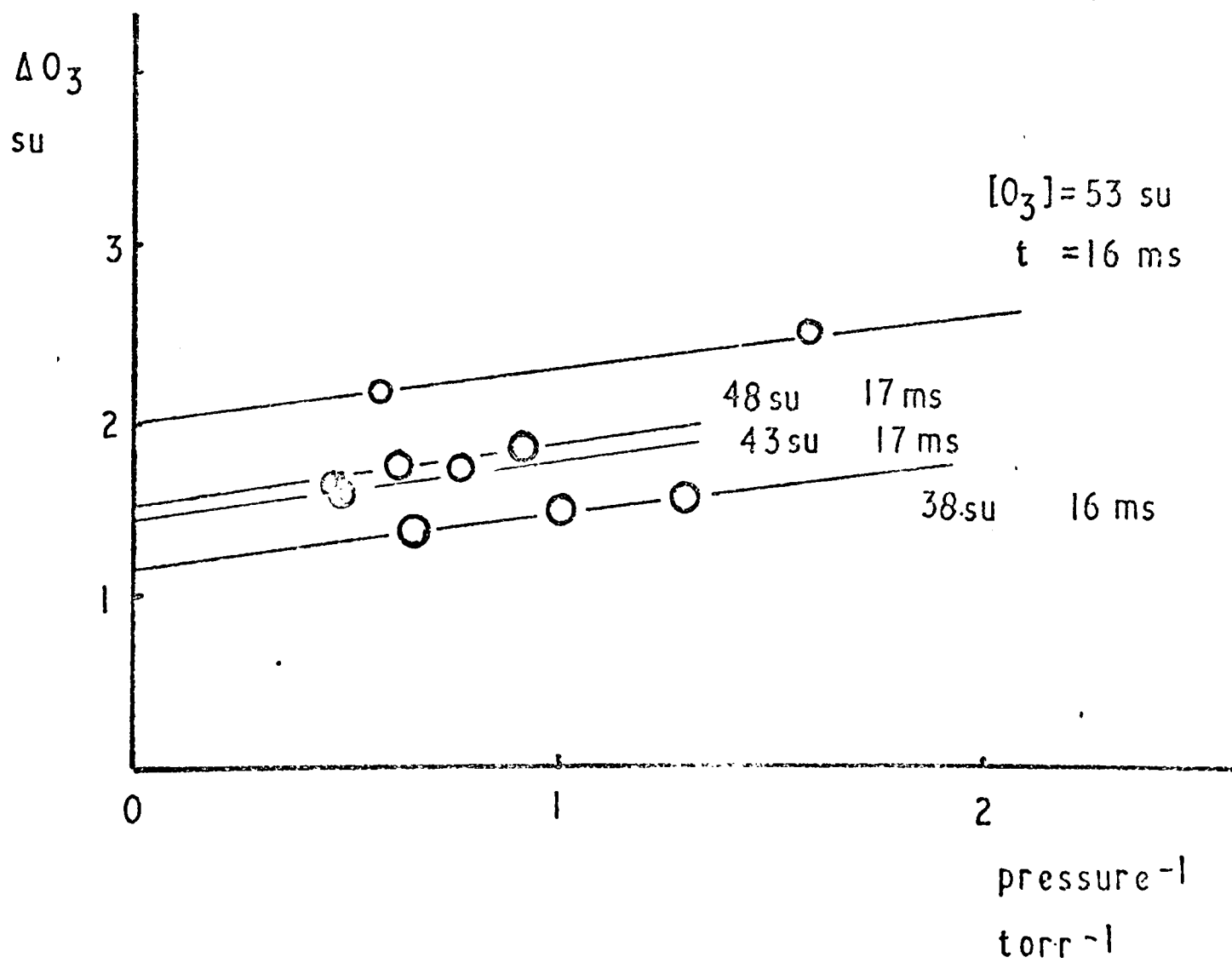
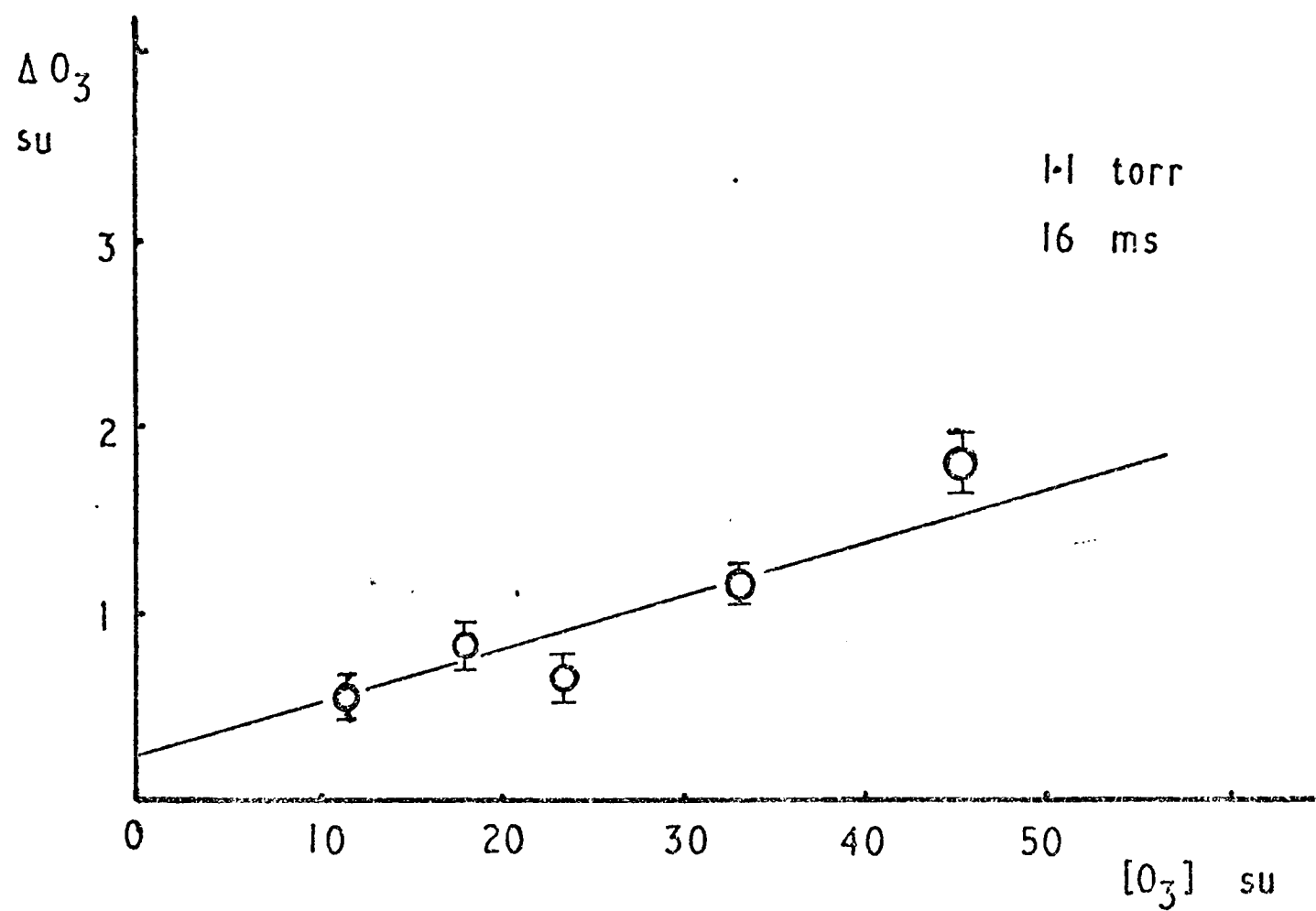
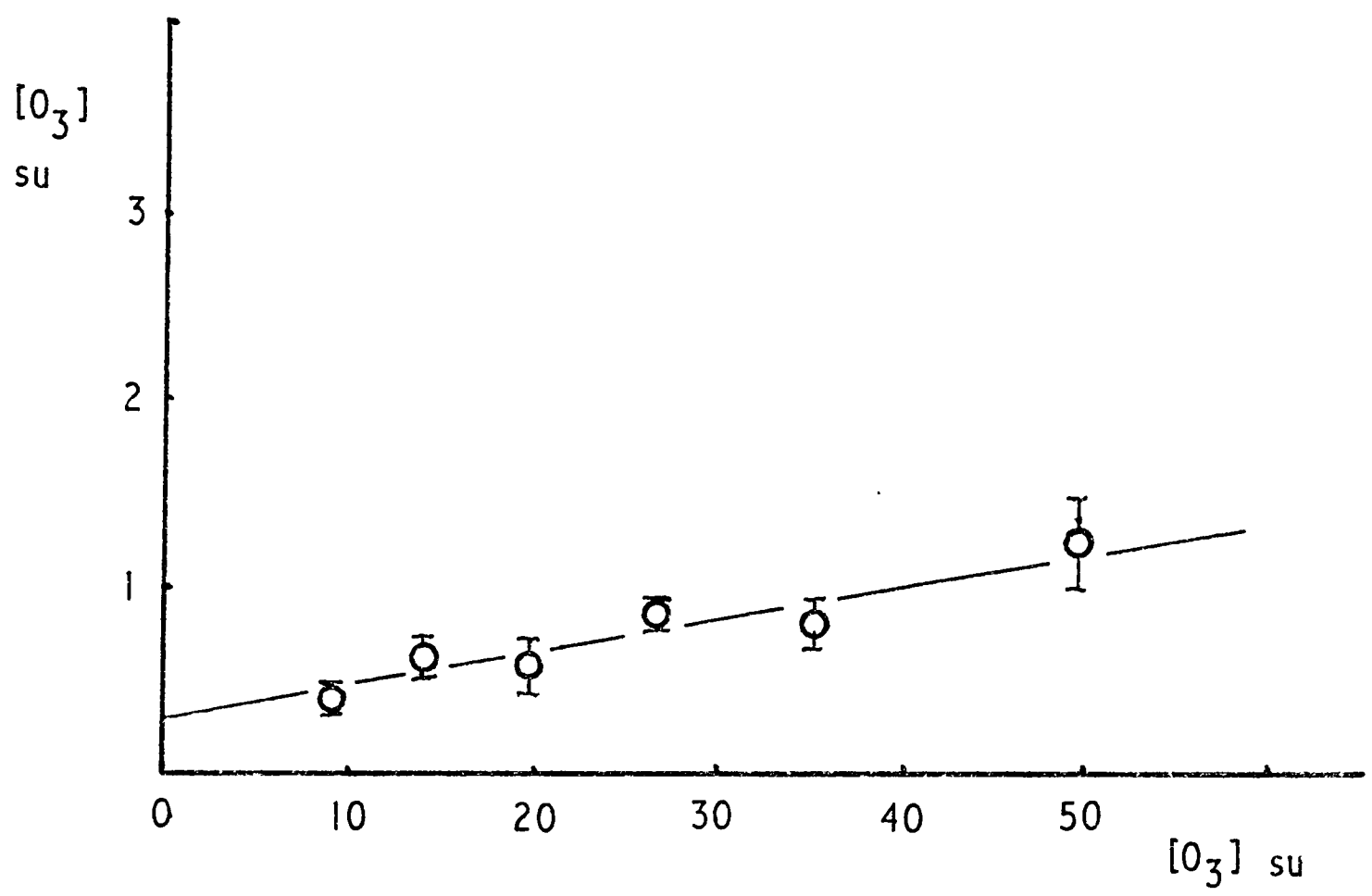


Figure 5,3 Photolysis $O_2/O_3/H_2O$



contains only a few points. The gradients nevertheless show a fair consistency. The $\Delta O_3 / [O_3]$ gradients obtained are summarised in Table 5,7. The four values were averaged by weighting according to the number of points comprising each line.

Table 5,8 compares the averaged values of $\Delta O_3^{cor} / [O_3] t$ obtained in the O_2/O_3 system by the two methods of calculation described above. The numbers in brackets represent the results of the linear least squares fitted data whilst the unbracketed numbers represent the weighted least squares fitting results.

To calculate our value of α we have compared the weighted mean value of $\Delta O_3^{cor} / [O_3] t$ for the O_2/O_3 data with the value of $\Delta O_3^{cor} / [O_3] t$ for the $O_2/O_3/H_2O$ data to obtain a Ratio. We believe, for the reason given above, that the weighted mean value of the Ratio obtained using the weighted least squares fit (constrained to pass through $\Delta O_3 = 0.3$) of the O_2/O_3 data at constant t and pressure is the more reliable value.

This bracketed value of the weighted mean Ratio is obtained from a number weighted combination of the bracketed linear least squares value of $\Delta O_3^{cor} / [O_3] t$ in the O_2/O_3 system at constant t and pressure, with the value of $\Delta O_3^{cor} / [O_3] t$ at constant t and $[O_3]$. This is then compared to the bracketed linear least squares fitted value of $\Delta O_3^{cor} / [O_3] t$ at constant time and pressure in the $O_2/O_3/H_2O$ system, to obtain the bracketed mean Ratio value. This is the value of α which would be obtained by using linear least squares fits of the O_2/O_3 and $O_2/O_3/H_2O$ data at constant time and pressure, rather than the constrained weighted fits. The difference in the Ratios obtained in these two slightly different treatments of the data only amounts to a 6% discrepancy in the value of the Ratio but

a 14% discrepancy in the value of α . However, the bracketed value of the O_2/O_3 weighted mean Ratio falls well within the experimental error limits quoted, viz. $= 0.63 \pm 0.18$.

This value of α is slightly higher than the value found by Giachardi and Wayne (1972, revised 1975) in a similar experimental system and is rather more consistent with the higher values favoured by Snelling and coworkers (1971-1974). Values of α found in the literature are summarised in Table 5,9. Our value of α is consistent with all the literature values apart from two early measurements by Izod and Wayne (1968a,b) and Jones and Wayne (1970), which values were revised by the authors in subsequent publications.

TABLE 5, 1. Reactions: $O_2/O_3/H_2O$ System.

J5	O_3	+	$h\nu (\lambda = 2537\text{\AA})$		$O(^1D) + O_2(^1\Delta_g)$
R4	$O(^1D)$	+	O_3	$\longrightarrow$	products
R6	$O(^1D)$	+	O_2	$\longrightarrow$	$O + O_2(^1\Sigma_g^+)$ $O + O_2$
R12	$O(^1D)$	+	H_2O	$\longrightarrow$	$OH + OH$
R80	$O_2(^1\Sigma_g)$	+	O_3	$\longrightarrow$	$O + 2O_2$
R81	$O_2(^1\Sigma_g)$	+	O_2	$\longrightarrow$	$O_2 + O_2$
R82	$O_2(^1\Sigma_g)$	+	H_2O	$\longrightarrow$	$O_2 + H_2O$

R35	OH	+	O_3	$\longrightarrow$	$HO_2 + O_2$
R	OH	+	O_2	$\longrightarrow$	
R3	O	+	O_3	$\longrightarrow$	$O_2 + O_2$
R2	$O + O_2$	+	O_2	$\longrightarrow$	$O_3 + O_2$
R10	$O_2(^1\Delta_g)$	+	O_3	$\longrightarrow$	$O + 2O_2$
R8	$O_2(^1\Delta_g)$	+	O_2	$\longrightarrow$	$O_2 + O_2$
R	$O_2(^1\Delta_g)$	+	H_2O	$\longrightarrow$	$O_2 + H_2O$

TABLE 5, 2 Rate Constants.

(Units: Second Order $l \text{ mole}^{-1} \text{ s}^{-1}$; third order $l^2 \text{ mole}^{-2} \text{ s}^{-1}$)

Reactants		Rate constant	Reference.
$O(^1D) + O_2$	R6	3×10^{10}	Noxon (1970)
		1.5×10^{11}	Young and Black (1967)
		2.4×10^{10}	Young et al (1968)
		4×10^{10}	Griggs (1968)
		4.44×10^{10}	NBS recommended value.
$O_2(^1\Sigma_g) + O_3$	R80	4.2×10^9	Becker et al. (1971)
		4.3×10^9	Izod and Wayne (1968b)
		1.5×10^{10}	Gilpin et al. (1971)
		1.38×10^{10}	Snelling (1974)
		1.5×10^{10}	Filseth et al. (1970) NBS recommended value.
$O_2(^1\Sigma_g) + O_2$	R81	6×10^4	Noxon (1970)
		9×10^4	Becker et al. (1971)
		6×10^5	O'Brien and Myers (1970)
		2.8×10^4	Thomas and Thrush 197) NBS recommended value.
$O_2(^1\Delta_g) + O_3$	R10	2×10^6	Clark et al. (1970)
		1.73×10^6	Findlay and Snelling (1971)
		2.13×10^6	Becker et al (1972) NBS recommended value.
$O + O_3$	R3	6.36×10^6	Davis et al. (1973)
		4.50×10^6	McCrumb and Kaufmann (1972)
		7.83×10^6	Husain et al. (1972) NBS recommended value.
$O_2(^1\Delta_g) + O_2$	R8	1.3×10^3	Findlay et al.(1969) NBS recommended value.
$O(^1D) + O_3$	R4	1.5×10^{11}	Gilpin et al.(1971)
		1.38×10^{11}	Snelling (1974)
		4×10^{10}	Biedenkapp and Bair (1970)
		1.62×10^{11}	Griggs (1968)
		3.18×10^{11}	NBS recommended value.

TABLE 5,2 continued.

Reactants		Rate constant		Reference.
$O_2(^1\Sigma_g) + H_2O$	R82	2.8	$\times 10^9$	Derwent and Thrush (1971)
		2.8	$\times 10^9$	Thomas and Thrush (197)
		2.0	$\times 10^9$	Filseth et al. (1970)
		3.3	$\times 10^9$	Stuhl and Niki (1970)
		2.4	$\times 10^9$	O'Brien and Myers (1970)
				NBS recommended value.
$O(^1D) + H_2O$	R12	2.1	$\times 10^{11}$	NBS recommended value.
OH + O_3	R35	3.0	$\times 10^7$	Simonaitis and Heicklen (1973)
		3.0	$\times 10^7$	Kaufman and Anderson (1973)
		3.0	$\times 10^8$	Kaufman (1964)
$O + O_2 + O_2$	R 2	2.34	$\times 10^8$	Kaufman and Kelso (1967)
		2.30	$\times 10^8$	Stuhl and Niki (1971)
		1.36	$\times 10^8$	Huie et al. (1972)
				NBS recommended value.

TABLE 5.3.

Lifetimes of Reactive species.

System	$[O_2]$ mole l^{-1}	$[H_2O]$ mole l^{-1}	$\dot{O}_2(^1\Sigma_g^-)$ s	$O(^1D)$ s
O_2/O_3	5×10^{-5}	-	$7 \times 10^{-4}(R80)$	$7 \times 10^{-5}(R6)$
$O_2/O_3/H_2O$	5×10^{-5}	1×10^{-5}	$5 \times 10^{-5}(R82)$	$7 \times 10^{-5}(R4, R12).$

for $[O_3] = 1 \times 10^{-7}$ mole l^{-1}

TABLE 5,4 THE PHOTOLYSIS OF OZONE IN O₂ CARRIER GAS.

Flow Pressure O ₂ torr	mean ΔO ₃ su	mean [O ₃] su	t ms	Number of points	H ₂ O torr	[H ₂ O] [O ₃]	Y	T ms	standard deviation ΔO ₃ s ⁻¹
0.626	2.480	53.30	16.39	23	-	-	-	63	0.380
0.770	1.550	39.30	15.60	18	-	-	-	60	0.202
1.011	1.480	36.90	15.47	28	-	-	-	59	0.151.
1.319	1.700	41.80	16.92	31	-	-	-	65	0.329
1.512	1.350	37.90	16.63	18	-	-	-	64	0.226
1.754	2.180	53.50	16.38	28	-	-	-	63	0.322
2.093	1.530	44.50	17.24	26	-	-	-	66	0.357
0.437	3.51	56.94	12.49	34	-	-	-	48	0.361
	2.59	70.70	12.49	24	-	-	-	48	-
	1.09	15.30	12.49	44	-	-	-	48	0.104
	1.65	30.78	12.49	41	-	-	-	48	0.227
1.094	1.823	45.15	16.22	28	-	-	-	61	0.139
	1.153	33.16	16.22	20	-	-	-	61	0.103
1.076	0.673	23.59	16.05	23	-	-	-	60	0.119
	0.854	17.97	16.05	29	-	-	-	60	0.124
	0.549	12.33	16.05	26	-	-	-	60	0.107
1.602	1.727	49.89	17.73	33	-	-	-	67	0.265
2.109	1.585	48.34	18.45	24	-	-	-	70	0.176

TABLE 5.5 THE PHOTOLYSIS OF OZONE IN O₂ IN THE PRESENCE OF H₂O

Flow pressure O ₂ torr	Mean ΔO ₃ su	Mean [O ₃] su	t ms	Number of points	[H ₂ O] torr	[H ₂ O] [O ₃]	Y	*	T ms	Standard deviation ΔO ₃ s ⁻¹
1.108	1.251	49.74	15.25	35	0.277	191	0.963		58	0.248
	0.803	35.16	15.25	27	0.230	223	0.968		58	0.141.
	0.828	26.81	15.25	24	0.186	237	0.971		58	0.119
	0.540	19.85	15.25	20	0.155	267	0.964		58	0.143
	0.640	14.17	15.25	27	0.113	273	0.974		58	0.095
	0.377	1.94	15.25	27	0.065	251	0.973		58	0.079

* Y *

$$\frac{k_{82} [H_2O]}{k_{82} [H_2O] + k_{80} [O_3]}$$

i.e. fraction of O₂(¹Σ_g) quenched by H₂O in relation to total quenching by water and ozone.

TABLE 5.6 LEAST SQUARES REGRESSION FITS * of O_2/O_3 and $O_2/O_3/H_2O$ data.

System	Fit	Gradient $\frac{\Delta O_3}{[O_3]}$	Intercept	$\frac{\Delta O_3^{cor}}{[O_3] t}$	Comments.
O_2/O_3	linear	$0.0369^{+}.007$	$0.032^{+}.21$	2.332	5 points only
(t =16.12ms)weighted		0.0275	0.299	1.730	constrained to intercept of 0.3
$O_2/O_3/H_2O$	linear	$0.0191^{+}.003$	$0.246^{+}.09$	1.265	
(t=15.25ms)weighted		0.0170	0.299	1.127	constrained to intercept of 0.3

* fitted to equation ΔO_3 (measured) = gradient x $[O_3]$ + intercept.

TABLE 5,7

O_2/O_3 data of Figure 5,2

Extrapolation of ΔO_3 measured values to infinite pressure.

O_3 su	t ms	ΔO_3 at infinite pressure ¹	$\frac{\Delta O_3}{[O_3]}$	$\frac{\Delta O_3^{cor}}{[O_3] t}$ s ⁻¹
53.4	16.4	2.00	3.75×10^{-2}	2.32
47.8	17.4	1.43	2.99	1.74
43.1	17.1	1.25	2.90	1.72
37.9	15.9	1.15	3.03	1.93
weighted ² mean				1.909

1. at infinite flow tube pressure the "intercept" found in the ΔO_3 vs $[O_3]$ plots tend to zero (see Chapter 4).
2. weighted according to the number of points through which each line at constant t and $[O_3]$ is drawn.

TABLE 5,8

CALCULATION OF THE EFFICIENCY α .

System	$\frac{\Delta O_3^{cor}}{[O_3]t}$	Ratio	Method.
O_2/O_3	1.730	1.53	ΔO_3 vs $[O_3]$
	(2.332)	(1.84)	at constant time and pressure
	1.909	1.69	ΔO_3 vs (pressure) ⁻¹
			at constant time and $[O_3]$
	weighted ² mean		* (1.73)
$O_2/O_3/H_2O$	1.127	1.00	* ΔO_3 vs $[O_3]$
	(1.265)	(1.00)	at constant time and pressure.

2. Weighted according to the number of points from which each determination is derived.

* The standard error on each of the two relative quantum yields measurements as estimated from the standard errors in Table 5,6 is $\pm 15\%$. The value of α is thus 0.63 ± 0.18

TABLE 5.9

LITERATURE VALUES OF α .

α	REFERENCE	METHOD
0.63 ± 0.18	This work	Relative quantum yield method using O_2/O_3 and $O_2/O_3/H_2O$ systems.
$0.53 < \alpha < 0.62$	Giachardi and Wayne (1972) (revised 1975)	Relative quantum yield method using He/O_3 , O_2/O_3 and N_2/O_3 systems; ^{3} and ^{2} also oxygen atom resonance fluorescence.
$\alpha < 10^{-2}$	Izod and Wayne (1968 a,b)	Monitoring $O_2(^1\Sigma_g)$ produced by oxygen photolysis.
$0.6 < \alpha < 1.0$	Biedenkapp and Bair (1970)	Flash photolysis of He/O_3 , O_2/O_3 and N_2/O_3 mixtures, curve fitting to O_3 concentration/time profile.
$0.7 < \alpha < 1.0$	Snelling and Gauthier (1971)	Absolute intensity measurements of $O_2(^1\Sigma_g)$ and $O_2(^1\Delta_g)$ in O_2/O_3 photo-system.
$\alpha \leq 0.7$	McCullough and McGrath (1971)	Flash photolysis O_2/O_3 .
$0.3 < \alpha < 1.0$	Noxon (1970)	Photolysis O_2 ; absolute measurements $O(^1D)$ and $O_2(^1\Sigma_g)$ emission intensities.
α near unity	Young and Black (1967)	O_2 photolysis; estimate from diffusion rates and wall losses.
$\alpha = 0.37 \pm 0.1$	Langley and McGrath (1971)	Flash photolysis N_2/O_3 and O_2/O_3 mixtures. Relative quantum yield measurements.
$\alpha \geq 0.6$	Gauthier and Snelling (1971)	Photolysis O_2/O_3 mixture, $O_2(^1\Sigma_g)$ emission intensity measurements.
$\alpha = 0.85 \pm 0.15$	Gauthier and Snelling (1971)	O_2/O_3 photolysis; $O_2(^1\Sigma_g)$ and $O_2(^1\Delta_g)$ emission measurements.

TABLE 5, 9 (continued)

α	REFERENCE	METHOD
$\alpha \geq 0.75$	Snelling (1974)	O_2/O_3 flash photolysis; curve fitting of $[O_3]$ time dependence.
$\alpha < 0.3$	Jones, Kaczmar and Wayne (1970)	Photolysis of O_2/O_3
$\alpha \sim 0.3$	Jones and Wayne (1971)	mixtures at long contact times.

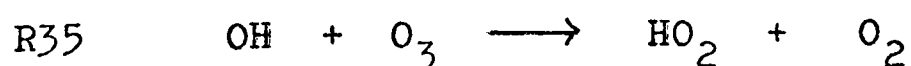
C H A P T E R 6

THE REACTION $\text{OH}^* + \text{O}_3$

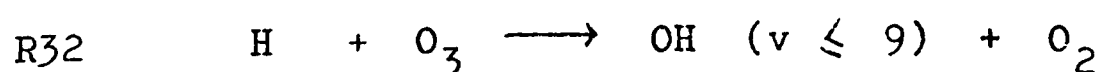
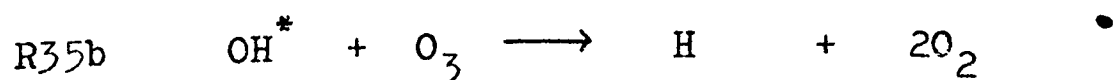
This chapter describes an attempt made to infer the products of the reaction of vibrationally excited OH in its electronic ground state (denoted by the symbols OH^*) with ozone. It is to be expected that the production of H atoms in the reaction would lead to a fast catalytic chain decomposition of the ozone; whereas if HO_2 is produced no chain decomposition should be observed under the conditions of these experiments.

6, 1 Introduction.

As was discussed in Chapter 1, the first attempts to explain the large differences in stratospheric ozone concentrations between the observed values and those predicted by the Chapman scheme of reactions invoked catalytic chain processes involving HO_x species (see Hunt, 1966). There was early evidence that the presence of water or other hydrogen-containing species promoted the decomposition of ozone when photolysed with ultra-violet light (Norrish and Wayne, 1965). The following chain mechanism was proposed



The mechanism was criticised by DeMore (1966) on the ground that R35 and R39 were both too slow to explain the experimental observations, and he proposed a chain involving H atoms and OH^*

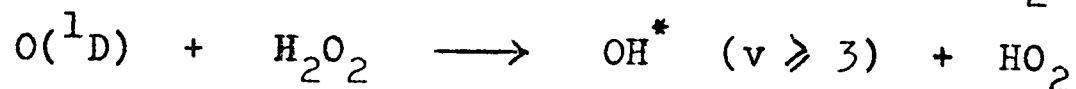


R35b is endothermic by only 38 kJ mole^{-1} and is thus energetically feasible for the $v = 1$ state of OH^* which has 43 kJ mole^{-1} of vibrational energy (and may feasibly be produced by the $\text{O}(^1\text{D}) + \text{H}_2\text{O}$

reaction). It was suggested that a vibrationally excited HO_2^* species, which could either be quenched, or decompose to form H atoms or OH, might be involved. This chain would have been faster than the previous suggestion since R35b could have been expected to be faster than R35 (and is now known to be so; Coltharpe et al, 1966; Potter et al. 1971) and R32 is a fast reaction.

In experiments in liquid argon at 87K DeMore (1967) showed that H atoms reacted with O_3 in a manner leading to chain decompositions of at least 25 O_3 molecules per H atom; an observation consistent with OH^* being the chain carrier since at these temperatures OH and HO_2 were shown not to react with ozone. It appears that in these experiments the Norrish mechanism could not operate.

Kaufman (1969) reviewed known rate data for hydrogen species and accepted DeMore's conclusions. Langley and McGrath, however, in a $\text{O}_3/\text{H}_2\text{O}$ flash photolysis study did not observe at short times a chain initiated by the reaction of $\text{OH}^* (v \leq 3)$ (from the $\text{O}(^1\text{D}) + \text{H}_2\text{O}$) reaction with ozone, and proposed that DeMore's $\text{O}_3/\text{H}_2\text{O}$ steady state photolysis experimental results could be explained on the basis of a chain reaction producing $\text{OH}^* (v \leq 3)$ involving hydrogen peroxide (generated for example by the $\text{HO}_2 + \text{HO}_2$ reaction).



This reaction could not occur in the flash photolysis experiments since all the $\text{O}(^1\text{D})$ would be lost before significant build-up of H_2O_2 had occurred.

Fortin et al. (1972) in another $\text{O}_3/\text{H}_2\text{O}$ flash photolysis experiment, whilst asserting that the $\text{H} + \text{O}_3$ (R32) reaction occurred in their system could not detect any effect attributable to a chain involving vibrationally excited hydroxyl radicals; particularly in view of the rate constants for the reaction of OH^*

in the $v = 1$ to 9 vibrational levels with ozone, which had just been published by Coltharpe et al. (1971). These latter authors, although not identifying the reaction products, could hardly have failed to notice a fast chain involving regeneration of OH^* by the $\text{H} + \text{O}_3$ reaction.

Anderson and Kaufman (1973) measured the rate of reaction of ground vibrational level OH, produced by the $\text{H} + \text{NO}_2$ reaction, with O_3 . DeMore (1973) and DeMore and Tschuikow-Roux (1974) side-stepped the original problem by photolysing $\text{O}_2/\text{H}_2\text{O}$ mixtures at $1849 \text{ \AA}$, under conditions such that the $\text{H} + \text{O}_3$ reaction could not contribute, measured the rates of reaction of OH and HO_2 with ozone, and observed the Norrish mechanism chain decomposition.

Simonaitis and Heicklen (1973 1,3) also observed the Norrish mechanism operating in the presence of excess oxygen in the photolysis of $\text{O}_3/\text{H}_2\text{O}$ mixtures at $2537 \text{ \AA}$ confirming that it does indeed occur at least to some extent, and apparently discounting the DeMore mechanism.

In a static photolysis experiment, which comes the closest to the experiment to be described later in this chapter, Kurylo (1973) flashed O_3/H_2 mixtures at wavelengths longer than $1650 \text{ \AA}$. OH was monitored by resonance fluorescence and O_3 was followed by optical absorption. Kurylo did not report the presence of a fast chain of the DeMore type.

It would therefore appear from the evidence that the gas phase reaction $\text{OH}(v \gg 1) + \text{O}_3$ generates HO_2 rather than H atoms as products. A question mark hangs over the liquid argon experiments of DeMore (1967) which may, however, be explicable in terms of H_2O_2 involvement.

In the present experiments O_3/H_2 mixtures were photolysed at $2537 \text{ \AA}$ in a fast flow system (at times and concentrations such

that contribution to the ozone loss quantum yield would largely not arise due to the Norrish chain mechanism) and evidence for a fast chain sought.

6, 2 The H_2/O_3 experiments.

The fast-flow/mass spectrometer system described in Chapter 3, together with the method of relative quantum yields described in Chapter 4 was used in an attempt to determine whether the reaction of vibrationally excited OH with ozone generates H atoms or HO_2 as products. If H atoms were produced it is expected that a catalytic chain loss of ozone would occur, whereas the generation of HO_2 species would lead to no significant enhancement of the quantum yield for ozone loss owing to the slowness of the $HO_2 + O_3$ reaction in our experimental concentration-time régime.

Ozone was photolysed at $2537\text{\AA}$ in the presence of H_2 and in helium carrier gas. In an ideal experiment the H_2 would be in large excess so that all the $O(^1D)$ produced would react only with the hydrogen to generate vibrationally excited OH. However, it was not found possible to work with excesses of hydrogen because of the reaction $OH + H_2$ which apparently generates H atoms, and might lead to a chain reaction on its own account despite the slowness of the reaction (see Table 6,2).

In order to calculate the fraction of $O(^1D)$ which reacts with the added H_2 to generate OH^* (here taken to denote OH in its ground electronic state and in vibration levels up to and including $v = 9$) it was necessary to know accurately both the relative rate constants for the attack of $O(^1D)$ on H_2 and O_3 , and also the relative concentrations of H_2 and O_3 . To avoid the possible errors inherent in calibrating the mass spectrometer with respect to both O_3 and H_2 and comparing the measured concentrations,

mixtures of O_3 and H_2 were made up and their respective pressures measured. This was a particularly dangerous procedure and led to spontaneous explosion of the O_3/H_2 mixtures and complete destruction of the 5 litre pyrex storage bulb on more than one occasion; and is not to be recommended ! However, it enabled W (where $W = k_{51} [H_2] / (k_{51} [H_2] + k_4 [O_3])$) to be measured precisely subject to the ratio of $k_{51} : k_4$ being known accurately.

This procedure was used also to enable a series of experiments to be carried out at constant W (see Figure 6,3). In experiments at constant $[O_3]$ (see Figure 6,2) the hydrogen concentration was measured either using a capillary flowmeter or as the H_2^+ signal at $m/e = 2$.

6, 3 Results and Discussion.

The results of the H_2/O_3 experiments are shown in Table 6,3; which shows the quantum yields for ozone loss at various values of W (the fraction of $O(^1D)$ reacting with H_2) and various values of $[O_3]$. Table 6,3 also shows computer predicted values for the quantum yield in the case where H atoms, and the case where HO_2 are reaction products.

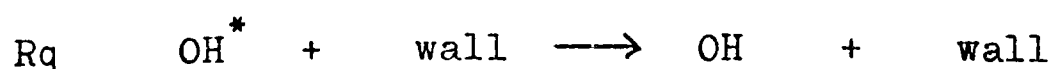
Foner and Hudson(1961) have undertaken a comprehensive investigation into the production and investigation of HO_2 radicals by mass spectrometric observation of the HO_2^+ ion. However, we were unable to detect any HO_2^+ ($m/e = 33$) in our experiments, perhaps in view of the large O_2^+ ($m/e = 32$) ^{present} peak which varies in response to the flashing photolysis lamp, and arises from fragmentation of O_3 .

The quantum yields shown in Table 6,3 generally lie above 2.0; the value to be expected if reactions J5, R4, R51 and R32 alone occur. The increase above a quantum yield of 2.0 is largely due to the enhanced rate of reaction of OH^* with ozone relative to the rate of reaction of ground vibrational state OH . In the computer

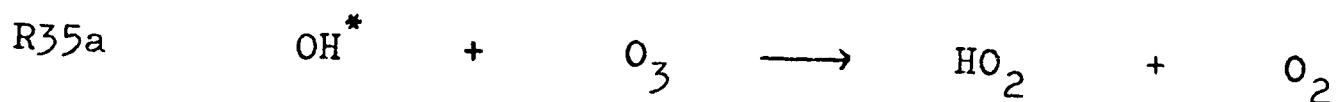
simulation the value of the rate constant of R35a and R35b was set to its highest value (Coltharpe et al. 1971) corresponding to the reaction of OH in its highest vibrational level as produced by the $\text{H} + \text{O}_3$ reaction, viz. the $v = 9$ level. This is undoubtedly an overestimate since Coltharpe et al. found evidence to show that OH^* was quenched to its next lowest vibrational level on substantially every collision with the reactor walls. The mean radiative lifetime of the transition OH^* ($v = 9 - 8$) has a value of 94 ms (Coltharpe et al. 1971). Other radiative lifetimes are in excess of this and therefore radiative vibrational deactivation was disregarded in the presence of a half life for reaction with ozone in the region of 2 ms.

The wall deactivation rate of OH^* to OH was set to various values, the highest being 1500 s^{-1} . An order of magnitude estimate based on the assumption that the rate of deactivation is controlled by the rate of diffusion to the walls; and taking the diffusion coefficient of OH^* through helium to be $0.6 \text{ cm}^2 \text{ s}^{-1}$ and the flow tube cross sectional area to be 0.81 cm^2 , indicates that the wall quenching rate would be in the region of 2200 s^{-1} . However, this assumes that OH^* is quenched to the ground vibrational level in one collision whereas in fact up to eight collisions with the wall may occur before OH reaches the $v = 1$ level, the last level in which it retains enough energy to generate H atoms, in principle.

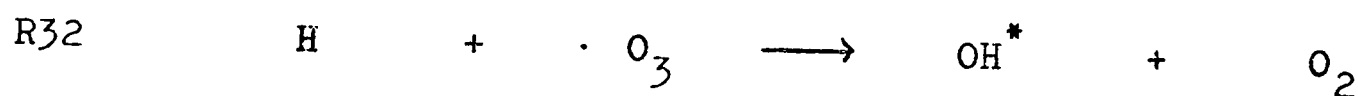
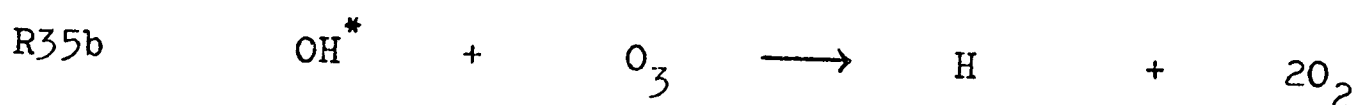
Consideration of the reaction scheme shown in Table 6,1 shows that it should be possible to calculate k_q from the experimental data. The relevant reactions are



and either;



or the sequence;



If the chain length is a ; the number of times R35b occurs per H atom originally produced in R51 ($a = 1$ if R35a operates), then the quantum yield in excess of 2.0 is given by

$$\begin{aligned} (\phi - 2) &= a \text{ (fraction of OH}^* \text{ reacting with ozone)} \\ &= \frac{a k_{35b} [\text{O}_3] \times [\text{OH}^*]}{k_{35b} [\text{O}_3] + k_q} \end{aligned}$$

$$\text{now } [\text{OH}^*] = W = k_{51} [\text{H}_2] / (k_{51} [\text{H}_2] + k_4 [\text{O}_3])$$

thus:

$$(\phi - 2) = \frac{a k_{35b} [\text{O}_3] \cdot k_{51} [\text{H}_2]}{(k_{35b} [\text{O}_3] + k_q) (k_{51} [\text{H}_2] + k_4 [\text{O}_3])}$$

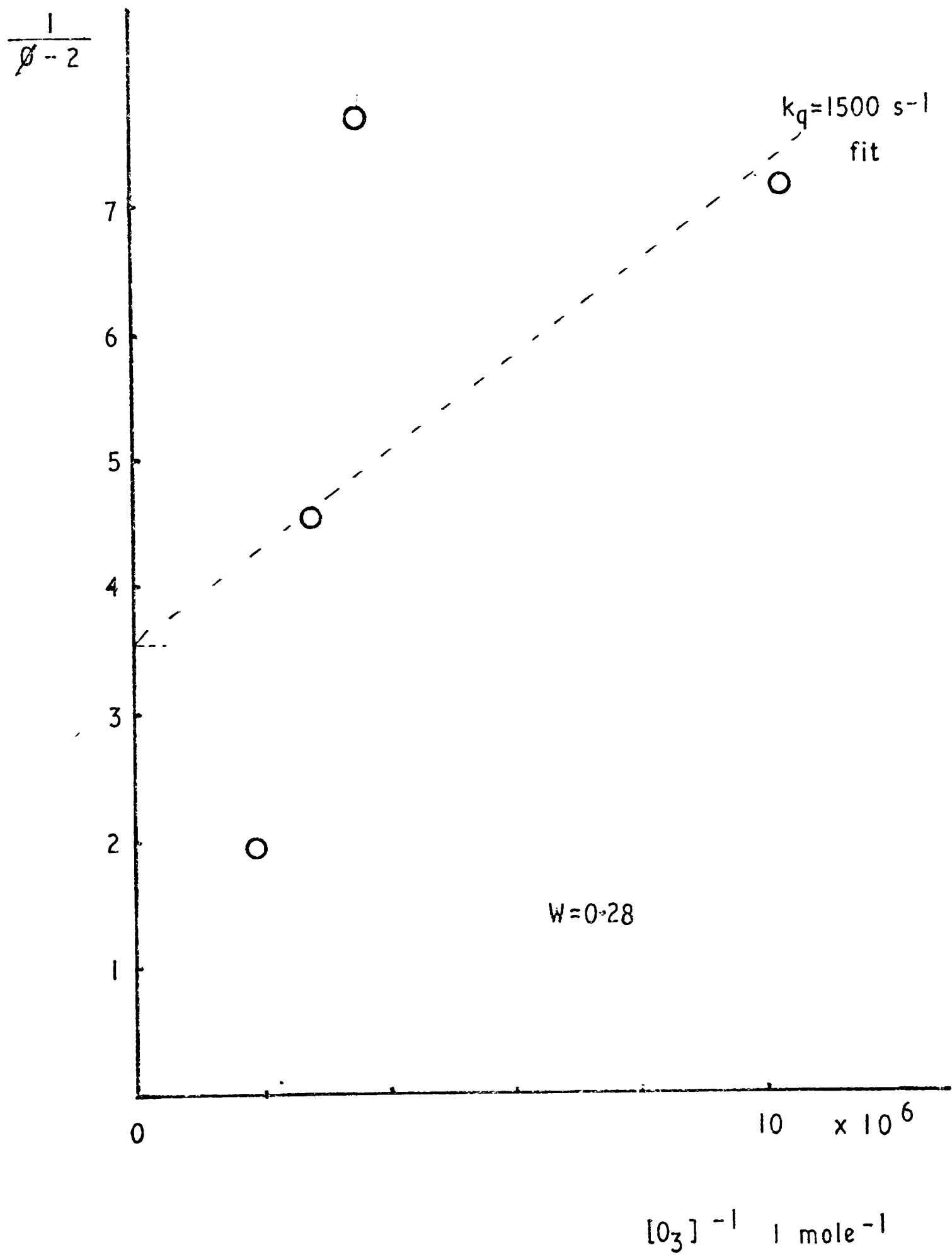
this simplifies to:

$$\frac{a}{(\phi - 2)} = 1 + \frac{k_4 [\text{O}_3]}{k_{51} [\text{H}_2]} + \frac{k_q}{k_{35b} [\text{O}_3]}$$

Therefore, plotting $1/(\phi - 2)$ against $1/[\text{O}_3]$ for those experimental runs in which $[\text{O}_3]/[\text{H}_2]$ is approximately constant should give a gradient k_q/k_{35b} . It should be possible to tell from the intercept whether a is greater than or equal to unity.

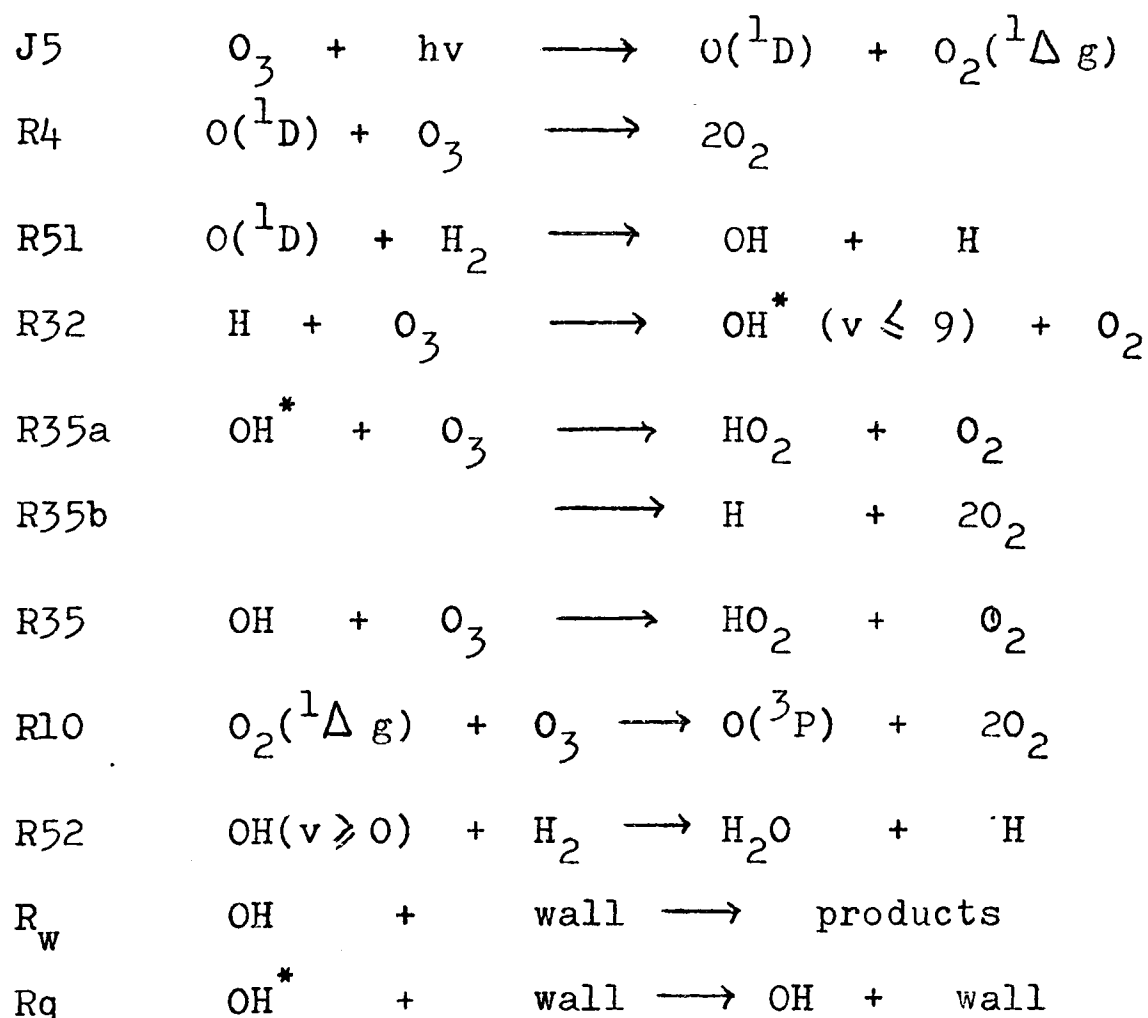
Experimental results at a value of $k_4 [\text{O}_3]/k_{51} [\text{H}_2]$ equal to 2.57 ($W = 0.28$) are shown in Figure 6,1. The plot should have an intercept of 3.57 if $a = 1$, however, the data are too scattered to draw any positive conclusions, the size of the quantities plotted lying within the limits of the experimental deviation of the data. The line drawn has a gradient of 3.5×10^{-7} and at the fastest rate of R35b (viz. $4.6 \times 10^9 \text{ l mole}^{-1} \text{ s}^{-1}$) corresponds to a wall quenching rate $k_q = 1500 \text{ s}^{-1}$ very approximately. However, no weight can be put on this estimate.

Figure 6,1 Wall loss OH^*



Reference to Table 6,3 shows that generally the quantum yields are equal to or lower than the value of the quantity $(2 + W)$ which would be expected if no chain operates (i.e. R35a occurs and $a = 1$) and the rate of wall loss of OH^* is small compared to its rate of reaction with ozone. This implies that R35a and not R35b occurs. However, the same qualitative result would ensue if the chain did occur but the rate of wall loss of OH^* were very large compared to rate of reaction with ozone.

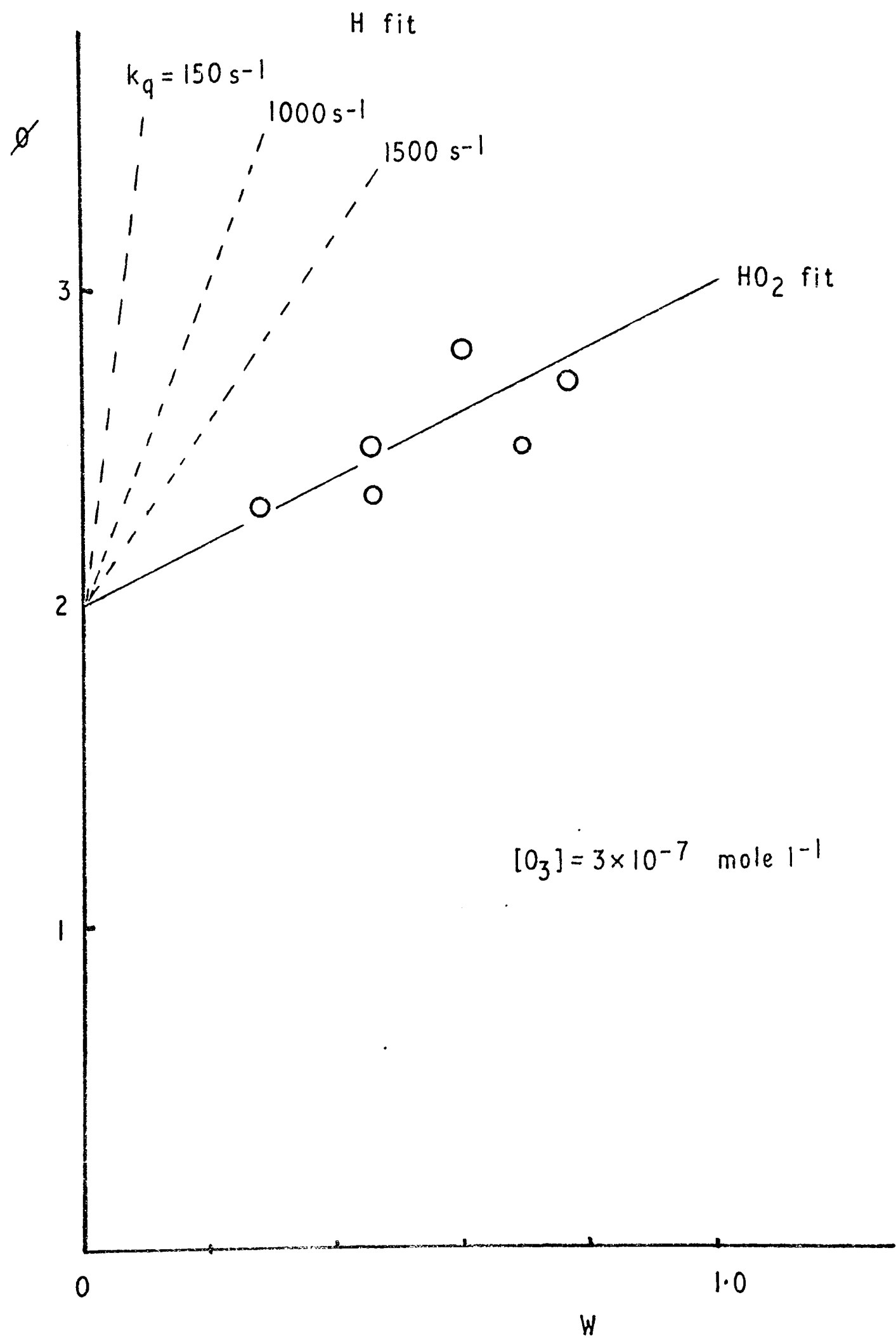
To investigate these two alternatives a computer simulation was developed. The program is shown in Appendix 1. It was based on the following reaction scheme.



Either R35a or R35b could be invoked, and the value of kq could be varied.

Table 6,3 shows the results simulated on the basis of the experimental data for the alternative cases of H or HO_2 production; kq being set to 1500 s^{-1} in both cases. Figure 6,2 shows a plot of quantum yield versus W (a measure of the amount of OH^* generated initially) at constant $[\text{O}_3]$; lines drawn in show

Figure 6,2 Photolysis $\text{H}_2/\text{O}_3/\text{He}$ - constant $[\text{O}_3]$



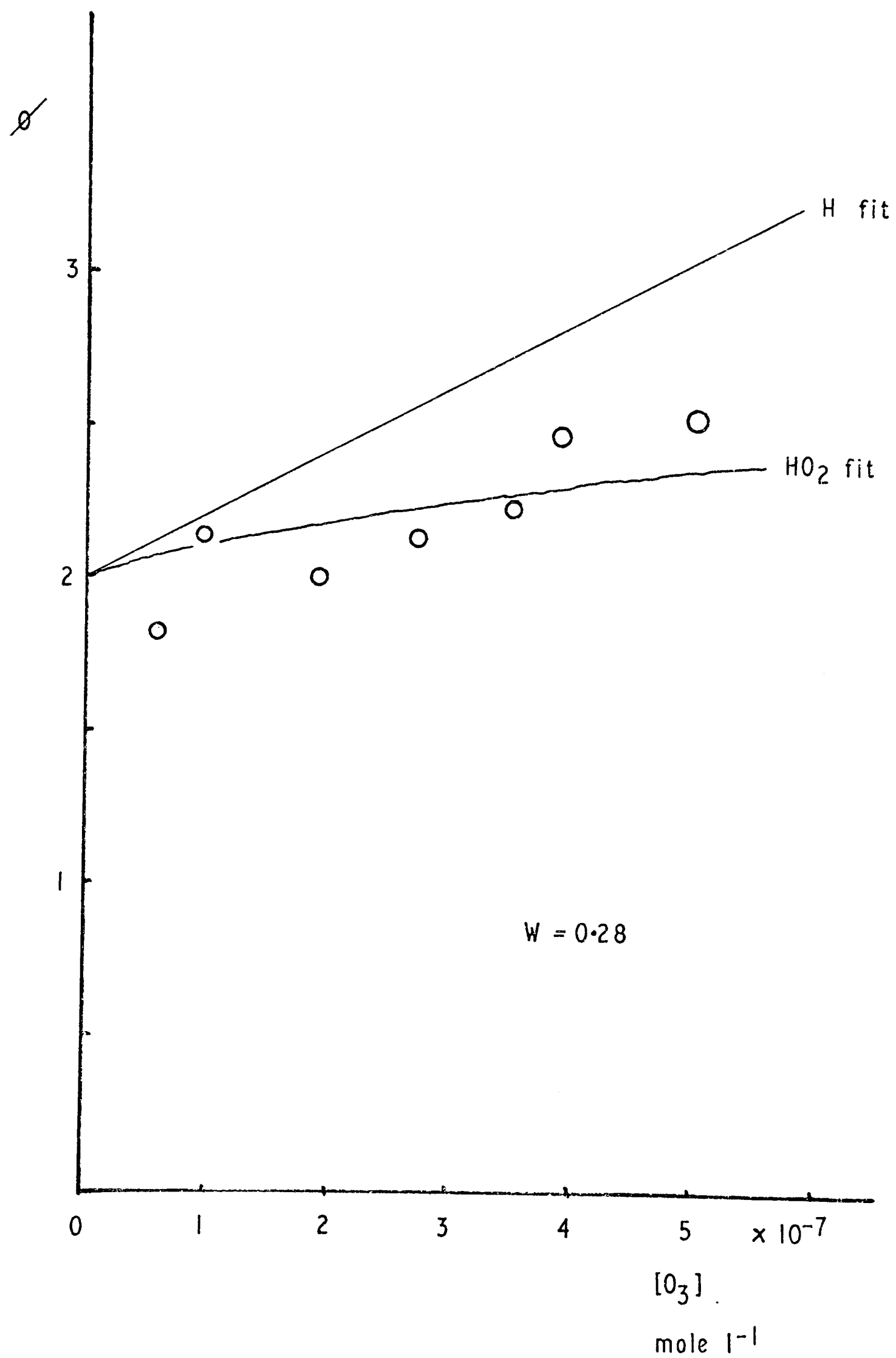
computed plots for the case of H atom production at various values of kq , and also the computed plot for HO_2 production. The results lie around the plot computed for HO_2 production at $kq = 1500 \text{ s}^{-1}$ and none lies close to any of the computed lines corresponding to H atom production even at $kq = 1500 \text{ s}^{-1}$. Even at this high OH^* wall quenching rate it is possible to distinguish the H propagated chain process from the non-chain process.

Figure 6,3 shows the plot of quantum yield versus O_3 at constant W. Again the experimental points lie close to the HO_2 fitted line, although, due to the relatively low value of W ($W = 0.28$), the difference between the H and HO_2 simulated plots is not so marked in this case.

The treatment of the wall quenching of OH^* has been rather simplified, the probability of cascading through the vibrational levels being disregarded, the effect however is to overestimate its value (and thereby reduce the difference between the H and HO_2 simulated plots) rather than the reverse. The value of $R35a/R35b$ must also be an over-estimate since the value used was for the reaction of $\text{OH}(v=9)$ with ozone; the effect of this is also to reduce the difference between the H and HO_2 simulated plots. We have set the rate constant for the minor reaction R52 equal to the value for reaction of ground vibrational state OH with H_2 , whereas in effect the reaction of OH^* with H_2 may be somewhat faster. The contribution of the reaction $\text{HO}_2 + \text{O}_3$ (R39) to the quantum yield was regarded as being negligible in view of its low rate constant ($k_{39} = 1.8 \times 10^6 \text{ mole}^{-1} \text{ s}^{-1}$; De More, 1973).

In view of the foregoing, the difference between the plots simulated for the H propagated chain process and the simulation of the production of HO_2 may be an underestimate. In spite of this it is clear from Figure 6,2 and 6,3 that the experimental data

Figure 6,3 Photolysis $\text{H}_2/\text{O}_3/\text{He}$ - constant W



are better represented by the simulation based on the production of HO_2 from the $\text{OH}^* + \text{O}_3$ reaction, than the simulation based on the production of H atoms. We, therefore find ourselves in agreement with the conclusions of previous authors that the reaction of OH, even in elevated vibrational levels, with ozone does not generate H atoms as product.

TABLE 6,1

 H_2/O_3 reaction scheme.

J5	O_3	+	$\text{hv}(\lambda = 2537\text{\AA})$	$\longrightarrow$	$\text{O}({}^1\text{D})$	+	$\text{O}_2({}^1\Delta_g)$
R4	$\text{O}({}^1\text{D})$	+	O_3	$\longrightarrow$	products		
R51	$\text{O}({}^1\text{D})$	+	H_2	$\longrightarrow$	OH	+	H
R32	H	+	O_3	$\longrightarrow$	$\text{OH}^*(v \leq 9)$	+	O_2
R35a	OH^*	+	O_3	$\longrightarrow$	HO_2	+	O_2
R35b				$\longrightarrow$	H	+	2O_2
R35	OH	+	O_3	$\longrightarrow$	HO_2	+	O_2
R10	$\text{O}_2({}^1\Delta_g)$	+	O_3	$\longrightarrow$	$\text{O}({}^3\text{P})$	+	2O_2
R52	$\text{OH}(v \geq 0)$	+	H_2	$\longrightarrow$	H_2O	+	H
R_w	OH	+	wall	$\longrightarrow$	products.		
R_q	OH^*	+	wall	$\longrightarrow$	OH	+	wall.
R39	HO_2	+	O_3	$\longrightarrow$	OH	+	2O_2

TABLE 6.2. Values of rate constants used in analysis.

units: 1 mole⁻¹s⁻¹ (second order); seconds⁻¹ (first order).

Reaction.			Rate constant	Reference.
R4	O(¹ D)	+ O ₃	3.2 x 10 ¹¹	NBS tables (Oct.73)
R51	O(¹ D)	+ H ₂	1.7 x 10 ¹¹	NBS tables (Oct.73)
R32	H	+ O ₃	1.6 x 10 ¹⁰	NBS tables (Oct.73)
R35, a,b.	OH* (V =9)	+ O ₃	4.6 x 10 ⁹	Coltharp and Potter.
R35	OH	+ O ₃	3.5 x 10 ⁷	NBS tables (Oct.73)
R10	O ₂ (¹ Δ _g)	+ O ₃	2.2 x 10 ⁶	NBS tables (Oct.73)
R52	OH	+ H ₂	5.2 x 10 ⁶	NBS tables (Oct.73)
R _w	OH	wall loss	50	---
R _q	OH*	deactivation	1500	see text.

TABLE 6,3

The Photolysis of Ozone in Helium in the Presence of H₂.

Flow pressure torr.	mean [O ₃] x 10 ⁷ mole l ⁻¹	mean [H ₂] x 10 ⁶ mole l ⁻¹	t ms	Number of points	W	Quantum Yield ϕ	T ms	Computer fit values. $\phi_H \phi_{HO_2}$ Kq = 1500 s ⁻¹
0.371	3.09	1.42	7.48	29	0.710	2.48	59	3.89 2.70
	3.78	0.25	7.48	20	0.260	2.48	59	2.73 2.26
	3.43	0.54	7.48	22	0.455	2.52	59	3.18 2.42
	3.41	-	7.48	26	-	2.00*	59	- 2.03
	3.15	1.46	7.48	28	0.711	2.81	59	3.94 2.71
	3.48	0.84	7.48	29	0.562	2.33	59	3.53 2.54
	3.19	1.97	7.48	21	0.766	2.52	59	4.27 2.83
0.392	1.94	0.142	8.21	36	0.280	1.95	65	2.40 2.18
	3.55	0.260	8.21	33	0.280	2.22	65	2.74 2.27
	1.12	0.019	8.21	32	0.280	1.54	65	2.23 2.12
	2.75.	0.201	8.21	34	0.280	2.13	65	2.57 2.25

II 2/03 cont.

6,3 cont.

Flow pressure torr.	mean $[O_3]$ $\times 10^7$ mole l ⁻¹	mean $[H_2]$ $\times 10^6$ mole l ⁻¹	t ms	Number of points	W	Quantum Yield ϕ	T ms	Computer fi values.	
								ϕ_H	ϕ_H
Kq = 1500 s ⁻¹									
0.592	5.14	0.576	8.21	20	0.280	2.52	65	3.06	2.55
	0.97	0.710	8.21	53	0.280	2.14	65	2.20	2.10
	0.64	0.470	8.21	29	0.280	1.79	65	2.13	2.07
0.425	0.859	0.169	8.19	54	0.510	2.36	65	2.33	2.17
	0.893	0.039	8.19	36	0.188	2.42	65	2.13	2.07
	0.957	-	8.19	27	-	2.00*	65	-	2.01
	0.953	0.118	8.19	11	0.396	2.84	65	2.28	2.14

* Quantum yields measured relative to photolysis of O₃ alone normalised to 2.00 for these runs.

C H A P T E R 7

THE REACTION OF $O(^1D)$ WITH FREONS.

This chapter examines the reaction of $O(^1D)$ with various fluorine and/or chlorine containing compounds (and including sulphur hexafluoride). $O(^1D)$ atoms are generated by the ultraviolet photolysis of ozone and the reactions studied in a development of the fast flow - mass spectrometer apparatus described previously.

7. 1. The atmospheric freon hypothesis.

From March 1977 it will be illegal to sell aerosols containing fluorochlorocarbon propellants in the state of Oregon U.S.A. The use of fluorochlorocarbon propellants (FCC's) in aerosol cannisters is to be banned on the largely unproved ground that FCC's are instrumental in depleting the stratospheric ozone layer. Let us examine this surprising assertion, involving what have hitherto been regarded as totally inert non-toxic substances.

Ironically it is just this inert quality on which the FCC-ozone hypothesis is based. FCC's are anthropogenically generated substances with no known natural sources. They are produced principally in the industrially developed countries of the Northern hemisphere and released into the troposphere at ground level. Table 7,1 shows that FCC's are used mainly as aerosol propellants (which are released almost immediately into the atmosphere), as refrigerants (released slowly to the atmosphere; large fraction recovered and reused) and as plastics foaming agents (uncertain fate). The most widely used FCC's are Freon 11 ($CFCl_3$) and Freon 12 (CF_2Cl_2).

The possible effects of chlorine containing compounds, and in particular FCC's, on the stratosphere ozone concentration were

first pointed out by Molina and Rowland (1974). These authors examined the possible involvement of chlorine and fluorine species in catalytic ozone loss processes and attempted to define the respective sources and sinks of such compounds in the atmosphere.

Because of their chemical inertness FCC's are not lost by reaction in the troposphere. However, there is evidence (Lovelock, Maggs & Wade, 1973) that CFCl_3 dissolves in the oceans to some extent, although Rowland and Molina (1974) discount this as a major loss process. The FCC's diffuse upwards through the atmosphere and are ultimately lost mainly by photodissociation (reportedly with a half life of the region of 40 - 150 years) as they encounter high energy solar ultraviolet radiation (less than about $2200\text{\AA}$) in the 20 to 40 km altitude region of the atmosphere. Absorption of UV occurs principally in the $1750\text{-}2200\text{\AA}$ window between the O_2 and O_3 absorption bands. Figure 7,1 shows election impact obtained ultraviolet absorption cross sections as a function of wavelength for CFCl_3 and CF_2Cl_2 (Heubner et al. 1975). This region of the atmosphere, however, coincides with the stratospheric ozone layer (see Chapter 1) and it is the FCC photodissociation products which may give rise to a chlorine-chlorine oxide catalysed chain decomposition loss of ozone.

It has been demonstrated that the photolysis of a CF_2Cl_2 molecule produces one Cl atom when employing longer wavelength ultraviolet radiation ($\lambda = 2139\text{\AA}$) and that the use of progressively shorter wavelenths tends to produce two Cl atoms per absorbed photon (Rebbat and Ausloos, 1975). The atomic chlorine reacts quickly with ozone (see Table 7,3 for rate constants and references) to generate ClO. This ClO regenerates Cl by reaction with the atomic oxygen which is present in significant quantities in the stratosphere (see Figure 1, 5). The reaction of ClO with the other

Figure 7,1 Absorption cross sections CFCl_3 , CF_2Cl_2

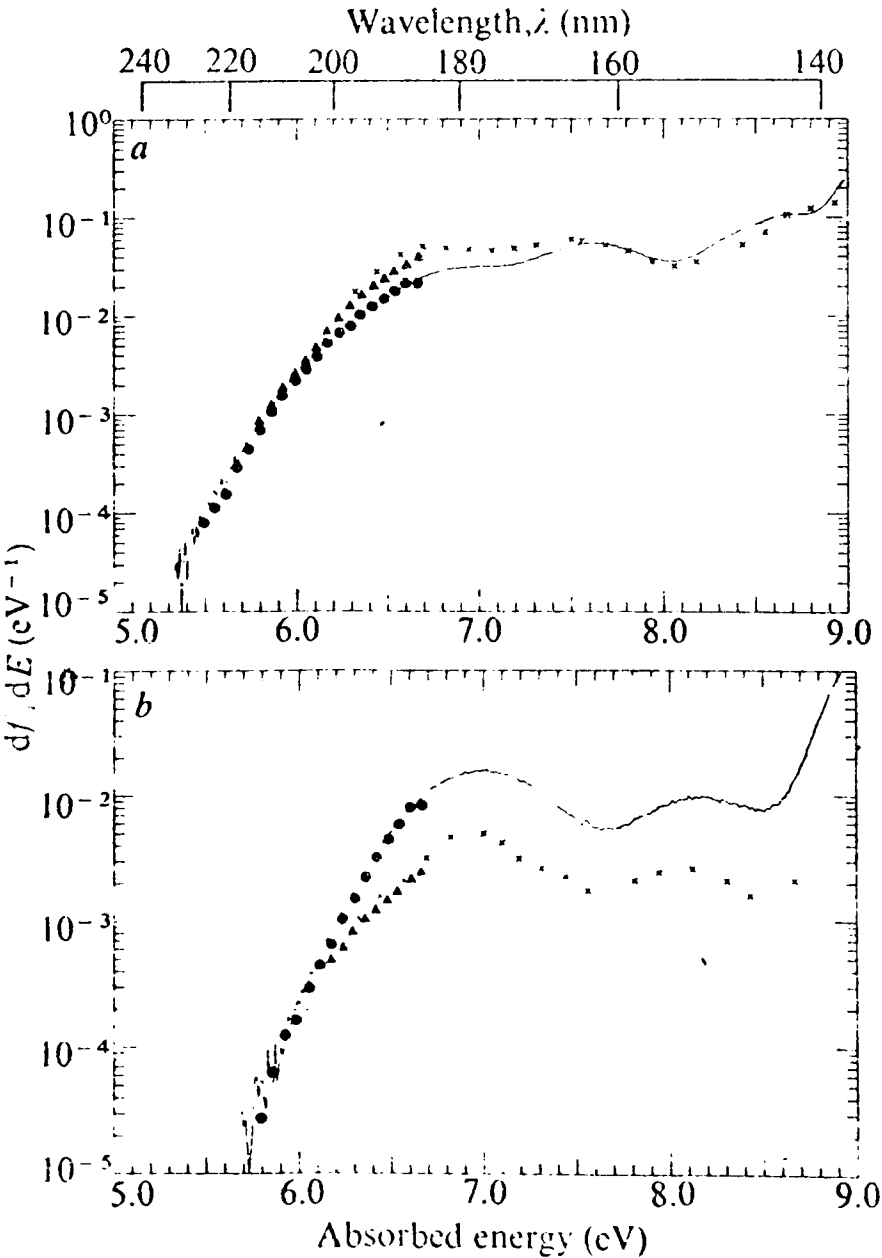
Apparent photoabsorption cross sections for CFCl_3 and CF_2Cl_2 derived from electron energy-loss measurements

Huebner et al.
(1975)

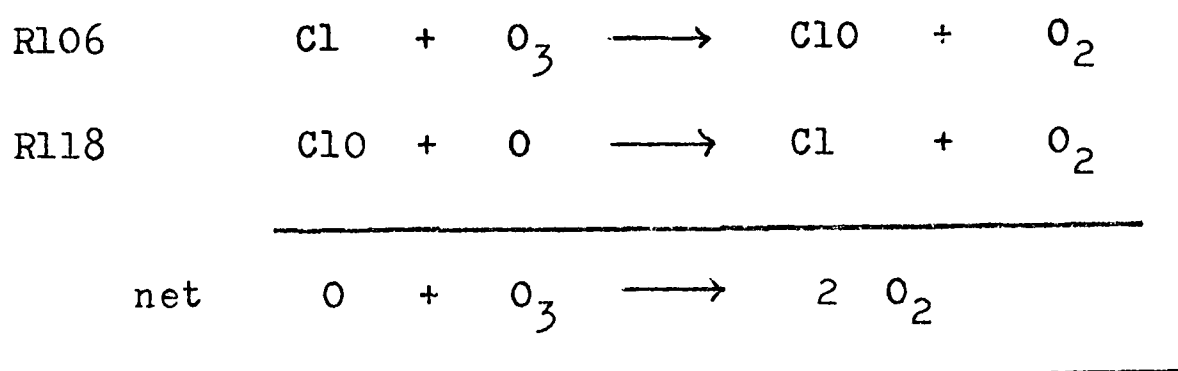
λ (nm)	Apparent photoabsorption cross section* (cm^2) CFCl_3	CF_2Cl_2
225	1.11 (-20)	—
221	2.20 (-20)	—
218	4.55 (-20)	1.97 (-21)
214	9.77 (-20)	4.50 (-21)
210	1.64 (-19)	1.08 (-20)
207	2.90 (-19)	2.63 (-20)
203	4.77 (-19)	5.16 (-20)
200	6.82 (-19)	1.02 (-19)
197	9.77 (-19)	2.10 (-19)
194	1.35 (-18)	3.44 (-19)
191	1.78 (-18)	5.65 (-19)
188	2.29 (-18)	8.42 (-19)
185	2.77 (-18)	1.15 (-18)
182	3.23 (-18)	1.49 (-18)
177	3.49 (-18)	1.76 (-18)
172	3.68 (-18)	1.39 (-18)
168	4.75 (-18)	8.91 (-19)
163	5.88 (-18)	5.98 (-19)
159	5.15 (-18)	6.87 (-19)
155	3.89 (-18)	9.46 (-19)
151	4.76 (-18)	1.07 (-18)
148	7.74 (-18)	9.45 (-19)

*The number in parentheses is the exponent of the power of ten to be multiplied by the value of the cross section tabulated

Comparison of oscillator strengths for halocarbon 11 (CFCl_3) in the ultraviolet absorption region: —, present electron impact results; x, optical values from ref. 2; $\blacktriangle$, optical values from ref. 2 as quoted in ref. 3; $\bullet$, optical values from ref. 3. b, Comparison of oscillator strengths for halocarbon 12 (CF_2Cl_2) in the ultraviolet absorption region (identifications as in a).

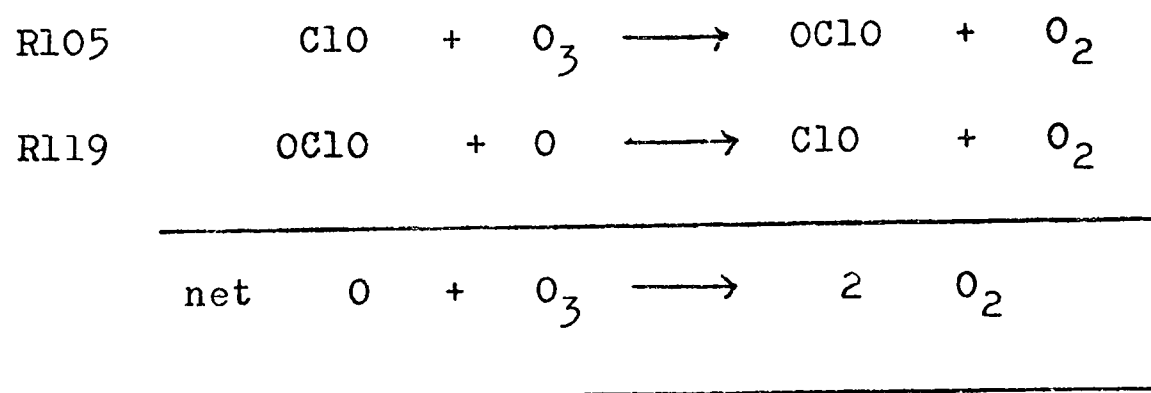


principal odd oxygen species O_3 is acknowledged (Clyne and Watson, 1974) to be a slow reaction (second order rate constant less than $3 \times 10^6 \text{ l mole}^{-1} \text{ s}^{-1}$).



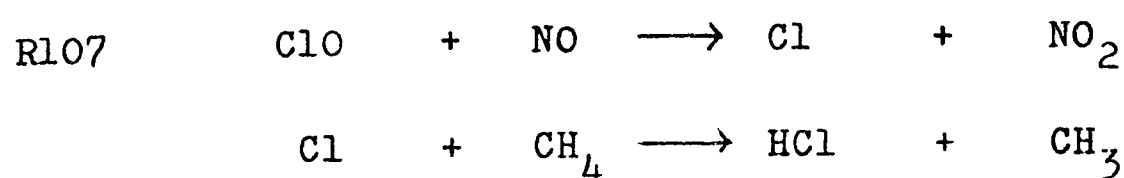
Both R106 and R118 are fast reactions and the chain decomposition is therefore a fast catalytic loss process.

A second possible catalytic cycle, involving ClO and OClO is much slower.



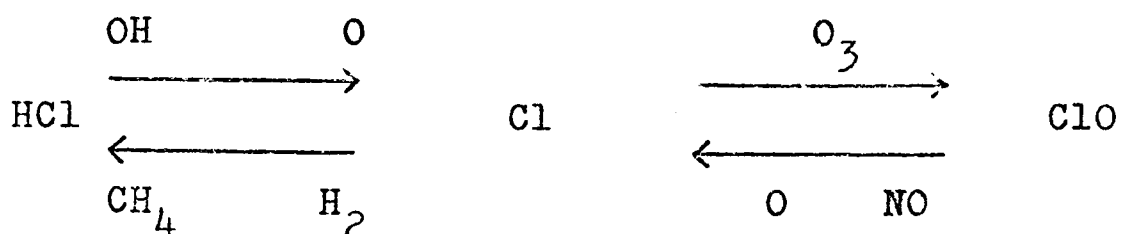
Reaction R105 produces OClO, which will henceforth be denoted by the formula ClO_2 , as distinct from the relatively unstable peroxy radical ClOO (Clyne and White, 1971) which is believed to be generated by the reaction $\text{Cl} + \text{O}_2 + \text{M}$.

The chlorine catalytic chain reactions are, of course, coupled into the other stratospheric reaction chains by way of reactions with hydrocarbons and NO (amongst others).



Cl may also react with ammonia and it is these last two processes which provide a sink, in the form of HCl (and analogous to the role played by HNO_3 in the NO_x catalytic cycle), for stratospheric

chlorine. All the chlorine oxides undergo photodecomposition to ultimately regenerate chlorine atoms, in the absence of other loss processes so that they do not act as stable sinks. HCl may, however, diffuse to lower levels of the atmosphere where it is rained out. Alternatively, reaction with O or OH may regenerate Cl atoms. The processes involving chlorine containing species may be simplified and summarised as:-



Interaction of the chlorine catalytic cycle with the NO_x cycle may promote the depletion of stratospheric ozone, whilst the presence of hydrocarbons may significantly reduce ambient Cl concentrations. The situation is complex, however, and work on modelling the overall stratospheric reaction scheme including FCC's has been done.

Stolarski and Cicerone (1974), using a sixteen reaction scheme involving only chlorine containing compounds, (although the interaction with other catalytic cycles was also considered later) demonstrated that the contribution from chlorine catalytic cycles became significant for an altitude uniform mixing ratio of ClX (defined as the sum of HCl, Cl, ClO, OClO, ClOO and Cl_2 concentrations) of 1 part per billion (presumably 10^{12}). The contribution to ozone depletion from the chlorine catalytic cycle became of equal significance as the NO_x cycle at a ClX mixing ratio of 10 ppb. Clearly the assumption of ClX species distributed uniformly with respect to height, or even the assumption of a ground source of ClX, is a gross oversimplification; especially as the stratospheric photolysis of FCC's has been postulated as the major source of Cl atoms in this region. Stolarski and Cicerone do not consider the details of ClX production.

There have been a number of measurements of the concentrations of ground level FCC's and other halogen containing compounds such as CH_3Cl and CCl_4 . Interest initially stemmed from the use of freons as inert tracers for atmospheric air movements, since, as freons are anthropogenically produced, their sources, being regions of high population density, are easily defined. Lovelock, Maggs and Wade unwisely observed in 1973 "The presence of these compounds (FCC's) constitutes no conceivable hazard; indeed the interest lies in their potential usefulness as inert tracers for the study of mass transfer processes in the atmosphere and oceans". Figure 7,2 shows the results of ocean level measurements of CFCl_3 , CH_3I and CCl_4 obtained by these authors.

Figure 7,2 includes ocean level measurements of CCl_4 and CFCl_3 made by another group of workers, Wilkniss, Lamontague, Larson, Swinnett, Dickson and Thompson (1973) and Wilkniss et al (1974). Figure 7,2 also shows an analysis of the increase in CFCl_3 concentrations in the period 1971 to 1974 by the same group of workers (Wilkniss et al. 1975).

Figure 7,2, shows measurements of halomethane concentrations by Lovelock 1974 and 1975. Included are measurements of the variation of CCl_4 and CFCl_3 concentrations with height in the troposphere over central England. The more rapid fall-off of CCl_4 concentration with height together with its uniform global distribution, both point to a natural ground level perhaps oceanic, source of CCl_4 . The evidence is inconsistent with a northern hemisphere industrial source, and sequential gas phase chlorination of methane is kinetically unlikely. Atmospheric concentrations of species such as CHCl_3 and CH_3CCl_3 have also been measured. The source of natural CCl_4 thus remains a mystery.

The measured FCC concentrations are in good mutual agreement

Table 7,1

Applications of FCC's in the United States in 1972

Compound	Aero- sol propel- lants ($\times 10^6$ kg)	Refrigerants ($\times 10^6$ kg)		Sol- vents ($\times 10^6$ kg)	Foam- ing agent ($\times 10^6$ kg)	Total ($\times 10^6$ kg)
		Prefab- ricated units	Large com- mercial units			
CCl_3F	111		4		21	136
CCl_2F_2	119	31	29		20	199
CHClF_2		21	15			36
$\text{CClF}_2\text{CFCl}_2$				23		23
$\text{CClF}_2\text{CClF}_2$	9					9
Total	239	52	48	23	41	403
Percentage of total	59	13	12	6	10	100

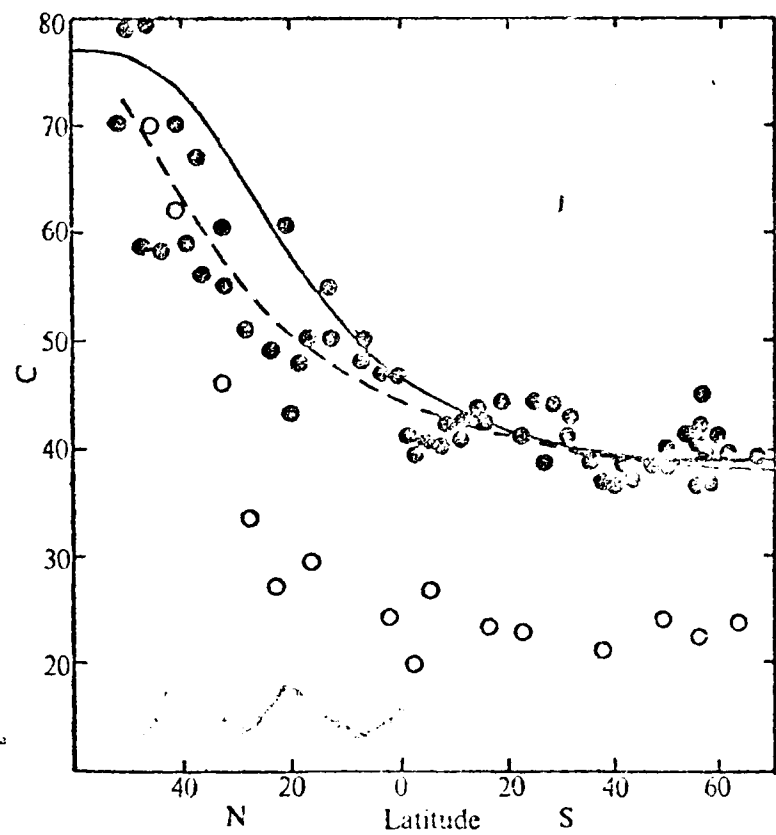
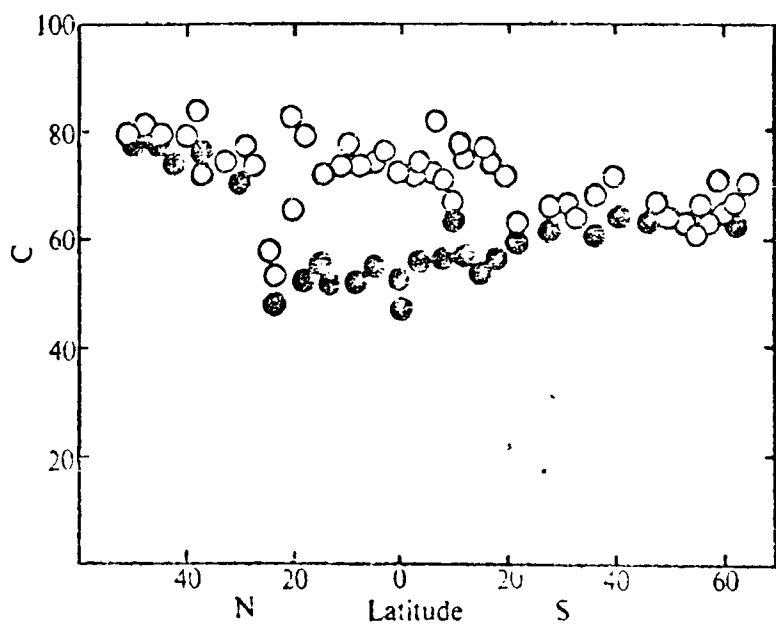


Figure 7,2

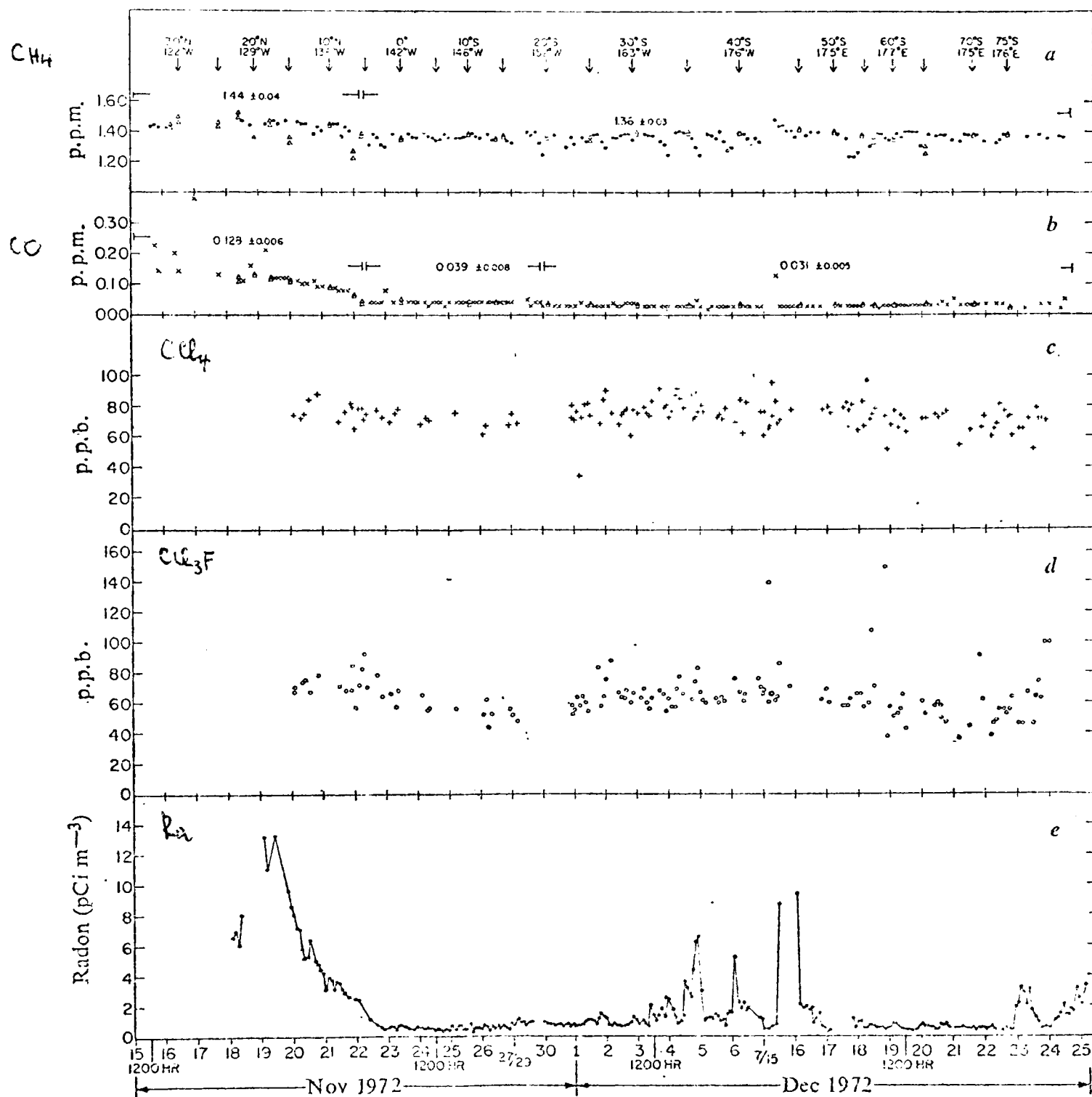
Lovelock et al. 1973

Distribution of CCl_3F in and over the North and South Atlantic Ocean. ●, Aerial concentrations ($\times 10^{-12}$) by volume. ○, Seawater concentrations ($\times 10^{-12}$); as aerial concentrations in equilibrium with water. —, Theoretical prediction. ---, Best fit third degree polynomial.



●, Aerial distribution of CCl_4 ; ○, marine concentration ($\times 10^{-12}$) by volume. Water concentration ($\times 10^{-12}$) as aerial concentration in equilibrium with water.

Figure 7,2 (cont.)



Wilkniss et al. 1975

Concentrations of five trace gases over the North and South Pacific and the Ross Sea. Concentrations for methane and carbon monoxide are by volume in p.p.m. (1 part in 10^6). Those for carbon tetrachloride and Freon are by volume in p.p.b. (1 part in 10^{12}). Radon is in pCi m^{-3} . a, Methane; b, carbon monoxide; c, carbon tetrachloride; d, Freon; e, radon.

and lie in the region 100 parts per billion (10^{12}). However, the uniform global distributions of species such as CH_3Cl and CCl_4 together with calculations of the maximum possible CCl_4 atmospheric concentrations based on industrial production to date (Lovelock, 1974, shows that had industrially produced CCl_4 accumulated in the atmosphere without loss it could account for only less than 3% of the observed ambient CCl_4 concentration) tend to show that anthropogenically generated FCC's contribute to only a minor extent to the overall atmospheric concentration of chlorine containing compounds. The calculations of Wofsey and McElroy (1974) using this concentration data as input indicate a 2% reduction of stratospheric ozone attributable to their presence. Unless there is some special effect arising from the injection of chlorine at higher altitudes from the photolysis of FCC's rather than, for example, CCl_4 which is destroyed by photolysis lower down in the atmosphere, there do not appear to be strong grounds for singling out the FCC's as being more hazardous than the other halocarbons which penetrate the tropopause.

One particularly effective way of generating catalytically active species at stratospheric altitudes is by the reaction of $\text{O}(^1\text{D})$ atoms, which are present due to the photolysis of ozone at these heights, with the chlorocarbons. Although this process can never compete effectively with quenching of $\text{O}(^1\text{D})$ by atmospheric nitrogen or oxygen, the fact that ClX species are injected into the precise level of the atmosphere where they can be most effective in destroying ozone may go some way to compensate for the estimate (Rowland, New Scientist, 2 October 1975) that inclusion of $\text{O}(^1\text{D})$ reactions reduces the atmospheric lifetime of CF_2Cl_2 by only a few percent.

A second reason for studying the reaction of $\text{O}(^1\text{D})$ with FCC's

is that it is believed that the attack of $O(^1D)$ on freons may be a convenient alternative source of species analagous to those generated by the ultraviolet photolysis of FCC's.

The involvement of fluorine species catalytic chains is much less likely than the analogous chlorine chains for at least two reasons. The first is that the photodetachment of F atoms from FCC's has not been demonstrated, Cl atoms being preferentially lost. The second is that HF is a more stable sink for fluorine than HCl is for chlorine, since the reaction $OH + HF$ being endothermic by 72 kJ Mole^{-1} will not occur to regenerate F atoms, in the stratosphere.

It may be convenient to enter here a caveat concerning the nomenclature used to describe the most important industrial fluorochlorocarbons. The scheme is used to describe the composition of compounds sold by DuPont under the Trade Mark "Freon" and by I.C.I. under the Trade Mark "Arcton". The last figure of the number denotes the number of fluorine atoms in the molecule; the penultimate figure is equal to the number of hydrogen atoms plus one, and the first figure is equal to the number of carbon atoms minus one. Thus, for example, CF_4 is called Freon 14; CF_3Cl is Freon 13; CF_2Cl_2 is Freon 12; CFC_2Cl_3 is Freon 11, and $CHFCl_2$ is Freon 21. The system of numbering quickly becomes unwieldy and is not widely used for higher homologues.

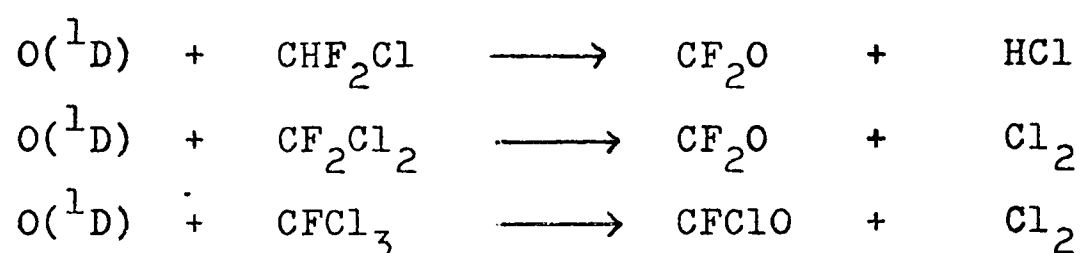
The abstraction of chlorine from the rupture of a C-Cl bond is endothermic by around 12 kJ mole^{-1} for ground state, $O(^3P)$, oxygen atoms, but for $O(^1D)$ atoms the rupture of C-Cl bond is very exothermic (by 130 kJ mole^{-1} for CF_3Cl , Gillespie and Donovan, in press). The rupture of a C-F bond is energetically possible for $O(^1S)$ atoms.

In the flash photolysis of O_3/CF_3Cl mixtures in argon

Clerc (1965) observed the production of ClO, arising from the attack of $O(^1D)$ on the freon, with an efficiency of around 4% based on the number of oxygen atoms (which could apparently also include a proportion of ground state $O(^3P)$ atoms) generated by the photolysis of ozone. The ClO concentration was measured by optical absorption at $2920\text{\AA}$ using the absorption coefficient of Edgcombe (1957). Similar results were obtained with O_3/CCl_4 mixtures. ClO_2 was observed several seconds after the flash, with absorptions at wavelengths of 4082, 3972, 3869, 3772, 3680, 3594, 3511, 3434, 3360, 3290, 3220 and 3160 angstroms.

Meaburn et al (1968) observed ClO in the pulse radiolysis of $CO_2/O_2/CCl_4$ mixtures and attributed its formation to the reaction of singlet atomic oxygen with CCl_4 . However, the dissociative recombination reaction $O_2^+ + e$ put forward as the source of singlet atomic oxygen is also believed to be a major source of $O(^1S)$ in the atmosphere and it is possible that this species was also present in these experiments.

Pitts and coworkers (Sandoval, Atkinson and Pitts, 1974 and Pitts, Sandoval and Atkinson, 1974) investigated the products and relative rate of reaction of $O(^1D)$, generated by the photolysis, of NO_2 at $\lambda = 2288\text{\AA}$, with the freons CHF_2Cl (1.6 ± 0.2), CF_2Cl_2 (2.4 ± 0.3), $CFCI_3$ (2.65 ± 0.4), $CF_2Cl.CF_2Cl$ (1.5 ± 0.2), $CF_2ClCFCI_2$ (2.5 ± 0.3) and CF_4 (< 0.1). The numbers in brackets are the rate constants relative to the reaction $O(^1D) + N_2O$. Control runs in which the freon alone was irradiated at $2288\text{\AA}$ showed no loss of freon. The products, identified by IR absorption, were CF_2O from CHF_2Cl (0.5 ± 0.1) and CF_2Cl_2 (0.85 ± 0.1) and $CFCIO$ from $CFCI_3$. The numbers in brackets are the yields based on the amount of $O(^1D)$ lost by the first two of the reactions



in relation to the overall loss of $\text{O}(^1\text{D})$ atoms respectively.

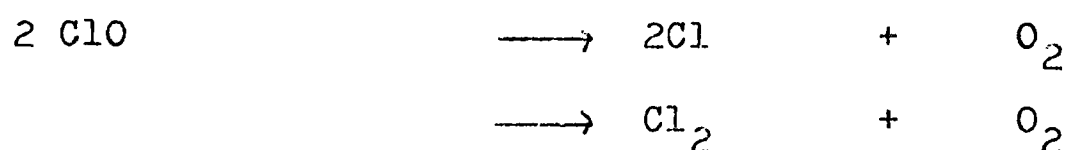
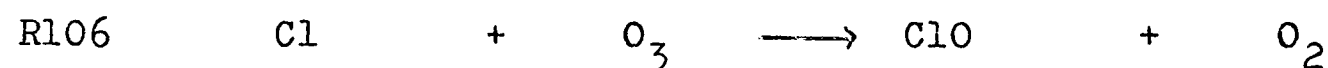
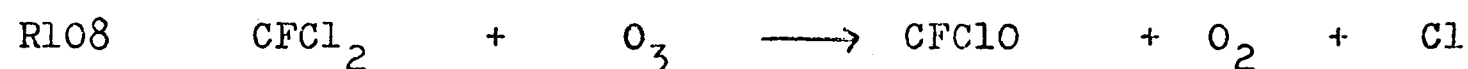
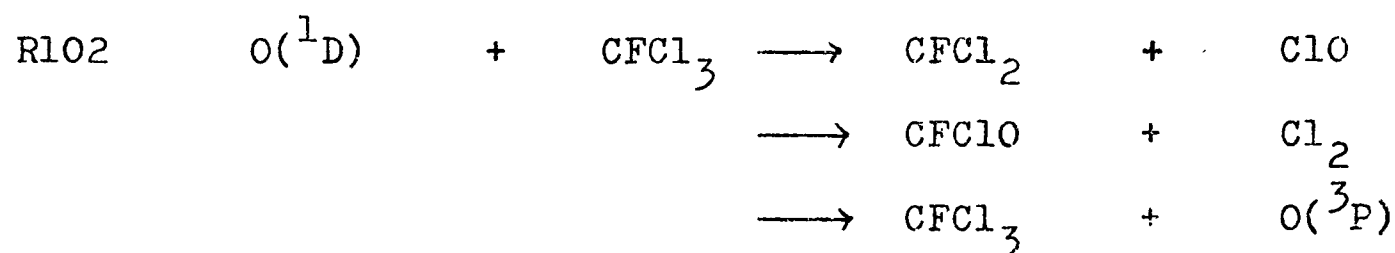
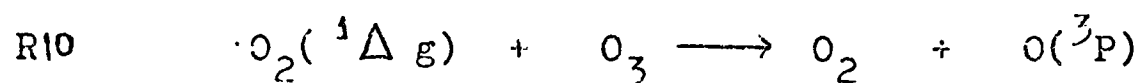
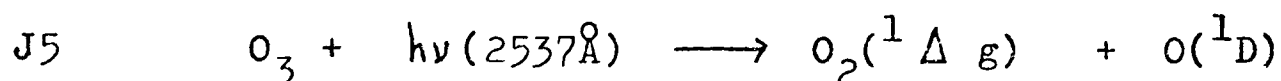
The alleged products HCl and Cl_2 were not identified.

Jayanty, Simonaitis and Heicklen (1975) photolysed fluoro-chloromethanes at $2139\text{\AA}$ in a static system in the presence of O_2 or O_3 ; and also photolysed O_3 /fluoro-chloromethane mixtures at $2537\text{\AA}$ in order to study the reactions of $\text{O}(^1\text{D})$ with CFCl_3 , CF_2Cl_2 , CF_3Cl and CCl_4 . The following rate constants for the reaction of $\text{O}(^1\text{D})$ with the freons relative to the reaction $\text{O}(^1\text{D}) + \text{N}_2\text{O}$ were measured; O_3 (2.5), CFCl_3 (1.5), CF_2Cl_2 (1.2), CF_3Cl (0.52) and CCl_4 (2.1.). The products CFClO and CF_2O were measured gas chromatographically after conversion to CO_2 . N_2 formed by the reaction $\text{O}(^1\text{D}) + \text{N}_2\text{O}$ was also measured on a gas chromatograph; whilst analysis for Cl_2 was made by UV absorption. The photolysis of CFCl_3/O_2 and $\text{CF}_2\text{Cl}_2/\text{O}_2$ mixtures at $2139\text{\AA}$ gave quantum yields for production of CFClO and CF_2O of 0.9 ± 0.15 and 1.0 ± 0.2 respectively; and, for production of Cl_2 , quantum yields of $0.50 - 0.63$ and $0.52 - 0.66$. The photolysis of CFCl_3/O_3 at $2139\text{\AA}$ gave product quantum yields of 0.9 ± 0.15 (CFClO) and $0.50 - 0.63$ (Cl_2) whilst the quantum yield for ozone loss increased from 2.75 at high CFCl_3 pressures (48 torr) to 4.6 at low pressures (10 torr).

For the reactions of the fluoro-chloromethanes with $\text{O}(^1\text{D})$ the same products, in the same yields, were found as for the $2139\text{\AA}$ photolysis experiments.

The quantum yields for ozone loss were found to be 5.7 ± 1.0 , 6.3 ± 1.0 and 6.0 for the CFCl_3/O_3 , $\text{CF}_2\text{Cl}_2/\text{O}_3$ and CCl_4/O_3 systems respectively.

The $O(^1D) + CFCl_3$ results were explained in terms of the following reaction scheme, (an analogous mechanism being applicable to CF_2Cl_2).



On the basis of unit $CFClO$ product yield, the physical quenching pathway of $R102$ was deduced to be insignificant. However the pathway of $R102$ which generates $CFClO + Cl_2$ cannot occur with unit efficiency unless a chain process propagated by the generation of Cl atoms by the recombination $ClO + ClO$ is important, since otherwise the quantum yield is predicted to be 3.0. The involvement of a Cl propagated chain was however demonstrated, the authors, quantity β being found to be 4 rather than the 2 to be expected if Cl atoms are not regenerated by the recombination of ClO . In the presence of this $Cl - ClO$ catalytic chain loss process it is therefore, hard to evaluate the authors' conclusion that the pathway of $R102$ which produce ClO , occurs with unit efficiency. (This would imply that $R108$ and $R106$ each contribute one unity increment

to the ozone loss quantum yield, and lead to a quantum yield in excess of 5.0).

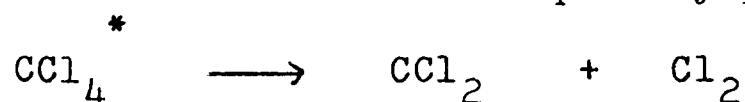
The same authors have also done work on the reaction of $O(^1D)$ with the compounds CCl_2O , $CFCIO$ and CF_2O which are postulated as the stable products in the above reaction scheme (Jayanty, Simonaitis and Heicklen in press). The results apparently show that the reactions are fast, although the paper is not definitive in that no attempt is made to identify products or take account of possible photolysis of the oxy-halo compounds. CO was found as a product with 40% to 80% yield, but could arise as a result of photodecomposition.

Gillespie and Donovan (in press) have investigated the reaction of $O(^1D)$ with CF_3Cl , CF_2Cl_2 and $CFCI_3$ by flash photolysis with time resolved absorption spectroscopy for the detection of ClO . The reaction pathway to produce ClO has been shown to occur with efficiencies of 0.33 (CF_3Cl), 0.40 (CF_2Cl_2) and 0.33 ($CFCI_3$) for these freons. The production of Cl atoms by freon photolysis was precluded by filtering out radiation of wavelength shorter than 2400Å. However, the authors do not say whether precautions were taken to prevent photolysis of ozone in the visible region, by the broad band flash, which would result in ozone loss but not production of $O(^1D)$ nor consequently production of ClO . Since the efficiency of ClO production was measured relative to the loss of ozone this could cause the apparent efficiency for ClO production to drop below its true value.

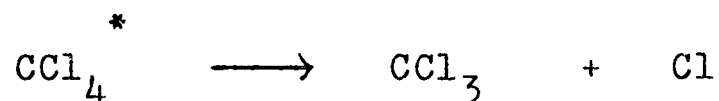
There is thus some evidence that the reaction $O(^1D) + \text{freon}$ does not produce ClO with unit efficiency, and it was one object of this work to investigate this phenomenon.

Figure 7,1 shows electron impact obtained UV spectra for $CFCI_3$ and CF_2Cl_2 . Studies of the photolysis of freons have been conducted by Simonaitis, Jayanty and Heicklen (1975), by

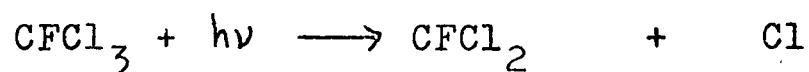
Davies et al (1975) and by Rebbert and Ansloos (1975). Simonaitis et al. photolysing CCl_4 only at $2139\text{\AA}$ interpreted their results in terms of an excited molecule primary process at low pressures.



although they believed that at higher pressures the process



should occur. Davies et al photolysed CCl_4 at wavelengths of 2537, 1849, 1470 and $1067\text{\AA}$ whilst Rebbert and Ansloos photolysed CFCl_3 and CF_2Cl_2 at 2139, 1849, 1633 and $1470\text{\AA}$. Both these authors showed that the principle process at $2537\text{\AA}$ is loss of one chlorine atom e.g.



whilst the probability of loss of two chlorine atoms (either as 2Cl or Cl_2) increased rapidly with increasing photon energy, e.g.



becoming the predominant process at the shorter wavelengths.

Much excellent and definitive work on the formation, observation and kinetics of halogen radicals has been performed by Clyne and coworkers (kinetic Studies of Diatomic Free Radicals using Mass Spectrometry, Parts 1 and 2; Reactions of Chlorine Oxide radicals, Parts 1 to 5). The radicals FO , ClO , BrO and IO , and the atoms Br , Cl and F have been detected mass spectrometrically and the kinetics of many of their reactions investigated. The kinetic results relevant to this work are summarised in Table 7.3. In particular Clyne and Watson (1974) note that the reaction of $\text{ClO} + \text{O}_3$ is immeasurably slow even at temperatures up to 670 K and attribute earlier reports of a fast rate constant to the effects of Cl atoms generated by the $\text{ClO} + \text{ClO}$ reaction. Rate constants for the reactions of Cl and O atoms with ClO_2 have also been measured (Bemand, Clyne and Watson, 1973).

In our experiments chlorine dioxide was prepared by the method described by McHale and von Elbe (1968) in a paper on the explosive decomposition of ClO_2 . Preparations of the other chlorine oxides are also reported in this paper. Lipscomb, Norrish and Thrush (1956) report the spectrum of ClO_2 and its photolysis to ClO and O_2 .

The flash photolysis of Cl_2O in the presence of oxygen has been described by Edgecombe, Norrish and Thrush (1957) and results in the production of ClO and ultimately ClO_2 .

Work on the oxidation of freons by $\text{O}(^3\text{P})$ and Cl atom initiation has been performed by Sanhueza and Heicklen and is reported in various papers (1974 to 1975). The results indicate long free radical chain processes producing polymeric materials as well as substituted phosgenes.

7, 2 Quenching of $O(^1D)$ by SF_6 and CF_4

It has long been assumed that $O(^1D)$ is quenched relatively infrequently on collision with sulphur hexafluoride or carbon tetrafluoride. Similarly it has been assumed that only physical quenching of $O(^1D)$ into its electronic ground state occurs in those quenching collisions, and that no net chemical reaction occurs. No evidence has been presented to date for the extraction of a fluorine atom in the form of FO by the reaction of $O(^1D)$ with fluorine containing substances, in a manner analogous to the abstraction of hydrogen in the form of HO from hydrocarbons, hydrogen or water. Since the question of whether $O(^1D)$ abstracts chlorine as ClO from chlorine containing substrates is at present open to question, it was felt necessary to establish initially the facts in relation to the abstraction of fluorine atoms.

In experiments designed to both measure the rate of quenching of $O(^1D)$ by SF_6 and by CF_4 , and, by inference, to establish whether any chemical reaction (as opposed to physical quenching) occurs, ozone was photolysed in the flow system described in Chapter 3 in the presence of SF_6 or CF_4 as carrier gas.

It was necessary to use SF_6 or CF_4 as carrier gases (in place of helium) so as to obtain the largest possible ratio of SF_6 or CF_4 over ozone, in view of the previously reported low rates of $O(^1D)$ quenching by the former, completely fluorinated, compounds. (We shall not in this case stretch the label "freon" to include SF_6 , in the way that this label has been previously defined as including CCl_4 !). Capillary constant data for SF_6 and CF_4 has already been presented in Chapter 3, and the calibrated flowmeters enabled the flow velocities in these new carrier gases to be measured. By observing the expected decrease in ozone destruction relative quantum yield, below the value of 2.0 normally obtained

for the relative quantum yield in an inert carrier gas (normally helium), it was possible to measure the ratio of the rate constant for quenching of $O(^1D)$ by SF_6 or CF_4 to the rate constant for reaction of $O(^1D)$ and O_3 ; viz. R_{120}/R_4 .

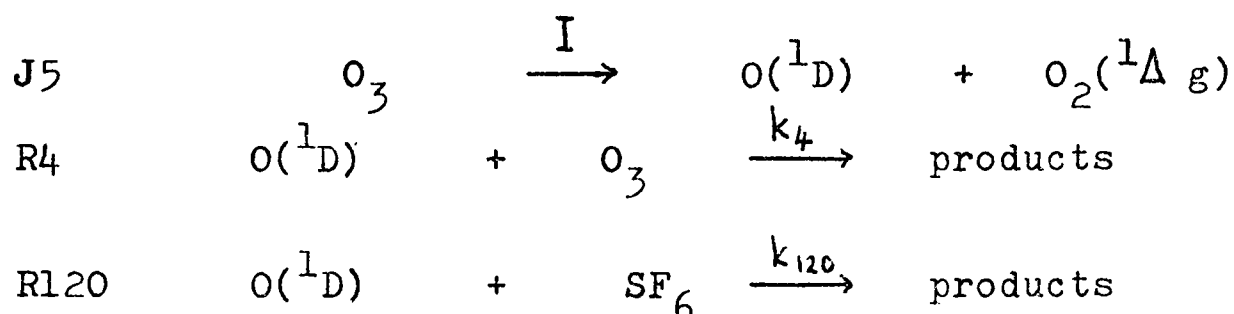
One of the major problems encountered was that of maintaining the nitrogen (or air) impurity in the SF_6 and, in particular, in the CF_4 to as low a level as possible since the quenching of $O(^1D)$ by these impurities occurs on approximately one in seven collisions, whereas quenching of $O(^1D)$ by SF_6 or CF_4 appears to occur on less than about two in 10^4 collisions.

A second problem encountered in these experiments, and, to an even greater extent, in those experiments involving freons which are described later in this chapter, was the problem of interfering broad background peaks, due to the reactants, at mass number 48 - the O_3^+ peak. In the presence of large excesses of SF_6 or CF_4 , the background at $m/e = 48$ which was due to overlap from the substantial peaks at $m/e = 51$ and $m/e = 50$ corresponding to SF^+ and CF_2^+ respectively, was much larger in many cases than the signal due to ozone. Two problems arose. The first was that the ozone "peak" went off scale and it was necessary to use a less sensitive amplifier range; and the second was that small fluctuations in carrier gas pressure caused correspondingly large fluctuations in the ozone signal baseline, leading to a lower signal-to-noise ratio and less precise measurements.

To solve the first of these problems a variable back-off facility was built into the mass spectrometer amplifier by the simple and effective expedient of introducing a variable bias into the negative feedback stabilisation loop. This enabled the background signal arising from the carrier gas to be backed-off before admitting ozone into the system. This did not, of course, affect the second

problem - which is essentially that of measuring small differences between large quantities - and this second problem was ameliorated by allowing the carrier gas pressure to reach a stable value before conducting experiments, and by taking background readings before and after each set of 20 to 30 readings of ΔO_3 and $[O_3]$.

Before presenting the experimental results we shall examine the kinetics involved since their solution is not intuitive. Consider the photolysis of ozone in SF_6 carrier gas.



where I has units s^{-1} .

It will be assumed initially that only physical quenching occurs, and this will be justified later in the discussion of the experimental results.

The relevant loss rates are

$$\begin{aligned}
 - \frac{d[O_3]}{dt} &= I[O_3] + k_4 [^1D][O_3] \\
 - \frac{d[^1D]}{dt} &= k_4 [^1D][O_3] + k_{120} [^1D][SF_6] - I[O_3]
 \end{aligned}$$

where $[^1D]$ denotes the concentration of $O(^1D)$ atoms. To a good approximation (see Appendix 6) a steady state exists in $[^1D]$, then

$$[^1D] = I[O_3] / (k_4[O_3] + k_{120}[SF_6])$$

substitution gives the rate of loss of ozone

$$- \frac{d[O_3]}{dt} = I[O_3] \left(1 + \frac{k_4 [O_3]}{k_4 [O_3] + k_{120} [SF_6]} \right)$$

The expression may be integrated to give the time dependence of the ozone concentration. The term in round brackets clearly depends on the ozone concentration and will therefore be a time dependent function since $[O_3]$ decreases owing to photolysis. However, a 10% reduction in $[O_3]$, the upper limit for most experiments, causes the bracketed term to change by only 1.7% (calculated for the nominal conditions of $[O_3] = 1 \times 10^{-7}$ mole l^{-1} and $[SF_6] = 1 \times 10^{-4}$ mole l^{-1}). To a good approximation the term in round brackets may therefore be regarded as independent of $[O_3]$ or t .

$$- \int_{[O_3]_0}^{[O_3]_t} \frac{d[O_3]}{[O_3]} = I \left[1 + \frac{k_4 [O_3]}{k_4 [O_3] + k_{120} [SF_6]} \right] \int_0^t dt$$

Integration and substitution gives

$$\ln \frac{[O_3]_t}{[O_3]_0} = - I \left[1 + \frac{k_4 [O_3]}{k_4 [O_3] + k_{120} [SF_6]} \right]$$

Now

$$\Delta O_3 = [O_3]_0 - [O_3]_t$$

Substitution and rearrangement gives

$$\frac{\Delta O_3}{[O_3]_0} = 1 - \exp \left\{ - I t \left(1 + \frac{k_4 [O_3]}{k_4 [O_3] + k_{120} [SF_6]} \right) \right\}$$

$$- \frac{1}{t} \ln \left(1 - \frac{\Delta O_3}{[O_3]_0} \right) = I \left(1 + \frac{k_4 [O_3]}{k_4 [O_3] + k_{120} [SF_6]} \right)$$

The term on the left hand side of the equation is equivalent to the quantity $\Delta O_3^{\text{cor}} / [O_3] t$, the value of $\Delta O_3 / [O_3] t$ corrected for finite ozone photolysis, as derived in Chapter 4; and I is equivalent to β , the value used in establishing relative quantum yields (experimentally $\beta = 2.187 \text{ s}^{-1}$). The relative quantum yield ϕ is thus given by

$$\phi = 1 + k_4 [O_3] / (k_4 [O_3] + k_{120} [SF_6])$$

rearrangement gives

$$(\phi - 1)^{-1} = 1 + k_{120} [SF_6] / k_4 [O_3]$$

Plots of $(\phi - 1)^{-1}$ versus $[SF_6] / [O_3]$ should give a straight line through an intercept of unity on the y axis, and with gradient k_{120} / k_4 ; if the reaction scheme on which the kinetics are based is valid. A completely analogous kinetic treatment may be applied to the SF_4/O_3 system.

Figure 7,3 shows the experimental plot obtained for the SF_6/O_3 system. The experimental results are tabulated in Table 7,4. The results show good agreement with prediction - the straight line of slope 2.07×10^{-4} passes almost exactly through $(\phi - 1)^{-1} = 1.0$.

Figure 7,4 shows the preliminary experimental data obtained from the CF_4/O_3 system. This data is tabulated in Table 7,5. It is not possible to draw any detailed conclusions from the data except to note that our cylinder CF_4 appeared to contain about five times as much impurity nitrogen as our Cylinder SF_6 ; and that, taking this into account it appears that $O(^1D)$ is quenched (if so it is) by CF_4 at least as slowly as it is quenched by SF_6 .

Let us now consider what the experimental results can tell us concerning the products of the reaction. It has already been pointed out the results fit fairly well the kinetic expression appropriate to a process in which $O(^1D)$ is physically quenched by SF_6 . This interpretation is, however, not an exclusive explanation - the results would, for example, be fitted equally well by an insertion process of the type $O(^1D) + SF_6 \longrightarrow SF_5OF$

Figure 7,3 Photolysis SF_6/O_3

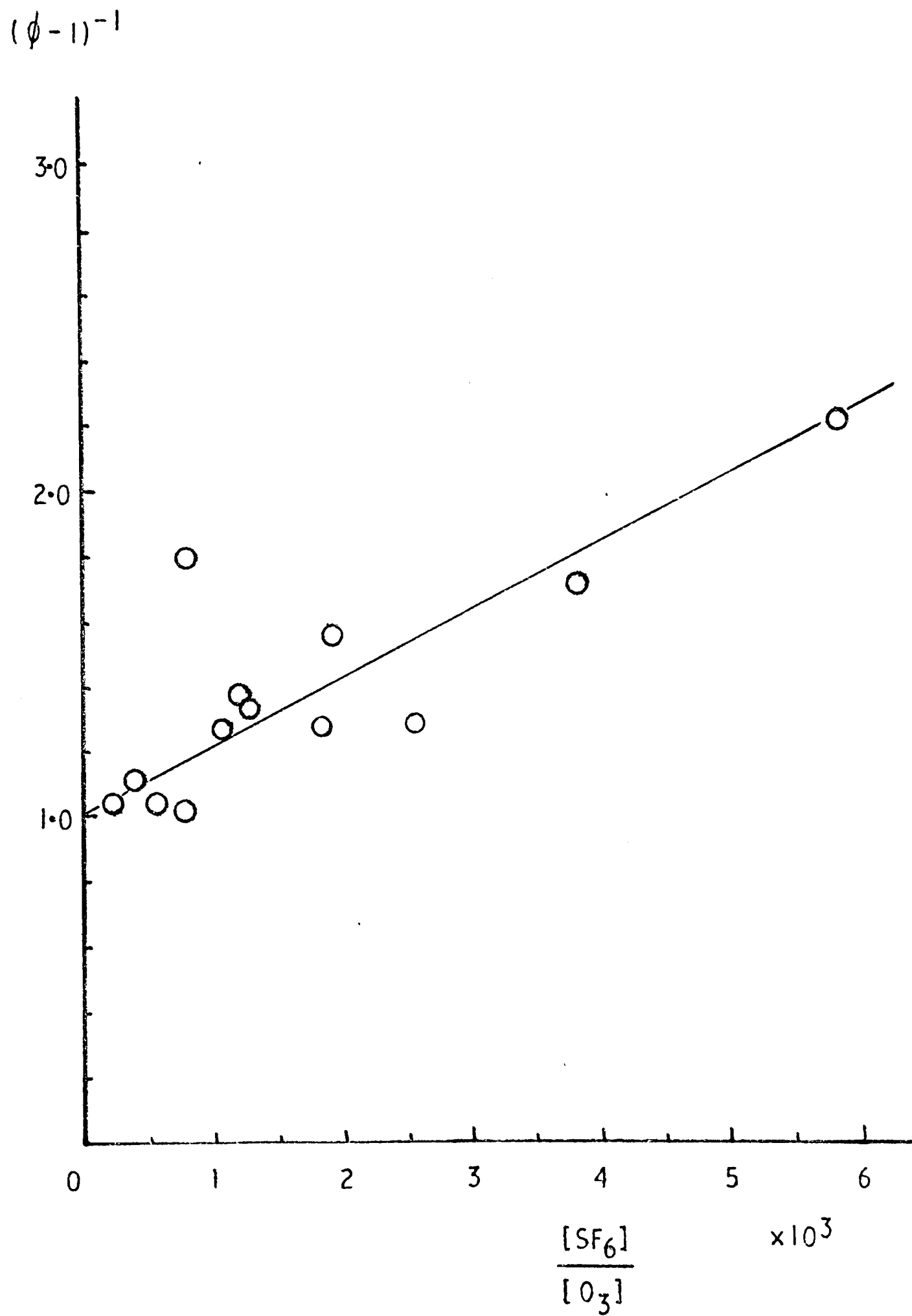
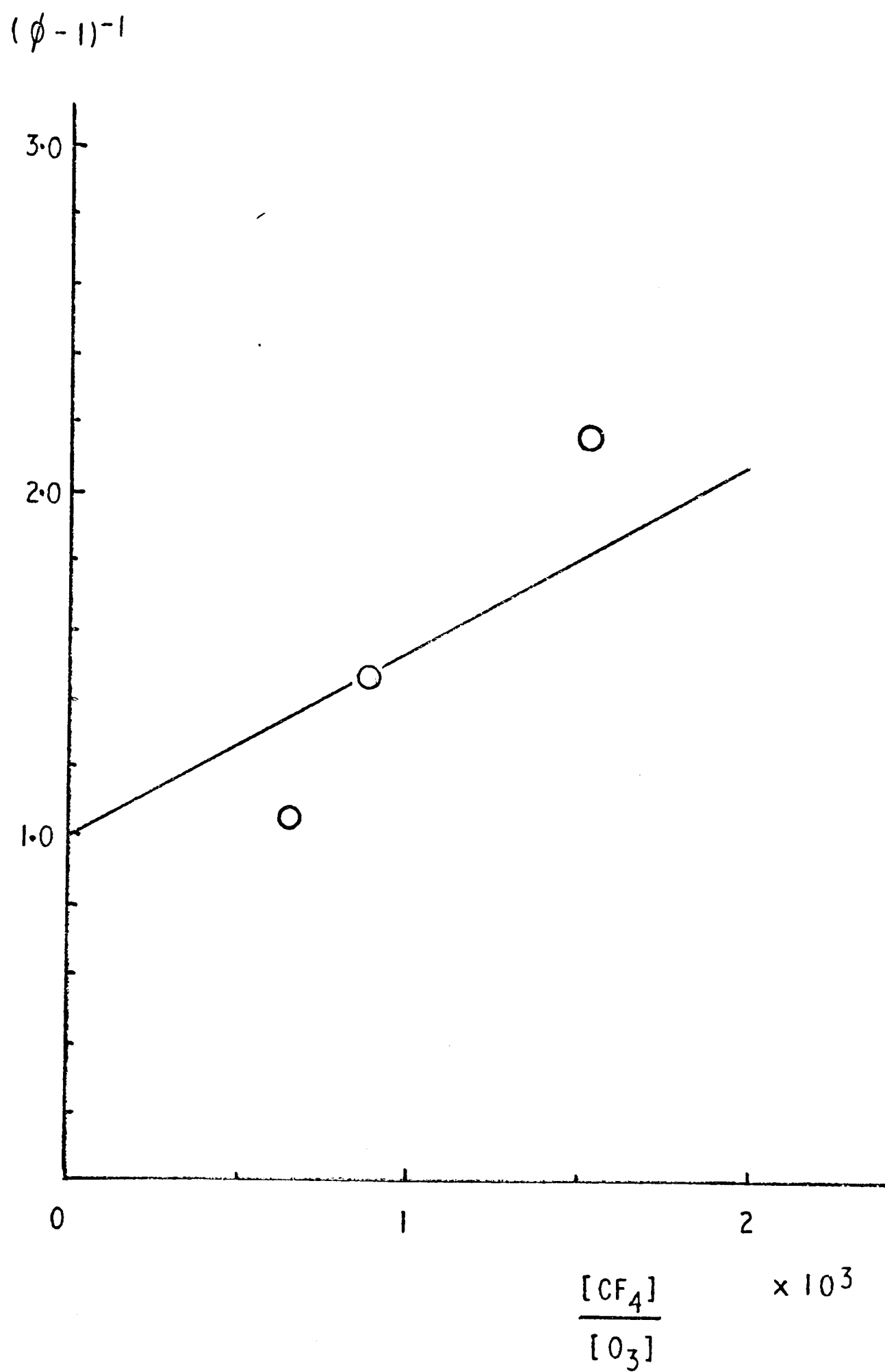


Figure 7,4 Photolysis CF_4/O_3



provided that the hypothetical product was not reactive toward ozone on the time scale of this experiment or led to the formation of such a species.

This second stated alternative is in effect equivalent, taken overall, to an abstraction reaction of the type $O(^1D) + SF_6 \longrightarrow SF_5 + FO$. It is clear that in this situation, where one if not both of the reaction products could be expected to react rapidly with ozone, the quantum yield would be 2.0 or $(2.0 + A)$ (where A is the fraction of $O(^1D)$ reacting with SF_6) respectively. The quantum yield would not fall below 2.0, as we observed in our experiments. It is, of course, always possible to produce hypothetical reaction schemes in which the reaction $O(^1D) + SF_6$ may occur partly by quenching and partly by reaction, and still produce a quantum yield of less than 2.0. If such a situation did occur then our rate constant would be high and our reaction mechanism incorrect. We can only comment that this would appear to be an improbable alternative.

Thus, ultimately basing our assignment of the mechanism of $O(^1D) + SF_6$ on the twin facts of good fit to the predicted reaction kinetics and a quantum yield which does not exceed 2.0, we believe quenching is by far the most plausible explanation.

The gradient of Figure 7,3 is found to be 2.07×10^{-4} . However, the nitrogen impurity was measured to be less than 5×10^{-8} mole l^{-1} , so that 15% or even up to 35% of the quenching could be due to N_2 impurity. Bearing this in mind we would put the ratio $R_{120}/R_4 = 2.07 \times 10^{-4}$ as an upper limit and estimate the error to be at least $\pm 50\%$. This value compares fairly well with the semi-qualitative value derived from the relative rate data of Gauthier and Snelling, 1975, of approximately 4×10^{-4} .

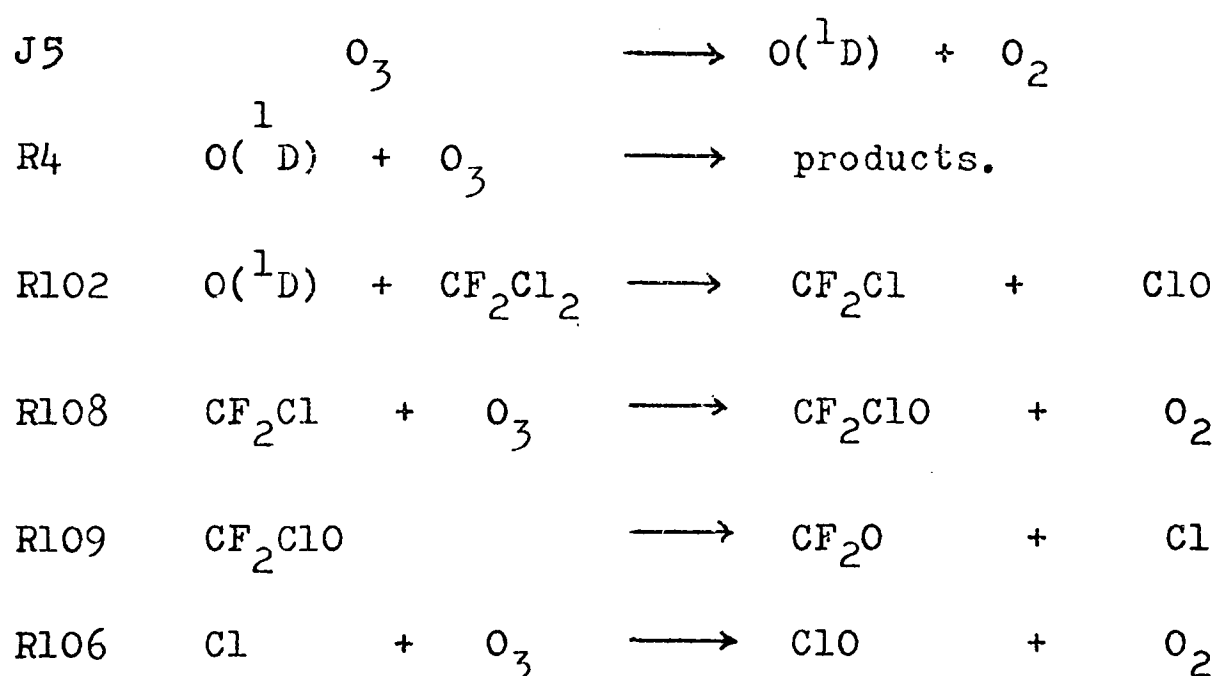
Taking R_4 to be 3.2×10^{11} l mole $^{-1}$ s $^{-1}$ we calculate R_{120} to be $(6.6 \pm 3.3) \times 10^7$ l mole $^{-1}$ s $^{-1}$ for the quenching

of $O(^1D)$ by SF_6 . The rate of quenching of $O(^1D)$ by CF_4 is not expected to exceed this value.

7.3 Kinetics.

On the basis of ~~his~~^{their} work on the static photolysis of O_3 /freon mixtures, as described in Section 7.1, Jayanty, Simonaitis and Heicklen proposed the following reaction scheme to account for their observations. The basic piece of data was the fact that, within experimental uncertainty, the overall quantum yield for the decomposition of ozone by UV radiation was unchanged by the presence of freon.

The immediate conclusion is that the added freon does not take part in the reactions, however on the basis of their finding species, in particular CF_2O , which appeared to be products of reaction involving freons, the following reaction scheme was proposed (in this case for CF_2Cl_2)



(Jayanty et al. in fact combined R108 and R109 into one reaction).

In treating the kinetics in relation to our experimental conditions we have omitted the slow reactions of $ClO + O_3$ and $ClO + ClO$, which are, however, important in the experiments of Heicklen et al.

The scheme is plausible in that CF_2O is a product, and if the reaction of $ClO + O_3$ dominates the loss of ClO in the reaction

$\text{ClO} + \text{ClO} \longrightarrow \text{Cl}_2 + \text{O}_2$, the quantum yield for ozone loss including the reactions of $\text{O}_2(^1\Delta_g)$ and $\text{O}(^3\text{P})$, is 5.0.

The quantum yield for the static photolysis of pure dry ozone is taken to be around 5.5 - the same as 5.0 taking experimental uncertainty into account. Pitts et al. did, however, observe Cl_2 as a product which points to the $\text{ClO} + \text{ClO}$ reaction perhaps being important at least in their experimental regime.

In the presence of excess freon so that the reaction $\text{O}(^1\text{D}) + \text{O}_3$ is negligible, and under our fast flow conditions, we can identify three principal kinetic variations based on the above reaction scheme.

1) R102, R108, R109, and R106 all go to completion:
yielding a quantum yield of 3.0.

11) R109 is the rate determining reaction:
leading to a first order dependence of the quantum
yield on T.

111) R108 is the rate determining reaction:
leading to a second order dependence of the quantum
yield on T and $[\text{O}_3]$.

As shown in Table 7,3 R102 and R106 are known to be fast and consequently go to completion under our typical concentration-time régimes.

Preliminary experiments indicated that the quantum yield for the photolysis of O_3 /freon mixtures was somewhere around two. Alternative 1) was therefore disregarded.

In order to test the experimental data in relation to the two remaining kinetic schemes, the detailed kinetics were worked out.

7.3 (1) Case 11) - the first order kinetics.

We shall simplify the treatment by regarding the photolysis zone as a point source, and consider the fast reactions (here taken to be R102 and R108) to occur entirely within it. The first order loss of CF_2ClO will be regarded as occurring entirely outside the photolysis zone. The loss rates are

$$- \frac{d[\text{O}_3]}{dt} = I[\text{O}_3] + k_4[{}^1\text{D}][\text{O}_3] + k_{108}[\text{CF}_2\text{Cl}][\text{O}_3] + k_{106}[\text{Cl}][\text{O}_3]$$

$$\frac{d[{}^1\text{D}]}{dt} = I[\text{O}_3] - k_4[{}^1\text{D}][\text{O}_3] - k_{102}[{}^1\text{D}][\text{CF}_2\text{Cl}_2]$$

$$\frac{d[\text{CF}_2\text{Cl}]}{dt} = k_{102}[{}^1\text{D}][\text{CF}_2\text{Cl}_2] - k_{108}[\text{O}_3][\text{CF}_2\text{Cl}]$$

$$\frac{d[\text{CF}_2\text{ClO}]}{dt} = k_{108}[\text{O}_3][\text{CF}_2\text{Cl}] - k_{109}[\text{CF}_2\text{ClO}]$$

$$\frac{d[\text{Cl}]}{dt} = k_{109}[\text{CF}_2\text{ClO}] - k_{106}[\text{Cl}][\text{O}_3]$$

Applying the steady state approximation to $[{}^1\text{D}]$ and $[\text{CF}_2\text{Cl}]$

$$[\text{CF}_2\text{Cl}] = \frac{k_{102}[{}^1\text{D}][\text{CF}_2\text{Cl}_2]}{k_{108}[\text{O}_3]}$$

$$[{}^1\text{D}] = \frac{I[\text{O}_3]}{k_4[\text{O}_3] + k_{102}[\text{CF}_2\text{Cl}_2]}$$

Since the steady state approximation (see Appendix 6) may not be applicable to $[Cl]$ in this case, an expression for $[Cl]$ was derived.

$$d \frac{[Cl]}{dt} = k_{109} [CF_2ClO] - k_{106} [Cl][O_3]$$

integration between $t = 0$ and $t = T$ yields.

$$- (k_{106} [O_3])^{-1} \cdot \ln (k_{109} [CF_2ClO] - k_{106} [Cl][O_3]) = T + \text{constant}$$

when $T = 0$; $[Cl] = 0$; thus

$$\text{constant} = - (k_{106} [O_3])^{-1} \ln(k_{109} [CF_2ClO])$$

substitution yields

$$\ln \frac{(k_{109} [CF_2ClO] - k_{106} [Cl][O_3])}{k_{109} [CF_2ClO]} = - k_{106} [O_3] T$$

$$[Cl] = \frac{k_{109} [CF_2ClO]}{k_{106} [O_3]} (1 - \exp(-k_{106} [O_3] T))$$

Under our typical conditions $[O_3] \approx 1 \times 10^{-7}$; $T \approx 1 \times 10^{-1}$ and $k_{106} \approx 1 \times 10^{10}$. The product $k_{106} [O_3] T$ is thus approximately 1×10^2 . The experimental term is thus negligible compared to unity and

$$[Cl] = \frac{k_{109} [CF_2ClO]}{k_{106} [O_3]}$$

This is the same result as that which would be given by the steady state approximation, but has been obtained by regarding $[CF_2ClO]$ as time independent, which is not strictly the case, but nevertheless a fair assumption as $k_{109} [CF_2ClO] \ll k_{106} [Cl] [O_3]$.

We shall now derive expressions for the loss of O_3 in the lamp zone, and hence the concentration of CF_2ClO in the lamp zone; and the conc of CF_2ClO outside the lamp.

Reactions within the lamp zone:- substitution of the steady state concentrations of $(\frac{1}{2}D)$, CF_2Cl and Cl into the above

expression for the ozone loss rate shows that

$$-\frac{d[O_3]}{dt} = 2 I [O_3] + k_{109} [CF_2ClO]$$

As pointed out before, we shall regard R109 as occurring exclusively outside the lamp zone, then

$$-\frac{d[O_3]}{dt} = 2 I [O_3]$$

$$[O_3]_{tt} = [O_3]_o \exp (-2 I t t)$$

where tt is a time such that $tt \leq t$ (the total time spent by the gas in the lamp zone).

now

$$\Delta O_3 = [O_3]_o - [O_3]_t \quad \text{and} \quad \beta = I$$

$$-\ln \left(\frac{1 - \Delta O_3}{[O_3]} \right) = 2 \beta t$$

This is the same result as obtained for photolysis of ozone in helium as detailed in Chapter 4 i.e. a quantum yield of 2.0. J5 produces a quantum yield increment of 1.0 and R102 followed by R108 produce the second increment of 1.0.

The concentration of CF_2ClO at time t viz. $[CF_2ClO]_t$ is therefore equal to approximately $\Delta O_3/2$.

If R109 hasn't gone to any significant extent at time t

$$\frac{d[CF_2ClO]}{dt} = AI [O_3] \quad \text{where} \quad A = \frac{k_{102} [CF_2Cl_2]}{k_{102} [CF_2Cl_2] + k_4 [O_3]}$$

integration gives

$$[CF_2ClO]_t = AI [O_3] t$$

where $[O_3]$ has been corrected to allow for finite percent photolysis.

First order loss of CF_2ClO outside lamp zone:- the loss rate

for CF_2ClO outside the lamp zone is given by

$$\frac{d [CF_2ClO]}{dt} = AI [O_3]_t - k_{109} [CF_2ClO]$$

outside the lamp zone $I = 0$. Integration from $t = t$ to $t = T$ gives

$$[CF_2ClO]_T = [CF_2ClO]_t \exp (-k_{109} T_1)$$

where $T_1 = T - t/2$ since T is measured from the mid-point of the lamp zone in these experiments.

If ΔO_3^T is the amount of ozone lost between times $t = t$ and $t = T$ (and is in addition to the amount of ozone lost up to time t) then

$$\begin{aligned} \Delta O_3^T &= [CF_2ClO]_t - [CF_2ClO]_T \\ \frac{\Delta O_3^T}{[CF_2ClO]_t} &= 1 - \exp (-k_{109} T_1) \end{aligned}$$

Substitution of the value for $[CF_2ClO]_t$ gives

$$\frac{\Delta O_3^T}{[O_3]_t} = AI (1 - \exp (-k_{109} T_1))$$

In Chapter 4 the generalised method of correction to allow for finite percent photolysis of ozone was outlined. Thus measurement of ΔO_3 , $[O_3]$ and T , should allow k_{109} to be found.

$$\phi - 2 = A (1 - \exp (-k_{109} T_1))$$

since the quantum yield at time t is 2.0. ϕ is the overall relative quantum yield.

$$\ln (A/(A - \phi - 2)) = k_{109} T_1$$

Plotting this function should give a straight line through the origin of gradient k_{109} if the system follows these first order kinetics.

7.3 (2) Case 111) - the second order kinetics.

In this case R108 is the rate determining step and is

followed by rapid decomposition of CF_2ClO in R109. The reaction is thus effectively



The quantum yield in the presence of excess freon should vary between 1.0 and 3.0 as a function of $[\text{O}_3]$ T; in contrast to the previous case where the quantum yield varies between 2.0 and 3.0 as a function of T.

As before, concentrations of intermediate species are:-

$$[\text{CF}_2\text{Cl}] = \frac{k_{102} [\text{I}_D] [\text{CF}_2\text{Cl}_2]}{k_{108} [\text{O}_3]}$$

$$[\text{I}_D] = \frac{\text{I} [\text{O}_3]}{k_4 [\text{O}_3] + k_{102} [\text{CF}_2\text{Cl}_2]}$$

and the Cl concentration corresponding to reaction R208 is

$$\begin{aligned} [\text{Cl}] &= \frac{k_{208} [\text{CF}_2\text{Cl}] [\text{O}_3]}{k_5 [\text{O}_3]} \\ &= k_{208} [\text{CF}_2\text{Cl}] / k_5 \end{aligned}$$

The loss of ozone within the lamp zone is given by

$$-\frac{d[\text{O}_3]}{dt} = \text{I} [\text{O}_3] + k_4 [\text{I}_D] [\text{O}_3] + k_{208} [\text{CF}_2\text{Cl}] [\text{O}_3] + k_{106} [\text{Cl}] [\text{O}_3]$$

substituting for $[\text{I}_D]$, $[\text{CF}_2\text{Cl}]$ and $[\text{Cl}]$ and taking

$$\frac{k_4 [\text{O}_3]}{k_4 [\text{O}_3] + k_{102} [\text{CF}_2\text{Cl}_2]} \approx 1 - A$$

gives

$$-\frac{d[\text{O}_3]}{dt} = \text{I} [\text{O}_3] (2-A) + 2 k_{208} [\text{CF}_2\text{Cl}] [\text{O}_3]$$

Making the approximation that R208 does not occur to any significant extent within the lamp zone,

$$-d \frac{[O_3]}{dt} = I [O_3] (2 - A)$$

Integration yields

$$[O_3]_t = [O_3]_0 \cdot \exp (- I t (2 - A))$$

letting $\Delta O_3^t = [O_3]_0 - [O_3]_t$ and since $\beta \equiv I$, gives

$$- \ln \left(1 - \frac{\Delta O_3^t}{[O_3]_0} \right) = (2 - A) t$$

The relative quantum yield at time t is thus $2 - A$.

In the presence of excess freon A approaches 1 and the relative quantum yield is thus unity.

The concentration of CF_2Cl inside the lamp zone is found from the expression for its formation rate.

$$d \frac{[CF_2Cl]}{dt} = I [O_3] \frac{k_{102} [CF_2Cl_2]}{k_{102} [CF_2Cl_2] + k_4 [O_3]} - k_{208} [O_3] [CF_2Cl]$$

Making the approximation that R208 occurs only to a negligible extent within the lamp zone, and integrating gives

$$[CF_2Cl]_t = AI [O_3] t$$

Second order loss of CF_2Cl outside lamp zone:- the only loss process is by reaction with ozone;

$$-d \frac{[CF_2Cl]}{dt} = k_{208} [O_3] [CF_2Cl]$$

integration from $t = t$ to $t = T$ gives

$$[CF_2Cl]_T = [CF_2Cl]_t \exp (- k_{208} [O_3] T_1)$$

where again $T_1 = T - t/2$

substitution for the value of $[CF_2Cl]_t$ derived above yields

$$[CF_2Cl]_T = AI [O_3] t \exp (-k_{208} [O_3] T_1)$$

If, as before, the amount of ozone lost by reaction outside the lamp zone, between times $t = t$ and $t = T$ is denoted by ΔO_3^T then

$$\Delta O_3^T = 2([CF_2Cl]_t - [CF_2Cl]_T)$$

Since each reactive encounter between an O_3 molecule and a CF_2Cl molecule ultimately leads to the loss of two ozone molecules through reactions R108 and R106.

Substitution gives

$$\Delta O_3^T = 2AI [O_3]_t (1 - \exp(-k_{208} [O_3] T_1))$$

$$\frac{\Delta O_3^T}{[O_3]_t} = 2AI (1 - \exp(-k_{208} [O_3] T_1))$$

This expression is entirely analogous to that derived for the first order kinetic situation. Expressed in terms of the overall relative quantum yield for ozone loss ϕ as measured at the detection point

$$\phi = 2A (1 - \exp(-k_{208} [O_3] T_1)) + (2 - A)$$

Since the quantum yield at time t is $2 - A$

Rearrangement gives.

$$\ln \left(\frac{2A}{2 + A - \phi} \right) = k_{208} [O_3] T_1$$

Plotting the log function versus $[O_3] T_1$ should give a straight line through the origin of gradient k_{208} if the system follows these second order kinetics.

Apart from the differences in the kinetic dependences on $[O_3]$ and T of first and second order kinetics, the other major difference is that the quantum yield for ozone loss at the end of the lamp zone is constant at 2.0 (subject to the point photolysis source approximation) in the first order kinetics, whilst the quantum

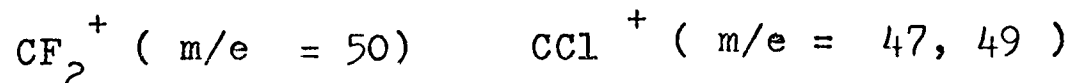
yield at the end of the lamp zone for the second order kinetics is $(2 - A)$. That is to say, that the quantum yield at time t depends in this second case on the ratio of freon to ozone, and is unity only in the special case of excess freon when $A = 1$.

These kinetic schemes are the simplest cases envisageable, and although some preliminary data appeared to be consistent with case 111) it later became clear that the photolysis of O_3 /freon mixtures followed much more complicated kinetics. Section 7,5 includes a description of a computer model developed to calculate the results to be expected from these more complicated reaction schemes, which were not amenable to simple kinetic treatments such as those which have just been described.

7.4 $O(^1D)$ + freons - The Experiments.

The reactions of $O(^1D)$ with the "freons" CF_3Cl , CF_2Cl_2 , $CFCl_3$ and CCl_4 were studied by photolysing ozone in the presence of excess freon; helium being used as carrier gas. The basic experimental techniques have already been described in Chapter 3 and the method of relative quantum yields has been detailed in Chapter 4. Some special problems arose in the experiments with freons, which experiments were by far the most difficult to perform of any described so far in this thesis.

Appendix 4 shows the experimental mass spectra of various freons obtained at an electron beam energy of 90 eV and trap current of 150 microamps (the optimum conditions for observation of the O_3^+ ion). It will be noted that every freon gives rise to at least one of the following fragment peaks which lie close (under the mass resolution régime occurring as a result of typical experimental conditions) to the ozone positive ion peak at mass number 48:



As we have already explained in section 7.2, with reference to the quenching of $O(^1D)$ by SF_6 and CF_4 , it was necessary to back-off background signals in order to observe the ozone peak with any acceptable sensitivity. In the case of the experiments to be described in this section very large backgrounds, often amounting to over ten times the O_3^+ signal, had to be backed off. It was necessary to strike a compromise between having a large enough excess of freon, so that substantially all the $O(^1D)$ reacted with the freon rather than with ozone, and maintaining an acceptable signal-to-noise ratio. In the Tables 7.6 to 7.9 inclusive, values of the quantity A are presented. A is the fraction of $O(^1D)$ reacting with freon in relation to overall loss of $O(^1D)$, and is

calculated using the relative rate data of Jayanty et al (1975).

A further objection to the use of large excesses of freon is that the flow conditions would be perturbed and the flow velocities, which were calculated on the basis of the measured helium flow rates, would not be correct.

The experiments are broadly divided into three groups; the basic freon/ O_3 relative quantum yields measurements, the freon/ O_3 /NO experiments, the search for mass peaks corresponding to ClO^+ and ClO_2^+ and related calibrations. The latter two groups of experiments were attempts to identify reaction mechanisms and products.

7.4 (1) Photolysis of freon/ O_3 mixtures.

Ultimately, ozone was photolysed in the presence of CF_3Cl , CF_2Cl_2 , $CFCl_3$ and CCl_4 in helium carrier gas. The initial experiments were carried out using CF_2Cl_2/O_3 mixtures; the reason being that, in addition to being gaseous and therefore easier to handle, CF_2Cl_2 also contains two chlorine atoms and can therefore take part in loss processes involving secondary chlorine abstraction reactions. The fact makes CF_2Cl_2 more typical of the series of freons than is CF_3Cl , the other gaseous member of the series.

Although $CFCl_3$ and CCl_4 have significant vapour pressures at room temperature (15° to $20^\circ C$, nominal) they both remain as liquids under normal atmospheric pressure. The freon inlet system was adapted so that it could be either attached to a gas cylinder or to a U-tube apparatus for handling liquids and equipped with greaseless taps and greaseless seals, (since both liquid freons are excellent solvents for greases). CF_3Cl and CCl_4 were trap-to-trap distilled between the two arms of the U-tube at least four times until the vapour pressure became fairly constant.

The U-tube containing the freons was held in a room temperature water bath to avoid the excessive cooling which otherwise occurred when freon was pumped off into the inlet system, and thence the flow tube. Because the freons solidify at cardice-trichlorethylene baths temperatures they were not passed through cold-traps. The impurity of the freons with respect to nitrogen (and by inference air) was checked mass spectrometrically and ^{such impurity} was always at an insignificant level.

The experimental system used in the freon experiments, a development of that used in the experiments described previously, is represented in Figure 7,5. However, a greater flexibility than is shown enabled almost any reactant to be introduced at almost any desired inlet point.

Reactant concentrations were measured by means of calibrated peaks in their mass spectra. Ozone concentrations were measured at $m/e = 48$; the particular freon peaks used are marked with a * in Appendix 4. As previously explained in Chapter 3 each peak used for calibration purposes was chosen with regard to convenient sensitivity and with regard to avoidance of interfering neighbouring peaks.

Consideration of published kinetic schemes by Heicklen and coworkers (1975) resulting from work on the static photolysis of ozone and freon mixtures led to the impression that the kinetics might be adequately described by either of the first or second order kinetic schemes detailed in section 7,2. Since both schemes involve a dependence on T (the "contact time") in early experiments, particularly those of CF_2Cl_2/O_3 mixtures, this parameter was altered by moving the photolysis lamp along the quartz section of the flow tube to obtain values of T in the region of 5 to 80 milliseconds.

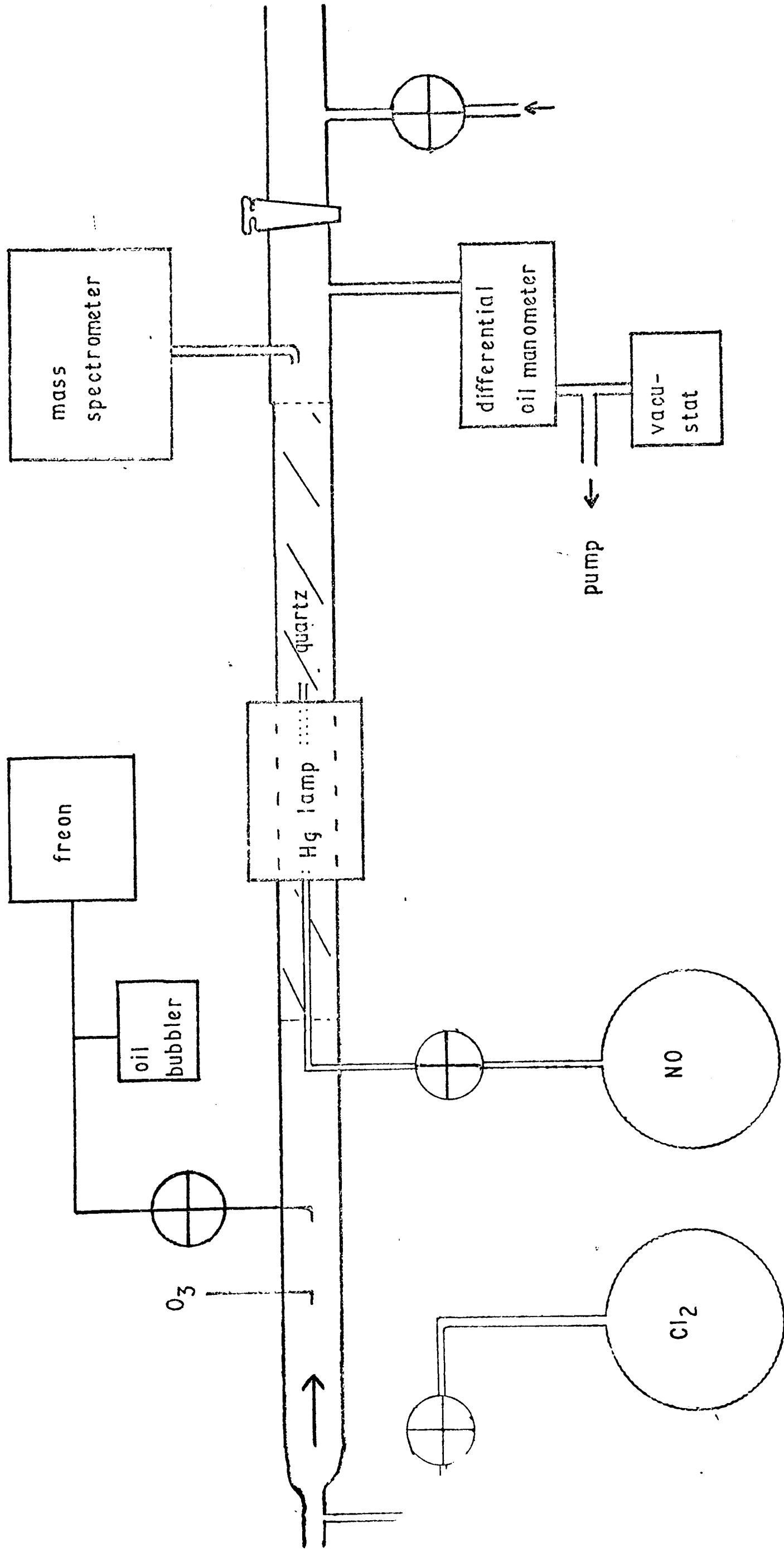


Figure 7,5 Flow system

Longer contact times were obtained in certain runs by reducing the flow velocity to only a few metres per second. This, of course, resulted in larger percent photolysis but was to an extent undesirable in that correspondingly large corrections needed to be made to the resulting values of $\Delta O_3 / [O_3]$.

Experimental data, including the freon/ O_3 runs, are presented in Tables 7,6 and 7,9 inclusive.

Some of the early misleading data, where troubles were experienced in measuring the O_3^+ baseline correctly due to the presence of drifting background signals; and the predictions of Heicklen and coworkers, were not in agreement with the conclusions of the main body of data. This led us to perform further "diagnostic" experiments.

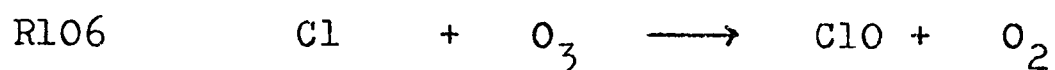
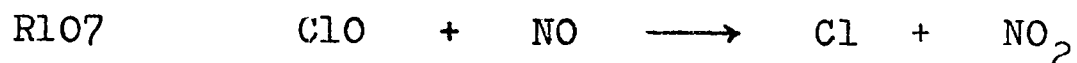
The mass range 0 to 200 (nominal) was examined for peaks which varied in response to the pulsed photolysis lamp (and hence the concentrations of $O(^1D)$ and consequent derived species). It was found that the broad peak corresponding to Cl^+ increased strongly, when the photolysis lamp was on, in mixtures of ozone with every freon. The F^+ peak ($m/e = 19$) showed no detectable variation under the same conditions. The peak at around $m/e = 67$ also increased when the photolysis lamp was on, but the enhancement, although approximately the same for the same concentration of $O(^1D)$ produced ^{by photolysis} in the case of all the freons, was very much smaller.

These observations will be discussed as part of a more comprehensive analysis of results in section 7,5; suffice to note here that CF_2O^+ and ClO_2^+ ^{predominantly} occur at $m/e = 66$ and 67 , respectively. The Cl_2^+ ^{predominantly} peak occurs at approximately $m/e = 71$.

7,4 (2) Photolysis of freon/O₃/NO mixtures.

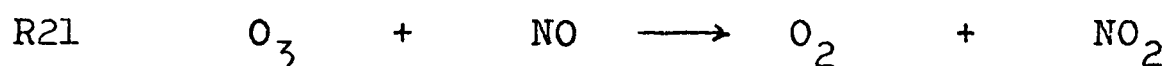
The object of photolysing freon/O₃ mixtures in the presence of NO was to demonstrate (or not) the production of ClO as a reaction product.

If ClO is present the following reactions may occur



ClO is regenerated and O₃ is lost in a chain decomposition reaction sequence. If ClO is present the addition of NO should cause the quantum yield for ozone loss to increase markedly.

In some of the experiments the concentrations of NO used were sufficiently large to cause significant loss of ozone in the slow reaction.



However, this was not a particular problem since it simply reduced the effective ozone concentration in the flow tube without affecting the value of $\Delta \text{O}_3 / [\text{O}_3]$ when the photolysis lamp was on. If $[\text{O}_3]$ was reduced due to the presence of NO, this reduction did not depend on the photolysis lamp being on so that a balancing reduction in ΔO_3 occurred; the relative quantum yield thereby remaining the same. It was believed that the NO₂ produced did not have any affect on the quantum yield; its reaction with ozone being slower than the reaction of NO with O₃ on the twin counts of slower rate constant and lower NO₂ concentrations.

Partly to minimise the reaction NO + O₃ by reducing the time in which NO and O₃ were in contact, but largely to avoid many complicating reactions which would ensue from passing NO through the lamp zone, the NO was injected into the flow tube immediately downstream of the photolysis lamp. NO was admitted from a storage

bulb trapped in a cardice-trichlorethylene bath at -78°C to condense impurities, particularly any residual NO_2 , into the flow tube via a narrow nylon inlet tube which passed down the centre of the quartz flow tube and through the lamp zone. The presence of the nylon tube reduced the inside cross sectional area of the flow tube by only about 1% and its affect on the flow velocity was therefore negligible.

This inlet tube had the advantages of avoiding the glass blowing of inlet jets into the quartz flow tube with consequent possible affects on the ultraviolet transmission properties of the quartz, and also inhibiting the movement of the photolysis lamp along the flow tube. The length of the nylon tube could also be varied so as to vary the injection position.

The NO concentration was measured via its mass peak at $m/e = 30$. The mass spectrometer sensitivity to nitric oxide was the greatest of any gas used, and calibration was effected at a lower electron beam energy of 30 eV, and the usual 150 microamp trap current, so as to reduce the NO^+ signal to a convenient size.

Table 7,6 to 7,8 include the experimental data on the photolysis of $\text{CF}_3\text{Cl}/\text{O}_3/\text{NO}$, $\text{CF}_2\text{Cl}_2/\text{O}_3/\text{NO}$ and $\text{CFCl}_3/\text{O}_3/\text{NO}$ mixtures respectively. It was not possible to perform the equivalent experiment for CCl_4 in the time available.

7,4 (3) Experiments to Observe directly the reaction products.

These experiments had as their objective the identification of products of the general reaction of $\text{O}(^1\text{D}) + \text{freon}$ by the direct observation of product ions in the mass spectrometer. In particular it was desired to establish whether or not ClO was a reaction product by looking for the ClO^+ ion.

When it had been established that the reaction sequence which occurred in real life did not appear to be satisfactorily

modelled by either of the predicted kinetic schemes that have been described in section 7,3, attempts were made to gain insight into the reaction routes by attempts to establish the identity of the products. The experiments aimed at inferring the presence of ClO indirectly by the addition of nitric oxide have just been described in section 7,4 (2). These experiments, however, due partly to the use of rather low NO concentrations and partly as a result of unexpected kinetic results, did not initially give any positive indication of the presence of ClO. Attempts to observe directly ClO and other reaction products were made using the mass spectrometer.

The method involved a search of the mass scale looking for peaks which responded to the flashing of the photolysis lamp. Complications arose from the presence of background signals, for example O_2^+ , which also fluctuated in response to the photolysis lamp. The product signals were in any case expected to lie close to the limits of detectability of our comparatively low sensitivity detection system.

In the event the search for ClO^+ ($m/e = 51$) was rendered very difficult by the presence of O_3^+ ($m/e = 48$) and CF_2^+ and CCl^+ peaks ($m/e = 50, 47$ and 49 respectively) at neighbouring mass numbers. ClO was never directly observed as a product of the photolysis of O_3 /freon mixtures.

In order to establish the limits of detectability of the mass spectrometer to ClO, and also to calibrate the detection system with respect to ClO, chlorine monoxide was generated in the flow tube by the reaction $Cl + O_3 \longrightarrow ClO + O_2$ (R106).

Figure 7,5 shows the Cl_2 inlet system. Cl atoms were generated by passage of Cl_2 in helium through a microwave discharge upstream of the ozone inlet jet. Chlorine was handled in a grease-free system. After flushing and filling the storage bulb the chlorine

was trapped down in liquid nitrogen, pumped on and subsequently allowed to vapourise; the procedure being repeated several times to remove any possible air impurities. Chlorine was admitted to the flow tube via a double-stage stainless steel needle valve.

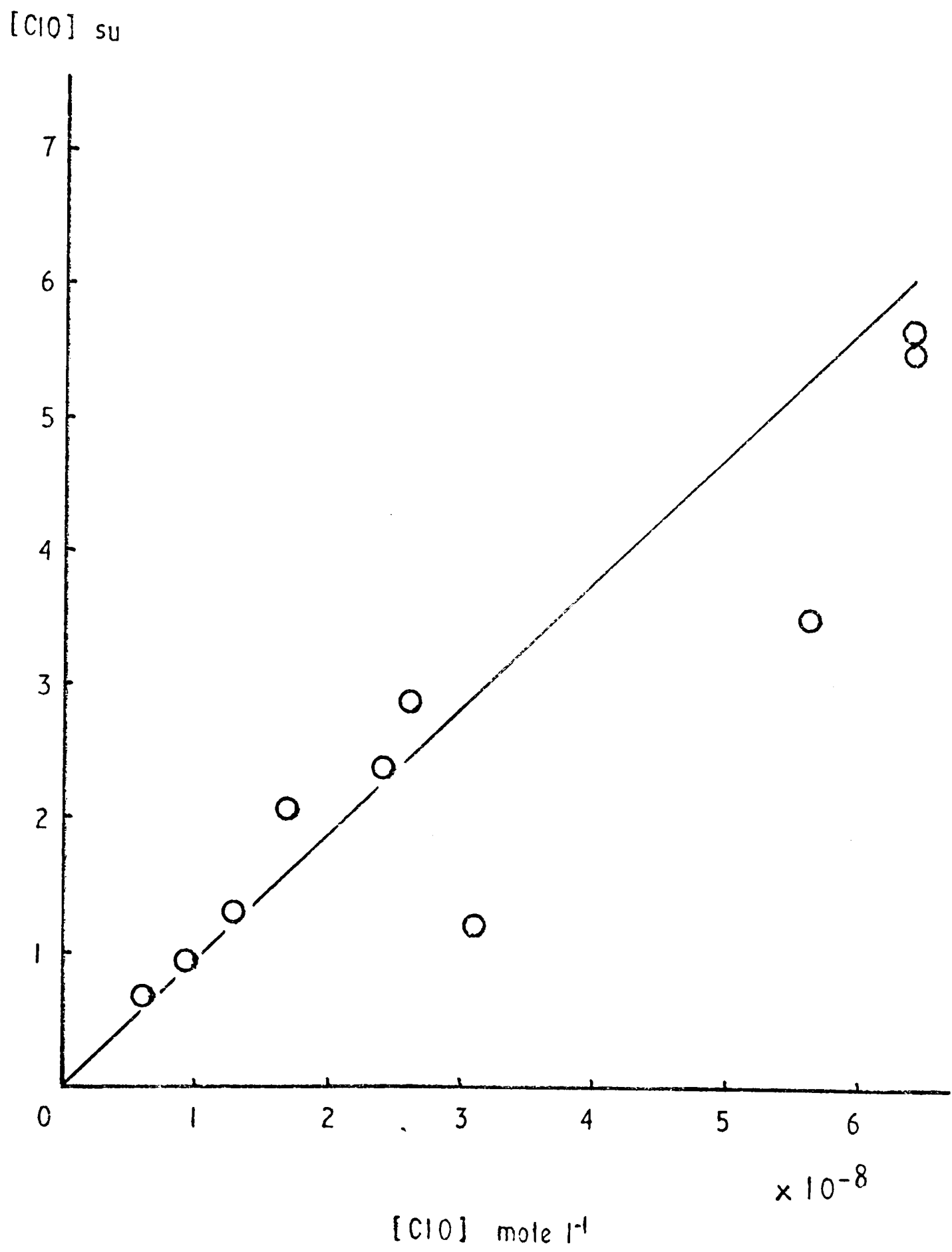
The reaction $\text{Cl} + \text{O}_3$ is very fast whilst the reaction $\text{ClO} + \text{O}_3$ is generally accepted as being sufficiently slow that it goes to a negligible extent during the typical contact time of around 40 ms used in these particular experiments. This conclusion was confirmed in that the ClO^+ peak did not appear to depend on the $[\text{O}_3]$ present.

The concentration of ClO produced was assumed to be equal to the concentration of Cl atoms present. The Cl concentration was measured by noting the decrease in $[\text{O}_3]$ when the microwave was switched on. No evidence of any reaction of Cl_2 with O_3 was found. By moving the discharge in relation to the ozone inlet jet it was established that no significantly large loss of Cl on the walls of the pyrex part of the flow system occurred.

Figure 7,6 shows the calibration plot of chart deflection ($m/e = 51$) versus $[\text{ClO}]$ in the flow tube. For a typical ozone concentration in the O_3/freon photolysis experiments of 8×10^{-8} mole l^{-1} and a typical value of 5% photolysis if the ClO were produced with unit efficiency a concentration of 4×10^{-9} mole l^{-1} would be produced in the absence of any loss processes. This corresponds to a chart deflection of about 0.5 cm which should be observable even in the presence of large fluctuating background signals, but is close to the limits of detectability.

To check that ClO could be observed in the presence of freons, it was generated by the reaction of Cl with O_3 in an O_3/freon mixture. It was possible to observe ClO^+ even in the presence of large amounts of freon (around 1×10^{-6} mole l^{-1}).

Figure 7,6 MS calibration ClO



The addition of NO also caused a large enhancement in the quantum yield for ozone decomposition, confirming the use of NO addition as a diagnostic test for the presence of ClO.

In view of the ClO calibration it appeared that if ClO were a reaction product it did not appear to be produced with unit efficiency from the reaction $O(^1D) + O_3$ since ^{contrary to expectation} ClO^+ was never observed in the photolysis of O_3 /freon (or O_3 /freon/NO) mixtures. The presence of peaks at mass numbers corresponding to other possible products was therefore investigated.

As pointed out previously, it was found in the photolysis of O_3 /freon mixtures that the Cl^+ peak showed a large positive enhancement when the photolysis lamps were on. No enhancement was found in the F^+ peak ($m/e = 19$); nor was any enhancement at $m/e = 87$, corresponding to Cl_2O^+ discovered. The only other peak to show any enhancement when the photolysis lamps were on was the peak at $m/e = 64 - 68$. The resolution was insufficient to positively identify the mass number. CF_2O^+ lies at $m/e = 64$, and ClO_2^+ ^{mean} lies at $m/e = 67.5$; both CF_2O and ClO_2 are possible reaction products. Both could be expected to be long lived in our system if formed, since both are stable species, nor would either be expected to be lost by reaction in our concentration-time régime.

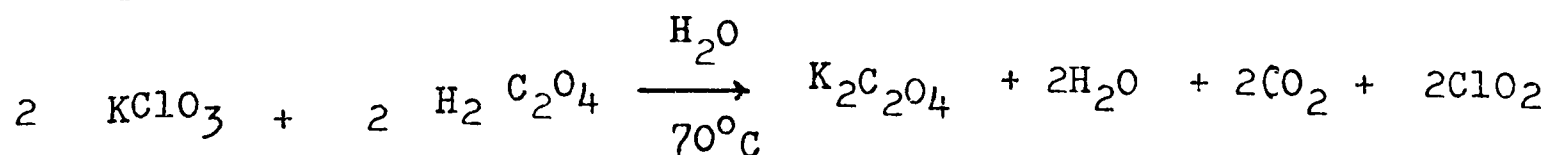
In order to observe the peak at $m/e = 64 - 68$ it was usually necessary to work with slower flow velocities and higher ozone concentrations than normal in order to produce a greater concentration of $O(^1D)$ and thereby greater concentrations of reaction products. However, for all the freons the photolysis of O_3 /freon mixtures produced qualitatively equal signals at $m/e = 64 - 68$ for the same initial concentration of $O(^1D)$, as shown in Table 7,10. If ClO were not a reaction product, or at least one which was not generated with unit efficiency, as appeared possible from initial experiments,

then ClO_2 seemed to be a conceivable alternative. Therefore experiments were performed to calibrate the mass spectrometer to ClO_2 .

Our thanks are due here to Dr. M.A.N. Clyne who kindly shared his experimental expertise in the preparation and handling of chlorine dioxide and who also took part in invaluable discussions about the implications of the experiments.

Despite this help considerable difficulty in preparing samples of chlorine dioxide was encountered. It is believed that at least part of this trouble was due to the long time taken to condition the preparation apparatus to ClO_2 , a much longer time than was usually required for conditioning pyrex to ozone, for example.

Chlorine dioxide was prepared from potassium chlorate and oxalic acid dihydrate by the method described by McHale and von Elbe (1968). The preparation apparatus is represented in Figure 7,7. The object was to produce not more than 50 torr of ClO_2 in a 5 l pyrex storage bulb. Since the reaction yield is approximately 80% (M.A.N. Clyne, personal communication) a mixture of about 2g of KClO_3 and 2g of $\text{H}_2\text{C}_2\text{O}_4$ were mixed into a slurry with a little distilled water in a bulb and heated to about 70° on a heated mantle under a slow stream of nitrogen. The bulb was adapted to be remotely manouvered onto the mantle. The whole apparatus was contained in a darkened fume cupboard to prevent decomposition of ClO_2 and operated with the front closed for safety. Chlorine dioxide produced from the reaction



together with carbon dioxide was flushed out of the bulb by the nitrogen, passed over P_2O_5 to remove traces of water vapour and collected in a liquid nitrogen trap. After completion of the

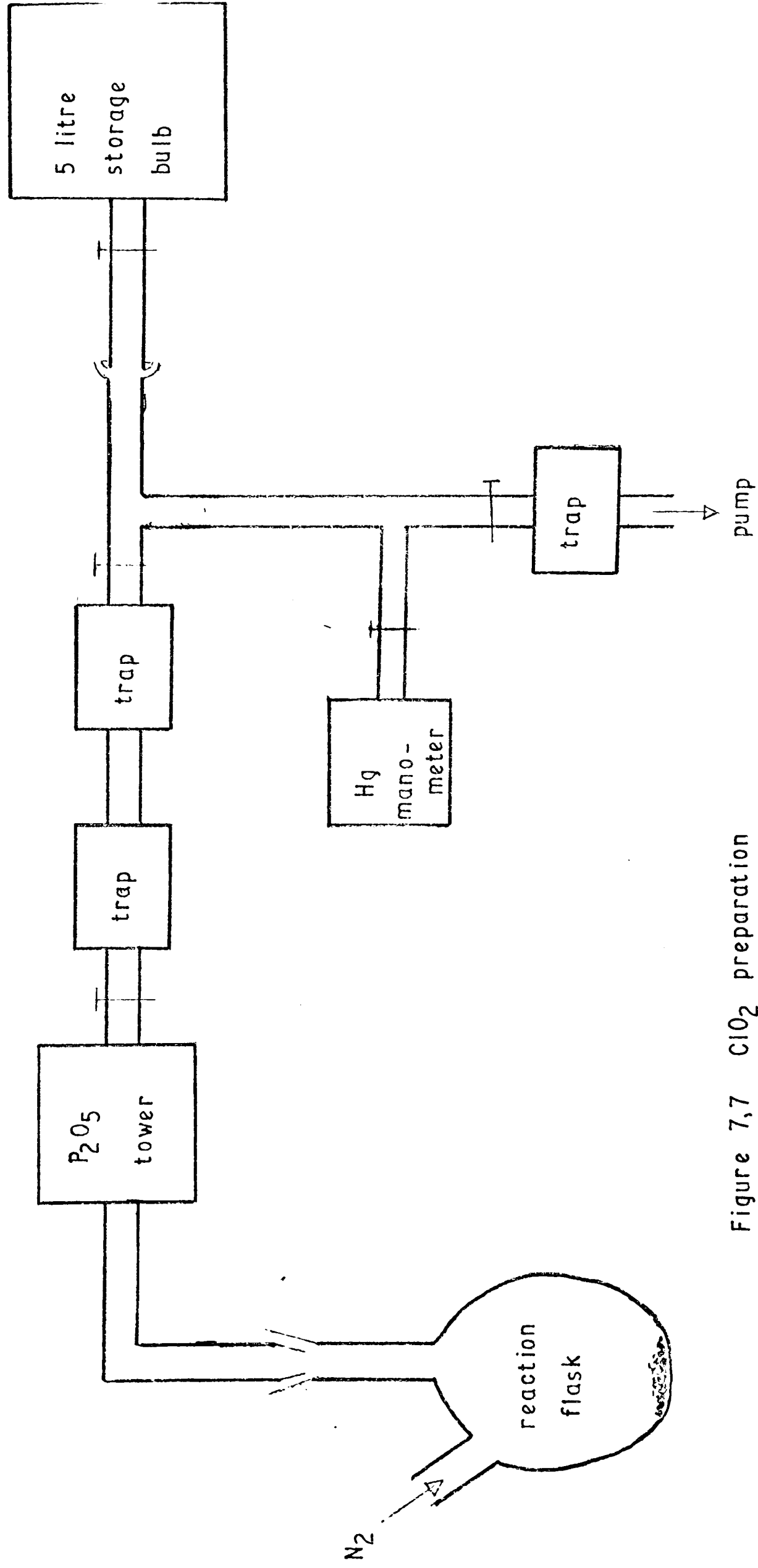


Figure 7,7 ClO_2 preparation

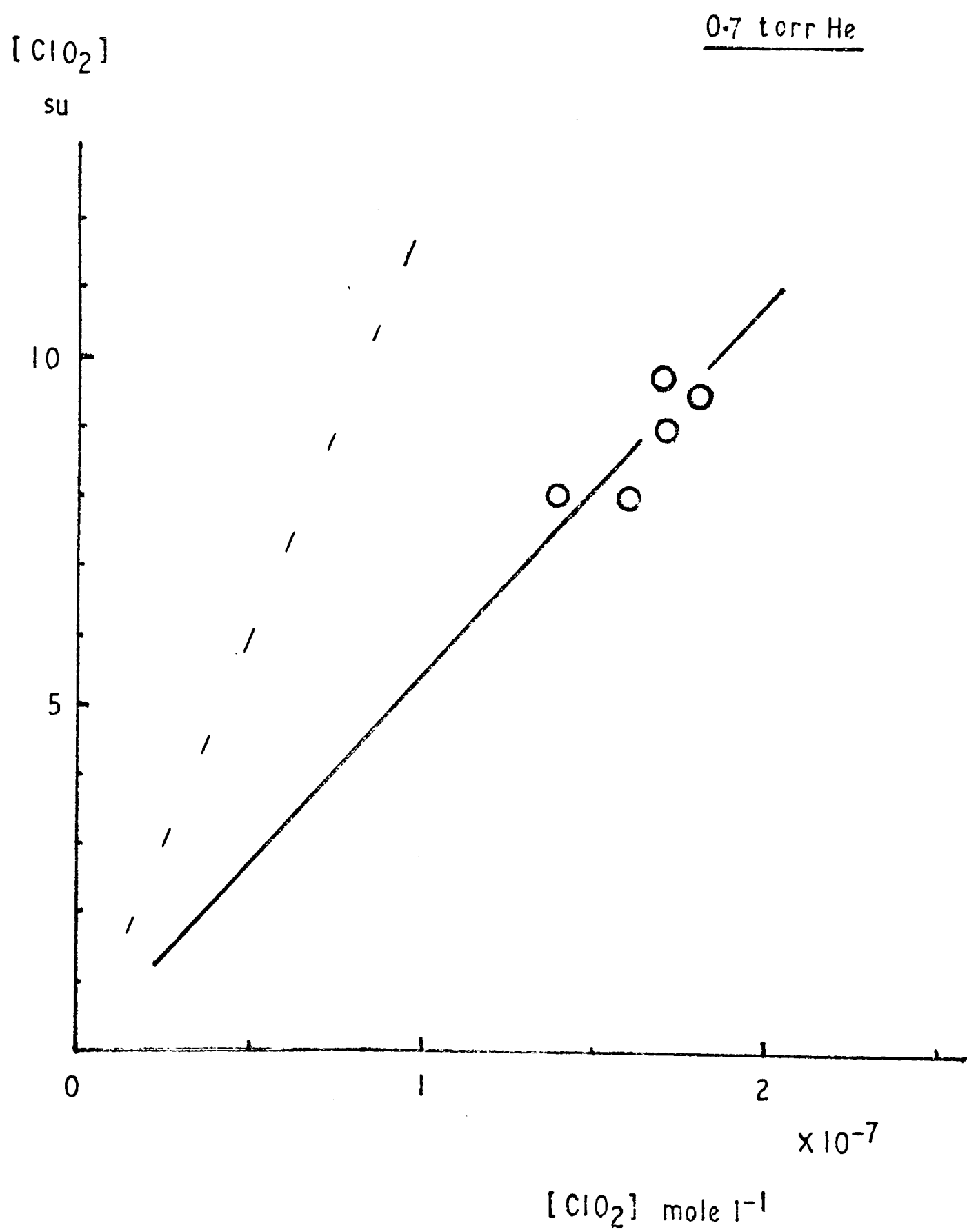
reaction 3 to 6 hours) the liquid nitrogen trap was replaced by a cardice-trichlorethylene trap and the CO_2 pumped off. The remaining chlorine dioxide was then allowed to warm up and fill the evaluated storage bulb. The purity of the sample was established from its UV optical density at $3515\text{\AA}$. Here the peak of the UV absorption occurs with ϵ equal to approximately $3000 \text{ l, cm}^{-1} \text{ mole}^{-1}$.

It was not possible in the time available to obtain any more than a preliminary calibration of the mass spectrometer to ClO_2 in the flow tube, since we were never able to produce ClO_2 consistently in sufficient amounts. It is not necessary to produce pure ClO_2 since its UV absorption around $3500\text{\AA}$ is very strong, whilst that due to chlorine, for example, is rather weak and does not mask the ClO_2 peak to any significant extent even when present in large excess. Figure 7,8a shows a preliminary calibration plot of signal at $m/e = 67.5$ versus $[\text{ClO}_2]$ in the flow tube. Calibration was performed as described in Chapter 3.

The points and the full straight line in the ClO_2 calibration plot express the ClO_2 concentration found by measuring the optical density of the ClO_2 sample on a scanning SP 800 ultraviolet spectrometer ($\epsilon \approx 3000$ at $\lambda = 3520\text{\AA}$). The dotted line reflects the lower purity calculated from measurements of the same sample on an SP 500 spectrometer. The considerable discrepancy is probably a consequence of the low ClO_2 content of the sample. The data are presented as preliminary calibrations in the absence of more reliable data.

Taking as a hypothesis that the peak at $m/e = 66 - 68$ found in the photolysis of O_3/freon mixtures was due to ClO_2 , the concentrations of ClO_2 which would be inferred from the preliminary calibration of the mass spectrometer with respect to ClO_2 are not inconsistent with ClO_2 being a product of the photolysis of

Figure 7,8a MS calibration ClO_2

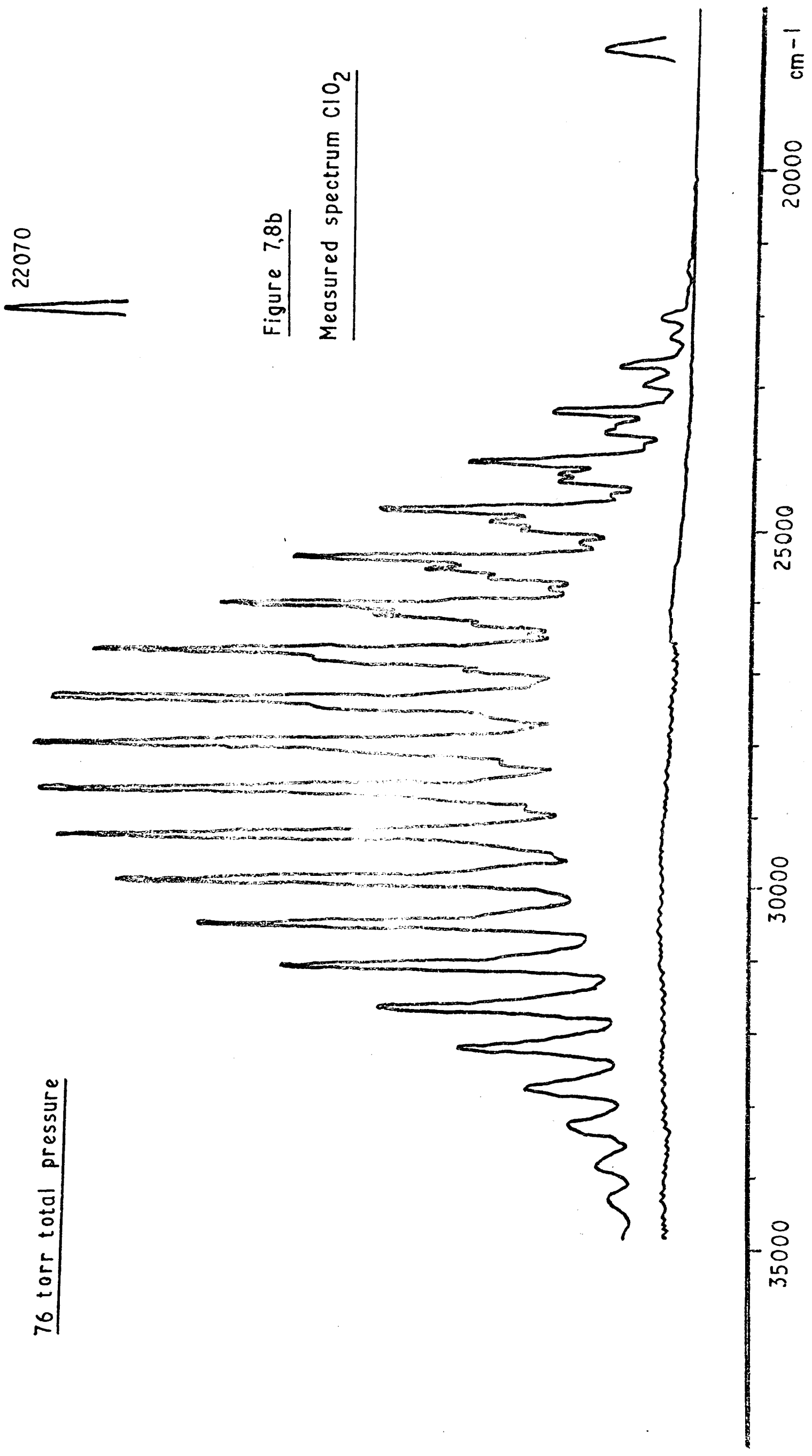


22070

76 torr total pressure

Figure 7,8b

Measured spectrum ClO₂



O₃/freon mixtures.

As shown in Table 7,10 the ratio of signals at m/e = 68 and 48 are generally in the approximate ratio 2.2:100. i.e. a concentration ratio [ClO₂] : [O₃] of about (1.8 - 4.0) x 10⁻⁸ : 1.5 x 10⁻⁷. In order to observe ClO₂ the O(¹D) concentration was increased to generally around 30% by reducing the flow velocity and thereby increasing the fractional photolysis. The ratio [ClO₂] : [O(¹D)] is therefore around (1.8 - 4.0) x 10⁻⁸ : 5 x 10⁻⁸. Thus the efficiency of ClO₂ production for each O(¹D) molecule appears to be in the region 0.4 to 0.8, with an average efficiency of approximately 0.6. This is consistent with ClO₂ being a reaction product.

7,5 Results and Interpretation of ozone-freon Experiments.

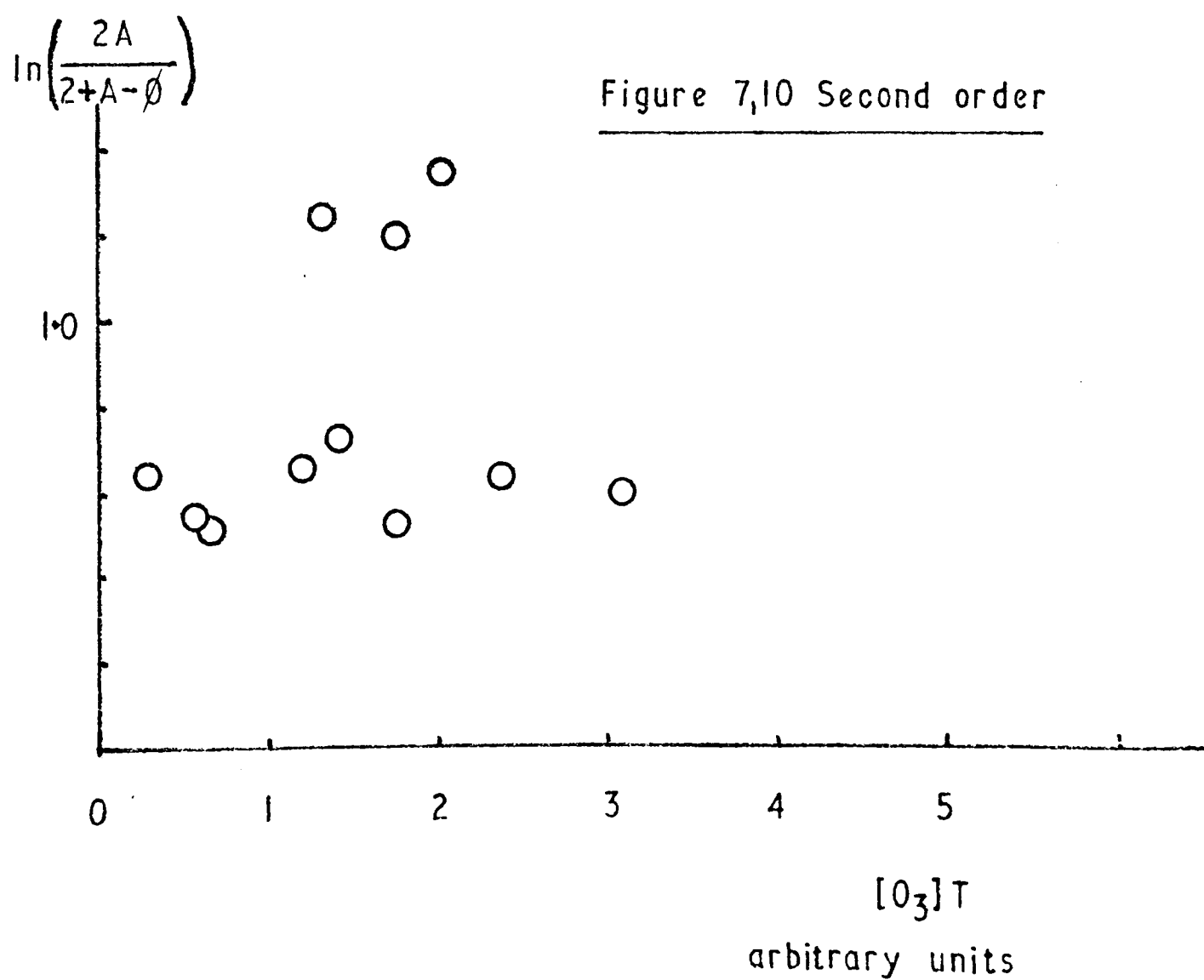
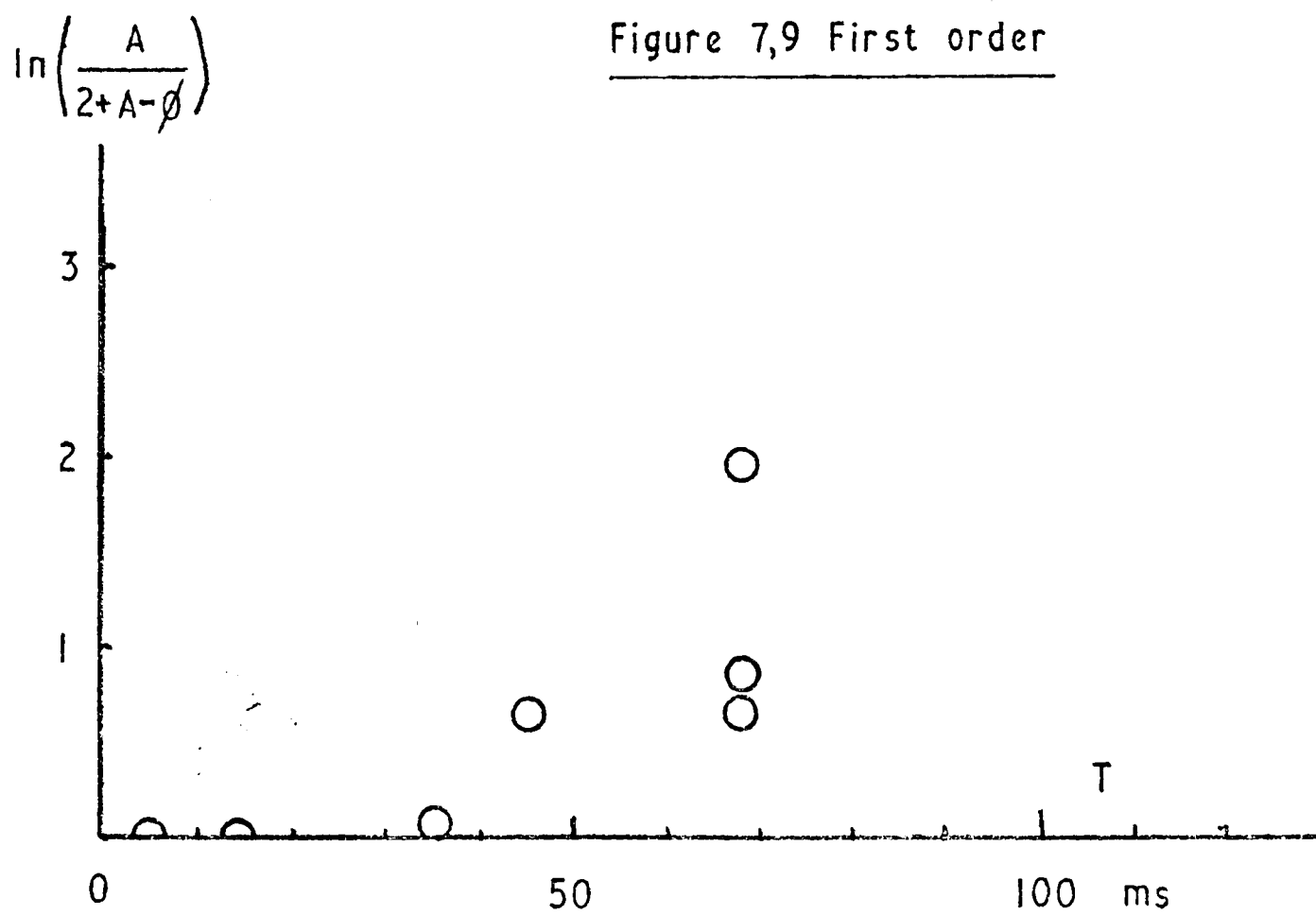
As explained in section 7,3 consideration of previously published work indicated that the photolysis of O_3 /freon mixtures might be expected to follow the simple first or second order kinetics described in that section. A third alternative, wherein all the reactions whose rate constants were unknown went to completion (viz. R108 and R109 in the case of O_3/CF_2Cl_2 photolysis), was quickly discounted when preliminary experiments showed that the experimental quantum yields were inconsistent with the relative quantum yield of 3.0 predicted by this alternative.

In the preliminary experiments O_3/CF_2Cl_2 mixtures were photolysed in helium carrier gas. Figure 7,9 shows a first order plot of the initial results. The data do not lie on a straight line through the origin, as would be expected if the kinetics showed a first order dependence.

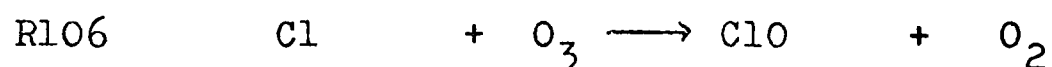
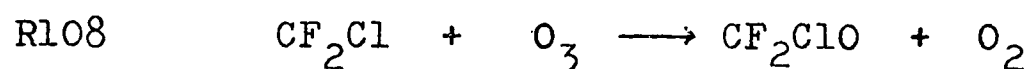
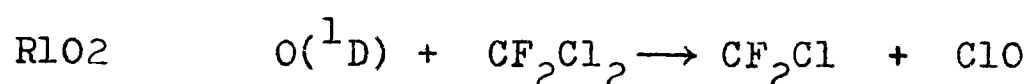
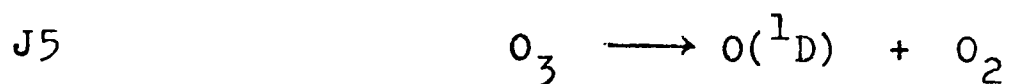
The same data, and some of the subsequent data are plotted according to the predicted second order kinetic relationship in Figure 7,10. The preliminary data (seven points at flow pressures of 1.024 and 0.986 torr helium) appeared to lie on a straight line through the origin; however, data obtained subsequently showed no dependence on $[O_3]T$, within experimental uncertainty. It proved impossible to reproduce the preliminary observations and it is certain that the high quantum yields recorded were due to incorrect measurement of the ozone baseline in these initial experiments after backing-off the background at $m/e = 48$ due to freon fragment ions. Thereafter, as the data in Table 7,7 shows, a relative quantum yield of around 2, independent of T or $[O_3]$, was obtained for the photolysis of O_3/CF_2Cl_2 mixtures.

It was thus established that the data did not fit either of the simple first or second order kinetic schemes in which R 109 or

Plots CF_2Cl_2 data



R108, respectively, is the rate determining step. Moreover, to be consistent with the reaction scheme examined in section 7,3 and reproduced here for convenience, a quantum yield of 2 requires R102 and R108 to have gone to completion whilst R109 has not occurred to any measurable extent i.e. the postulated CF_2ClO species is either stable under our time scale or does not decompose according to R109.



For CF_2ClO to be stable on our time scale puts an upper limit of between 10 and 100 sec^{-1} on the first order rate constant R109. CF_2ClO is an electron deficient radical species like CF_2Cl and therefore even if R109 were slower than 10 - 100 sec^{-1} it would be remarkable if the reaction $\text{CF}_2\text{ClO} + \text{O}_3$ (R110) had an even longer half life. This would require R110 $< 1 \times 10^8 \text{ l mole}^{-1} \text{ s}^{-1}$ whilst at the same time the analogous reaction of CF_2Cl occurred at a rate approaching the gas kinetic rate i.e. R108 = 1×10^{10} to $1 \times 10^{11} \text{ l mole}^{-1} \text{ s}^{-1}$.

Whilst such an oversimplified comparison of postulated radical reaction rates is not meant to be in any way conclusive, it is all the same difficult not to be sceptical of a reaction scheme which requires the hypothetical CF_2ClO species to be stable with respect both to unimolecular decomposition and to reaction with ozone.

Before continuing any further it would be desirable to examine the evidence that reaction between $O(^1D)$ and freons indeed occurs. A quantum yield of 2 is that quantum yield which would also be expected from the photolysis of O_3 in helium in the absence of freon.

As discussed already in section 7,1, both in the work of Pitts, Sandoval and Atkinson (1974) and in the work of Jayanty, Simonaitis and Heicklen (1975) the reaction rate of $O(^1D)$ with various freons is measured to be close the gas kinetic frequency. It is of interest to note that the relative reaction rate constants quoted by Jayanty et al (see Table 7,3) increase monotonically with increasing chlorine content of the freon. Thus the relative rate constants for reaction of $O(^1D)$ with CF_3Cl , CF_2Cl_2 , $CFCl_3$, and CCl_4 were measured to be 0.52, 1.2, 1.5 and 2.1 respectively. The ratio is remarkably close to 1: 2: 3: 4 - the ratio of the number of chlorine atoms in the respective freon molecules. This circumstantial evidence is in accord with the findings of section 7,2 wherein the totally fluorinated CF_4 is shown to result in the loss of an $O(^1D)$ atom on less than approximately 1 in 10^4 collisions, and points to the reaction of $O(^1D)$ with freons involving chlorine atoms in the freon molecule.

Both the aforementioned groups of workers identified products arising from the static photolysis of O_3 /freon mixtures. Pitts et al. identified CF_2O by IR absorption whilst Jayanty et al. inferred the presence of CF_2O , which was analysed gas chromatographically as carbon dioxide. The quantitative yields of these products ruled against the reaction being initiated by products from the ultraviolet photolysis of the freons; none of which (with the possible exception of CCl_4) has any significant absorption at the photolysis wavelengths used. At this point we are not concerned with the nature

of the products but with the fact that products which indicate that reaction has occurred between $O(^1D)$ and the freon, are formed.

Experimentally it has been observed that the F^+ ($m/e = 19$) peak remains constant and does not depend on the photolysis lamp, whilst a strong increase in the Cl^+ ($m/e = 36$) peak is observed when the photolysis lamp is on. This points to the formation of some chlorine containing species which fragment inside the mass spectrometer to form Cl^+ more easily than does the parent freon. Chlorine atoms if formed will be present in the flow tube only in very low concentration due to their fast reaction with ozone. It is unlikely that sufficient of these Cl atoms will survive passage through the pinhole inlet to account for the observed increase in the Cl^+ peak.

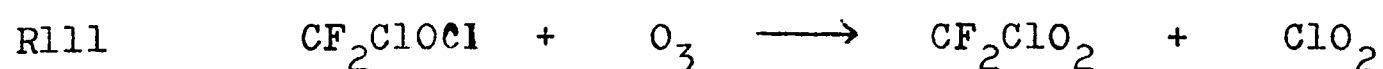
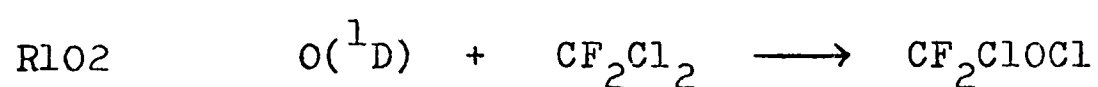
No decreases in any of the freon peaks (the parent mass peaks were not generally observed) in response to the flashing photolysis lamp were detected. This test would have unequivocally proved that reaction involving the freon occurs. Under normal conditions of excess freon the freon concentration is several hundred times greater than the ozone concentration. Since the $O(^1D)$ concentration produced is generally only about 5% of the ozone concentration, percentage changes in the freon concentration consequent on reaction amount to less than 0.1%. The most favourable conditions for observing a decrease in freon concentration occur when the rate of $O(^1D)$ reaction with ozone and with the freon is equal, since then, for example, for a 5% photolysis of ozone a 2.5% change in freon concentration should be observed. However, despite apparently favourable signal-to-noise ratios in many cases the expected decrease in freon fragment peak was never detected.

Other experimental tests to be described viz. the addition of NO to O_3 /freon mixtures after photolysis, and the observation of

a product ion peak at $m/e \approx 68$ have confirmed that reaction between $O(^1D)$ and the freons (except CF_4) does in fact occur.

In order to obtain more information about the reaction mechanism, as described in section 7.4, the mass spectrometer was calibrated with respect to ClO and ClO_2 concentrations in the flow tube. Observations had shown the presence of a product peak at $m/e \approx 68$, but had failed to show the presence of ClO^+ ($m/e = 51$). The calibrations showed that if ClO were produced with unit efficiency from the photolysis of O_3 /freon mixtures it should produce a detectable change at $m/e = 51$. However, since the $m/e = 51$ mass spectral region was overlapped by the ozone signal and the freon background it would not be possible to positively detect ClO if produced with an efficiency of, say, less than 0.5.

The product peak at $m/e \approx 68$ could be due either to ClO_2^+ or to CF_2O^+ (or both). It is unlikely that it could be due to Cl_2^+ at $m/e = 71$ in view of the gross miscalibration which would be involved. It was envisaged that ClO_2 could perhaps be produced as a result of an insertion reaction of $O(^1D)$ and the freon followed by reaction of the product with ozone.



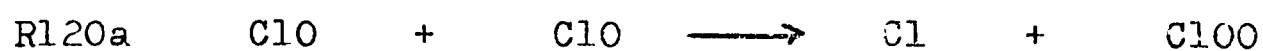
To check these schemes diagnostic tests involving the photolysis of ozone with freons other than CF_2Cl_2 were performed.

If the peak at $m/e \approx 68$ were due to CF_2O^+ it would not be observed in the photolysis of $CFCl_3$ and ozone, since the $CFCl_3$ molecule only contains one fluorine atom. Were the $m/e \approx 68$ peak due to ClO_2^+ it would be observed in the photolysis of any of the chlorine containing freons, but only if it involved an insertion reaction.

If ClO were abstracted with unit efficiency on the reaction of $O(^1D)$ with the freon and the ClO_2 were the product of some secondary reaction of the freon fragment with ozone, then no ClO_2^+ would be observed in the case of the photolysis of freons containing only one chlorine atom, e.g. CF_3Cl with ozone.

The experimental results are shown in the third and fourth columns of Table 7,10. A product peak was observed in the photolysis of $O_3/CFCl_3$ mixtures, wherein CF_2O cannot be a product, in approximately the same amount for a given amount of $O(^1D)$ produced as in the case of other freons. Photolysis of O_3/CF_2Cl_2 , O_3/CF_3Cl and O_3/CCl_4 mixtures also gave approximately the same amounts of ClO_2^+ , showing that ClO_2 is probably produced as a result of the primary reaction of $O(^1D)$ with the C-Cl bond in the freon.

In an alternative hypothetical reaction model to the production of ClO_2 in consequence of the insertion reaction of $O(^1D)$ and the freon described above, chlorine dioxide ($OCIO$ and/or $ClOO$) is generated indirectly by the reaction of ClO either with itself or with ozone. The bimolecular reaction of ClO with itself,



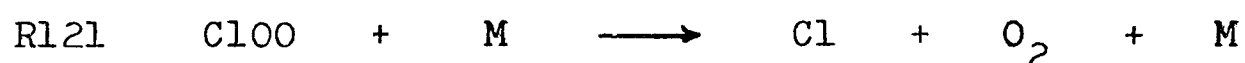
has always been shown to be strictly second order (wall quenching efficiency for ClO on pyrex being apparently very low and the wall loss rate contributing to a negligible extent to the total loss of ClO) with a rate constant $k_{120} = (1.32 \pm 0.18) \times 10^7 \text{ l mole}^{-1} \text{ s}^{-1}$ (Clyne, McKenney and Watson, 1975). Although $R120b$ is a reversible reaction with an equilibrium constant $R120b/R120$ at 298K calculated by Clyne et al. (1975) to be 0.04, the reaction in our system should go essentially to completion

owing to the removal of Cl atoms by reaction with ozone which is present in excess. However, the work of the above-mentioned authors shows that OClO (the more thermally-stable of the two isomers of chlorine dioxide and which has hitherto been denoted by the formula ClO₂) is produced in R120b with an efficiency of only about 0.05 with respect to the overall reaction R120.

In view of the fact that the results of the preliminary calibration of the mass spectrometer to ClO₂ (i.e. OClO) were consistent with a unity efficiency for the production of OClO from O(¹D), it is believed that R120b cannot account for the observed chlorine dioxide concentrations.

The pathway R120a which generates ClOO has been shown by Clyne et al. (1975) to be the major pathway at 298K.

However, the ClOO ^eproxy radical decays rapidly at 298K due to the reaction



It has been suggested that K_{121} lies within the range $2 \times 10^6 \leq k_{121} \leq 3 \times 10^8 \text{ l mole}^{-1} \text{ s}^{-1}$ based on estimates of ΔH_f° 298 and the reverse reaction. At 1 torr total flow tube pressure the longest corresponding half-life for ClOO loss would be 7 ms. Since the $m/e \approx 68$ signal attributed to ClO₂ was observed at contact times very much longer than this, this signal is unlikely to be due to the ClOO isomer.

In addition, the Cl atoms generated in R120 and R121, would lead to an increased quantum yield for the decomposition of ozone concurrent with the observation of the $m/e \approx 68$ signals. Such quantum yield enhancements might, on the basis of observations of an efficiency of 0.5 for the production of Cl atoms in R121 found by Clyne et al. (1975) be expected to be in the region of 0.75 - an increment which would have been observable in our

experiments.

Finally, probably the most significant argument against the formation of ClO_2 by the bimolecular homogenous recombination of ClO molecules is that reaction R120 is too slow. Based on pseudo-first order estimates of the ClO lifetimes with respect to reaction R120 under our experimental conditions, the half-life of the reaction is about one hundred times longer than the reaction times at which products with mass numbers of approximately 68 were observed.

Generation of OClO by the reaction $\text{ClO} + \text{O}_3$ (R105) may also be discounted on similar grounds since R105 is apparently too slow to generate significant amounts of ClO_2 at the reaction times employed.

($k_{105} \approx 3 \times 10^6 \text{ mole}^{-1} \text{ s}^{-1}$; Clyne et al. 1975).

Moreover, it is observed that the addition of NO downstream of the lamp zone does not effect the size of the ClO_2^+ peak. If ClO_2 were generated by the reaction $\text{ClO} + \text{O}_3$ or by the reaction $\text{ClO} + \text{ClO}$ then the addition of NO would considerably reduce the ClO concentration due to the fast reaction

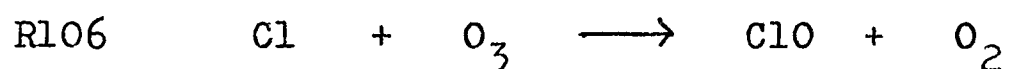
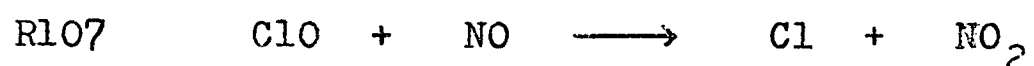


and thereby greatly reduce the amount of ClO_2 produced. It is also observed that altering the contact time T by moving the photolysis lamp up and down the flow tube also has no effect on the ClO_2^+ peak, which would imply that R105 had gone to completion and require k_{105} to be some four orders of magnitude higher than its presently accepted value.

The body of evidence thus favours the identification of the

$m/e \approx 68$ peak as being ClO_2^+ rather than CF_2O^+ . The preliminary calibration of the mass spectrometer to ClO_2 is consistent with ClO_2 being produced with freon about 40 to 80% efficiency from the reaction of $\text{O}(^1\text{D})$ with freon.

These conclusions were rather surprising since it has always been accepted that ClO is generated by the reaction of $\text{O}(^1\text{D})$ and chlorine containing freons. Initial experiments were, however, unable to demonstrate the production of ClO , either by direct observations of $m/e = 51$ or by inference from the addition of NO to the photolysis mixture downstream of the lamp zone. The addition of NO did not appear to cause a chain decomposition of ozone according to the scheme



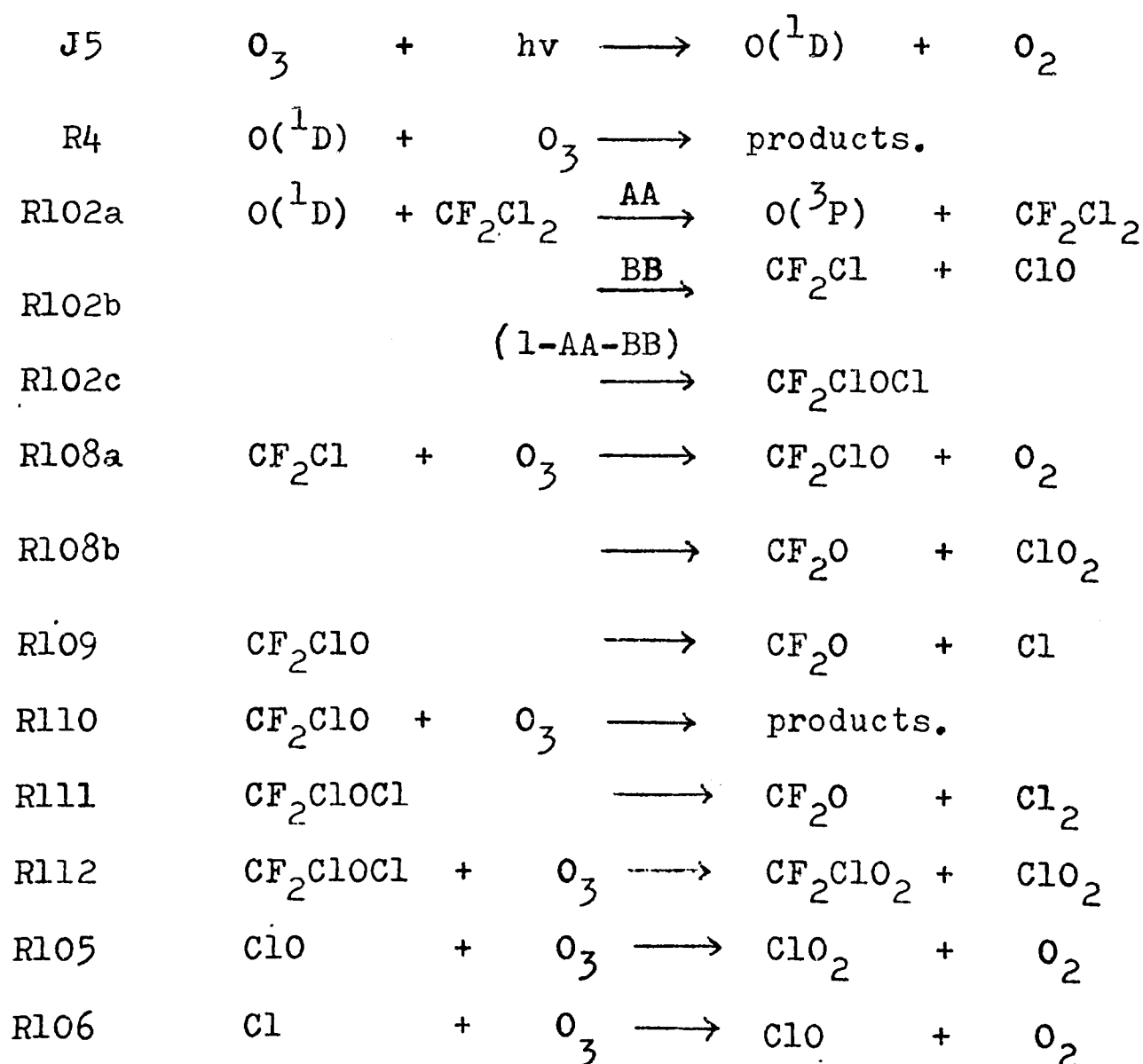
However, subsequent experiments using much higher NO concentrations than had initially been thought to be sufficient have indeed demonstrated enhancements in the ozone decomposition relative quantum yields in the (see Table 7,10) $\text{O}_3/\text{CF}_3\text{Cl}/\text{NO}$, $\text{O}_3/\text{CF}_2\text{Cl}_2/\text{NO}$ and $\text{O}_3/\text{CFCl}_3/\text{NO}$ photolytic systems. The analogous $\text{O}_3/\text{CCl}_4/\text{NO}$ experiment has not yet been attempted due to the lack of time available.

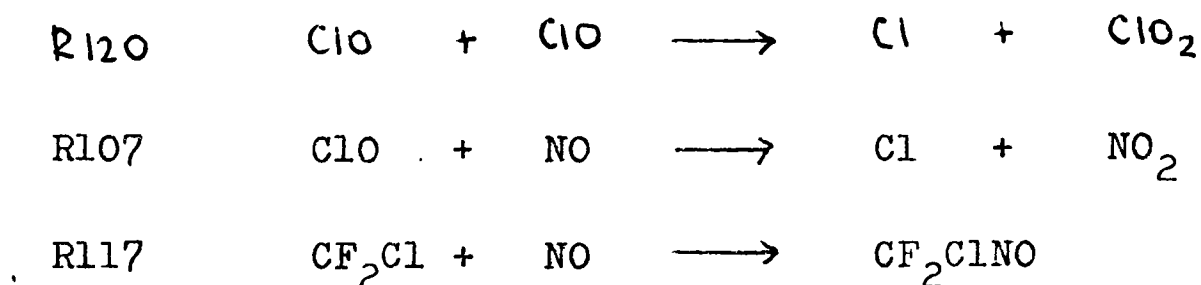
The reason for the initial lack of success was that the enhancement was much smaller than expected and almost always less than a unity increment of quantum yield. This is surprising in the apparent absence of any fast ClO loss processes other than reaction with NO .

The Cl atom wall loss rate is expected to be of the order 100 sec^{-1} , and was in any case demonstrated to be negligible by moving the microwave discharge relative to the ozone inlet in the ClO generation experiments described previously in Section 7,4.

The most plausible explanation of the low quantum yield enhancements attending the addition of NO to the O_3 /freon photolyses is that ClO is in fact produced, but with an efficiency of considerably less than unity. Although it may be that at least some of the reason for the lower than expected enhancements is due to reaction of NO with CF_2Cl (in the case of $O_3/CF_2Cl_2/NO$ photolysis) or other species, and consequent reduction of the basic quantum yield (i.e. the observed quantum yield after subtraction of the enhancement due to the ClO/NO chain) below the value of 2.

The experimental observations appear to show, therefore, that ClO is produced with less than 100% efficiency and also that ClO_2 is produced with around 60% efficiency on the reaction of $O(^1D)$ with freons. The third piece of relevant information is that the basic quantum yield (in the absence of NO) for O_3/CF_2Cl_2 photolysis is two. The following experimental scheme (shown also in Table 7,2b) was developed to account for these three facts.





In the absence of added NO the quantum yield for the photolysis of $\text{O}_3/\text{CF}_2\text{Cl}_2$ mixtures is predicted to be 2.0 (J5: R102 followed by R108a or R108b^{then R112}). If R108a occurs then, provided that the product CF_2ClO is stable, the quantum yield will be 2.0; if R109 occurs rapidly then the quantum yield will be $(2.0 + \text{BB})$ since R109 is followed by the fast reaction $\text{Cl} + \text{O}_3$ (R106).

The quantum yield, however, is observed to be approximately 2. It is therefore likely, in accordance with the previous observations on the probable lifetime of CF_2ClO in our system, that R108b rather than R108a occurs. It is unlikely, however, that R108b is the sole source of ClO_2 .

Let us make the assumption that the reaction of $\text{O}(^1\text{D})$ with freons occurs in an analogous way for the freons CF_3Cl , CF_2Cl_2 , CFCl_3 and for CCl_4 . Anticipating the results of the computer simulation to be described later in this section, it was found that the abstraction of ClO in R102c was a minor pathway. This means that the amount of ClO_2 produced in R108b is less than that produced in the reaction $\text{CF}_2\text{ClOCl} + \text{O}_3$ (R111). In the case of the photolysis of $\text{O}_3/\text{CF}_3\text{Cl}$ mixtures it is not possible for R108b to occur since this demands the abstraction of a second chlorine atom. However, observations of the amount of ClO_2 produced by the photolysis of $\text{O}_3/\text{CF}_3\text{Cl}$ mixtures, showed it to be present in qualitatively the same concentrations as the ClO_2 produced in the photolysis of ozone with the other chlorine containing freons. Thus R108b cannot be the only source of ClO_2 .

Another explanation for the basic quantum yield being 2 is that the efficiencies AA and BB is R108a and R108b respectively are

equal, and that R108a is followed by the rapid reactions R109 and R106. It is unlikely that R102a is a major pathway, however, in view of the almost quantitative yield of products found by Pitts et al. (1974) and Jayanty et al. (1975) in the static photolysis experiments. The efficiency AA will, therefore, be assured hereafter to be negligibly small.

In order to calculate the efficiency BB of ClO production in R102b and $O_3/CF_2Cl_2/NO$ system and the enhancements to be expected from the addition of given concentrations of NO have been modelled in a computer simulation of the above reaction scheme. Reaction R117' was not included, but its possible effects will be discussed later in connection with the discussion of the photolysis of ozone with the other chlorine containing freons. The total loss rate for ClO in the flow tube was arbitrarily taken to be 300 s^{-1} . The Cl wall loss rate was not included since it is likely to be negligible in the presence of the fast reaction with ozone (R106).

The computer program is included in Appendix 1. An Euler type step integration was used and a sufficient number of integration steps were used such that the use of a larger number of steps did not alter the resulting concentrations. To avoid the very large errors attending the application of this simple approach to the build up from zero and fast drop back to zero of $O(^1D)$ concentrations, the products of reaction R102 were allowed to be present at the start of the simulation.

The program also allows for optionally including R110 and R112. In general R110 was not included. The rate of R109 was set to the maximum value of $2.1 \times 10^7\text{ sec}^{-1}$ which was estimated on the basis of decomposition on every collision with a helium carrier

gas molecule. The inclusion of R109 however leads to a quantum yield in the absence of NO of $(2.0 + BB)$ which is contrary to experimental observation, and therefore R109 was omitted from the computer reaction scheme for the simulations reported here. The omission of R109 means that the results of the simulation are not dependent on whether the reaction $CF_2Cl + O_3$ goes by route R108a or R108b since neither route generates species which react further with ozone.

R108 was allocated a rate constant $k_{108} = 5 \times 10^{10} \text{ l mole}^{-1} \text{ s}^{-1}$; R110 was allocated a rate constant $k_{110} = 1 \times 10^{10} \text{ l mole}^{-1} \text{ s}^{-1}$, and R112 was allocated a rate constant $k_{112} = 1 \times 10^{10} \text{ l mole}^{-1} \text{ s}^{-1}$. There is no rational behind the choice of these specific values except to ensure that the reactions, when included in the simulation, go essentially to completion on the time scale of these experiments.

The relatively slow reaction $NO + O_3$ (R21) was included in the computer model only as a loss process for NO since only the ozone loss processes consequent on photolysis of ozone contribute to the quantum yield. Reaction R21 reduces the lamp-off background ozone concentration, without affecting the quantum yield, since there are no processes which occur downstream of the lamp zone which are particularly sensitive to $[O_3]$.

Table 7,12 shows the results of the computer simulation predicted on the basis of reactions J5, R4, R102, R108, R112, R105, R106 and R107 only. Reactions R109, R110 and R111 have not been included. The fractional efficiency BB of ClO production in R102b was varied to give the optimum fit to the observed quantum yields in the $O_3/CF_2Cl_2/NO$ system. The best fit value of BB was found to be 0.3.

The quantum yield figures in brackets are the

experimentally obtained results for the same O_3 , CF_2Cl_2 , and NO concentrations. It is clear that there is good agreement, within the error limits, between the experimental and simulated enhancements upon the addition of nitric oxide. The results depend on the choice of the ClO loss rate since, in the absence of a significant sink for ClO, the chain process propagated by reactions R107 and R106 leads to predicted quantum yields which are very much higher than those observed. However, in order for BB to be unity the ClO total loss rate is simulated to be around $1000s^{-1}$. It was found that the experimental results could be modelled satisfactorily (see Table 7,11) using a value of $BB = 0.3$ and a pseudo-first order ClO loss rate (to include all ClO loss processes other than reaction with NO) of around $300s^{-1}$. Modelling using two such adjustable parameters is clearly undesirable; however, reduction of the ClO loss rate below $300s^{-1}$ leads to concomitant reduction of the efficiency BB to surprisingly low values, below even 0.3.

Figure 7,11 shows a sample of the computer output. Calculation shows that, for example, the final chlorine dioxide concentration corresponds closely to the theoretical figure predicted on the basis of production with efficiency $(1 - AA - BB)$ in R102c and R112; and confirms the numerical accuracy of the integration method used.

The photolysis of an O_3/CF_2Cl_2 mixture was carried out in the presence of sulphur hexafluoride as carrier gas instead of helium. Table 7,7 shows that the relative quantum yield measured ($2.17 \pm .13$) was in good agreement with the experiments in helium carrier gas, in giving a quantum yield substantially equal to 2.0.

We shall now consider the results of the photolysis of the other chlorine containing freons with ozone; and the enhancements found on the addition of NO.

Reference to Table 7,10 shows that photolysis of O_3/CF_3Cl mixtures in the presence of excess freon ($A \approx 1.0$) apparently gives a quantum yield of about 1.5. Insufficient data is

Figure 7,11 Output $\text{CF}_2\text{Cl}_2/\text{O}_3/\text{NO}$ simulation

INITIAL O3 = 0.41800?+03
 DELTA O3 = 0.53345?+02
 FREON = 0.20100?+05
 NO = 0.73900?+03
 NO = 0.70253?+03
 TIME IN LAMP = 0.15670?-01
 TIME AFTER LAMP = 0.54700?-01
 FINAL CLO2 = 0.96568?+01
 FINAL F2C = 0.00000?+00
 FINAL F2C2O = 0.50008?-08
 FINAL F2CO = 0.41386?+01
 FINAL CL = 0.39362?+00

T SEC	OZONE	QYIELD	CLO
0.27350?-03	0.40363?+03	0.10207?+01	0.41386?+01
0.30085?-02	0.39090?+03	0.19561?+01	0.12916?+01
0.57435?-02	0.38625?+03	0.23052?+01	0.11258?+01
0.84790?-02	0.38324?+03	0.25332?+01	0.10189?+01
0.11213?-01	0.38091?+03	0.27113?+01	0.92418?+00
0.13948?-01	0.37893?+03	0.28637?+01	0.83894?+00
0.16683?-01	0.37717?+03	0.29992?+01	0.76189?+00
0.19418?-01	0.37559?+03	0.31214?+01	0.69214?+00
0.22153?-01	0.37417?+03	0.32322?+01	0.62894?+00
0.24888?-01	0.37288?+03	0.33330?+01	0.57163?+00
0.27623?-01	0.37171?+03	0.34247?+01	0.51965?+00
0.30358?-01	0.37065?+03	0.35081?+01	0.47248?+00
0.33093?-01	0.36969?+03	0.35840?+01	0.42966?+00
0.35828?-01	0.36881?+03	0.36531?+01	0.39077?+00
0.38563?-01	0.36802?+03	0.37160?+01	0.35545?+00
0.41298?-01	0.36730?+03	0.37732?+01	0.32335?+00
0.44033?-01	0.36664?+03	0.38253?+01	0.29418?+00
0.46768?-01	0.36605?+03	0.38727?+01	0.26766?+00
0.49503?-01	0.36551?+03	0.39158?+01	0.24355?+00
0.52238?-01	0.36502?+03	0.39551?+01	0.22163?+00

CONCS IN UNITS E-10 MOLES PER LITRE

available to determine whether this depends on $[O_3]$ or T . Addition of NO gives both positive and negative enhancements in the quantum yield (see Figure 7,12). This fact is clearly shown by the pairs of alternate runs with and without added NO, at the flow pressure of 1.416. The small positive enhancements implies that ClO is present. The negative enhancements in the presence of larger NO concentrations imply that in addition NO is competing successfully for a species reactive with ozone. In the presence of large excess of NO the quantum yield approaches 1.

Considering our proposed reaction scheme, we may speculate that the CF_3Cl analogue of R108 and/or R112 does not occur quickly or indeed at all. In addition the injection of increasing amounts of NO reduce the quantum yield thereby implying that NO competes with ozone for either or both of the postulated species CF_3OCl or CF_3 . Further work is required before any definitive conclusions can be arrived at.

The results of the $O_3/CFCl_3$ experiments are shown in Table 7,8. In the absence of NO the quantum yield appears to increase with increasing T up to a value of around 1.7 (see Figure 7,13), however, most of the data has been obtained at similar values of $[O_3]$ so that it is difficult to determine whether $[O_3]$ is also an important parameter. The addition of NO, again produces much smaller enhancements than in the O_3/CF_2Cl_2 experiments, however, this may be due to some counterbalancing reaction involving NO such as competition with ozone in a reaction analogous to R117. Again a better understanding of the important processes is required before any detailed quantitative conclusions may be reached.

The photolysis of O_3/CCl_4 mixtures gives quantum yields in the region 2 to 4, with an average value of 3.3 which shows

Figure 7,12 Photolysis $\text{CF}_3\text{Cl} / \text{O}_3 / \text{NO}$

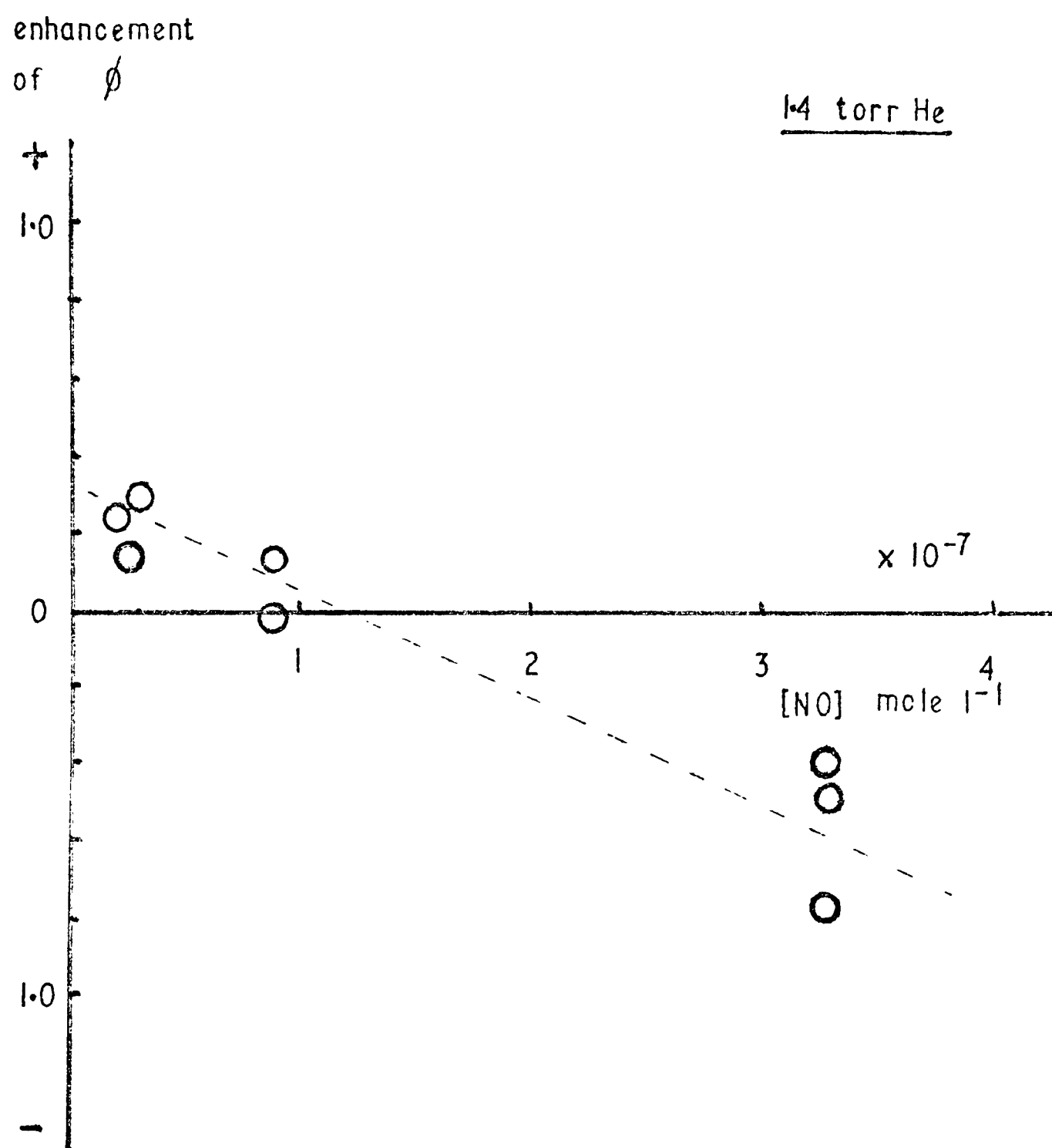
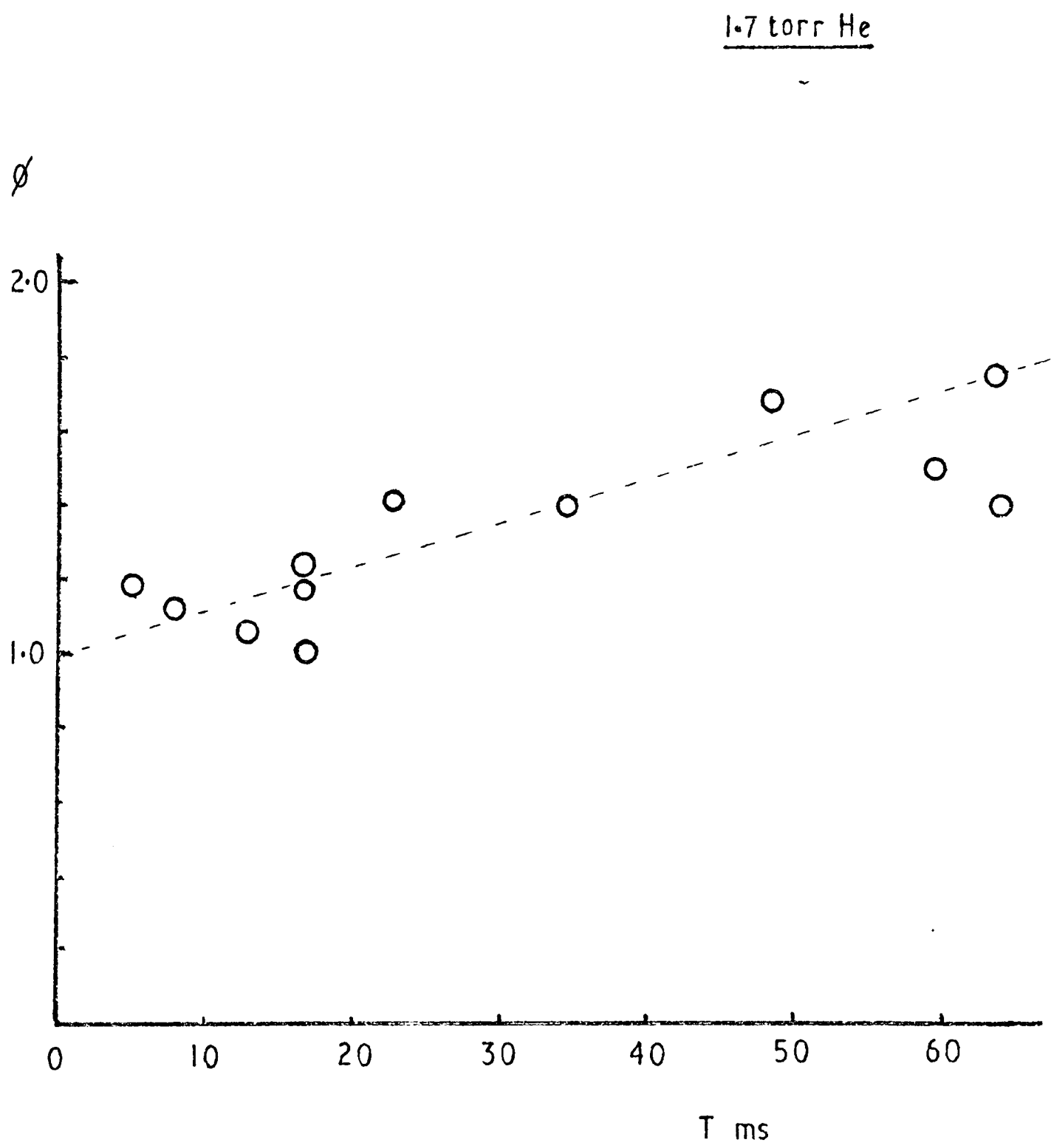


Figure 7,13 Photolysis CFCl_3/O_3



no apparent dependence on $[O_3]$ or T . It is possible that the quantum yield is affected by small amounts of CCl_4 UV photolysis products, particularly chlorine atoms.

The above results are in no way regarded as conclusive, although it is noted that the efficiency $BB = 0.3$ for ClO production from the reaction $O(^1D) + CF_2Cl_2$ agrees, with reasonable limits, to a recent value of 0.4 obtained by Gillespie and Donovan (1976) for the same process, and the ad hoc reaction scheme leaves many questions unanswered, particularly with respect to the freons CF_3Cl , $CFCl_3$ and CCl_4 . It is hoped that the final section of this Chapter will suggest future work to be done in order to define the situation more clearly.

7.6 Future Work.

The data presented in this chapter do not lead to any firm conclusions concerning the mechanism of the attack of $O(^1D)$ atoms on freons, except to confirm that ClO is produced, probably with less than unit efficiency. The three questions remaining are thus: what is the quantitative value of the branching ratio; what are the products of the complementary pathway; and, what is the nature of secondary reactions and their effect on the quantum yield.

In order to provide an answer to the first question it is necessary to measure the wall loss rate for ClO , although it is unlikely to be faster than the reaction $ClO + ClO$, so that it may be fed into the computer simulation. By generating Cl atoms at a fixed point upstream in relation to the sampling zone and adding O_3 to generate ClO at inlet jets of varying distance from the Cl inlet it should be possible to measure any ClO wall loss by observation of the time dependence of the ClO^+ peak; whilst the decay of Cl atoms before reaction with ozone may be monitored by monitoring the decrease in O_3^+ due to addition of Cl atoms.

To positively identify the $m/e \approx 65$ peak it will be necessary to calibrate the mass scale accurately by the use of a tracer with similar mass number. This may be ClO_2 ; and the calibrations with respect to this compound should be completed. Similar calibrations may be performed for CF_2O .

The nature of the secondary reactions should become clearer when the primary processes have been elucidated.

TABLE 7,2a

Freon/O₃/NO System-Selection of
Preliminary/Secondary Reactions.

J5	O ₃	+	hν (λ =2537Å)	→	O(¹ D)	+	O ₂ (¹ Δ _g)
R4	O(¹ D)	+	O ₃	→	products.		
R120	O(¹ D)	+	SF ₆	→	O(³ P)	+	SF ₆
R100	O(¹ D)	+	CF ₄	→	O(³ P)	+	CF ₄
R101	O(¹ D)	+	CF ₃ Cl	→	CF ₃	+	ClO
				→	CF ₃ OC1		
R102	O(¹ D)	+	CF ₂ Cl ₂	→	CF ₂ Cl	+	ClO
				→	CF ₂ ClOC1		
R103	O(¹ D)	+	CFC1 ₃	→	CFC1 ₂	+	ClO
				→	CFC1 ₂ OC1		
R104	O(¹ D)	+	CCl ₄	→	CCl ₃	+	ClO
				→	CCl ₃ OC1		
R105	ClO	+	O ₃	→	ClO ₂	+	O ₂
R106	Cl	+	O ₃	→	ClO	+	O ₂
R107	ClO	+	NO	→	Cl	+	O ₂
R21	NO	+	O ₃	→	NO ₂	+	O ₃
R118	ClO	+	O	→	Cl	+	O ₂

TABLE 7,2b

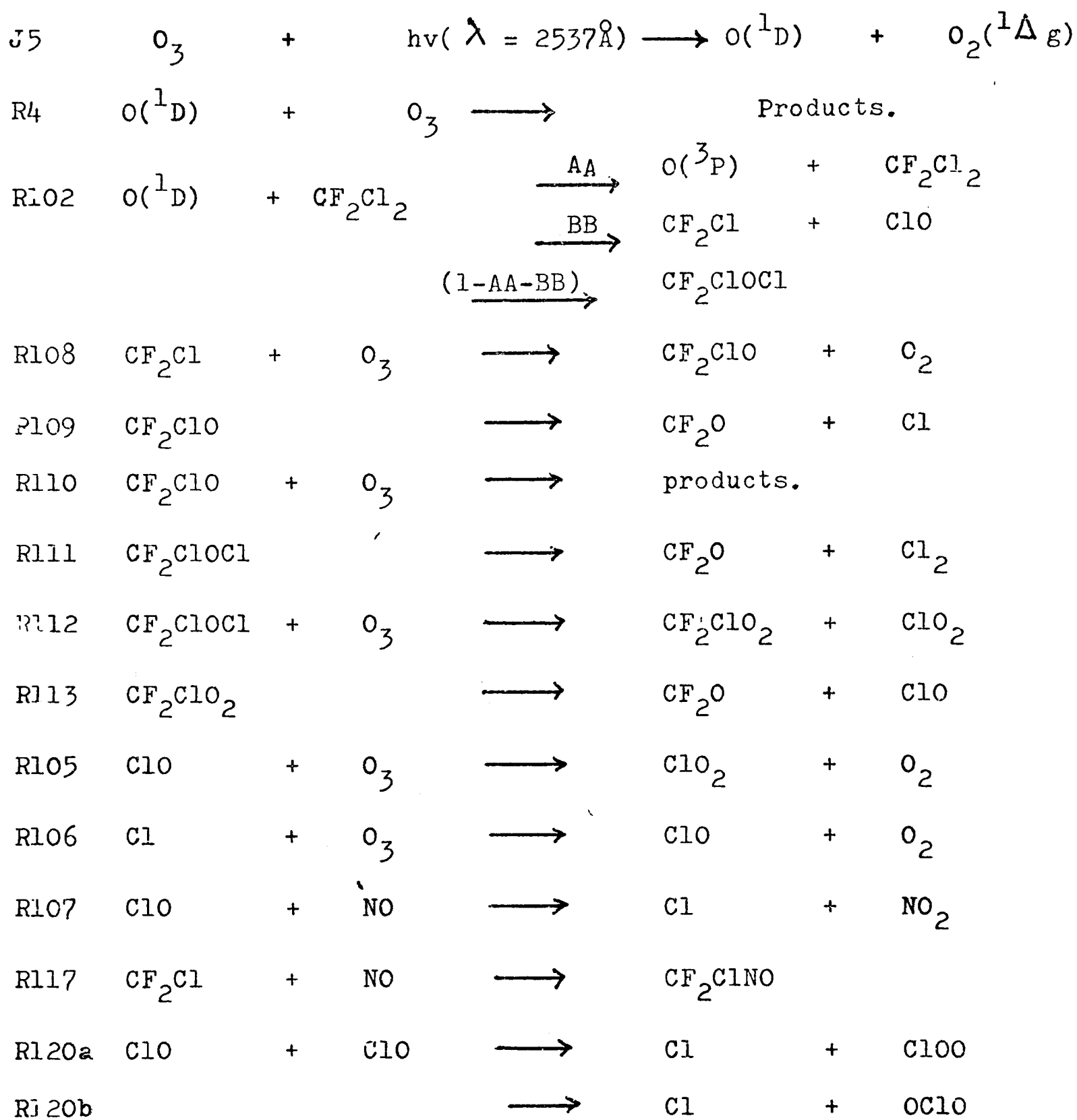
CF₂Cl₂/O₃/NO System - Reaction Scheme.

TABLE 7.3

Relative * Rate Constants - Freon/O₃/NO Systems.

Reaction	Jayanty et al (1975)	Pitts et al (1974)
R4 O(¹ D) + O ₃	2.5	-
R100 O(¹ D) + CF ₄	-	< 0.1
R101 O(¹ D) + CF ₃ Cl	0.52	-
R102 O(¹ D) + CF ₂ Cl ₂	1.2	2.4 ⁺ 0.3
R103 O(¹ D) + CFC1 ₃	1.5	2.7 ⁺ 0.4
R104 O(¹ D) + CCl ₄	2.1	-
R114 O(¹ D) + CHF ₂ Cl	-	1.6 ⁺ 0.2
R115 O(¹ D) + CF ₂ Cl. CF ₂ Cl	-	1.5 ⁺ 0.2
R116 O(¹ D) + CF ₂ Cl. CFC1 ₂	-	2.5 ⁺ 0.3

* Relative to the reaction O(¹D) + N₂O

where k_{N₂O} = (1.32 ⁺ 0.12) x 10¹⁰ mole l⁻¹ s⁻¹

TABLE 7,3 (cont)

Absolute Rate Constants.

Second order rate constant units: $\text{l mole}^{-1} \text{s}^{-1}$

Reaction.				Rate constant.	Reference.
R105				$\leq 3 \times 10^6$	Clyne and Watson (1974)
R106				$(1.1 \pm 0.2) \times 10^{10}$	Clyne and Watson (1974)
R107				$(1.0 \pm 0.1) \times 10^{10}$	Clyne and Watson (1974)
R119				$(3.0 \pm 0.3) \times 10^8$	Bemand, Clyne and Watson (1973).
R118				$(3.2 \pm 0.5) \times 10^{10}$	Bemand, Clyne and Watson (1973)
R120				$(1.3 \pm 0.2) \times 10^7$	Clyne, McKenney and Watson (1975).

TABLE 7.¹Photolysis of SF₆/O₃ Mixtures - Data.

[SF ₆] flow press. torr.	[O ₃] x 10 ⁸ mole l ⁻¹	[SF ₆] x 10 ⁵ mole l ⁻¹	$\frac{[\text{SF}_6]}{[\text{O}_3]}$	T ms	t ms	Number of points	$(\phi - 1)^{-1}$	Relative quantum yield.	Standar deviat
0.450	6.34	2.46	387	53	13.97	36	1.110	1.901 [*]	.242
0.673	6.39	3.68	576	58	15.22	37	1.035	1.966 [*]	.205
0.805	5.69	4.40	773	59	15.44	33	1.027	1.974 [*]	.256
1.074	4.60	5.87	1276	64	16.71	44	1.335	1.749 [*]	.293
1.281	6.58	7.01	1065	65	17.06	29	1.272	1.786 [*]	.128
0.377	9.56	2.06	216	39	10.24	46	1.046	1.956 [*]	.325
0.817	5.58	4.46	700	55	14.34	34	1.799	1.556 [*]	.312
1.199	5.51	6.55	1189	57	14.88	38	1.376	1.727 [*]	.260
1.550	4.41	8.48	1920	89	25.55	22	1.563	1.640	-
1.550	3.29	8.48	2572	89	25.55	22	1.277	1.783	-
1.550	2.22	8.48	3819	89	25.55	18	1.715	1.583	-
1.550	1.45	8.48	5852	89	25.55	24	2.212	1.452	-
1.550	4.55	8.48	1864	89	25.55	20	1.266	1.790	-

SF₆ cont.

TABLE 7.4 (cont)

* Corrected for the presence of an intercept, as described in Chapter 4

ϕ - Relative quantum yield

$$(\phi - 1.0)^{-1} = 1 + k_{120} [SF_6] / k_4 [O_3]$$

TABLE 7.5 Photolysis of CF₄/O₃ Mixtures - Preliminary Data.

[CF ₄] flow press. torr,	[O ₃] x 10 ⁸ mole l ⁻¹	[CF ₄] x 10 ⁵ mole l ⁻¹	$\frac{[CF_4]}{[O_3]}$	T ms	t ms	Number of points	($\phi-1$) ⁻¹	Relative Quantum Yield	Standard deviation.
0.904	7.63	4.95	648	9.2	16.70	34	0.80	2.25	-
0.904	5.66	4.95	875	9.2	16.70	36	1.05	1.95	-
1.504	5.40	8.23	1524	8.1	14.67	24	1.47	1.68	-

ϕ - Relative quantum yield.

$$(\phi - 1.0)^{-1} = 1 + k_{100} [CF_4] / k_4 [O_3]$$

TABLE 7.6 Photolysis of CF₃ Cl/O₃/NO Mixtures - Data.

Helium flow press. torr.	[O ₃] x 10 ⁸ mole l ⁻¹	[freon] x 10 ⁶ mole l ⁻¹	[NO] x 10 ⁸ mole l ⁻¹	T ms	t ms	Number of points	A	Relative Quantum Yield	Standard deviation.
1.554	3.82	-	-	62	17.04	22	-	2.059	.124
	4.48	0.32	-	62	17.04	26	0.602	1.725	.123
	3.54	0.28	-	62	17.04	20	0.621	1.898	.126
	2.33	0.27	-	62	17.04	20	0.704	1.819	.110
	2.15	0.26	-	34	17.04	18	0.713	1.502	.207
	5.40	0.24	-	34	17.04	20	0.479	2.073	.170
	4.64	0.22	-	9.4	17.04	22	0.498	1.846	.145
	2.95	0.21	-	9.4	17.04	20	0.594	1.574	.111
	4.23	0.19	1.39	63	17.04	20	0.487	2.115	.076
	5.04	0.19	2.69	63	17.04	20	0.444	1.982	.095
	3.24	0.19	2.69	63	17.04	20	0.555	1.853	.207

/ CF₃Cl cont.

TABLE 7.6 (cont)

Helium flow press. torr	[O ₃] x 10 ⁸ mole l ⁻¹	[freon] x 10 ⁶ mole l ⁻¹	[NO] x 10 ⁸ mole l ⁻¹	T ms	t ms	Number of points	A	Relative Quantum Yield.	Standard deviation
1.554	4.46	0.19	-	63	17.04	12	0.474	1.852	.127
	3.93	0.19	2.69	63	17.04	16	0.505	1.856	.169
	2.89	1.73	3.12	63	17.04	22	0.925	1.784	.234
	2.26	1.73	3.12	63	17.04	14	0.941	1.544	.189
1.542	14.43	1.29	-	594	106	14	0.650	1.684	.026
	15.20	1.29	-	106	106	12	0.639	1.648	.062
1.416	6.04	-	-	78	21.72	24	-	1.94*	.12
	6.75	1.96	-	78	21.72	24	0.860	1.49*	.14
	6.75	1.70	2.97	78	21.72	36	0.841	1.78*	.16
	3.59	1.47	-	78	21.72	24	0.896	1.56*	.27
	3.37	1.38	2.43	78	21.72	22	0.896	1.71*	.17

/CF₃Cl cont.

TABLE 7,6 (cont)

Helium flow. Press. torr.	$[O_3]$ $\times 10^8$ mole l^{-1}	$[freon]$ $\times 10^6$ mole l^{-1}	$[NO]$ $\times 10^8$ mole l^{-1}	T ms	t ms	Number of Points	A	Relative Quantum Yield	Standard deviation.
1.416	7.93	1.15	-	78	21.72	20	0.752	1.40*	.09
	8.12	1.00	1.93	78	21.72	20	0.719	1.65*	.14
	5.02	2.44	-	78	21.72	20	0.910	1.23*	.16
	4.52	2.28	8.95	78	21.72	22	0.915	1.21*	.12
	7.27	2.12	-	78	21.72	26	0.858	1.71*	.16
	6.65	1.97	8.95	78	21.72	22	0.860	1.85*	.12.
	6.03	1.80	-	78	21.72	22	0.861	1.13*	.12
	5.19	1.80	33.18	78	21.72	26	0.878	0.64*	.11
	7.58	1.80	-	78	21.72	26	0.833	1.38*	.15
	6.09	1.80	33.18	78	21.72	26	0.861	0.98*	.13
	2.02	1.80	-	78	21.72	22	0.947	1.46*	.33
	1.38	1.80	33.18	78	21.72	20	0.962	1.06*	.83

/CF₃Cl cont.

TABLE 7,6 (cont)

Helium flow press. torr	$[O_3]$ $\times 10^8$ mole l^{-1}	$[freon]$ $\times 10^6$ mole l^{-1}	$[NO]$ $\times 10^8$ mole l^{-1}	T ms	t ms	Number of points	A	Relative Quantum Yield	Standard deviation
1.416	1.75	1.80	-	78	21.72	24	0.957	1.62*	.26
	1.36	1.80	33.18	78	21.72	16	0.967	0.84*	.25
	8.07	-	-	78	21.72	30	-	2.06*	.16

* Normalised to the mean of the first and last He/O₃ measurements (a mean relative quantum yield = 1.710) taken to be 2.000.

where,

$$A = \frac{k_{101} [CF_3Cl]}{k_{101} [CF_3Cl] + k_4 [O_3]}$$

$k_4 : k_{101}$
4.81 : 1

(Jayanty et al. 1975)

TABLE 7.7.

Photolysis of CF₂Cl₂/O₃/NO Mixtures - Data.

Helium flow press. torr	[O ₃] x 10 ⁸ mole l ⁻¹	[freon] x 10 ⁶ mole l ⁻¹	[NO] x 10 ⁸ mole l ⁻¹	T ms	t ms	Number of points	A	Relative Quantum Yield.*	Standard deviation
1.396	6.22	-	-	55	15.49	32	0.945	2.000	.248
	5.85	1.43	-	55	15.49	12	0.949	1.813	.442
	4.15	1.43	3.53	55	15.49	18	0.963	3.094	.494
	3.56	1.43	-	55	15.49	15	0.968	1.731	.585
	2.05	1.43	-	55	15.49	20	0.981	2.201	.427
	1.50	1.43	3.53	55	15.49	24	0.986	2.801	.934
1.385	8.10	2.01	-	55	15.67	28	0.950	1.736	.241
	7.07	2.01	7.81	55	15.67	24	0.957	3.243	.262
	4.87	2.01	-	55	15.67	22	0.971	1.721	.302
	4.18	2.01	7.39	55	15.67	22	0.971	2.766	.574

/CF₂Cl₂ cont.

TABLE 7.7 (cont)

Helium flow press. torr	$[O_2]$ $\times 10^8$ mole l^{-1}	$[freon]$ $\times 10^6$ mole l^{-1}	$[NO]$ $\times 10^8$ mole l^{-1}	T ms	t ms	Number of points	A.	Relative Quantum Yield.	*	Standard deviation.
1.585	3.28	2.01	-	55	15.67	24	0.978	1.635		.434
	2.65	2.01	6.97	55	15.67	26	0.985	2.656		.618
	2.06	2.01	-	55	15.67	26	0.985	2.237		.416
	1.85	2.01	6.00	55	15.67	20	0.988	2.797		.575
	5.63	2.01	-	55	15.67	20	0.964	1.917		.198
	5.00	2.01	6.18	55	15.67	26	0.971	3.752		.523
	6.42	1.89	-	55	15.67	24	0.964	1.655		.564
	4.08	1.89	16.5	55	15.67	26	0.971	5.348		.514
	6.15	1.89	-	55	15.67	20	0.964	1.950		.368
	4.23	1.89	16.5	55	15.67	26	0.971	3.869		.615

* Relative Quantum Yields normalised to He/O₃ taken as 2.000 /CF₂Cl₂ cont.

TABLE 7.7 (cont)

Helium flow press. terr.	$[O_3] \times 10^8$ mole l ⁻¹	$[freon_6] \times 10^6$ mole l ⁻¹	$[NO] \times 10^8$ mole l ⁻¹	T ms	t ms	Number of Points	A	Relative Quantum Yield.	Standar deviati
1.024	7.08	2.90	-	69	18.20	58	0.966	3.038	.269
	4.74	2.90	-	69	18.20	22	0.977	2.839	.341
	3.07	2.90	-	69	18.20	18	0.985	2.782	.384
0.986	7.22	3.58	-	6.3	15.85	33	0.972	2.243	.226
	6.23	3.06	-	36	15.85	32	0.972	2.544	.312
	6.09	3.15	-	45	15.85	42	0.973	2.741	-
	6.86	3.22	-	15	15.85	37	0.970	2.084	-
1.489	5.57	1.58	-	14	17.12	25	0.951	2.144	.148
1.477	6.23	1.58	-	26	17.18	36	0.923	2.267	.157
1.484	6.28	1.56	-	37	17.06	34	0.922	2.097	.207
	6.23	1.56	-	50	17.06	35	0.922	2.229	.209
	6.38	1.54	-	64	17.06	22	0.920	2.191	.240

CF₂Cl₂ cont.

TABLE 7.7 (cont)

Helium flow press torr.	$[O_3] \times 10^8$ mole l ⁻¹	$[freon] \times 10^6$ mole l ⁻¹	$[NO] \times 10^8$ mole l ⁻¹	T ms	t ms	Number of Points	A	Relative Quantum Yield	Standa deviat
1.277	6.40	2.23	-	58	15.78	32	0.954	2.286	.265
0.968	5.50	2.72	-	45	11.71	18	0.972	2.093	.587
	9.40	2.72	-	43	11.71	18	0.972	2.280	.242
0.951	2.96	0.068	-	6.5	11.73	3/4	0.615	2.206	.445
	6.60	0.068	-	6.5	11.73	20	0.418	2.290	.553
	4.62	0.068	-	6.5	11.73	2/4	0.506	2.345	.533
	1.82	0.068	-	6.5	11.73	26	0.723	2.084	.582
	7.61	0.068	-	6.5	11.73	4/4	0.384	2.250	.450
1.621	5.18	-	-	6.2	17.77	20	0.970	2.000*	.853
	3.27	2.27	-	6.2	17.77	24	0.983	1.940*	.555
1.582	3.98	-	-	52	95.24	14	0.985	2.000*	.154
	2.15	3.36	-	332	95.24	16	0.991	2.090*	.216
SF ₆									
1.550	4.07	2.32	-	89	25.55	26	0.979	2.170*	.126

CF₂Cl

TABLE 7.7 (cont)

* Relative Quantum Yields normalised to He/O ₃ taken as 2.00		
A	$= \frac{k_{102} [CF_2Cl_2]}{k_{102} [CF_2Cl_2] + k_4 [O_3]}$	: the fraction of (¹ D) quenched by freon
where	$k_4:$ k_{104}	(Jayanty, Simonaitis and Heicklen, 1975)
	1.33:	1

TABLE 7.8

PHOTOLYSIS OF CFC1₃/O₃/NO Mixtures - Data

Helium Flow press. torr.	[O ₃] x 10 ⁸ mole l ⁻¹	[freon] x 10 ³ mole l ⁻¹	[NO] x 10 ³ mole l ⁻¹	T ms	t ms	Number of Points	A	Relative Quantum Yield	Standard deviation.
1.714	5.32	-	-	16.6	18.48	32	-	1.813	.156
	4.58	4.91	-	16.6	18.48	24	0.984	1.017	.200
	4.05	6.12	-	16.6	18.48	24	0.989	1.253	.247
	2.45	6.12	-	16.6	18.48	20	0.994	1.163	.246
	3.03	6.12	-	68	18.48	32	0.992	1.744	.295
	4.54	6.12	-	68	18.48	28	0.987	1.579	.154
	3.79	5.59	-	60	18.48	26	0.989	1.486	.293
	3.44	5.59	-	49	18.48	24	0.989	1.583	.251
	3.41	5.59	-	35	18.48	22	0.989	1.397	.289
	3.14	5.59	-	23	18.48	22	0.991	1.425	.274

/CFC1₃ cont.

TABLE 7.8. (cont)

Helium flow press. torr	$[O_2] \times 10^8$ mole l ⁻¹	$[freon_6] \times 10^6$ mole l ⁻¹	$[NO] \times 10^8$ mole l ⁻¹	T ms	t ms	Number of Points	A	Relative Quantum Yield	Standard deviation
1.714	3.30	5.59	-	13.9	18.48	28	0.989	1.044	.520
	3.12	5.59	-	8.3	18.48	24	0.991	1.122	.263
	3.30	5.59	-	5.5	18.48	22	0.989	1.189	.317
1.592	20.75	-	-	529	137	8	-	2.435	.029
	3.71	-	-	529	137	8	-	1.814	.105
	25.54	7.71	-	529	137	12	0.958	1.781	.370
	16.23	7.71	-	529	137	14	0.966	1.409	.021
	3.10	7.71	-	529	137	9	0.994	0.600	.025
1.395	5.35	-	-	56	15.13	20	-	2.101	.203
	4.07	-	-	56	15.13	18	-	1.797	.170
	2.06	-	-	56	15.13	16	-	1.556	.214
	6.53	-	-	56	15.13	28	-	1.976	.285
	1.89	-	-	56	15.13	18	-	2.102	.399

TABLE 7,8 (cont)

Helium flow press. torr.	$[O_3]$ $\times 10^8$ mole l^{-1}	$[freon]$ $\times 10^6$ mole l^{-1}	$[NO]$ $\times 10^8$ mole l^{-1}	T ms	t ms	Number of Points	A	Relative Quantum Yield.	Standard deviation.
1.395	5.31	5.74	-	56	15.13	26	0.985	1.230	.207
1.442	5.12	5.11	1.63	135	35.76	22	0.983	0.903	.174
	5.69	5.11	-	135	35.76	20	0.981	0.749	.059
	2.36	5.11	-	135	35.76	20	0.992	0.784	.195
	2.22	5.11	1.14	135	35.76	22	0.992	1.119	.169
	6.21	5.11	-	155	35.76	14	0.981	0.855	.115
	5.97	5.11	2.80	135	35.76	18	0.981	1.403	.087
	3.78	5.11	-	135	35.76	22	0.988	0.830	.175
	3.40	5.11	2.80	155	35.76	22	0.988	1.632	.158
	7.40	5.11	-	135	35.76	20	0.977	0.955	.110
	6.27	5.11	2.80	135	35.76	20	0.981	1.270	.127
	2.25	5.11	-	155	35.76	22	0.992	0.833	.175

/CFC13 cont.

TABLE 7,8 (cont)

TABLE 7.9 Photolysis of C Cl₄/O₃ Mixtures - Data.

Helium flow press. torr.	[O ₃] x 10 ⁶ mole l ⁻¹	[freon] x 10 ⁶ mole l ⁻¹	[NO] x 10 ⁸ mole l ⁻¹	T ms	t ms	Number of Points	A	Relative Quantum Yield [*]	Standard deviation.
1.185	4.27	-	-	230	76.5	20	-	1.96	.09
	6.86	2.72	-	230	76.5	10	0.971	2.84	.13
	5.39	2.72	-	230	76.5	20	0.971	5.35	.24
1.390	8.05	-	-	55	14.96	24	-	2.04	.28
	2.04	2.58	-	4.5	14.96	22	0.992	5.99	.10
	7.71	2.58	-	4.5	14.96	28	0.966	5.35	.49
	6.81	2.58	-	18	14.96	28	0.970	5.27	.50
	3.52	2.58	-	33	14.96	20	0.985	3.62	.38
	6.55	2.58	-	33	14.96	30	0.970	3.21	.54
	3.90	2.58	-	45	14.96	24	0.980	5.60	.80
	7.75	2.58	-	45	14.96	16	0.966	2.87	.48
	6.74	2.58	-	55	14.96	50	0.970	2.64	.55

CCl₄ cont.

TABLE 7.9 (cont)

* Relative Quantum Yields normalised to He/O₃ (linear mean value of experimental relative quantum yield = 1.612) taken as 2,000.

$$A = \frac{k_{104} [CCl_{l_i}]}{k_{104} [CCl_{l_i}] + k_4 [O_3]}$$

k_4
:
 k_{104}
(Jayanty et al 1975)

1.19
:
1

The linear mean value of the C Cl_l/O₃ relative quantum yields = 3.27

TABLE 7,10 Summary Observations O_3 /freon Photolysis

$-\phi\{o_3\}$	Addition of NO	Observation m/e $\approx$ 65	Approx. Ratio m/e 65:48	Observation m/e = 51.
CF_4	2	-	-	-
CF_3Cl	ca 1.5	positive and negative increments in observed	ca 2:100	not observed.
CF_2Cl_2	2	increases	Yes	qualitative as above
$CFCl_3$	1.2*	increases	Yes	2.2:100 [†] not observed.
CCl_4	2 - 4	not performed	Yes	2.2:100 [†] not observed.

* Quantum yield dependent on ozone concentration and contact time.

† Ratio when ϕ is equal to 2.

TABLE 7.11

Comparison of Computer Predicted and Experimentally
obtained Relative Quantum Yields for the
 $\text{CF}_2\text{Cl}_2/\text{O}_3/\text{NO}$ System.

$[\text{O}_3]$ $\times 10^8$ mole l^{-1}	$[\text{CF}_2\text{Cl}_2]$ $\times 10^6$ mole l^{-1}	$[\text{NO}]$ $\times 10^8$ mole l^{-1}	Quenching Fraction AA.	Efficiency ClO prod. BB	"ClO" wall loss s^{-1}	Quantum Yield
5.85	1.43	-	0.0	0.3	300	$2.0(1.8^{+}_{-} .5)$
4.15	1.43	3.53	"	"	"	$2.4(3.1^{+}_{-} .4)$
3.56	1.43	-	"	"	"	$2.0(1.7^{+}_{-} .3)$
2.05	1.43	-	"	"	"	$2.0(2.2^{+}_{-} .3)$
1.50	1.43	3.53	"	"	"	$2.4(2.8^{+}_{-} .7)$
8.10	2.01	-	"	"	"	$2.0(1.7^{+}_{-} .2)$
7.07	2.01	7.81	"	"	"	$2.8(3.2^{+}_{-} .2)$
4.87	2.01	-	"	"	"	$2.0(1.7^{+}_{-} .2)$
4.18	2.01	7.39	"	"	"	$2.8(2.8^{+}_{-} .3)$
3.28	2.01	-	"	"	"	$2.0(1.6^{+}_{-} .3)$
2.65	2.01	6.97	"	"	"	$2.7(2.7^{+}_{-} .4)$
2.06	2.01	-	"	"	"	$2.0(2.2^{+}_{-} .3)$
1.83	2.01	6.00	"	"	"	$2.6(2.8^{+}_{-} .4)$
5.63	2.01	-	"	"	"	$2.0(1.9^{+}_{-} .1)$
5.00	2.01	6.18	"	"	"	$2.7(3.7^{+}_{-} .2)$
6.42	1.89	-	"	"	"	$2.0(1.6^{+}_{-} .3)$
4.08	1.89	16.5	"	"	"	$3.7(5.3^{+}_{-} .4)$
6.15	1.89	-	"	"	"	$2.0(1.9^{+}_{-} .3)$
4.23	1.89	16.5	"	"	"	$3.7(5.9^{+}_{-} .5)$

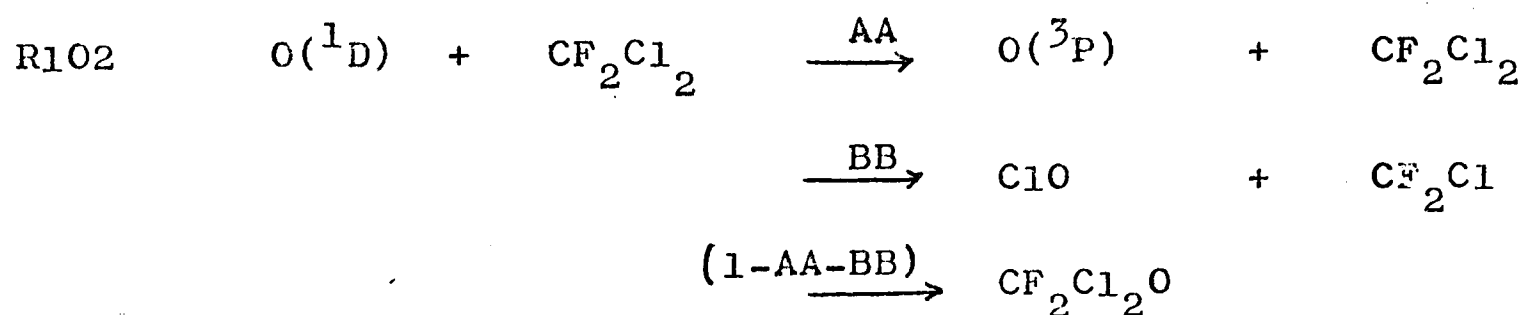
/cont.

TABLE 7,11 (cont)

$[O_3]$ $\times 10^8$ mole l^{-1}	$[CF_2Cl_2]$ $\times 10^6$ mole l^{-1}	$[NO]$ $\times 10^8$ mole l^{-1}	Quenching Fraction AA.	Efficiency ClO prod. BB	"ClO" wall loss s^{-1}	Quantum Yield.
4.18	2.01	7.39	0.0	0.3	zero	6.4
"	"	"	0.0	"	100	4.0
"	"	"	0.0	"	200	3.1
"	"	"	0.0	"	300	2.8
"	"	"	0.1	"	"	(2.8 $\pm$ 13) 2.7
"	"	"	0.0	0.5	300	3.3
"	"	"	0.0	1.0	500	3.6
"	"	"	0.0	1.0	1000	2.8

* Figures in brackets are the experimental results.

The fractions AA and BB relate to the relative efficiencies:



NB The O_3 , CF_2Cl_2 and NO concentrations correspond to the values used in the experiments summarised in Table 7,7.

The reaction scheme modelled above involves reactions J5, R4, R102, R112, R105, R106 and R107 only.

APPENDIX 1.

COMPUTOR PROGRAMS.

CF₂Cl₂/O₃/NO simulation

```

      SUBROUTINE FREEM INTEGRATIONS;
      DIMENSION N3(201),F2C(201),C17(201),F2C27(201),F2C7(201)
      DIMENSION C172(201),F27(201),C1(201),XN7(201),CY(201),F2C2(201)
      READ (1,30)
      READ(1)N3INIT,F7INIT,XN7(1),T,T1,F7,F5,AA,EB,F10
      C 2ND ORDER RATE CONSTANTS DIVIDED BY E10 TO AVOID OVERFLOW
      BETA=2.1E7
      R2=3.2F1
      R3=3.2F1
      R4=5.0
      R5=F5*1.0
      R6=2.1E7
      R7=F7*1.0
      R8=1.1
      R9=1.0
      R10=F10*100.0
      R11=7.5E-4
      DD73=(1.0-EXP(-BETA*T))*N3INIT
      FF=R3*F7INIT/(R3*F7INIT+R2*N3INIT)
      N3(1)=N3INIT-DD73-(1.0-FF)*DD73
      F2C2(1)=F7INIT-DD73*FF
      C17(1)=EB*FF*DD73
      F2C(1)=EB*FF*DD73
      F2C27(1)=(1.0-AA-EB)*FF*DD73
      F2C7(1)=0.0
      C1(1)=0.0
      C172(1)=0.0
      F27(1)=0.0
      CY(1)=0.0
      TS=T1/200.0
      DO 2 J=1,200,1
      10 C=R4*F2C(J)*N3(J)
      E=R5*F2C27(J)*N3(J)
      F=R7*F2C7(J)*N3(J)
      G=R8*C1(J)*N3(J)
      H=R9*C17(J)*XN7(J)
      Q=R6*F2C7(J)
      N3(J+1)=N3(J)-TS*(C+E+F+G)
      F2C(J+1)=F2C(J)-TS*(+C)
      IF (F2C(J+1)-1.E-16) 52,52,53
      52 F2C(J+1)=0.0
      53 CONTINUE
      C17(J+1)=C17(J)-TS*(+R10*C17(J)+F-G-H)
      IF (C17(J+1)-1.E-16) 80,80,81
      80 C17(J+1)=0.0
      81 CONTINUE
      F2C27(J+1)=F2C27(J)-TS*E
      IF (F2C27(J+1)-1.E-16) 60,60,61
      60 F2C27(J+1)=0.0
      61 CONTINUE
      F2C7(J+1)=F2C7(J)-TS*(-C+E+F)
      IF (F2C7(J+1)-1.E-16) 70,70,71
      70 F2C7(J+1)=0.0
      71 CONTINUE

```

```

C1P2(J+1)=C1P2(J)+TS*E
F2C(J+1)=F2C(J)+TS*(C+F)
C1(J+1)=C1(J)-TS*(C+F-F)
IF (C1(J+1)-1.E-16) 90,90,91
90 C1(J+1)=0.0
91 CONTINUE
XNP(J+1)=XNP(J)-TS*(F+K11*P3(J)*XNP(J))
X=AIPO(1.0-(P3INIT-P3(J))/P3INIT)
2 CY(J)=-X/(EFIA*1)
11 WRITE(2,30)
WRITE(2,31)P3INIT
DP3=P3INIT-P3(199)
WRITE(2,32)DP3
WRITE(2,33)FMINIT
WRITE(2,34)XNP(1),XNP(199)
WRITE(2,35)1
WRITE(2,36)T1
WRITE(2,39)C1P2(199)
WRITE(2,40)F2C(199)
WRITE(2,41)F2C2C(199)
WRITE(2,42)F2C(199)
WRITE(2,43)C1(199)
WRITE(2,37)
DO 12 J=1,200,10
13 XAT=J*TS
12 WRITE(2,38)XAT,P3(J),CY(J),C1P(J)
WRITE(2,48)
30 FORMAT(50F
31 FORMAT(14F INITIAL P3 = ,E12.5)
32 FORMAT(12F EFIA P3 = ,E12.5)
33 FORMAT(9F FMIN = ,E12.5)
34 FORMAT(6F MP = ,E12.5)
35 FORMAT(16F TIME IN LAMP = ,E12.5)
36 FORMAT(19F TIME AFTER LAMP = ,E12.5)
37 FORMAT(51F T SEC PZONE GYIELD C1P )
38 FORMAT(5(X,E12.5))
39 FORMAT(14F FINAL C1P2 = ,E12.5)
40 FORMAT(13F FINAL F2C = ,E12.5)
41 FORMAT(15F FINAL F2C2C = ,E12.5)
42 FORMAT(14F FINAL F2C = ,E12.5)
43 FORMAT(12F FINAL C1 = ,E12.5)
48 FORMAT(//36F CONCS IN UNITS F-10 MOLES PER LITRE)
PAUSE
END
%
&FT3;
&IPAD;
&RIH;

```

END OF PROGRAMME

END OF PROGRAMME

H₂/O₃ simulation

```
& JPB, FORNER;
& FORTRAN, INTEGRATION 2;
  GLOBAL, FORNER
  DIMENSION H2(401), O3(401), O21D(401), OH(401), EXOH(401), F(401), CYIELD
  READ(1,12)
  READ(1) O3INIT, H2INIT, R5A, R5B, R11, FVEL, CONST, T1
C  RATE CONSTANTS DIVIDED BY E10 TO AVOID NUMBER OVERFLOW
  R2B=1.6E1
  R2A=R2B
  R3=1.7E1
  R4=1.6E0
  R6=3.5E-3
  R10=5.2E-4
  R7=2.2E-4
  R13=1500.0
  PF=CONST*FVEL
  OZ=O3INIT*(1.0-PF)
  O1D=O3INIT*PF
  O21D(1)=O1D
  C=(R2A+R2B)*OZ+(H2INIT*R3)
  WRITE(2,43) OZ, O1D, C
  OH(1)=O1D*H2INIT*R3/C
  F(1)=OH(1)
  WRITE(2,44) OH(1)
  O3(1)=OZ-O1D*OZ*(R2A+R2B)/C
  H2(1)=H2INIT-OH(1)
  EXOH(1)=0.0
  WRITE(2,44) O3(1)
44  FORMAT(E10.3)
  CYIELD(1)=1.0 + OZ*(R2A+R2B)/C
  WRITE(2,43) OH(1), O3(1), CYIELD(1)
  TS=T1/400.0
  DO 1 J=1,400,1
  IF (J-400) 10,11,11
10  A=R7*O21D(J)*O3(J)
  B=R4*F(J)*O3(J)
  C=(R5A+R5B)*EXOH(J)*O3(J)
  D=R6*OH(J)*O3(J)
  E=R10*(OH(J)+EXOH(J))*H2(J)
  F=R10*OH(J)*H2(J)
  O3(J+1)=O3(J)-TS*(A+B+C+D)
  O21D(J+1)=O21D(J)-TS*A
  H2(J+1)=H2(J)-TS*E
  OH(J+1)=OH(J)+TS*(-D-F-R11*OH(J)+R13*EXOH(J))
  F(J+1)=F(J)+TS*(E-B+R5B*EXOH(J)*O3(J))
  EXOH(J+1)=EXOH(J)+TS*(B-C-R10*EXOH(J)*H2(J)-R13*EXOH(J))
  CYIELD(J)=(O3INIT-O3(J))/(PF*O3INIT)
1  CONTINUE
C  ITS ABOUT TIME THIS PROGRAM WORKED!
11  WRITE(2,12)
  WRITE(2,14) O3INIT
  WRITE(2,15) H2INIT
  WRITE(2,45) CYIELD(391)
  WRITE(2,13)
```

```

      DO 30 J=1,400,10
30    WRITE(2,22) J,P3(J),CYIELD(J),P21D(J),EXPH(J)
      WRITE(2,40)
      DO 31 J=1,400,10
31    WRITE(2,41) J,PH(J),P2(J),H(J)
      WRITE(2,42)
12    FORMAT(50F
14    FORMAT(9H P3INIT = ,E10.3)
15    FORMAT(10H P2INIT = ,E10.3)
13    FORMAT(/52F J      P3      CYIELD      P21D      EXPH      )
22    FORMAT(/13,4(2X,E10.3))
40    FORMAT(/40F J      PH      P2      P      )
41    FORMAT(/13,3(2X,E10.3))
42    FORMAT(///36H CONCS IN UNITS E-10 MOLES PER LITRE )
43    FORMAT(3(2X,E10.3)///)
45    FORMAT(/15H CYIELD(391) = ,E10.3)
PAUSE
END
%
&FT3;
&LOAD;
&RUN;

```

END OF PROGRAMME

```

&JPR,HQENFR;
&PORTRAN,DATA DEVIATIONS;
GLQRAL,MGH,SOPT,ALOG
DIMENSION D3(400),L3(400),OY(400)
      READ(1,30)
      READ(1)N,H,K,T,RANGE
      S03=0.0
      SD03=0.0
      DD03=0.0
      O0Y=0.0
      IF (K) 1,3,1
1    DO 2 J=1,N,1
2    READ(1)D3(J),DD3(J)
      GO TO 6
3    DO 4 J=1,N,1
4    READ(1)D3(J)
      DO 5 J=1,N,1
5    READ(1) DD3(J)
6    CONTINUE
      DO 7 J=1,N,1
      S03=S03+D3(J)
7    SD03=SD03+DD3(J)
      XM03=S03*RANGE/H
      XMD03=SD03*RANGE/H
      FI=XMD03/XM03
      A=1.0-FI
      FICOR=ALOG(A)
      FICORT=-FICOR/1
      OYIELD=FICORT/2.187
      DO 8 J=1,N,1
8    DD03=DD03+(XMD03-RANGE*DD3(J))**2
      VARD03=DD03/(H-1.0)
      RMSD03=SQRT(VARD03)
      DO 9 J=1,N,1
      AA=DD3(J)/D3(J)
      BB=1.0-AA
      CC=-ALOG(BB)
      DD=CC/1
9    OY(J)=DD/2.187
      DO 10 J=1,N,1
10   O0Y=O0Y+(OYIELD-OY(J))**2
      VAROY=O0Y/(H-1.0)
      RMSOY=SQRT(VAROY)
      WRITE(2,30)
      WRITE(2,20)XMD03
      WRITE(2,21)XM03
      WRITE(2,22)FI
      WRITE(2,23)FICOR
      WRITE(2,24)FICORT
      WRITE(2,26)OYIELD
      WRITE(2,31)RMSOY
      WRITE(2,27)RMSD03
      WRITE(2,28)H
      WRITE(2,29)1
20   FORMAT(25H MEAN DELTA D3 = ,F12.5)
21   FORMAT(25H MEAN OZONE CONC = ,F12.5)
22   FORMAT(25H DELTA D3 / D3 = ,F12.5)
23   FORMAT(25H DELTA D3 CORR / D3 = ,F12.5)
24   FORMAT(25H DELTA D3 CORR / D3*1 = ,F12.5)
26   FORMAT(25H QUANTUM YIELD O3 LOSS = ,F12.5)
27   FORMAT(25H RMSDEV DELTA D3 = ,F12.5)
29   FORMAT(25H SMALL 1 = ,F12.5)

28   FORMAT(25H NUMBER OF POINTS = ,F12.5)
30   FORMAT(50H
31   FORMAT(25H RMS DEV QUANTUM YIELD = ,F12.5)
PAUSE
END

```

$$Y=MX, Y=MX+C \quad \text{fit}$$

```

* JOB, FORNER LEAST SQUARES;
* FORTRAN, FORNER;
GLOBAL, M, F, SORT, ABS;
      DIMENSION X(400), Y(400)
      SX=0.0
      SY=0.0
      SXX=0.0
      SXY=0.0
      SYY=0.0
      XBAR=0.0
      YBAR=0.0
      READ(1) N, F, K, L, M
      IF (N) 30, 31, 30
30    DO 40 J=1, N, 1
40    READ(1) X(J), Y(J)
      GO TO 50
31    DO 41 J=1, N, 1
41    READ(1) X(J)
      DO 42 J=1, N, 1
42    READ(1) Y(J)
50    CONTINUE
      DO 1 J=1, N, 1
      SY=SY+Y(J)
      SX=SX+X(J)
      SYY=SYY+Y(J)*Y(J)
      SXY=SXY+X(J)*Y(J)
1     SXX=SXX+X(J)*X(J)
      IF (K) 5, 2, 5
4     IF (L) 6, 3, 6
2     SL=SXY/SXX
      WRITE(2, 11) SL
      E=(SYY-SL*SXY)/((F-2.0)*SXX)
      SE=SQRT(E)
      WRITE(2, 12) SE
5     GO TO 4
6     GO TO 20
3     WRITE(2, 13)
      XBAR=SX/F
      YBAR=SY/F
      SLOPE=(SXY-F*XBAR*YBAR)/(SXX-F*XBAR*XBAR)
      WRITE(2, 14) SLOPE
      VV=SLOPE*(SXY-F*XBAR*YBAR)
      WW=SYY-F*YBAR*YBAR
      Z=WW-VV
      IF (Z) 100, 101, 101
100   ZZ=ABS(Z)
      WRITE(2, 102)
      GO TO 103
101   ZZ=Z
103   VSL=ZZ/((F-2.0)*(SXX-F*XBAR*XBAR))
      IF (VSL) 300, 301, 301
300   VSL=ABS(VSL)
      WRITE(2, 303)
301   SESL=SQRT(VSL)
      WRITE(2, 12) SESL
      ZINT=YBAR-SLOPE*XBAR
      WRITE(2, 15) ZINT

```

```

      VINT=22*(1.0/F+(XBAR*XBAR/(SXX-F*XBAR*XBAR)))/(F-2.0)
      IF(VINT)200,201,201
200  VINT=ABS(VINT)
      WRITE(2,203)
201  SEINT=SEGT(VINT)
      WRITE(2,12)SEINT
20  WRITE(2,21)
      WRITE(2,305)
      DO 400 J=1,N,1
      YFIT=SLOPE*X(J)+ZINT
      RES=Y(J)-YFIT
400  WRITE(2,304) J,Y(J),YFIT,RES
304  FORMAT(13,3(2X,E12.5))
305  FORMAT(//45H J      Y      YFIT      RES      )
11  FORMAT(//,23HZERO INTERCEPT SLOPE = ,E12.5)
12  FORMAT(17HSTANDARD ERROR = ,E12.5)
13  FORMAT(//,22HDATA FIT TO Y = MX + C)
14  FORMAT(7HSLOPE = ,E12.5)
15  FORMAT(12HINTERCEPT = ,E12.5)
21  FORMAT(//,32HNOW LOOK UP VALUES OF STUDENTS T)
102  FORMAT(48HROUNDING PROBLEM IN ERROR OF SLOPE AND INTERCEPT)
203  FORMAT(33HVARIVANCE OF INTERCEPT IS NEGATIVE)
303  FORMAT(28HVARIVANCE OF SLOPE IS NEGATIVE)
      PAUSE
      END

%
&FT3;
&INAD;
&RUN;

```

Appendix 2. Treatment of Laminar Flow.

In this appendix a simplified expression for the concentration of species produced ^{by} photodecomposition under conditions of laminar flow is derived and this concentration is compared with that to be expected under conditions of "plug flow". The computer program written to integrate and evaluate the resulting expression is also included.

It should qualitatively be apparent that under conditions of laminar flow in a tube, wherein the gas close to the tube wall is flowing more slowly than the gas in the centre of the tube, a greater fractional photolysis will occur in that gas close to the tube wall; the time spent in the photolysis zone by the latter being longer. The optical density of that gas close to the tube wall will decrease due to photolysis and thus the absolute amount of gas photolysed per unit volume per unit contact time will fall below the value of that quantity for the gas in the centre of the flow tube.

Let us make the simplifying assumption that for a circular cross section tube the distribution of the gas velocities parallel to the tube axis follows the parabolic expression

$$V_x = A - kx^2$$

where V_x is the velocity at distance x radially out from the central axis of the flow tube

A is the velocity at the centre of the tube.

k is a constant dependent on the fluid dynamic properties of the gas.

and where $A \geq k R^2$ since V_x is never negative.

where R is the tube inside radius.

The quantity $(A - kR^2)$ is thus the slip velocity at the tube wall.

The time t_x spent in the photolysis zone (whose length is d cm) by an increment of gas travelling parallel to the tube axis, along the surface of the cylinder of radius x is given by:

$$\begin{aligned} t_x &= d/V_x \\ &= d/(A - kx^2) \end{aligned}$$

Due to photolysis of the gas, which is present in a large excess of carrier gas, the concentration C_t at time t is related to the initial concentration C_o by

$$C_t = C_o e^{-\beta t}$$

where β is a constant dependent on the lamp intensity, the geometry of the system and the gas absorption cross section.

The concentration of species at x after time t_x is

$$C_x = C_o \left[\exp(-\beta d/(A - kx^2)) \right].$$

The mean time MT spent in the photolysis zone by all gas increments from $x = 0$ to $x = R$ along any radius is given by

$$\begin{aligned} MT &= \frac{1}{R} \int_{x=0}^{x=R} t_x \cdot dx \\ &= \frac{1}{R} \int_0^R \frac{d}{(A - kx^2)} dx \\ &= \frac{d}{2R \sqrt{k} \sqrt{A}} \ln \left| \frac{\sqrt{A} + \sqrt{k} R}{\sqrt{A} - \sqrt{k} R} \right| \end{aligned}$$

The mean concentration of species CLMT along any radius after time MT in the laminar flow case is thus given by

$$\begin{aligned} CLMT &= \frac{1}{R} \int_0^R C_x dx \\ &= \frac{C_o}{R} \int_0^R \exp(-\beta d/(A - kx^2)) dx \end{aligned}$$

This is integrated numerically in the appended program.

Under plug flow conditions wherein the gas is in the

photolysis zone for the same mean time MT as above, the concentration of species CPMT is given by

$$CPMT = C_o \exp (- \beta .MT)$$

Comparison of CLMT and CPMT shows that CLMT is always less than CPMT and approaches it as the slip velocity approaches the velocity A of the gas in the centre of the tube.

The following table shows results computed for $A = 20 \times 10^3 \text{ cm s}^{-1}$, a typical experiment value for β , and various slip velocities.

Slip velocity, cm s^{-1}	$\frac{CLMT}{C_o}$	$\frac{CPMT}{C_o}$	mean time MT ms
0.01	0.962	0.895	5.55
1.0	0.962	0.924	3.95
10	0.960*	0.939	3.15
100	0.964	0.954	2.34
1000	0.971	0.969	1.56
10000	0.983	0.983	0.88
19000	0.986	0.986	0.72

* integration time step five times larger than for other values.

$CLMT/C_o$ represents the fractional concentration left after photolysis under laminar flow conditions.

$CPMT/C_o$ represents the fractional concentration left after photolysis for the same mean time MT under plug flow conditions.

The computer program is appended hereafter:-

```

& JOB, ABSORPTION OF LIGHT BY LAMINAR FLOW;
& FORTRAN, MCF;
C INBAL, MCF, IN, ABS, EXP, SQRT
      DIMENSION X(1000), CX(1000)
      READ(1) A, K, DX
      WRITE(2, 99)
      WRITE(2, 105) A
      WRITE(2, 107) K, DX
      D=14.0
      R=1.0
      CINT=0.0
      BETA=2.0
      X(1)=0.0
      SV=(A-K*K**2)
      WRITE(2, 106) SV
9      DO 10 J=1, 1000, 1
      CX(J)=(1-EXP(-BETA*D/(A-K*X(J)**2)))
      CINT=CINT+DX*CX(J)
      X(J+1)=X(J)+DX
10      IF (R-X(J)) 11, 11, 9
11      WRITE(2, 100) CINT
      WRITE(2, 102)
13      DO 12 J=1, 1000, 10
      WRITE(2, 101) X(J), CX(J)
      IF (R-X(J)) 12, 12, 13
C      CALC OF MEAN TIME SPENT IN IRRADIATION ZONE
12      T=(SQRT(A)+SQRT(K)*R)/(SQRT(A)-SQRT(K)*R)
      S=ABS(T)
      XMT=D*LN(S)/(2*K*SQRT(K)*SQRT(A))
      XBET=BETA*XMT
      CPMT=(1-EXP(-XBET))
      WRITE(2, 103) XMT
      WRITE(2, 104) CPMT
99      FORMAT(36H ABSORPTION OF LIGHT BY LAMINAR FLOW)
100      FORMAT(41H LAMINAR FLOW MEAN FRACTION PHOTOLYSIS = ,E10.3)
102      FORMAT(19H      X      CONC)
101      FORMAT(E10.3, 2X, E10.3)
103      FORMAT(41H MEAN TIME IN PHOTO ZONE, LAMINAR FLOW = ,E10.3)
104      FORMAT(46H PLUG FLOW FRACTION PHOTOLYSIS AT MEAN TIME = ,E10.3)
105      FORMAT(//27H VELOCITY AT TUBE CENTRE = ,E10.3)
106      FORMAT(25H SLIP VELOCITY AT WALL = ,E10.3)
107      FORMAT(5H K = ,E10.3, 6H DX = ,E10.3)
      PAUSE
      END
%
& FT3;
& INAD;
& RUN;

```

Appendix 3.Relaxation Times of First Order Reactions.

The rate of a first order reaction with respect to loss of species x has the form

$$\frac{dx}{dt} = -k x$$

where k may be a true first order rate constant, or the rate constant for a "pseudo first order" reaction. The integrated expression shows that at time t

$$x = x_0 \exp(-t/\tau)$$

where x is the concentration of species x at time t

x_0 is the initial concentration of species x

and $\tau = 1/k$

when 10% of x has been consumed

$$0.90x_0 = x_0 \exp(-t/\tau)$$

$$0.10\tau = t$$

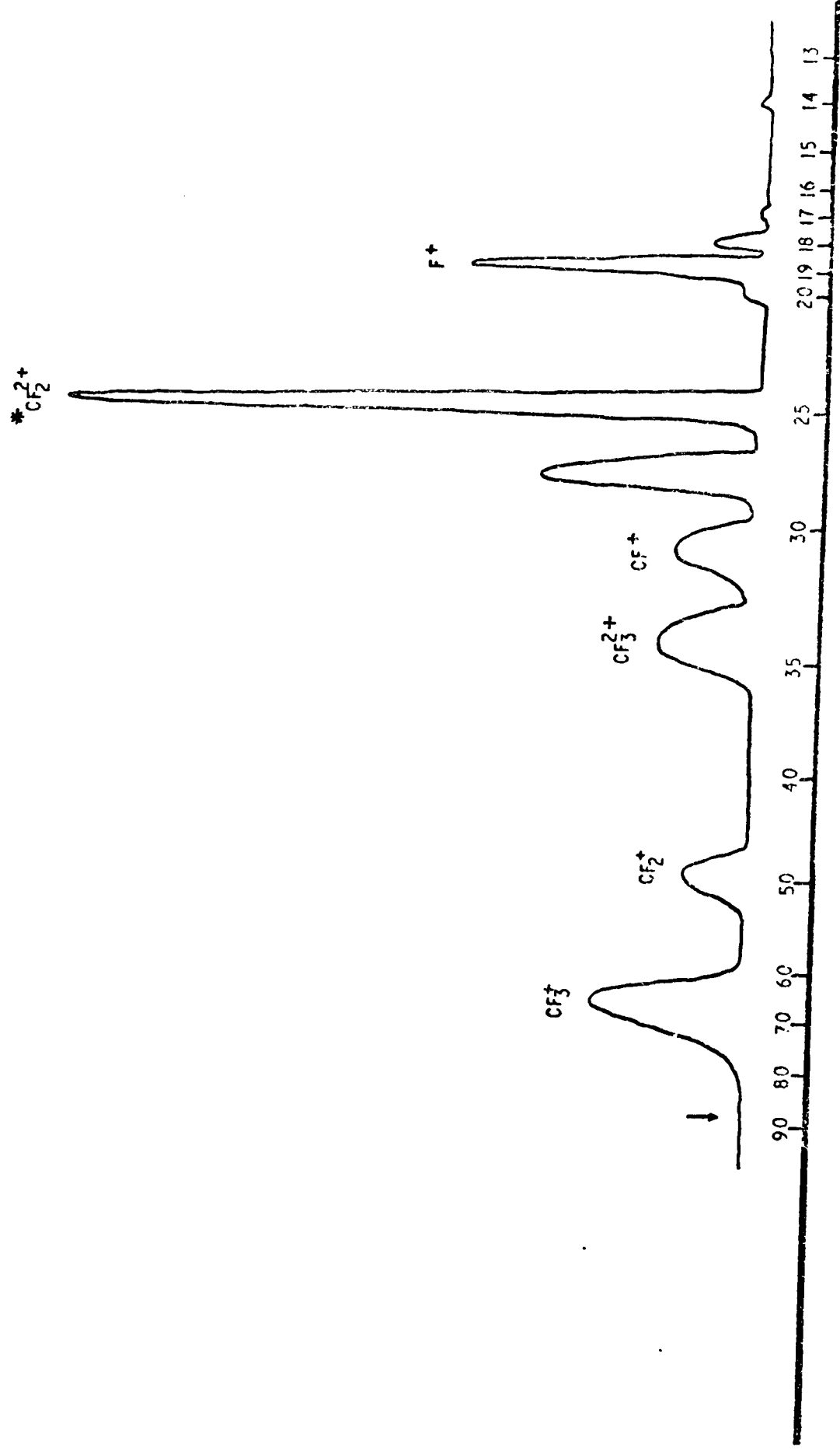
Thus 10% loss of reactant in a first order reaction occurs at a time equal to 0.1τ . The following results may be obtained in the same way.

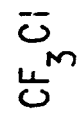
<u>Extent of reaction</u>	<u>No. of τ required.</u>
1%	0.01
5%	0.05
50%	0.69
95%	3.0
99%	4.6

APPENDIX 4.

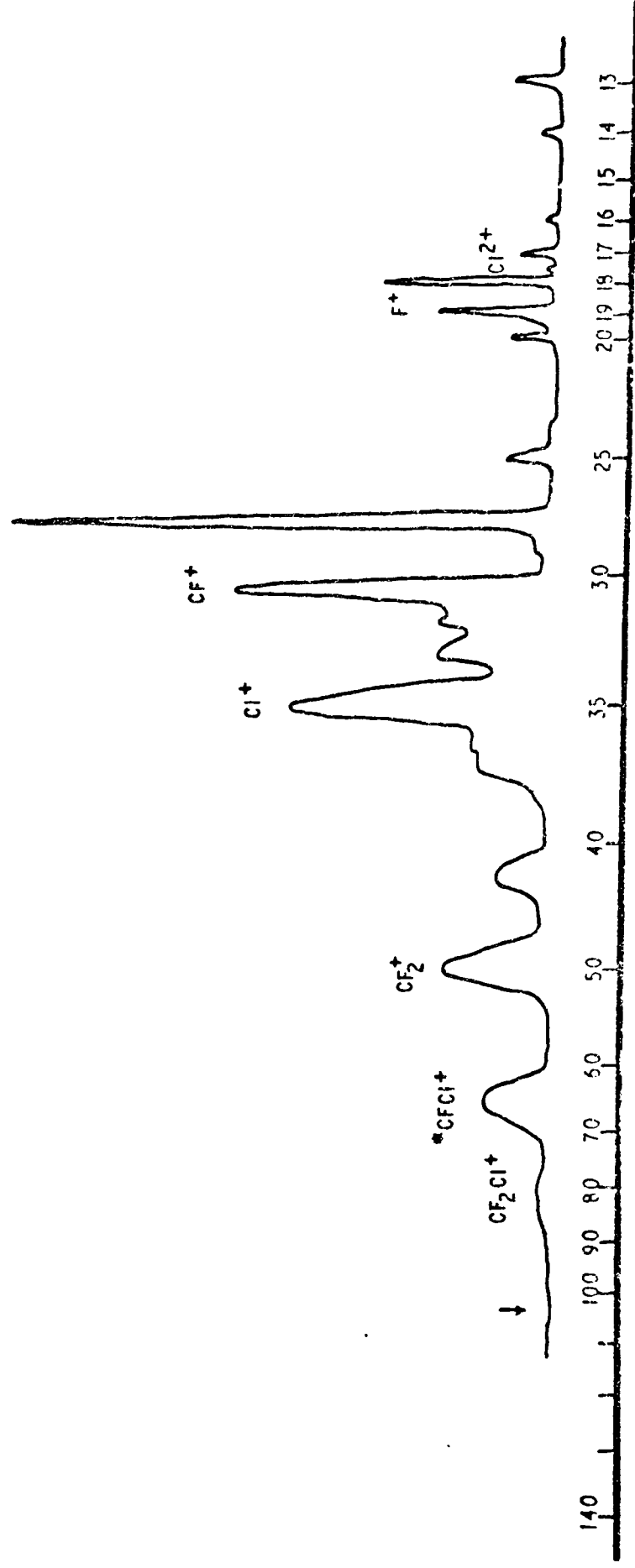
Mass Spectra.

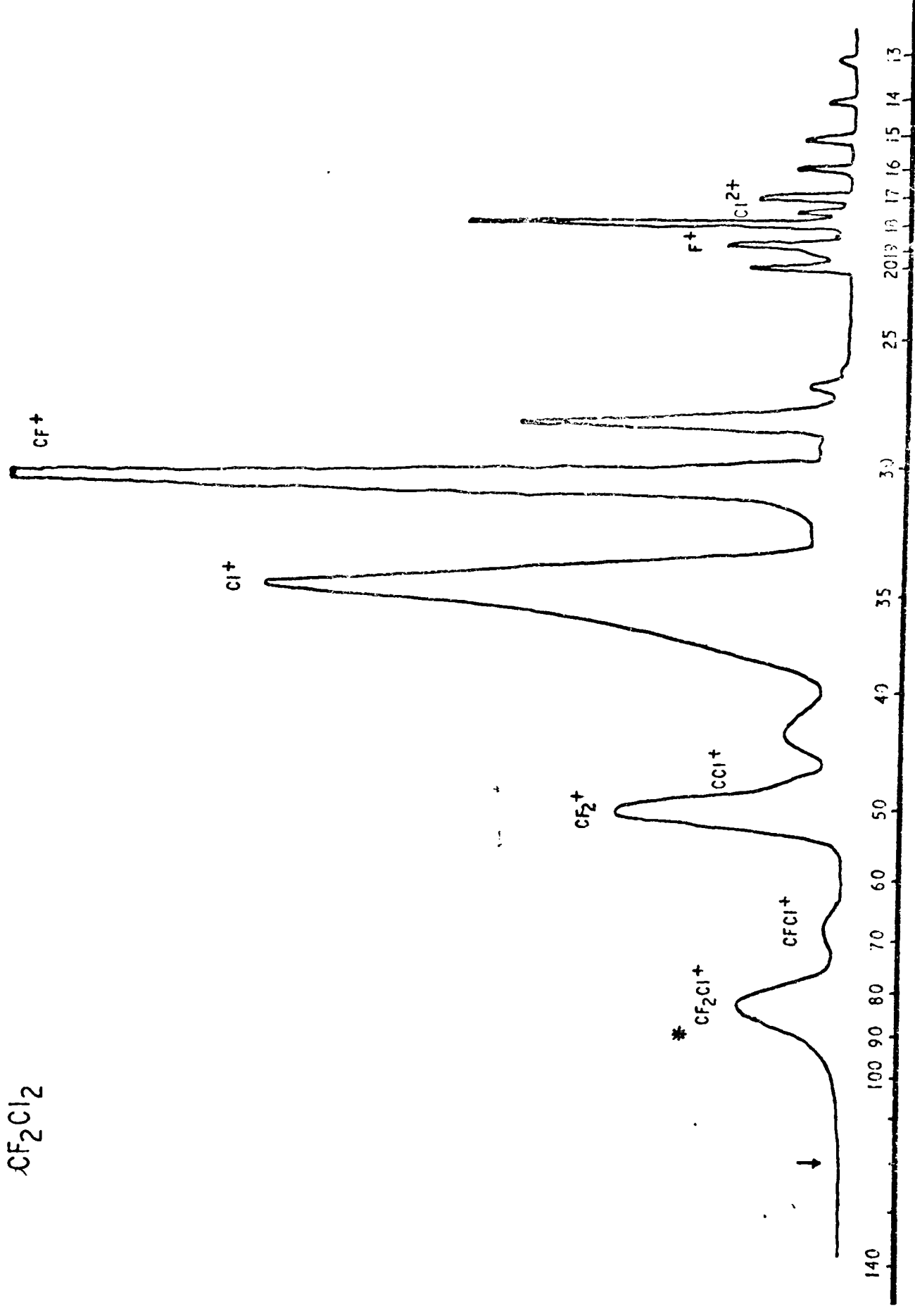
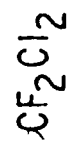
CF₄

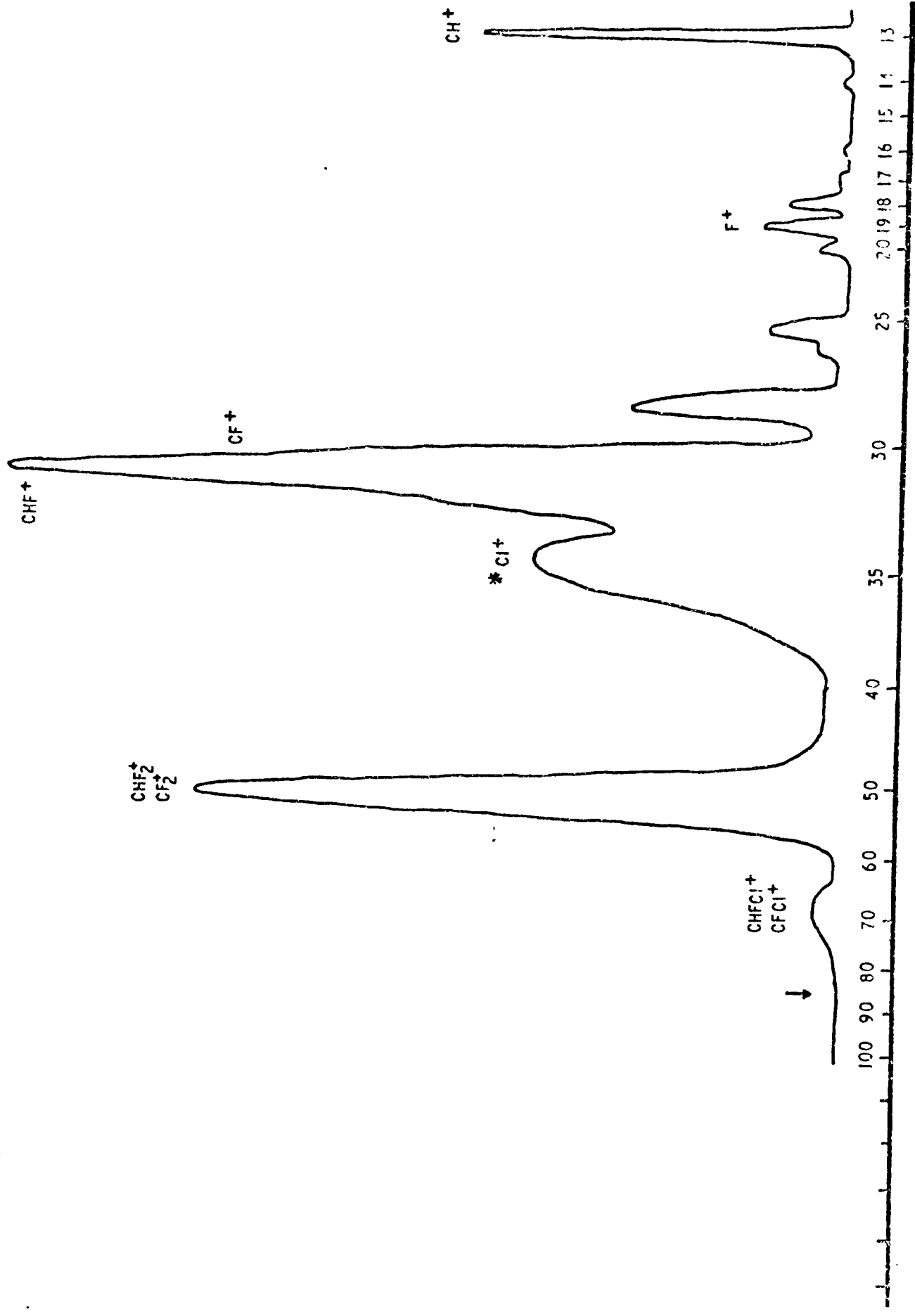




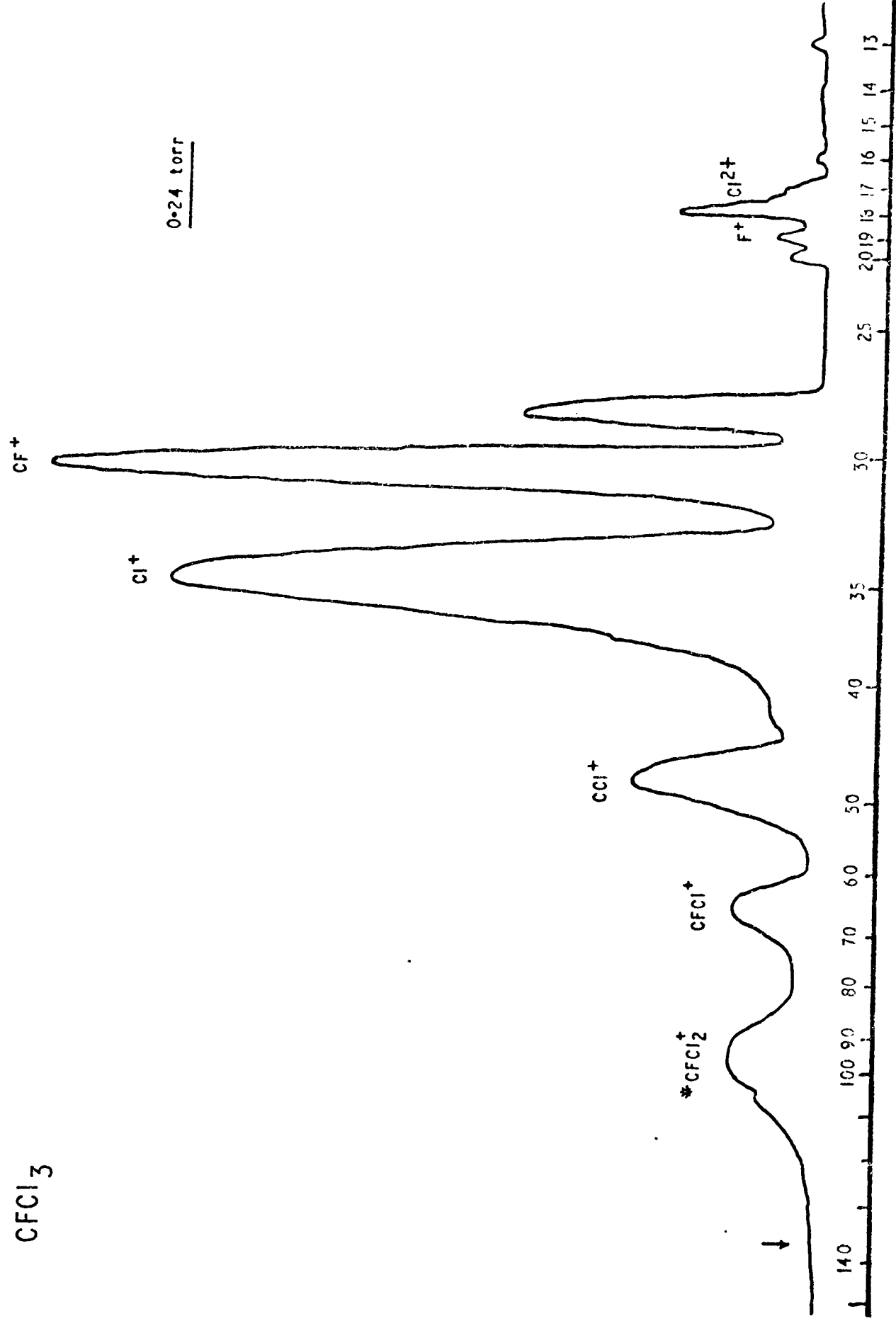
0.4 torr



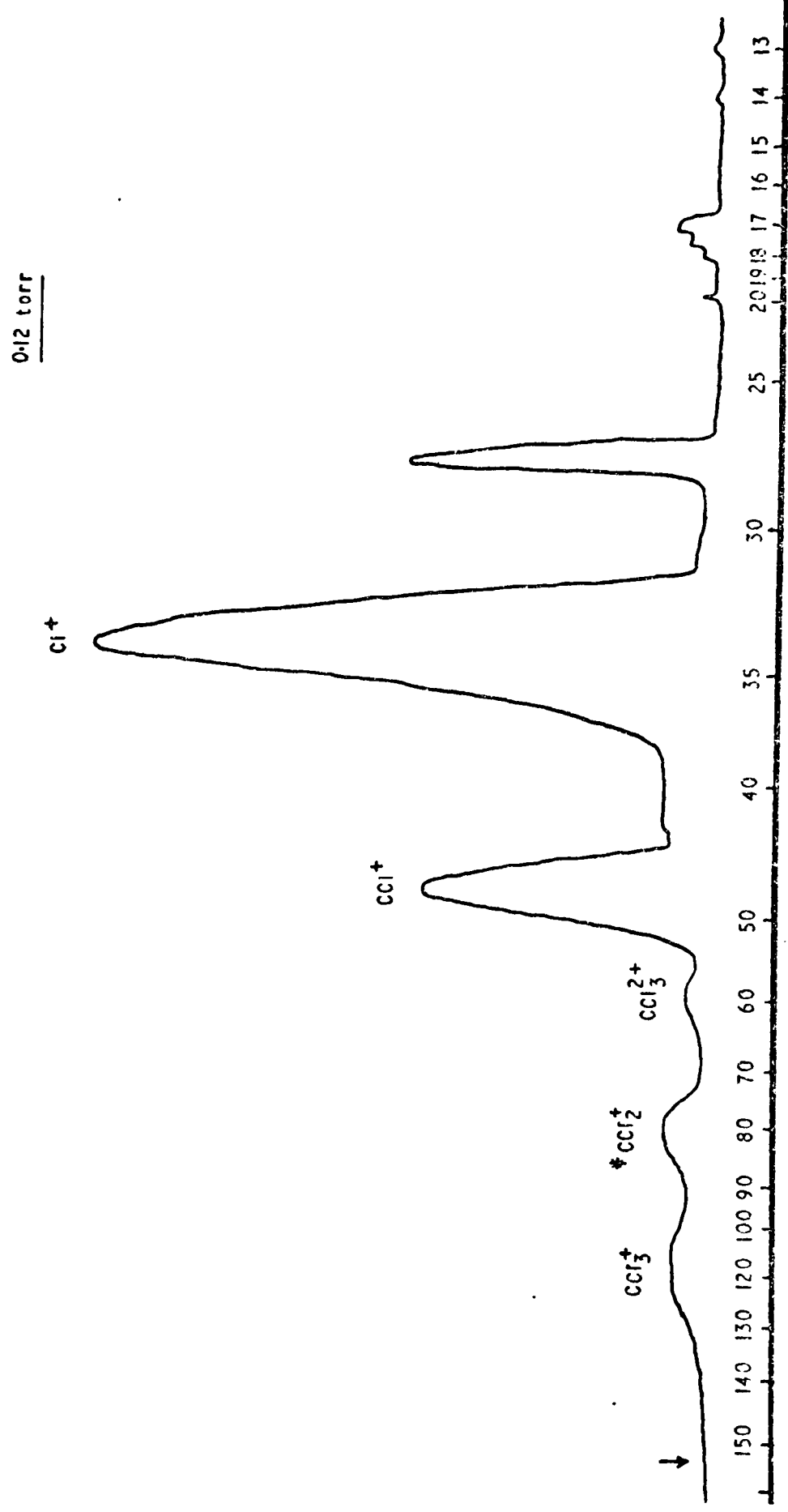




CFCl_3

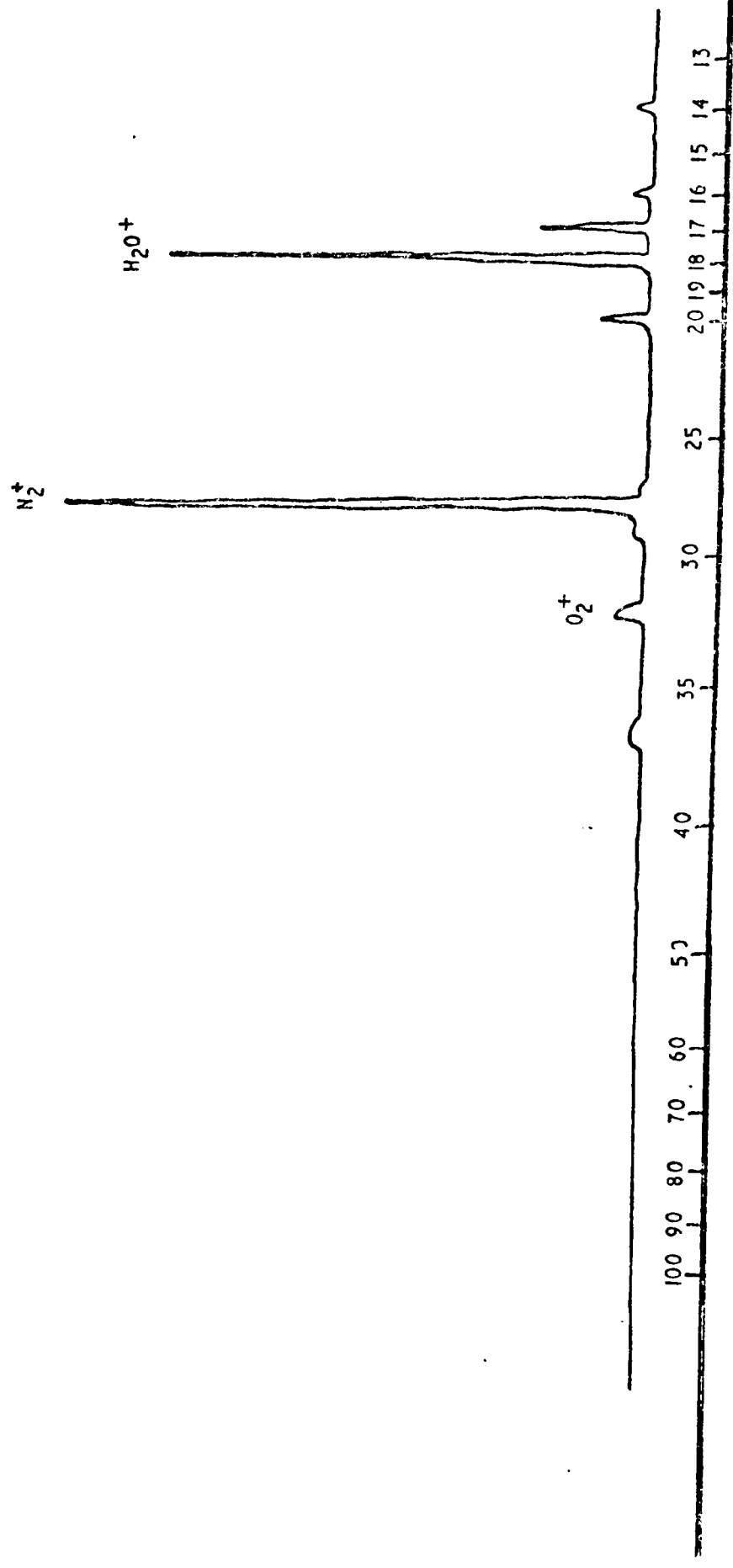


CCl_4

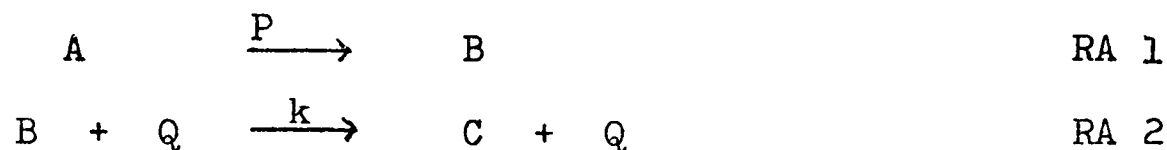


background

1.5 torr helium



If an excited state B is formed in a generation reaction
RA1 and removed by a quencher Q in reaction RA2,



$$\text{Then } \frac{dB}{dt} = P[A] - k[B][Q] \quad \text{A1}$$

and if we constrain $[A]$ to remain constant so that the rate of
formation of B is time independent, A1 may be integrated to give A2

$$[B] = \frac{P[A] (1 - \exp(-k[Q]t))}{k[Q]} \quad \text{A2}$$

It is clear from this expression that $[B]$ will only reach a constant
value when $t = \text{infinity}$. The steady state value, $[B]_{ss}$, is then
given by,

$$[B]_{ss} = P[A] / k[Q] \quad \text{A3}$$

For the actual concentration of B to reach within 1% of the steady
state concentration

$$\frac{[B]_{ss} - [B]}{[B]_{ss}} \leq 0.01 \quad \text{A4}$$

and substituting A2 and A3 into A4 yields

$$\exp(-k[Q]t) \leq 0.01$$

which gives

$$t \geq 4.6 / k[Q]$$

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ABSTRACT.

Three main catalytic chain processes are believed to contribute to the loss of ozone in the stratospheric region of the earth's atmosphere. These are the HO_x , the ClO_x and the NO_x catalytic processes. This thesis describes experiments conducted to elucidate mechanisms involved in the first two of these; the HO_x and the ClO_x chain processes. In addition the efficiency of energy transfer from $\text{O}(^1\text{D})$ to molecular oxygen is measured.

A fast-flow/photolysis system with mass spectrometric detection has been developed to study the reactions of $\text{O}(^1\text{D})$ generated by the photolysis of ozone at $2537\text{\AA}$. The method of relative quantum yields, wherein the quantum yield for loss of ozone in a series of reactions is quantified by reference to the loss of ozone in the photolysis of O_3/N_2 and O_3/He mixtures, is used to monitor ozone loss. Under suitable concentration-time conditions the ^{relative} quantum yield for ozone loss in the photolysis of O_3/N_2 and O_3/He mixtures is 1.0 and 2.0, respectively.

From measurement of the relative quantum yield for ozone loss in oxygen carrier gas the efficiency of energy transfer to produce $\text{O}_2(^1\Sigma^+_g)$ in the reaction $\text{O}(^1\text{D}) + \text{O}_2$ per $\text{O}(^1\text{D})$ atom deactivated is found to be 0.63 ± 0.18 .

Observations of the relative quantum yield for ozone loss in the photolysis of O_3/H_2 mixtures in helium carrier gas failed to show any evidence for the occurrence of a catalytic chain process. On this basis it is believed that the reaction of vibrationally excited OH^* , produced by the reaction $\text{H} + \text{O}_3$, with ozone does not generate H atoms as products. The observations are consistent with the reaction $\text{OH}^* + \text{O}_3$ producing HO_2 with unit efficiency. This result implies that the Norrish mechanism

is the one most likely to subsist in the HO_x catalytic loss of ozone in the gas phase.

The rate of quenching of $\text{O}(^1\text{D})$ by sulphurhexafluoride relative to the rate of reaction with ozone is found to be $(2.1 \pm 1.0) \times 10^{-4}$ from observations of the relative quantum yield for the photolysis of ozone in SF_6 carrier gas. Qualitative observations show that the relative rate of quenching of $\text{O}(^1\text{D})$ by carbon tetrafluoride is unlikely to be significantly faster than this.

The relative quantum yields for the photolysis of ozone in the helium carrier gas and in the presence of CF_3Cl , CF_2Cl_2 , CFCl_3 and CCl_4 are found to be ca 1.5, 2.0, 1 - 2 (dependant on $[\text{O}_3]$ and t , and 2 - 4, respectively. The quantum yields for the photolysis of $\text{CF}_3\text{Cl}/\text{O}_3$, $\text{CF}_2\text{Cl}_2/\text{O}_3$ and CFCl_3/O_3 mixtures show an increase on addition of nitric oxide. This is interpreted in terms of a catalytic chain involving formation of ClO by abstraction of chlorine from the freon by $\text{O}(^1\text{D})$, the reaction $\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$ and regeneration of ClO in the reaction $\text{Cl} + \text{O}_3$. Calculation shows that the efficiency for ClO production in the reaction $\text{O}(^1\text{D}) + \text{CF}_2\text{Cl}_2$ is approximately 0.3. The other major reaction pathway is believed not to be physical quenching of $\text{O}(^1\text{D})$. Observation of a product peak at $m/e \approx 66$ is interpreted in terms of the production of chlorine dioxide in the second reactive pathway.