THE PHOTOCHEMICAL OXIDATION OF FORMALDEHYDE

IN THE GASEOUS PHASE

by

JAMES HARRY SHARP

B. A., University of British Columbia, 1957

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the Department
of

CHEMISTRY

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

AUGUST, 1960

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Department of ___Chemistry___

The University of British Columbia,
Vancouver 8, Canada.

Date ___August 26, 1960___

ABSTRACT

The object of this work was the investigation
of the photochemical oxidation of formaldehyde in the
gaseous phase at $110^{\circ}C$. Reaction mixtures, where the
$O_2: CH_2O$ ratio was approximately 1:10, were irradiated
with ultra violet light at a wavelength of $3130A^{\circ}$ and
the reaction products analyzed. The major products were
found to be CO, H_2 and HCOOH. CO_2 was a minor product.
No peroxides were found and the reaction was oxygen
independent at low $O_2:CH_2O$ ratios.

The formation of the major products was found
to be directly proportional to the initial formaldehyde
pressure and to the intensity of the absorbed light.

A satisfactory mechanism is proposed to explain
the formation of the reaction products, and the following
kinetic equations were derived:

$$(1) \quad \frac{d\,[CO]}{dt} = \frac{2\oint' Ia(K_8 + K_3\,[HCHO]\,)}{K_8}$$

$$(2) \quad \frac{d\,[H_2]}{dt} = \frac{\oint' Ia(K_8 + 2K_3\,[HCHO]\,)}{K_8}$$

(3) $\dfrac{d\,[HCOOH]}{dt} = 2\,\phi'\,Ia\,\dfrac{K_3}{K_8}\,[HCHO]$

(4) $\dfrac{d\,[CO_2]}{dt} = \dfrac{2K_2\,\phi'\,Ia\,(K_8 + K_3\,[HCHO])}{K_1 K_8}$

Abstract Approved

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C O N T E N T S

C O N T E N T S

ACKNOWLEDGEMENT

I wish to express my sincere gratitude and
thanks to Professor C.A. McDowell for his generous
encouragement, supervision and enlightening discussions
throughout the course of the work. I also wish to ex-
tend my appreciation and thanks to Dr. K.M. Bell for
his many helpful suggestions, his kindness and his
interest in this work.

Appreciation and thanks are also expressed to
Dr. G. Porter and Dr. A.D. Kirk for their interest
and many encouraging discussions.

I am grateful to the University of British
Columbia for Student Assistantships during the 1958-
59 and 1959-60 sessions.

Finally, I wish to thank the glassblowing,
electronic and workshop staff for their assistance
in the construction of parts of the apparatus.

CHAPTER I

INTRODUCTION

1. The Thermal Oxidation

2. The Photolysis

3. The Photochemical Oxidation

CHAPTER I - INTRODUCTION

1. The Thermal Oxidation

The oxidation of many organic compounds, particularly hydrocarbons, produces aldehydes as intermediates. Hence, a knowledge of the mechanism by which aldehydes are themselves oxidized is of importance in the understanding of the general mechanism of hydrocarbon oxidation.
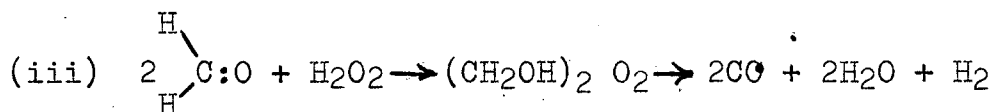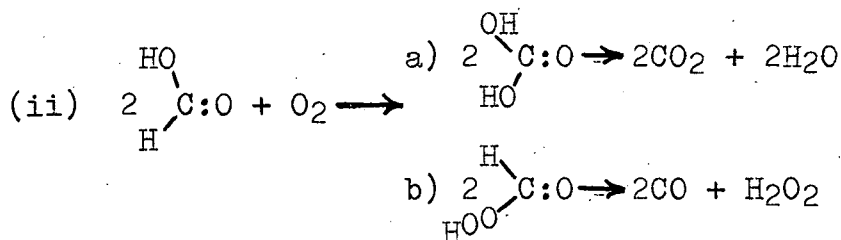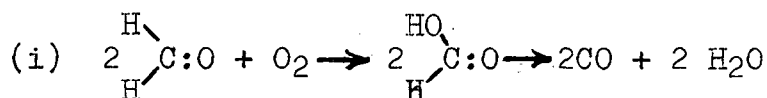
Although formaldehyde has been found to play an important role in the oxidation of many of the lighter hydrocarbons (1-9), and would appear to be the logical choice of aldehyde for the study of such mechanisms, it has not proved to be a very popular one. Several mechanisms and a number of free radicals and activated molecules have been postulated for the thermal oxidation of formaldehyde whereas there is general agreement as to the chain carriers in the slow combustion of acetaldehyde.

Askey (10), in 1930, was the first to study the oxidation of formaldehyde in the gaseous phase, Although his experiments were far from exhaustive, they did indicate that the oxidation of formaldehyde at $321°C$ was a chain mechanism and that the main products were H_2O, CO, H_2 and CO_2. No mechanism was proposed.

In the same year, Fort and Hinshelwood (11) were able to show that the rate of pressure rise was independent of the oxygen concentration and strongly dependent upon the formaldehyde concentration.

They also found that the activation energy was 20 kilo calories per mole.as determined from the times of half reaction at different temperatures. Once again their results indicated a chain mechanism, but no mechanism was proposed.

In 1936, Bone and Gardner (12) working at considerably higher pressures than the previous workers (1 atm.) studied the slow combustion between 250° and 290° C. Their experiments included 2:1 and 1:1 mixtures of formaldehyde and oxygen and they found that the former mixture was much more reactive at all temperatures. Although there was no observable induction period, they found that an increase in the surface to volume ratio of the silica reaction vessel from o.8 to 1.8 decidedly retarded the reaction. By an extensive analysis of the reaction products, they found that CO and H_2O were the major products whereas CO_2, H_2, HCOOH and peroxides were formed in smaller amounts. There was evidence that the peroxides were performic acid and dioxymethyl peroxide, $CH_2OH-O-O-CH_2OH$. These peroxidic substances were formed during the early stages of the reaction and were shown to disappear with time. They concluded that formic acid, performic acid and dioxymethyl peroxide were always intermediately formed and envisioned the following successive reations:

(i) $2 \begin{array}{c} H \\ \diagdown \\ \diagup \\ H \end{array} C{:}O + O_2 \rightarrow 2 \begin{array}{c} HO \\ \diagdown \\ \diagup \\ H \end{array} C{:}O \rightarrow 2CO + 2 H_2O$

(ii) $2 \begin{array}{c} HO \\ \diagdown \\ \diagup \\ H \end{array} C{:}O + O_2 \rightarrow$

    a) $2 \begin{array}{c} OH \\ \diagdown \\ \diagup \\ HO \end{array} C{:}O \rightarrow 2CO_2 + 2H_2O$

    b) $2 \begin{array}{c} H \\ \diagdown \\ \diagup \\ HOO \end{array} C{:}O \rightarrow 2CO + H_2O_2$

(iii) $2 \begin{array}{c} H \\ \diagdown \\ \diagup \\ H \end{array} C{:}O + H_2O_2 \rightarrow (CH_2OH)_2 \; O_2 \rightarrow 2CO + 2H_2O + H_2$

Later, in the same year, Spence (13) showed that in the presence of an extensive surface of powdered glass oxidation proceeded according to the following equation:

$$CH_2O + O_2 \longrightarrow H_2O + CO_2$$

In unpacked pyrex vessels, he showed that an increase in the diameter of the reaction vessel resulted in an increase in the rate of formation of carbon monoxide. From the variation of initial rates of pressure rise with temperature, Spence calculated an overall activation energy of 17.6 kilo calories per mole. Although oxygen had little influence on the rate of reaction, he found that the rate was strongly dependant on the formaldehyde concentration. In agreement with Bone and Gardner he found $HCOOH$, H_2, H_2O, CO and CO_2 as reaction products.

He suggested a reaction chain which is analogous to that given by Bäckstrom (14) for the oxidation of aldehydes in the liquid phase. The chain included HCO_3H, activated H_2CO and activated $HCOOH$. With the assumption of steady state for these molecules the following equation for the initial rate of disappearance of formaldehyde was obtained.

$$- \frac{dF}{dt} = K^i (H_2CO)^2 - K^{ii}(H_2CO) + K^{iii}$$

Although this equation is in fair agreement with his experimental results, little weight can be placed upon his mechanism.

Some time later, in 1939, Snowden and Style (15) reinvestigated formaldehyde oxidation at $344°C$ and using both analytical and monometric techniques along with a spectrophotometric method of determining formaldehyde, they found that CO, H_2O, H_2 and CO_2 were the main products. Their analyses clearly showed that CO and CO_2 were not the only carbon containing products, especially in the earlier stages of the reaction, and since only traces of peroxides were detected, they obtained evidence for the presence of $HCOOH$.

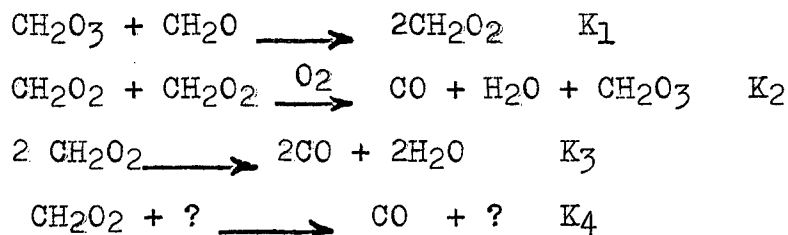They found that the rate of oxidation could be expressed by an equation of the form,

$$- \frac{dF}{dt} = KF(F-C)$$

where F is the formaldehyde concentration and where K and C are constants.

Both these constants varied erratically. This formula
was also shown to fit Spence's results satisfactorily.
The above expression can be formally deduced from the
following scheme.

$$X + F \longrightarrow 2X \quad Ka$$

$$X + X \longrightarrow \text{end products} \quad Kb$$

$$X \longrightarrow \text{end products} \quad Kc$$
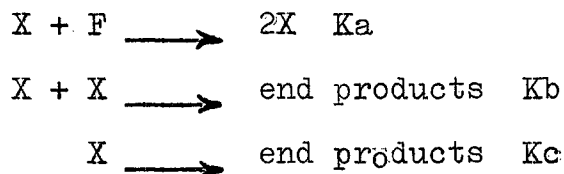
and, since they found evidence that CO_2 formation was,
in part at least, connected with a chain ending reaction,
they postulated the following tentative reaction scheme.

$$CH_2O_3 + CH_2O \longrightarrow 2CH_2O_2 \quad K_1$$

$$CH_2O_2 + CH_2O_2 \xrightarrow{O_2} CO + H_2O + CH_2O_3 \quad K_2$$

$$2\ CH_2O_2 \longrightarrow 2CO + 2H_2O \quad K_3$$

$$CH_2O_2 + ? \longrightarrow CO + ? \quad K_4$$

They also roughly examined the effect of various
surface treatments and found that concentrated nitric
acid produced the least changeable surface and, at the
same time, one which gave a reasonable rate of reaction.
Hydrofluoric acid and caustic soda solutions both gave
slow and unsteady rates and small yields of formic acid.
The presence of mercury vapour increased the rate of pressure
rise.

Axford and Norrish (16), in 1948, were the next investigators to study the oxidation of gaseous formaldehyde. They also followed the reaction analytically and monometrically in the region of 340° C. They found that CO and H_2O were the major products and that CO_2 and H_2, in almost equal amounts, were the minor products. No evidence for the presence of HCOOH or peroxides was found. The effect of varying the oxygen concentration on the rate of the reaction was negligible but they found that the initial rate was nearly proportional to the square of the formaldehyde concentration. They determined the activation energy of the reaction from variation of initial rates with temperature, and found it to be equal to 21.0 kilo calories per mole. Small quantities of oxygen were found to induce a slow decomposition of formaldehyde where it was normally quite stable. No observable diameter effect upon the rate of pressure rise was noted in any of their experiments. Hence several discrepancies were noted between their work and the work of previous investigators.

They criticized the mechanism of Snowden and Style on two points. First, although oxygen is present in their reaction scheme, it does not enter into their kinetics to obtain the resulting equation and hence its presence is obscure. Secondly, they made no suggestion as to the initial process, except to state that it probably occurred on the surface.

In order to explain their results, Axford and Norrish suggested a mechanism based on the oxidation of hydrogen and hydrogen - carbon monoxide mixtures and involving Hydrogen and oxygen atoms and hydroxyl and HO_2 radicals.

Work on the photolysis and the photo oxidation of formaldehyde had led to the suggestion that the reactions

$$H + HCHO = H_2 + CHO$$

$$O + HCHO = OH + CHO$$
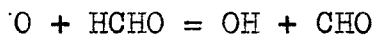
were involved. There was some doubt as to the stability of the formyl radical, but since Akeroyd and Norrish (17) in 1936 and Leermakers (18) in 1934 had concluded from their results that the formyl radical decomposed to CO and H atoms above 100°, Axford and Norrish assumed that, at elevated temperatures, the formyl radical would split to give CO and H. Hence, the preceding equation can be written.

$$H + HCHO = H_2 + CO + H$$

$$O + HCHO = OH + CO + H$$
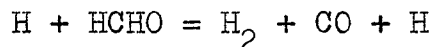
From their results and these assumptions, they postulated the following reaction ($F = CH_2O$).

1) $O_2 + F \longrightarrow H_2CO_2 + O$ K_1 initiation

2) $O + F \longrightarrow OH + H + CO$ K_2

3) $H + F \longrightarrow H_2 + CO + H$ K_3 propagation (decomposition)

4) $OH + F \longrightarrow H_2O + CO + H$ K_4

5) $H + O_2 + F \longrightarrow H_2O + CO + OH$ K_5 Propagation (oxidation)

6) $H + O_2 + F \longrightarrow H_2O + CO_2 + H$ K_6

7) $H + O_2 + O_2 \longrightarrow HO_2 + O_2$ K_7

8) $H + O_2 + X \longrightarrow HO_2 + X$ K_8 termination

9) $H + O_2 + Wall \longrightarrow HO_2$ K_9

With reference to (1) they point out that Bowen and Tietz (19) found that oxygen reacts rapidly with formaldehyde to give performic acid at low temperatures and hence it was reasonable to suppose, at higher temperatures, that the normal acid is formed. They found that this scheme fitted their experimental results well and were able to derive the following equation:

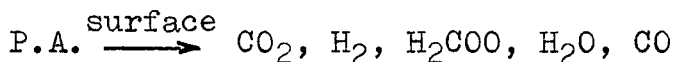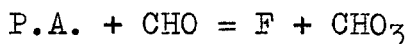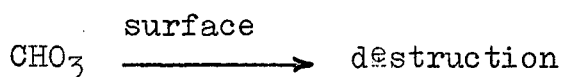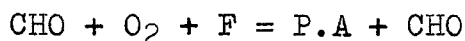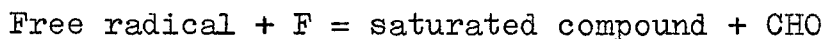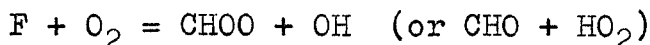$$-\frac{dF}{dt} = \frac{K_1}{K_7} 2K_5 (F)^2$$

However, it should be pointed out, that although they form formic acid in their proposed scheme they did not detect it in their experimental results.

Although there seemed to be a difference of opinion between the kinetic results of Axford and Norrish on the one hand and Spence, Snowden and Style on the other, Lewis and von Elbe (20) in 1951 attempted to reconcile these two views. They noted two important points. The first was that Snowden and Style had found that mercury vapour greatly increased the rate of pressure rise and that Axford and Norrish had used heated mercury seals leading to the reaction vessel. Secondly, Axford and Norrish obtained no induction period whereas Snowden and Style found induction periods varying with the type of surface. Lewis and von Elbe concluded that the experimental arrangement of Axford and Norrish may have introduced sufficient mercury vapour into the reaction vessel to cause rapid removal of peroxide by decomposition, thus simplifying the kinetics.

In reference to Gorin's (21) work, they give evidence that the formyl radical was much more stable than supposed by Axford and Norrish. Style and Summers (22) had also come to the conclusion that the formyl radical was more stable than had been anticipated.

With these facts, Lewis and von Elbe suggested a mechanism in which HCO_3H was formed by a chain reaction where the formyl radical was the predominent chain carrier.

The performic acid then diffused to the wall and
decomposed into CO, H_2O, CO_2, H_2 and HCOOH. Further
gas phase reactions of the intermediate performic
acid with HCO were neglected if the destruction was
rapid. If however, the vessel surface was inactive
toward peroxide destruction, gas phase reactions of the
performic acid were considered important and the kinetics
became more complex. Their reaction scheme may be written
as follows where F = HCHO, P.A. = HCOOOH.

$$F + O_2 = CHOO + OH \quad (or \ CHO + HO_2)$$
$$Free \ radical + F = saturated \ compound + CHO$$

$$CHO + O_2 + F = P.A + CHO$$
$$CHO + O_2 + M = CHO_3 + M$$

$$CHO_3 \xrightarrow{surface} destruction$$
$$P.A. + CHO = F + CHO_3$$
$$P.A. + F = CHOO + H_2O + CHO$$
$$P.A. \xrightarrow{surface} CO_2, H_2, H_2COO, H_2O, CO$$

Hence, the simple kinetics of Axford and Norrish
were attributed to a system which rapidly destroyed per-
oxides, whereas the more complicated kinetic data of Spence,

Snowden and Style, Bone and Gardner was attributed to a system where the intermediate P.A. was not rapidly destroyed.

More recently, Scheer (23) in 1954 also attempted to reconcile the difference between the kinetics of previous workers. CO, CO_2, O_2, H_2, $HCOOH$ and $HCHO$ were analysed mass spectroscopically. Products, condensable at $-110^{\circ}C$ from a reaction in an aged vessel showed the presence of formic acid plus some unidentified peaks which were assigned to performic acid. In systems containing mercury vapour, he found that the formic acid concentration was much reduced.

He envisioned the same overall reaction as Bone and Gardner to account for the products of the oxidation and proposed a rather complicated reaction scheme. Scheer states that although his mechanism provides a satisfactory explantation for most of the observations encountered for this reaction, there are several results reported by prevous investigators which do not fit into his scheme.

The history of the thermal oxidation of formaldehyde has been traced from the original work of Askey to the more recent work of Scheer and it is obvious that the mechanism is very complex and that the reaction is very dependent upon the area and type of surface.

Photochemical initiation has been used by several workers in non thermal oxidation studies of formaldehyde.

However, before discussing the work which has been
accomplished in this field, it is advantageous to re-
view some of the work on the photolysis of formaldehyde.

2. The Photolysis

   Formaldehyde was first investigated photochemically
by Berthelot and Gaudechon (24) in 1910. They found
that in the form of trioxymethylene it is mainly decomposed
into H_2 and CO with small quantities of CO_2 and CH_4 by
ultra violet light.

   In 1924, Bredig and Goldberg (25) studied the
reaction in the vapour phase and found that at 80° the
reaction proceeded almost quantitatively according to

$$CH_2O = H_2 + CO$$
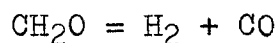
but found that at 195° considerable quantities of CO_2
and CH_4 were found. These authors did not attempt to
measure the quantum efficiency of the reaction or to
characterize the wavelength of the active radiation.

   Norrish and Kirkbride (26) in 1932 were the first
investigators to measure the quantum yield of form-
aldehyde at isolated wave lengths. They measured the
quantum efficiency for three spectral regions, 2540-
2800A°, 3030 - 3130A° and 3340 - 3650A° at 100°C and

found that the mean quantum efficiencies were o.9, 1.1 and 0.7 respectively.

Since the predissociation limit lies at 2800A$^{\circ}$ (27) they found no evidence for a photochemical threshold associated with it. In the predissociation range, they concluded that the reaction

$$h\nu + CH_2O = H_2 + CO$$
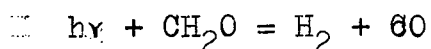
was spontaneous while in the region of fine structure it occurs as a result of a collision between an excited molecule and a second body, such a collision bringing about dissociation by a redistribution of the energy of activation.

$$h\nu + H_2CO = H_2CO*$$

$$X + H_2CO* = H_2 + CO + X$$
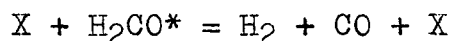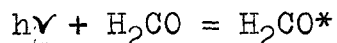
Akeroyd and Norrish (17) in 1936 in studying the chain photolysis of formaldehyde at higher temperatures came to the conclusion that CO was formed directly in the process of disruption and that the formyl radical and hydrogen atom are only set free in small amounts (10% of the decomposition).

They found that the quantum yeilds were 1.0 at 100°,
2.9 at 200°, 8.0 at 250° with increasing quantum yeilds
up to 100 at 350°. Their modified scheme for the photo-
lysis of formaldehyde may be written as follows:

1),2) $h\gamma + HCHO = H_2 + CO$ Primary
$= H + HCO = H + H + CO$ Process

3) $H + HCHO = H_2 + HCO$

4) $HCO = H + CO$

5) $H + H = H_2$
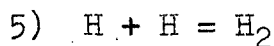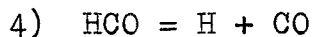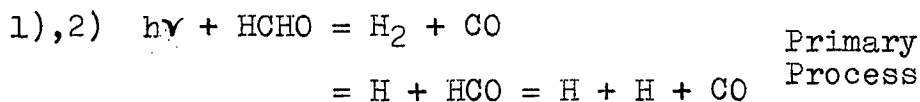
Gorin (21) in 1939 studied the photdysis in the
presence of iodine vapour which resulted in a contradiction
to the above mechanism. At 100° and a wavelength of
3130 A° he found that the permanent gases consisted al-
most entirely of CO. In addition, the ratio of HI/CO
was nearly two. These facts showed that the main reaction
was the splitting off of one hydrogen atom since it takes
102 kilo calories to pull off the two hydrogen atom from
formaldehyde and it is obvious tha a quantum of light at
3130A° possesses sufficient energy to detatch only one hydrogen
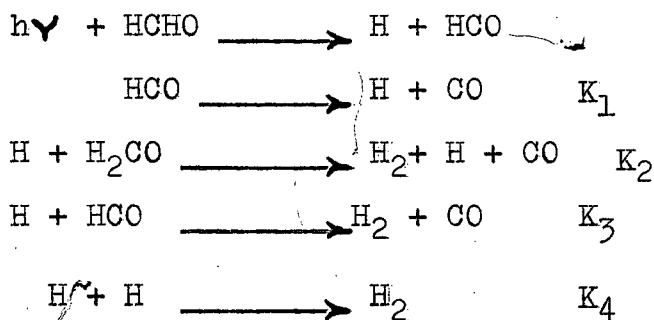atom.

Hence he postulated the primary process at 3130 A° as

$$h\gamma + HCHO = H + HCO$$
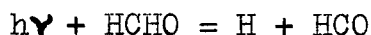
In the presence of iodine vapour this would be followed by

$$H + I_2 \longrightarrow HI + I$$

$$HCO + HCO \longrightarrow H_2CO + CO$$

The quantum efficiency for the formation of hydrogen iodide was unity and the rate of formation of CO in the presence of I_2 was $\frac{1}{2}$ as large as it was in the absence of iodine as required by the above mechanism.

From his results using light irradiation of wavelength 3650A° he was able to show that the formyl radical was much more stable than was previously anticipated, about 26 kilo calories being required to dissocia te it.

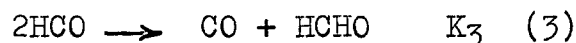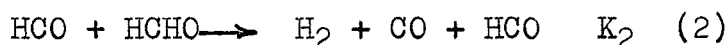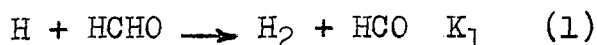Gorin's scheme for the chain photolysis is as follows:

$$h\gamma + HCHO \longrightarrow H + HCO$$

$$HCO \longrightarrow H + CO \qquad K_1$$

$$H + H_2CO \longrightarrow H_2 + H + CO \qquad K_2$$

$$H + HCO \longrightarrow H_2 + CO \qquad K_3$$

$$H + H \longrightarrow H_2 \qquad K_4$$

Since, K_1 had a large temperature coefficient, K_2 would be dominant at lower temperature s while K_3

would be the largest at high temperatures.

Style and Summers (22) in 1945 concluded that
since hydrogen atoms had been reported to react rapidly
with formaldehyde (28) neither of the mechanisms as pro-
posed by Norrish and Carruthers or by Gorin could be
considered satisfactory. They suggested the following
which was a simplification of Gorin's scheme.

$$CH_2O + h\nu \longrightarrow H + HCO \qquad A$$

$$H + HCHO \longrightarrow H_2 + HCO \qquad K_1 \qquad (1)$$

$$HCO + HCHO \longrightarrow H_2 + CO + HCO \qquad K_2 \qquad (2)$$

$$2HCO \longrightarrow CO + HCHO \qquad K_3 \qquad (3)$$
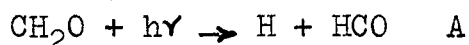
Steacie and Calvert (29) deduced an activation
energy of 13.5 kilo calories for the decomposition
of the formyl radical from their results on the photo-
lysis of formaldehyde. The mechanism they proposed is:

$$CH_2O + h\nu \longrightarrow H + HCO \qquad (i)$$

$$H + H_2CO \longrightarrow H_2 + HCO \qquad (ii)$$

$$HCO \longrightarrow H + CO \qquad (iii)$$

$$HCO \xrightarrow{\text{wall}} \text{products} \qquad (iv)$$
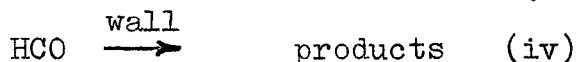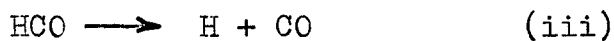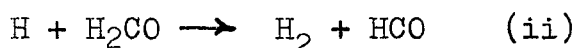
More recently, in 1954, Horner, Style and Summers
(30) in a discussion of the oxidation of formaldehyde
suggested that at 100°C, K_{iii} was zero.

At higher temperatures, when (iii) becomes sig-
ificant, they suggest that it should not be a first
order decomposition, but would more likely be a second
order process. Hence, (iii) would become

$$HCO + H_2CO \longrightarrow H + CO + H_2CO$$
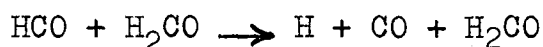
From these examples, we see that there was some
doubt as to the stability of the formyl radical and
as to the mechanism of the photolysis of formaldehyde.

3. The Photochemical Oxidation

In 1936, Carruthers and Norrish (31) studied
the photochemical oxidation of formaldehyde at $100^{\circ}C$.
Upon irradiation, they found a rapid decrease in pressure
and were able to account for this decrease by an analysis
of the reaction products. The products consisted of
HCOOH, H_2O and CO as major products and CO_2 and H_2 as
minor products. No peroxides were detected.

They explained their results by the primary ox-
idation of formaldehyde to formic acid according to the
equation,

$$HCHO + 1/2\ O_2 \longrightarrow HCO_2H$$
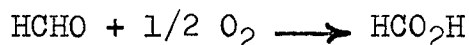
The presence of CO_2, CO, H_2 and H_2O was explained by the subsequent decomposition of the formic acid in two ways.

$$CO_2 + H_2 \longleftarrow H \cdot COOH \longrightarrow CO + H_2O$$
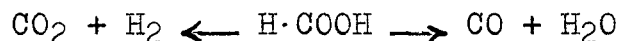
Evidence for the above decomposition at lower wavelengths had been noted by several workers (32).

They found that increasing the oxygen concentration had little effect on the course of the reaction. The quantum yield for a $CH_2O + O_2$ mixture was reported to be 12.6 whereas the quantum yield for a 2:1 mixture was reported to be 9.0.

The next study of the photo-oxidation of formaldehyde was made in 1945 by Style and Summers (22). They found the same products as Carruthers and Norrish but their quantum yields are considerably lower. Only traces of peroxides were detected.

Using light of wavelength $2650A^O$ and $2537A^O$ they found that $\phi_{HCOOH} \rangle \phi_{CO} \rangle \phi_{H_2} \rangle \phi_{CO_2}$ at 100^OC and that the quantum yield depended somewhat on the oxygen concentration. It is interesting to note that at low oxygen pressures, their quantum yields increased rapidly.

They concluded that the mechanism of the oxidation depended to some extent upon the photolysis of formaldehyde. Since the formyl radical was known to react rapidly with oxygen (33), they reasoned that reactions (2) and (3) of their proposed mechanism of the photolysis of formaldehyde could be neglected when the pressure of oxygen was above a few tenths of a millimeter of mercury. This assumption had already been made by Lewis and von Elbe (34).

The variation of ϕ_{H_2} with increased oxygen concentration led them to postulate a competition for (1)

$$H + O_2 + M \longrightarrow HO_2 + M$$
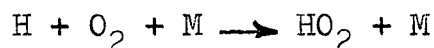
HO_2 would also be formed by the reaction of the formyl radical with oxygen,

$$HCO + O_2 \longrightarrow HO_2 + CO$$
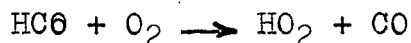
and since at low oxygen concentration, ϕ_{H_2} was greater than unity, they postulated a subsequent reaction of the HO_2 radical with formaldehyde to regenerate hydrogen atom,

$$HO_2 + CH_2O = CO + CO_2 + HCOOH + H$$
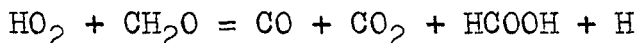
The chain breaking reaction was given as

$$HO_2 = ?$$
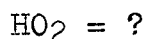
The above mechanism only partially accounted
for their experimental results and it is especially
weak in that formic acid, a major product, is not
satisfactorily accounted for.

In their paper of 1954, Horner, Style and Summers
(30) suggested the following mechanism at 100^0C,

$$H_2CO + h \longrightarrow H + HCO \qquad (i)$$

$$M + H + O_2 \longrightarrow HO_2 + M \qquad 1$$

$$H + CH_2O \longrightarrow H_2 + HCO \qquad 2$$

$$HCO + O_2 \longrightarrow HO_2 + CO \qquad 3$$

$$HO_2 + CH_2O \longrightarrow H + CO + ? \qquad 4$$

$$HO_2 \longrightarrow H_2 + CO \qquad 5$$
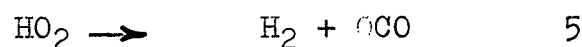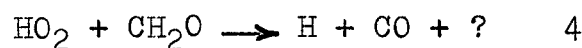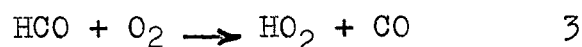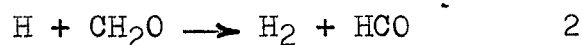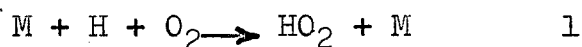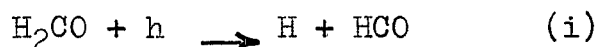
and although it is in fair agreement with their previous
results, it does not include formic acid.

At higher temperatures, $\sim 150^oC$, their results
had indicated that a new mechanism occurred and in this
region, they replaced reactions 4 and 5 by

$$HO_2 + CH_2O \longrightarrow P \qquad\qquad 4^1$$

$$P \longrightarrow R + \text{end products} \qquad\qquad 5^1$$

$$P + CH_2O \longrightarrow H + CO + \text{end products} \qquad 6^1$$

$$R + CH_2O \longrightarrow HCO + qH_2 + nCO + mCO_2 + 1HCO_2H \quad 7^1$$

$$R \xrightarrow{\text{WALL}} \alpha H_2 + \beta CO + - - - -$$

where $P = H_2 \ C \overset{O\cdot}{\underset{O_2H}{}}$, $R = HC \overset{O}{\underset{O.}{}}$
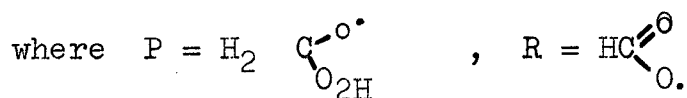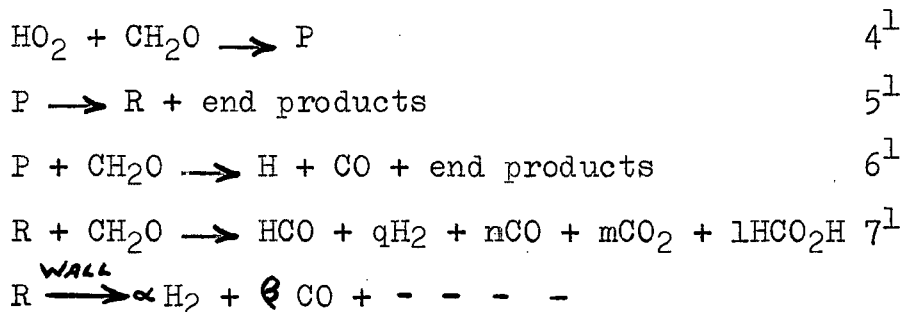
This mechanism was not unambiguously established and the true mechanism is obviously extremely complicated.

It is clear from the preceding discussions on the thermal oxidation, the photolysis and the photochemical oxidation of formaldehyde that there is a wide discrepancy of results, that the mechanisms are very complex, and that no one mechanism has been decidedly established.

The object of this investigation was to investigate the photochemical oxidation of formaldehyde at relatively low oxygen concentration. With the aid of gas chromatography it was hoped that a more complete analysis of reaction products could be made and that a satisfactory mechanism could be proposed for the photochemical oxidation at $\sim 100^\circ C$.

CHAPTER II

PREPARATION

A   Materials

B   Calibration

CHAPTER II - PREPARATION

A Preparation of Materials

1. Formaldehyde

Formaldehyde was prepared by the method of Spence and Wild (35) and stored at liquid nitrogen temperature. The apparatus, which was connected to the vacuum system, is shown in Fig. 1. Dow Corning Silicon high vacuum grease was used for the heated taps.

The distillation vessel was partially filled with chemically pure paraformaldehyde which had been dried over granular anhydrous magnesium perchlorate in a vacuum dessicator for 48 hours. A piece of glass wool was then introduced on top of the paraformaldehyde to prevent particles of the solid from being carried over into the condensing system during the distillation. The system was then pumped down with the mechanical and diffusion pumps. During this period, the separator and trap were heated with an electric gun to $\sim 150^{\circ}$C while the current in the electrical heating tapes (shaded area in Fig. 1) was adjusted, by means of a variac, to give a uniform temperature of 110°C.

Distillation was begun by heating the paraformaldehyde in a beaker of glycerine which rested on a small hot plate. The initial distillation temperature during this time was 110°C.

FIGURE 1

TO REACTION VESSEL

B-24

TRAP, -180°C

TO MECH & DIFF. PUMPS

4 FOLDED "U" TUBES

SEPARATOR, -78°C

B-24

GLASS WOOL

PARAFORM.

DISTILLATION VESSEL
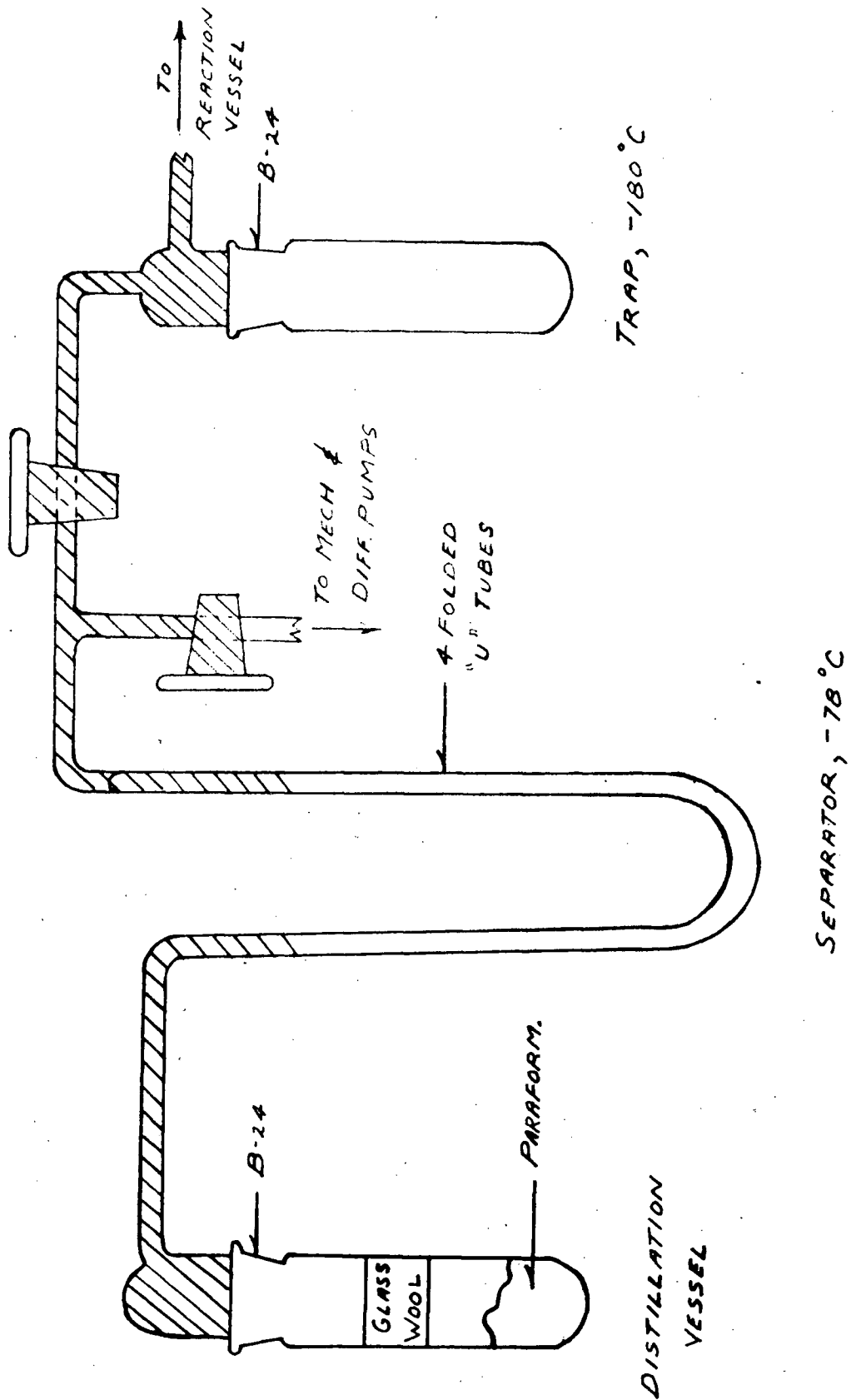
During the removal of the first fraction by the pumps, the
condensing vessels were continually heated with the electric
gun.

After the first fraction had distilled off, the
bottom portion of the separator was cooled in an ethanol -
dry ice mixture, the trap was immersed in liquid nitrogen
and the stopcock leading to the mechanical and diffusion
pumps was closed. As distillation proceeded, the rate
gradually became slower and slower and the temperature
of the glycerine bath was raised to 120°C.

When sufficient solid had collected in the trap,
the glycerine bath was removed and the apparatus once more
connected to the pumps. The cold bath was removed from the
separator and the trap was isolated from the separator
via the stopcock shown in Fig. 1.

It was found that pure monomeric formaldehyde could
be prepared in this manner and that very little polymerization
occurred as long as the trap was kept at liquid nitrogen
temperature.

2. Oxygen

Oxygen, 99.6 per cent pure, was taken from a cylinder, passed through a spiral trap immersed in an ethanol - dry ice bath and led to the main line of the vacuum system. The main line was flushed out 3 or 4 times with the oxygen and then the oxygen was allowed to enter a large evacuated bulb until atmospheric pressure had been attained. The oxygen was stored there until ready for use. The admitting system is shown in Fig. 2.

3. Actinometer Solutions

Actinometry was carried out according to the work of Hatchard and Parker (36). The following solutions were prepared.

a.) Potassium Ferrioxalate

Pure $K_3 Fe(C_2O_4)_3$ was prepared by mixing 3 volumes of 1.5 molar A.R. potassium oxalate with 1 volume of 1.5 molar A.R. ferric chloride with vigorous stirring. The ferrioxalate was then recrystallized 3 times from warm water and dried in a current of air at $45^{\circ}C$. A 6×10^{-3} molar solution was then made by dissolving 2.947 grams of the recrystallized product in 800 ml of water. 100 ml of $1.0N$ H_2SO_4 was then added and the solution diluted to 1 litre. This solution was stored in a black bottle until required.

FIGURE 2

TO VACUUM SYSTEM

COTTON WOOL

Hg

FROM O₂ CYLINDER

SPIRAL TRAP (-78°C)
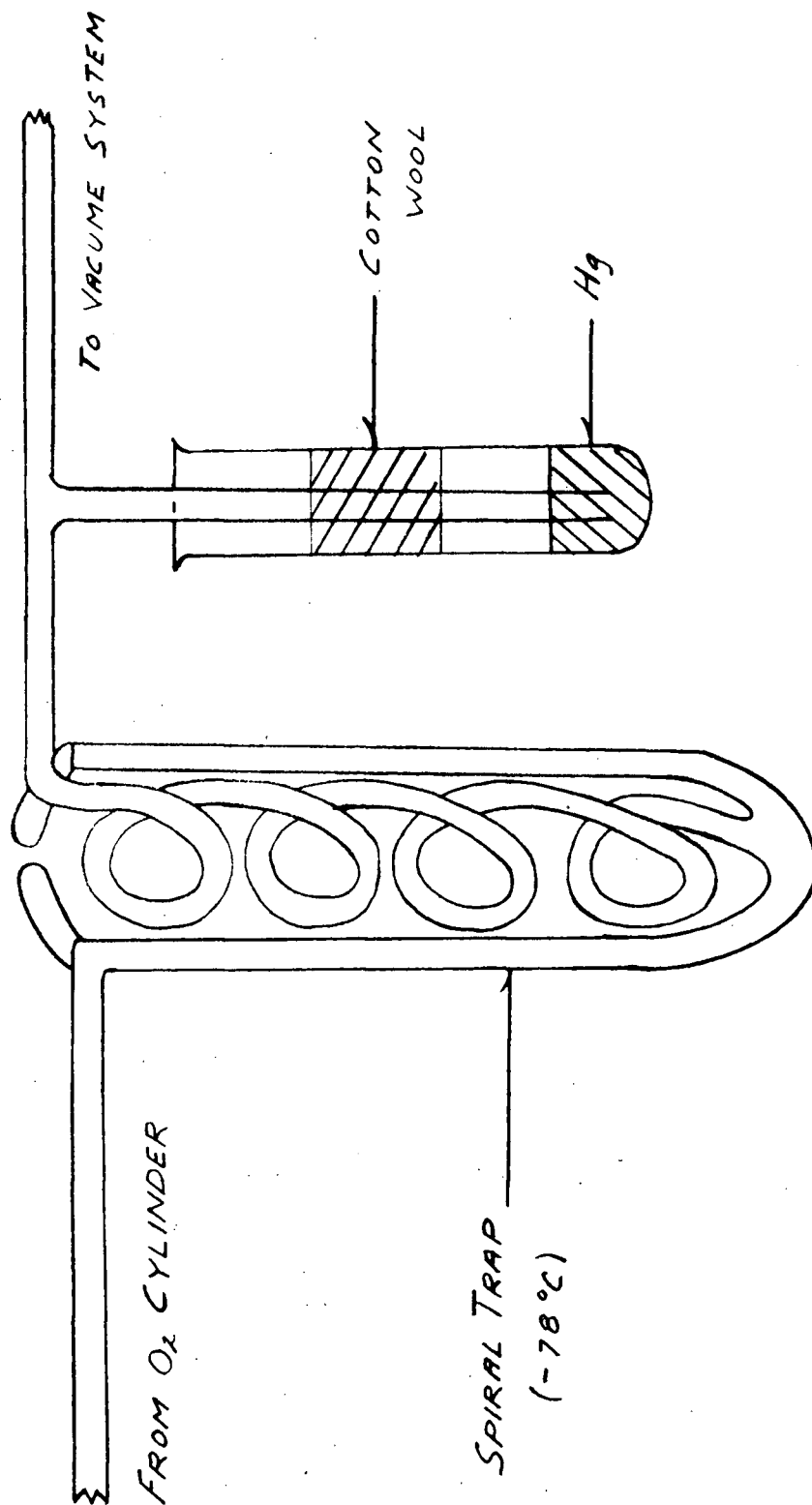
b.) <u>Potassium dichromate</u>

A 0.1 N solution was prepared by dissolving 2.5062 grams of A.R. $K_2Cr_2O_7$ in 500 ml of distilled water.

c.) <u>Ferrous Sulphate</u>

The 0.1 M $FeSO_4$ solution was prepared by dissolving 1.4 grams of A.R. $FeSO_4 \cdot 7H_2O$ in 50 ml of 0.1 N sulphuric acid. This solution was then standardized with the standard potassium dichromate. The proceedure was as follows:

A 10 ml sample of the ferrous sulphate solution was transferred to a 125 ml conical flask and 2 ml of conc. HCl and 3 ml of phosphoric acid (85%) were added. Several drops of barium diphenyl amine sulphonate indicator were then added and the resulting solution titrated with the standard dichromate until a permanent violet - blue colour was observed.

Hence, $N(FeSO_4) = \dfrac{(0.1) \ X \ Volume \ K_2Cr_2O_7 (ml.)}{10}$

The oxidation - reduction equations involved are,

$$6e + 14H^+ + Cr_2O_7^= \longrightarrow 2Cr^{+++} + 7H_2O$$

$$6Fe^{++} \longrightarrow 6Fe^{+++} + 6e$$

$$Cr_2O_7^= + 6Fe^{++} + 14H^+ \longrightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O$$
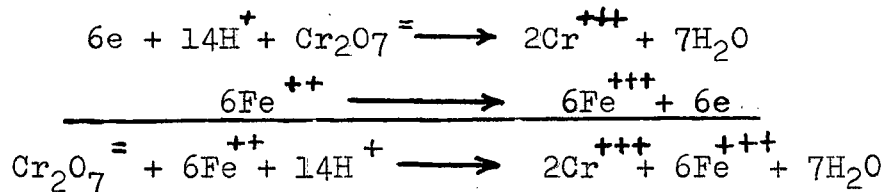
d.) <u>Phenanthroline</u>

A 0.1% phenanthroline solution was prepared by dissolving one gram of 1:10 phenanthroline monohydrate in 100 grams of distilled water.

e.) <u>Buffer Solution</u>

The buffer solution was prepared by mixing 600 ml of normal sodium acetate and 360 ml of normal sulphuric acid and diluting the resulting solution to one litre.

4) <u>Solutions for Peroxide Determination</u>

Tests for peroxides in the reaction products were made by employing the method of Young et al (37). The following solutions were prepared.

a.) <u>Ammonium Thiocyanate in Methanol</u>

A stock solution of ammonium thiocyanate was used for preparing a solution of ferrous thiocyanate. 5 grams of A.R. ammonium thiocyanate was dissolved in about 600 ml of absolute methanol, 0.5 ml of concentrated sulphuric acid was added, and the resulting solution diluted to one litre. This solution invariably had a very faint pink colouration, probably due to the presence of a minute amount of Fe^{+++} in the sulphuric acid.

No precautions to use perfectly dry methanol were taken
since the presence of varying proportion of water made
no difference to the accuracy of the test. The solution
was normally quite stable and was stored in an amber
coloured bottle until required for use.

b.) Ferrous Thiocyanate in Methanol

A solution of ferrous thiocyanate is slowly
oxidized by atmospheric oxygen with the formation of
a dark red solution of ferric thiocyanate complex.
For this reason, the solution of ferrous thiocyanate
was always made up just prior to being used. 50 ml of
the stock solution of ammonium thiocyanate was shaken
with 0.1 grams of A.R. ferrous ammonium sulphate for
one minute and allowed to stand for two minutes. The
solution was then decanted from the undissolved ferrous salt.

5. Light Filter Solutions

Two light filter solutions and a glass filter were
used in this work as recommended by Hunt and Davis (38)
to isolate a fairly narrow wavelength band close to the
3130A$^{\text{o}}$ mercury line.

a.) Potassium Hydrogen Phthalate

Five grams of A.R. potassium hydrogen phthalate was
dissolved in 500 ml of distilled water. This solution
was always used in conjunction with the two centimeter
filter cell.

Since this solution was not stable to the action of light, it was stored in the dark and a new filter had to be prepared after each run.

b.) Potassium Chromate

0.246 grams of potassium chromate was dissolved in 500 ml of distilled water. This solution was always used in conjunction with the one centimeter filter cell. It was quite stable to the action of light and this filter could be used for several runs.

c.) Glass Filter

A 2 mm Corning 9863 filter was used in conjunction with the above solutions.

6. Gas Chromatographic Columns

Essentially, two columns were used throughout this work. The first, a molecular sieve column, was used for the separation of hydrogen, oxygen, nitrogen and carbon monoxide. The second, designated as column "J" by Perkin Elmer was successfully used for the analysis of carbon dioxide.

a.) Molecular Sieve Column

This column was prepared by grinding molecular sieve (aluminium calcium silicate), obtained from the British Drug Houses Ltd., with a mortar and pestle so that it passed through a #10 and was retained on a #20 Tyler standard screen sieve.

The screened material was then packed into a 10' length
of copper tubing, $\frac{1}{4}$" O.D., and neatly folded. Helium
gas was then passed through the column at $100^{\circ}C$ for 8
hours. It was found that this column effectively separated
hydrogen, oxygen, nitrogen and carbon monoxide both
qualitatively and quantitatively. This column could
not be used for the analysis of carbon dioxide since it
was irreversibly absorbed.

b.) <u>Column "J"</u>

This column was obtained from the Perkin - Elmer
Corporation and consisted of silica gel, type 15, packed
in a two meter length of $\frac{1}{4}$" stainless steel tubing.

7. <u>Solutions for the Analysis of Formic Acid</u>

a.) <u>Indicator Solution</u>

This solution was prepared by dissolving 3 - 4 drops
of phenolphthalien in 100 ml of distilled water.

b.) <u>N/1000 Sodium hydroxide</u>

This solution was prepared by diluting $\sim$ N/10
sodium hydroxide.

It was standardized with N/100 hydrochloric acid which had been standardized against a known weight of mercuric oxide in potassium iodide. The standardized base was kept in a stoppered flask and although it was restandardized on several occasions, it was found to be quite stable.

B CALIBRATION

1. Actinometry

a.) Calibration Graph for Ferrous Iron

Four ml of the standardized 0.1M Ferrous sulphate solution was diluted to 500 ml with 0.1N sulphuric acid. The resulting solution contained 0.8×10^{-6} moles Fe^{++} per c.c. Next, 0, 1, 2, 4, and 6 ml aliquots of this solution were added to individual 50 ml volumetric flasks. A sufficient volume of 0.1N sulphuric acid was then added to each flask to make the total volume of acid equal to 25 ml. Five ml of the 0.1% 1:10 phenanthroline solution and 12.5 ml of the buffer solution were then added to each flask. The flasks were diluted to volume with distilled water and allowed to stand for $\frac{1}{2}$ hour. At the end of this time, the optical densities of the developed solutions were measured at 510 mμ on a Unicam Sp. 600 spectrophotmeter.

Distilled water was used as the reference in each case. A graph of the resulting optical densities as ordinate against the concentration of ferrous ion in micro moles as abscissae is shown in Figure 3. The tabulated results are shown in Table I.

TABLE I

ml. Fe solution	Micro moles Fe	Corrected optical Density
0	0	0
1	0.8	0.164
2	1.6	0.330
4	3.2	0.670
6	4.8	1.062

b.) Actinometric Calibration of the Light Source

The descriptions of the optical system, the photometer unit and the light source are given in Chapter III.

The lamp and the photometer unit were turned on and allowed to warm up for 15 minutes with the shutter S (Figure 12) closed. During this time, the reaction vessel was thoroughly evacuated and fresh filter solutions were put in cells F-1 and F-2 (Figure 12).
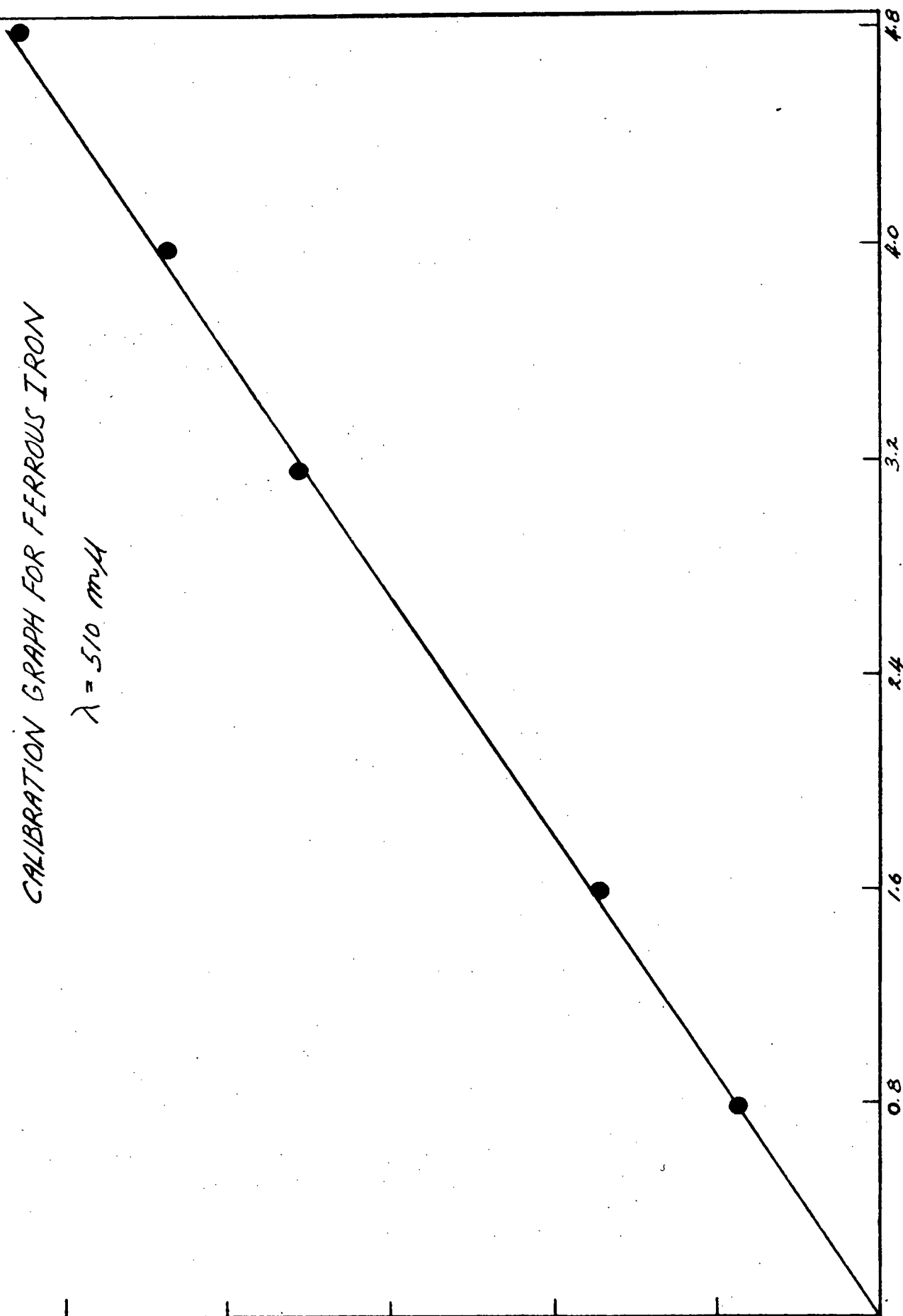
FIGURE 3

CALIBRATION GRAPH FOR FERROUS IRON

$\lambda = 510 \ m\mu$

When the lamp had attained a steady output, the shutter
was opened and light was allowed to fall on the photocell.
The potentiometric reading was taken by means of the
photometer unit and was designated as I_0 (initial).
The shutter was now closed and the photocell exactly
replaced by a cell containing 10 ml of the ferrioxalate
actinometer for a specified time interval. At the end
of this time, the actinometer was removed and the photocell
replaced. Another reading I_0 (final) was then taken.
(It was necessary to take both initial and final readings
since the potassium hydrogen phthalate solution slowly
photolyzed) The average of these I_0 readings was used.

After irradiation, the actinometer solution was
transferred to a 50 ml amber coloured flask and 5 ml of
the phenanthroline solution and 5 ml of the buffer solution
were added. The volume was then made up to 50 ml with
distilled water and the flask was allowed to stand for
$\frac{1}{2}$ hour. The optical density of the resulting solution was
then measured on the Unicam at a wavelength of 510 mμ.
The resulting optical density was then converted to micro
moles of ferrous ion produced. The above procedure was
carried out in duplicate and blanks were run along with
each determination.

Results and calculations are shown below.

Determination	I_o (initial)	I_o (final)	I_o Averg.	Time of Irradiation	O.D.	Corrected O.D.	Micro moles Fe
1	9080 Ω	8800 Ω	8940 Ω	15 min.	1.117	1.039	4.71
1-B					0.078		
2	8663 Ω	8530 Ω	8596 Ω	15 min.	1.058	0.980	4.44
2-B					0.078		

* The mean quantum yield as given by Hatchard and Parker (36) for the ferrioxalate actinometer at 3130A$^\circ$ is 1.23.

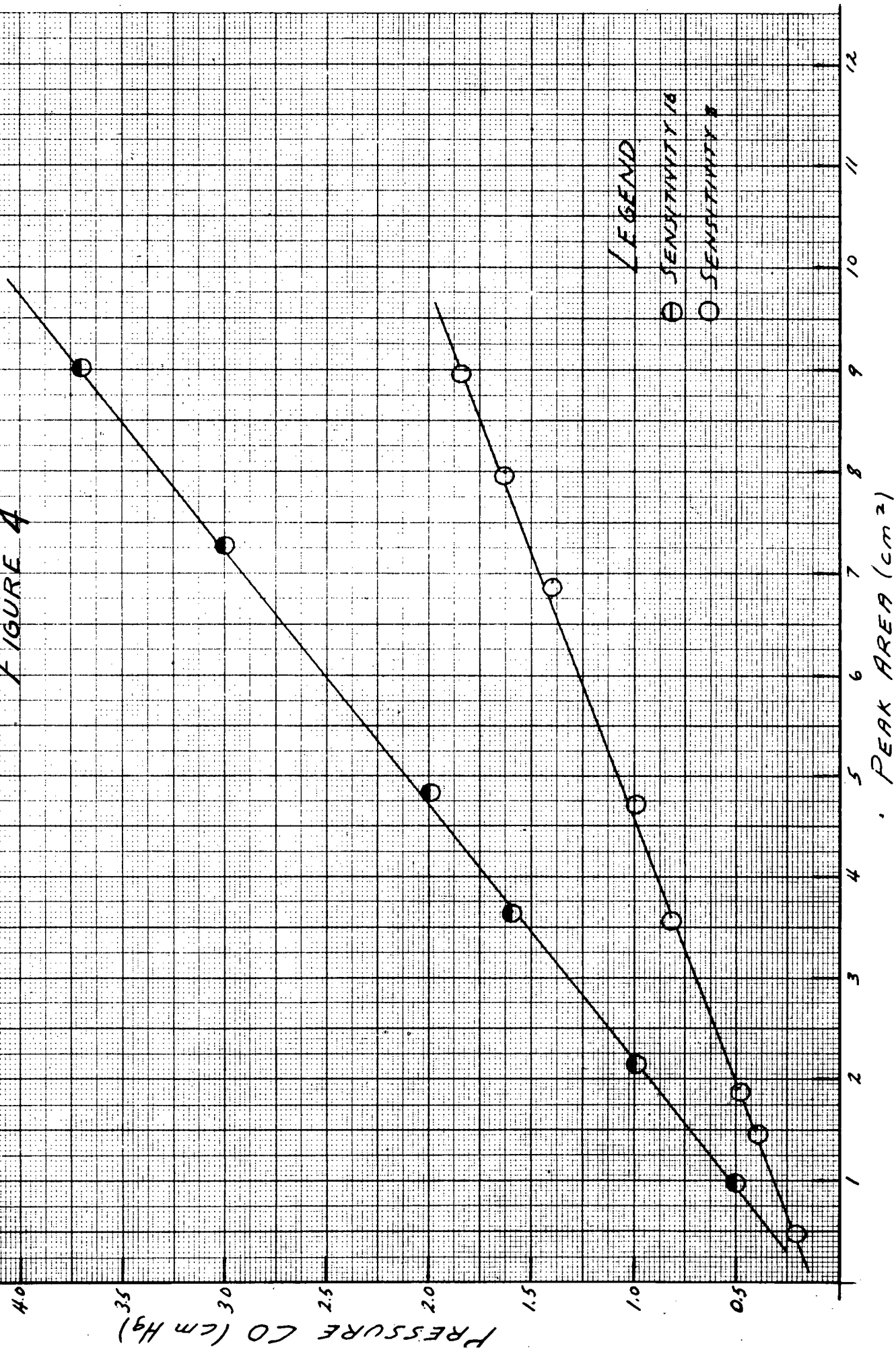Determination #1

Quanta per ohm per sec $= \dfrac{(4.71 \times 10^{-6})\ (6.02 \times 10^{23})}{(1.23)\ (15 \times 60)\ (8940)}$

$= 2.87 \times 10"$

Determination #2
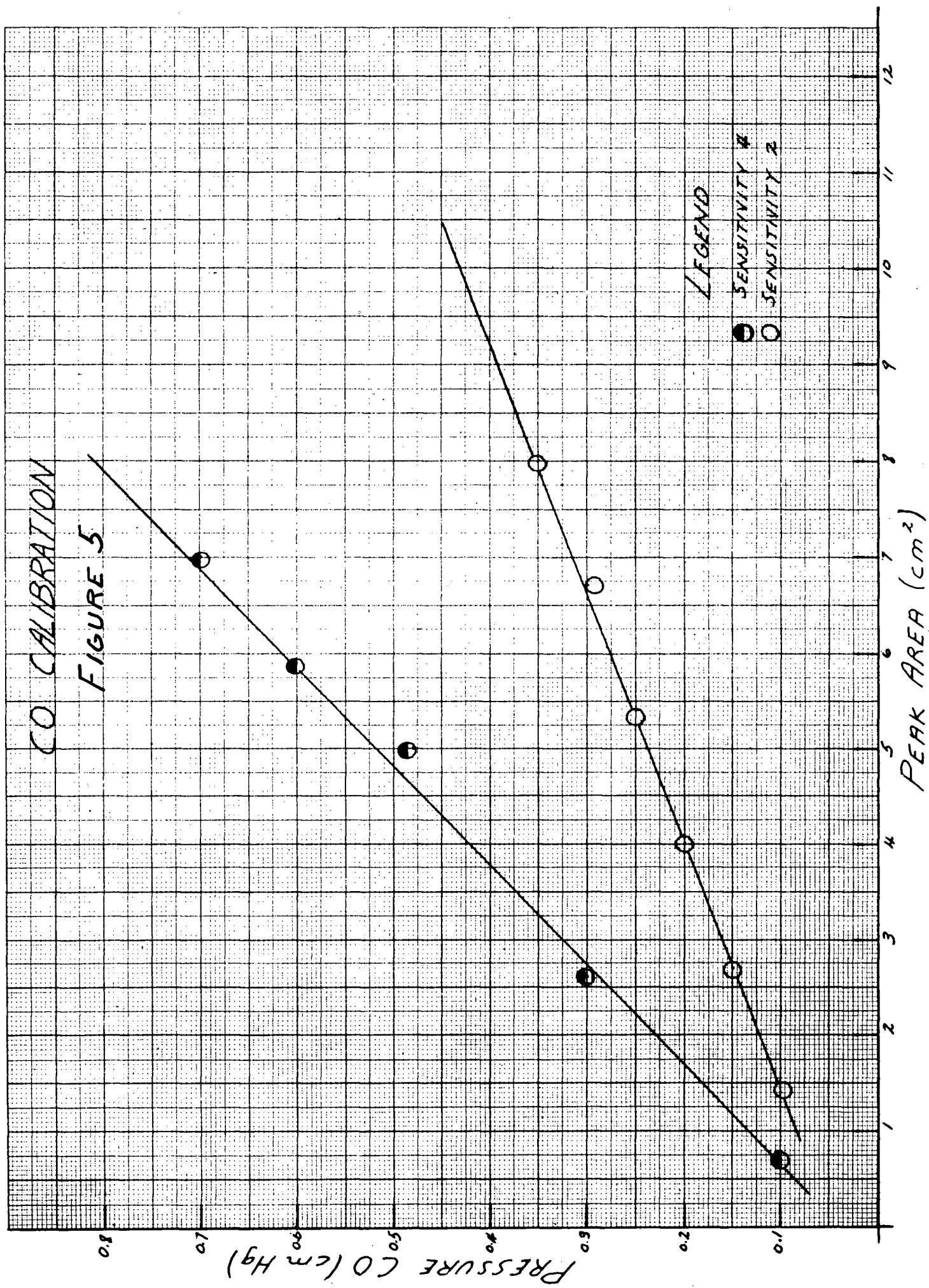
Quanta per ohm per sec $= \dfrac{(4.44)\ (6.03) \times 10^{17}}{(1.23)\ (15 \times 60)\ (8596)}$

$= 2.84 \times 10"$

Average Quanta per ohm per sec $= 2.85 \times 10"$

CO CALIBRATION

FIGURE 4

CO CALIBRATION

FIGURE 5

2. Calibration Graphs for Reaction Products

a.) Carbon Monoxide

Carbon monoxide, 99% pure, was taken from a cylinder and admitted to an evacuated gas sampling bulb. The bulb was then placed on the gas admission system for the Perkin Elmer Vapour Fractometer (Figure 16) and various pressures of the CO were admitted to the Fractometer. The molecular sieve column was used for analysis. Calibration graphs were then prepared in which the pressures of CO in mm was plotted against the area of the peak in cm^2 for different sensitivities. These graphs appear in Figure 4 and 5. The column temperature was maintained at $69^{\circ}C$, the column pressure was 0.2 $\#/in^2$ and the flow rate was approximately 150 cc He per minute.

b.) Hydrogen

Hydrogen was taken from a cylinder and admitted to an evacuated gas sampling bulb. Calibration was carried out in the same way that the CO calibration was done except that peak heights were used instead of peak areas. The results are plotted in Figure 6. Since the same column was utilized, the experimental conditions were maintained.

H_2 CALIBRATION

FIGURE 6

LEGEND
● SENSITIVITY ½
◐ SENSITIVITY ¼
○ SENSITIVITY ⅛

PRESSURE H_2 (cm Hg)

PEAK HEIGHT (cm)
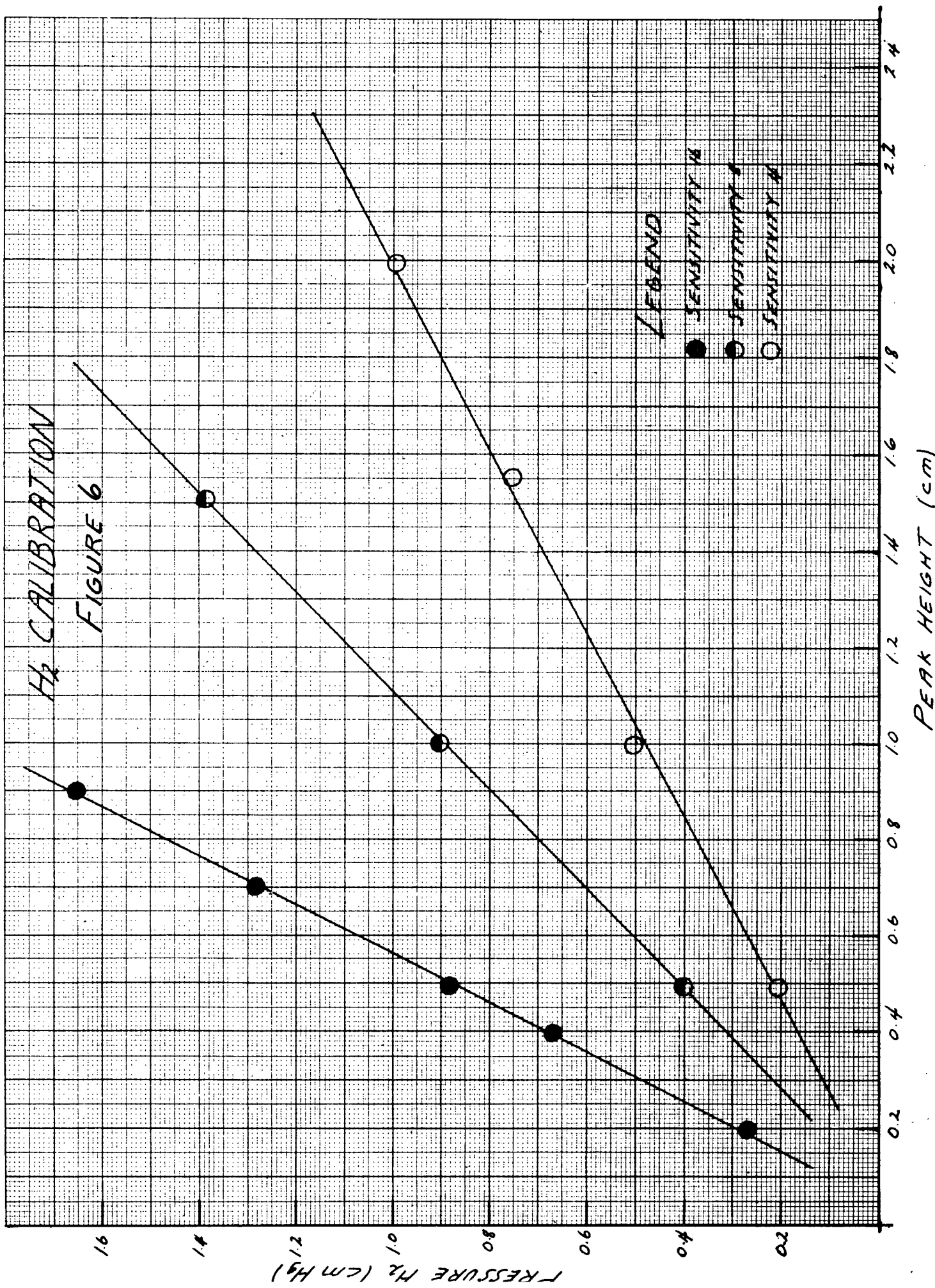
c.) Carbon Dioxide

Carbon dioxide was taken from a cylinder attributed to contain 99% CO_2. The same method of calibration was employed as above except that column "J" was used. The experimental conditions for the CO_2 analysis were: column temperature = 69°C; column pressure = $7^{\#}/in^2$; flow rate = 68 cc He per minute.

The results are plotted in Figure 7.

CO₂ CALIBRATION
SENSITIVITY 2
FIGURE 7
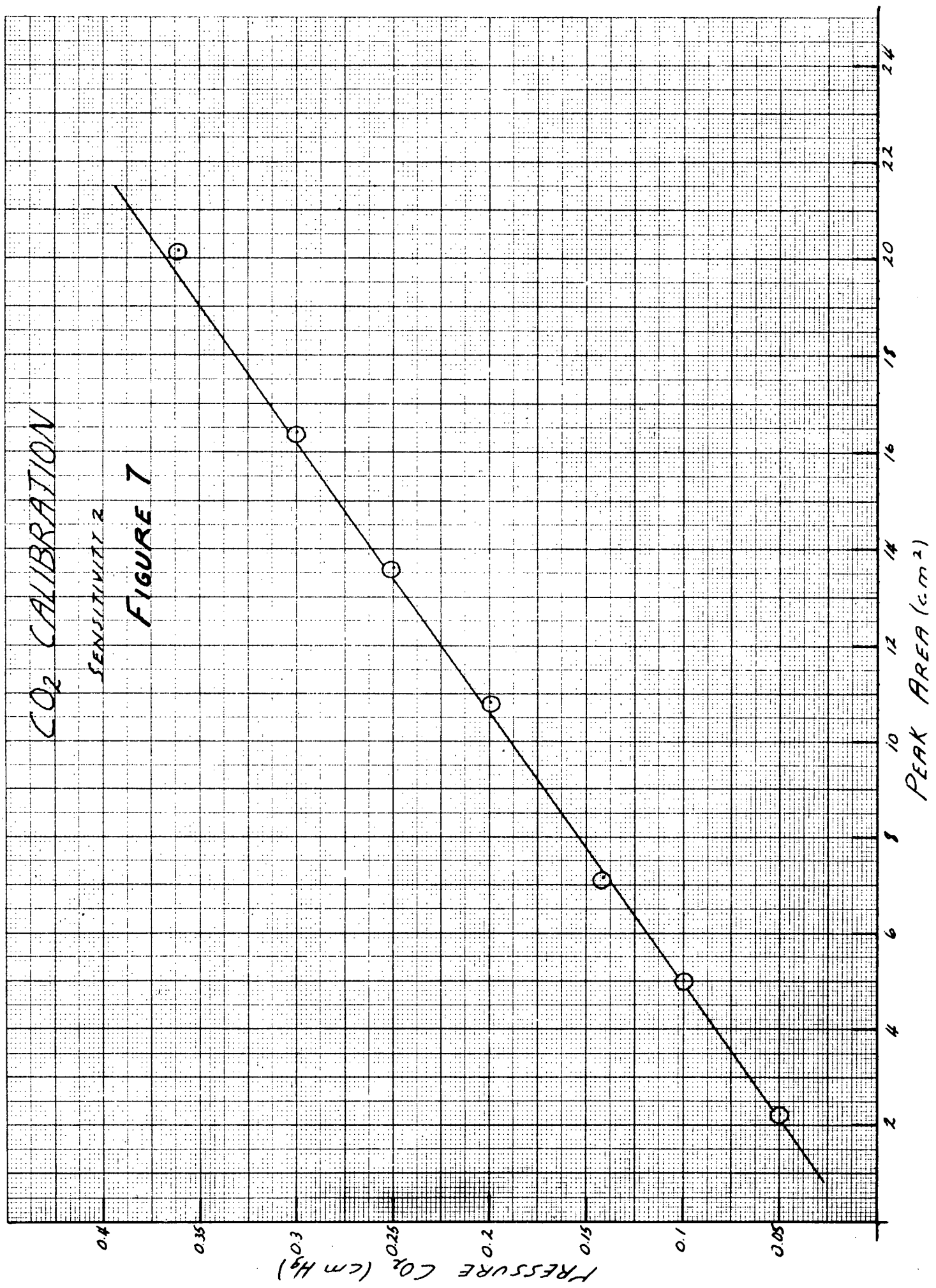
CHAPTER III

APPARATUS

1.   The Vacuum System

2.   The Furnace

3.   The Optical System

4.   The Lamp

5.   The Photometer Unit

6.   The Gas Admission System for the Perkin-Elmer Model 154-C Vapour Fractometer

7.   Temperature Measurement – The Thermal Couple

CHAPTER III - APPARATUS

1. The Vacuum System

The vacuum system as shown in Figures 8-A and 8-B
was of conventional design and constructed of pyrex
apart from the quartz reaction vessel. All the high
vacuum stopcocks were lubricated with Apiezon N grease
except those which were wound with electrical heating
tape. The latter were lubricated with Dow Corning
high vacuum Silicone grease which was stable to $400^{O}F$.

The evacuation system (not shown) comprised a one-
stage mercury diffusion pump of conventional design
backed by a "Hyvac" rotary oil pump. A P_2O_5 trap and
cold trap were also included.

The cold trap was detatchable and the refrigerant
was always liquid nitrogen. Using the liquid nitrogen
trap, the system could be readily evacuated to 10^{-5} mm Hg.

The one piece quartz reaction vessel was cylindrical
with flat ends and was connected to the vacuum system by
a quartz-to-pyrex graded seal. It was 10.0 cms long and
had an illuminated volume of 73.0 ml. The narrow gauge
tubing between the cell and the tap to the vacuum system
had a total volume of 3.0 ml and was not illuminated.

FIGURE 8-A

REMOVEABLE GAS SAMPLING BULB

TO REACTION VESSEL

REMOVEABLE TRAP

B10

TO PUMPS

2 WAY STOPCOCK
1. AIR
2. VACUME

Hg

BELL TRAP

TO PUMPS

B10

CALIBRATED BURETTE

VALVE

TOEPPLER PUMP

TO PUMPS
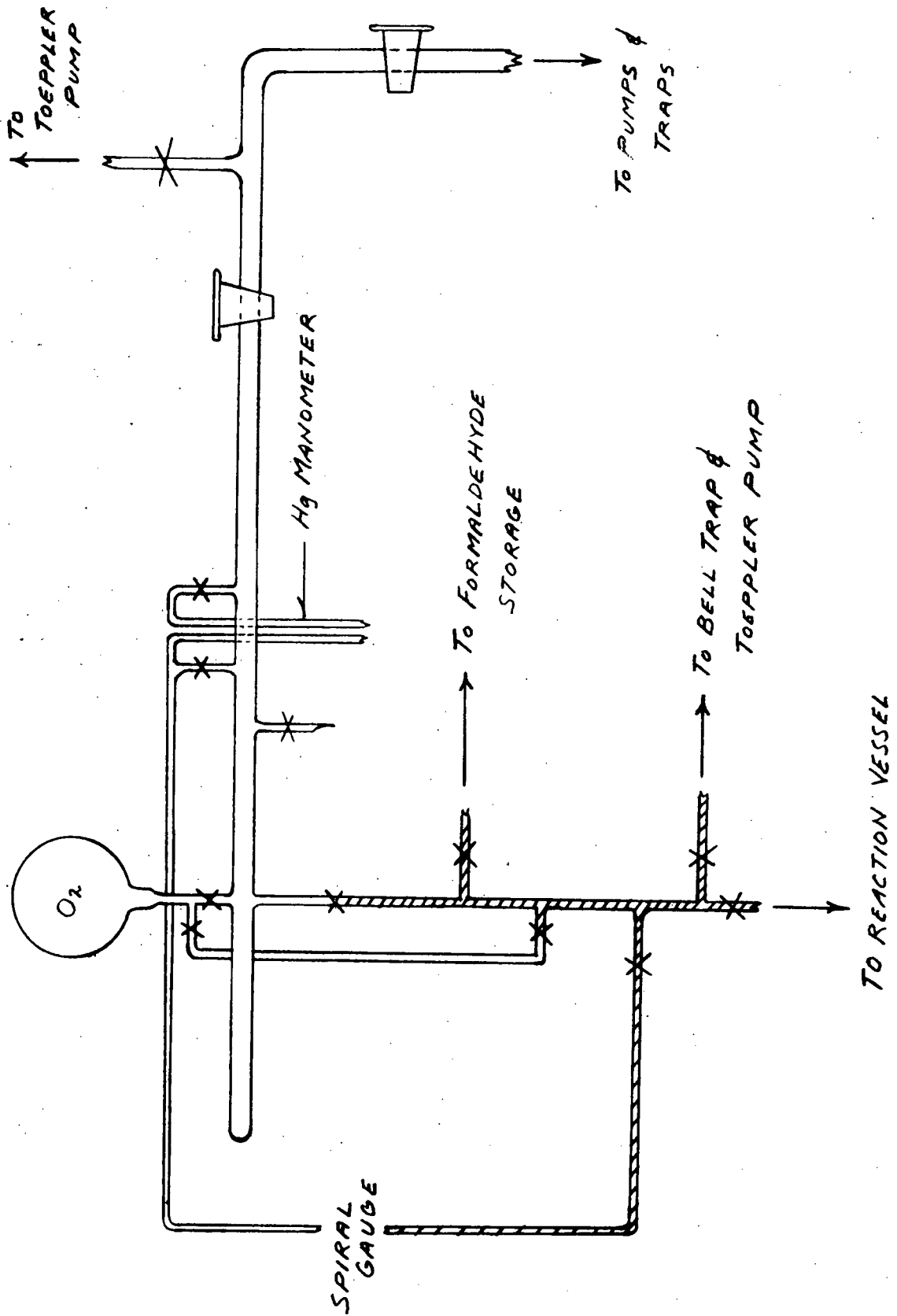
FIGURE 8-B

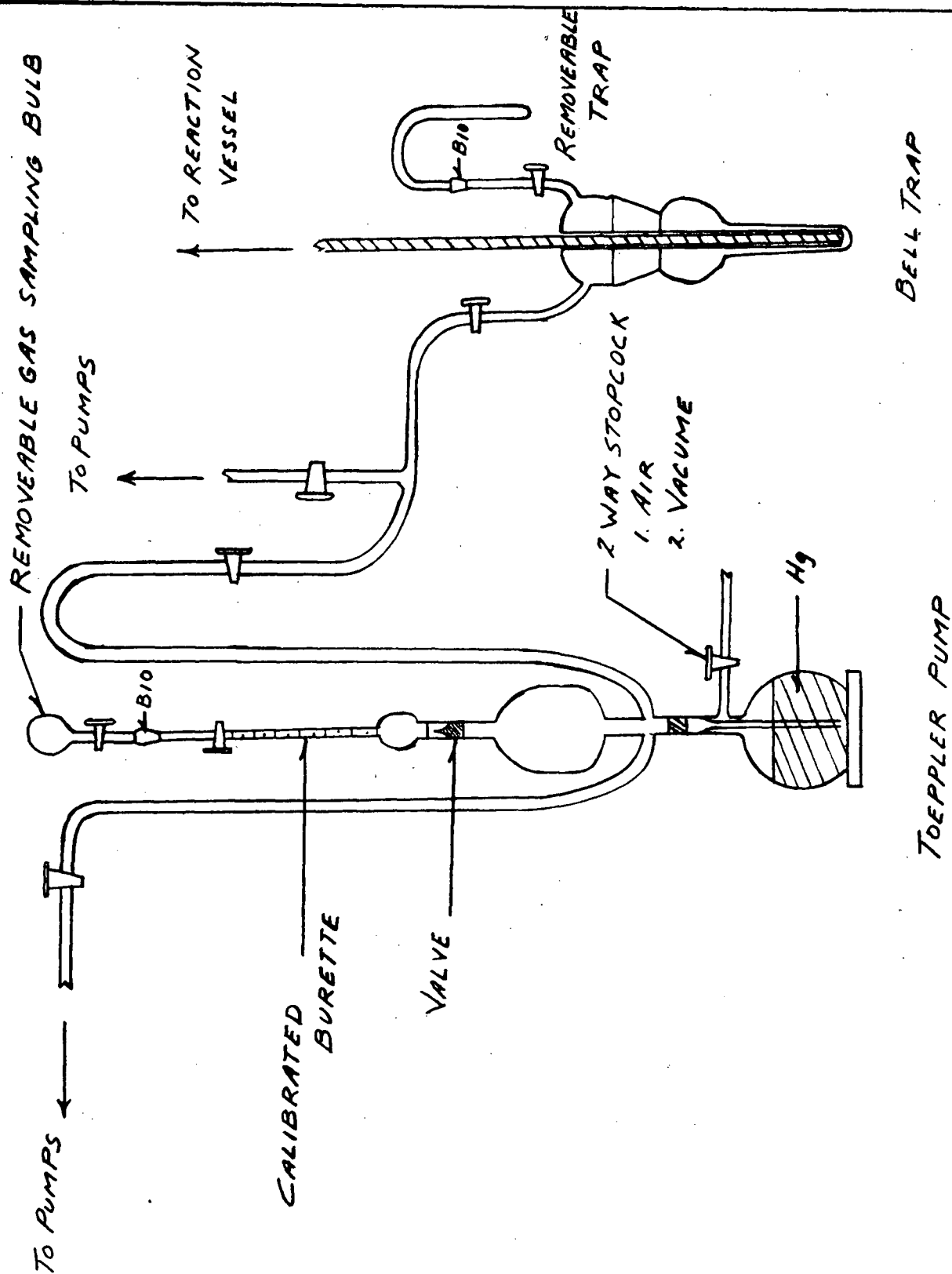Since formaldehyde rapidly polymerizes at room termperature, all tubing leading from the reaction vessel to the spiral gauge, the "Bell" trap (39) and the formaldehyde storage was wound with electrical heating tapes whose temperature was maintained at $100^{\circ}C$ by means of variacs. (Heating tapes are represented by the shaded areas in Figures 8A, 8B and 9)

Reactants were metered into the reaction vessel using a spiral gauge. The spiral gauge was calibrated as a direct reading manometer and was about 5 times as sensitive as a standard mercury manometer without a vernier scale. This gauge is illustrated in Figure 9 and the calibration graph is shown in Figure 10.

After an experiment had been carried out, the reaction products were led to the "Bell" trap which was cooled in liquid nitrogen. The permanent gases were then pumped over into the gas sampling bulb with the Toeppler pump. Hydrogen and carbon monoxide could then be analyzed on the Vapour Fractometer.

If formic acid was to be determined, the lower portion of the "Bell" trap was removed and the acid titrated directly. If carbon dioxide was to be determined, the condensible products were recondensed into the removable trap (Fig. 8-B) and analyzed on the Vapour Fractometer.

FIGURE 9
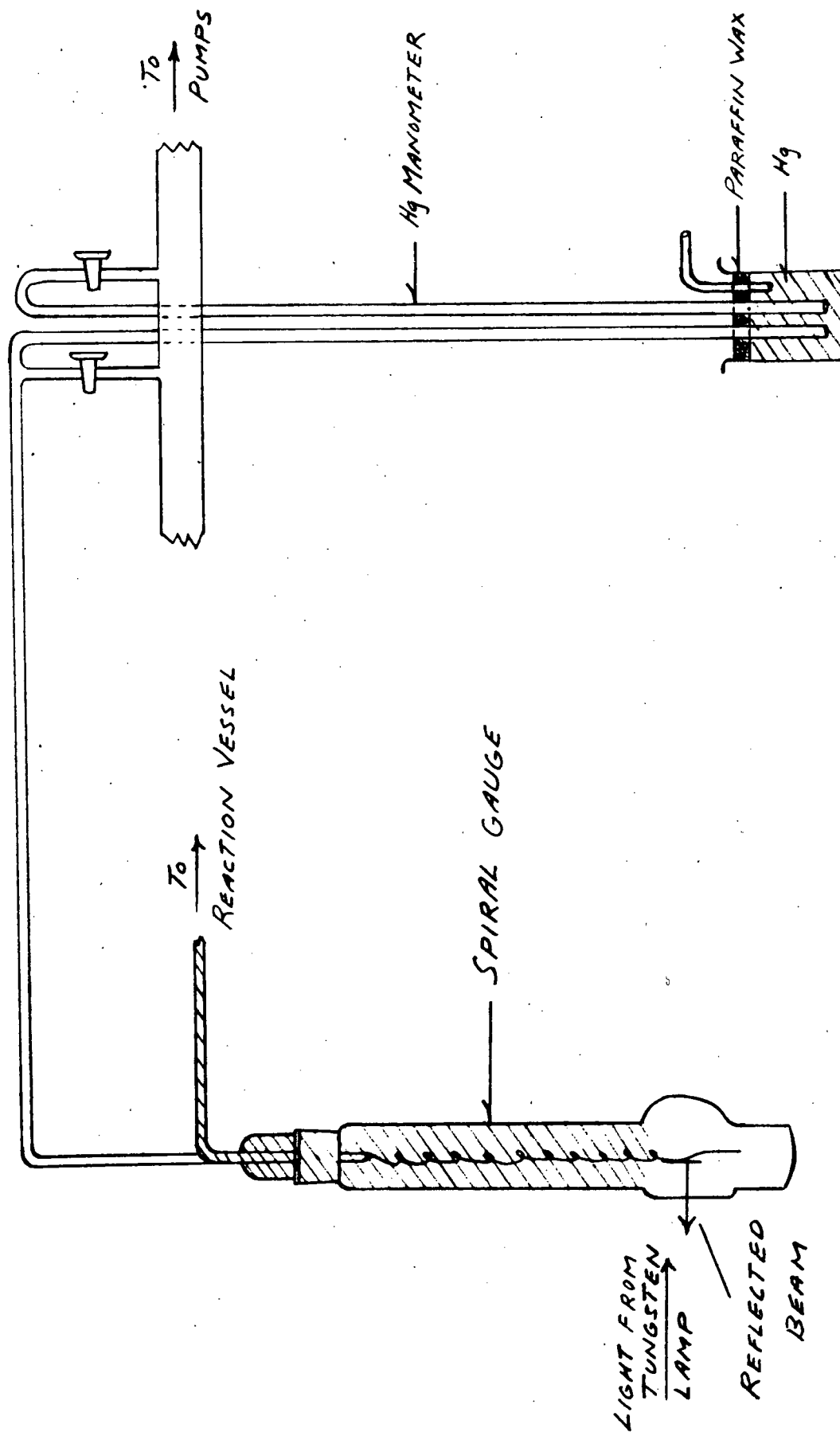
CALIBRATION OF SPIRAL GAUGE

FIGURE 10
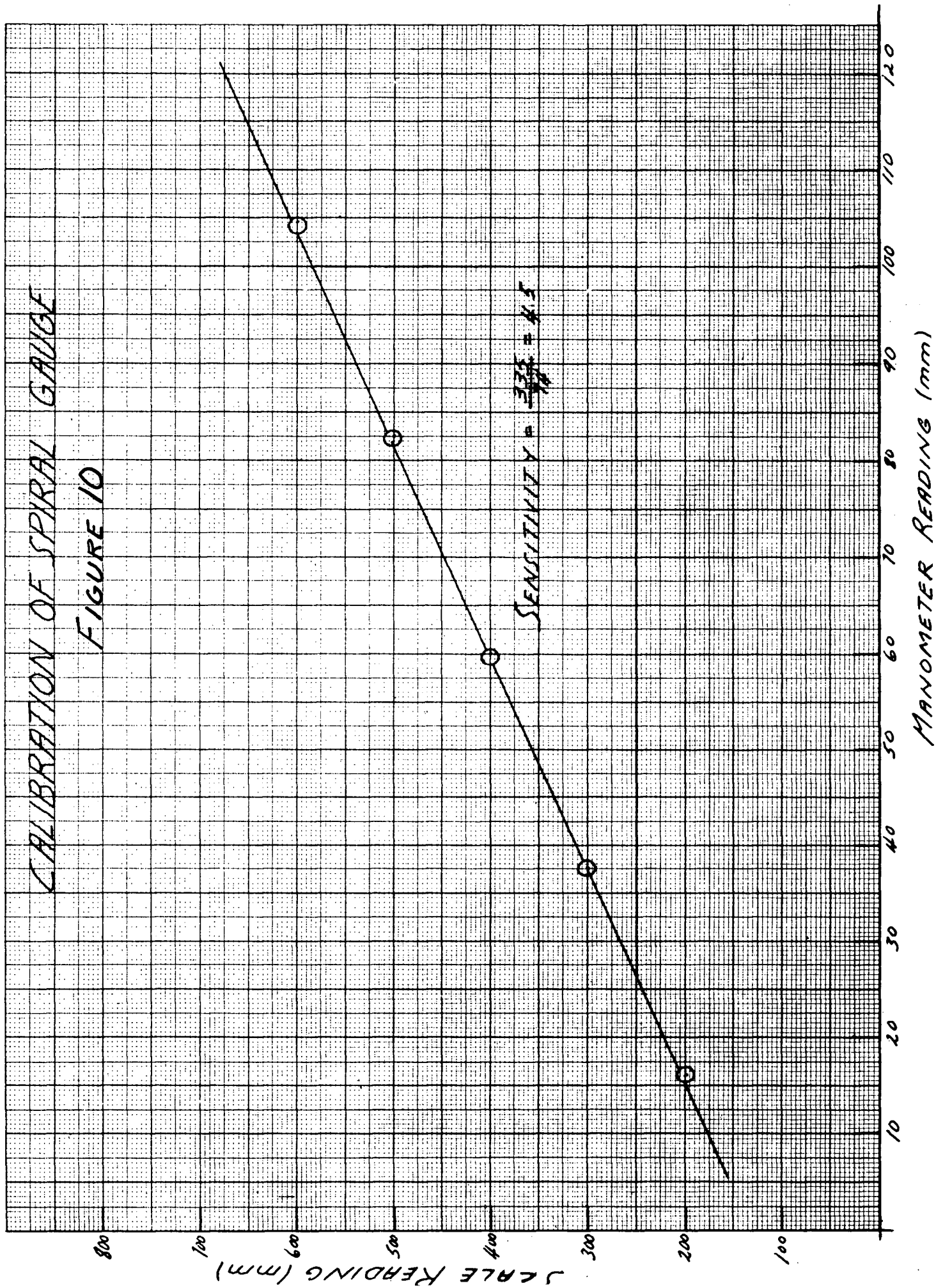
2. The Furnace

The aluminum - block furnace (Figure 11) was used to keep the reaction vessel at a chosen temperature. The furnace core comprised two aluminum cylinders, with 1.5 cm thick walls, which fitted snugly around each end of the reaction vessel, and which mated at the middle of the vessel. In this way the vessel could be easily removed. The mating aluminum cylinders were housed in a brass box which was adjustably mounted on a standard optical bench fitting. Each aluminum cylinder was separately wound with an electrical heating coil and the two coils were wired in series. With the aid of a variac transformer, voltages from 0 to 120 volts could be applied to the heating coils. It was found that a voltage setting of 82 volts was sufficient to keep the furnace at a temperature of $110^{o}C$. This temperature could be held constant to within one degree during the course of an experiment. There was a conveniently placed hole in the aluminum block to accommodate a thermocouple. The furnace was insulated by filling the space between the cylinders and the brass box with vermiculite.

THERMO-
COUPLE

O-RING

AL BLOCK

LENS

QUARTZ REACTION
VESSEL

FIGURE 11 FURNACE

ARC

D

S

A

V

B

P

GLASS
FILTER

F_1 F_2

FURNACE

OPTICAL BENCH
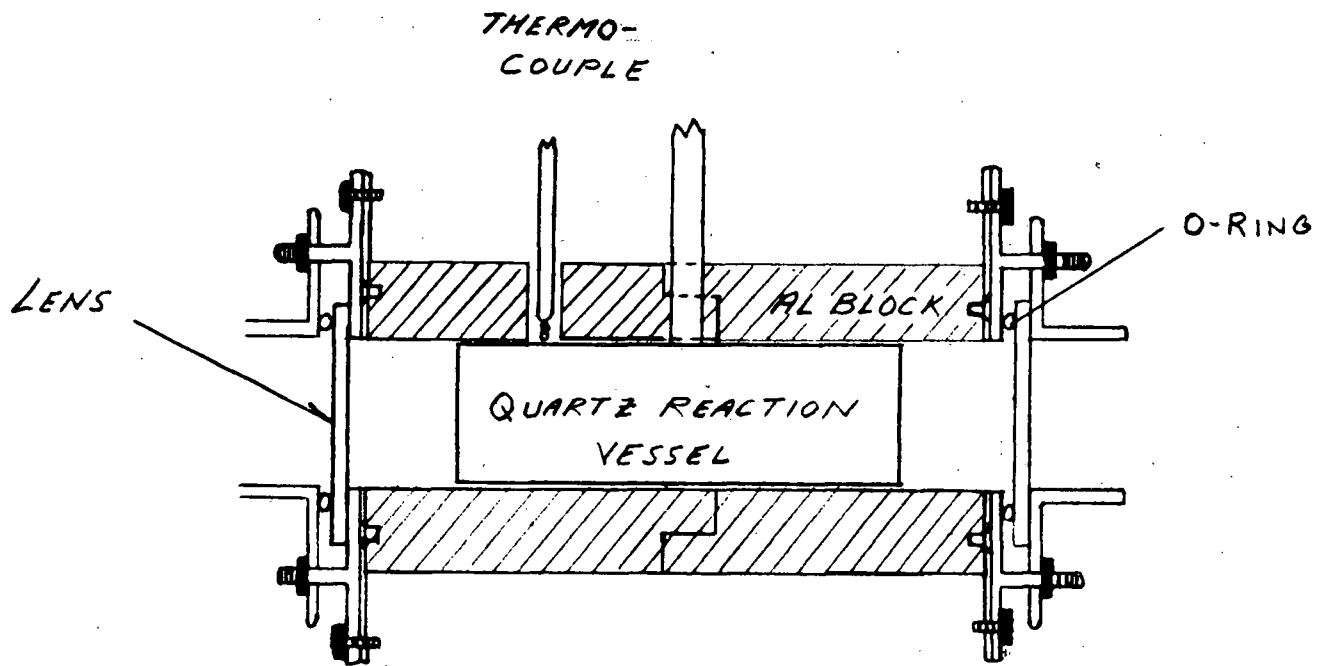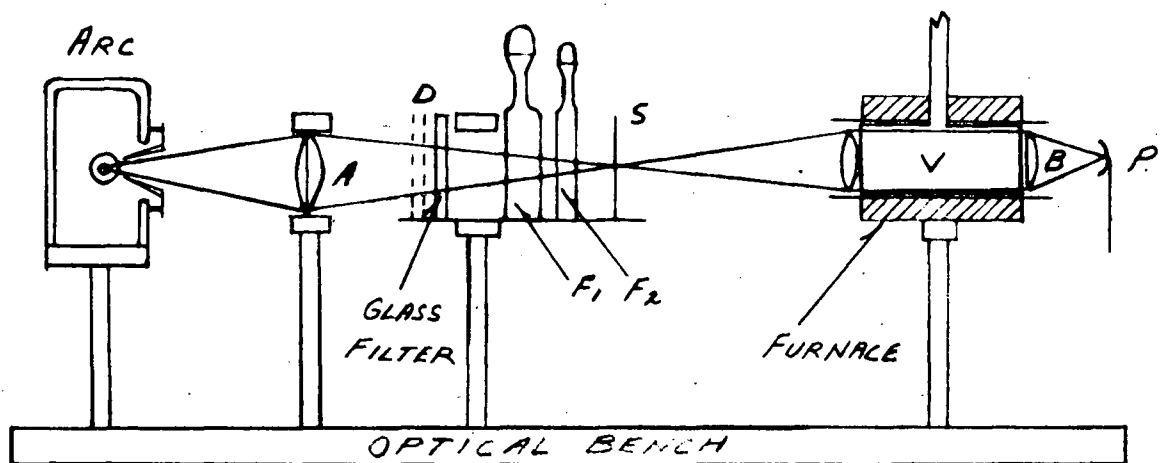
FIGURE 12 OPTICAL SYSTEM

3. The Optical System

The optical system is shown in Figure 12. The lamp
was a General Electric, water cooled AH6 high pressure
mercury arc with a housing designed to give a 3 mm.
diameter source. The position of the lamp and the quartz
lenses at A was adjusted so that a very nearly parallel
light beam completely filled the reaction vessel V.
The quartz lens B focussed the light onto the photocell P.
Very fine wire mesh screens,D, could be placed in the light
beam and their position was adjusted so that the screens
were out of focus along the length of the reaction vessel.
S was a manual shutter. F_1 was a 2 cm quartz filter cell
containing the potassium hydrogen phthalate solution. F_2
was a 1 cm quartz filter cell containing the potassium
dichromate solution.

The spectrum of the filter solution and glass filter
combination was measured against no blank on a Carey aut-
omatic - recording spectrophotometer. The spectrum is
shown in Figure 13. An absorption minimum is shown at
3130A$^{\circ}$. All experiments were carried out using this filter
combination.

4. The Lamp

The lamp, lamp housing and a.c. supply are shown in
Figure 14. The arc was rated at 1000 watts and was cooled
with water flowing at more then 3 litres per minute.

FIGURE 13

TRANSMISSION OF COMBINED FILTER SOLUTIONS & GLASS FILTER

WATER COOLED JACKET

ARC

WATER

QUARTZ
ENVELOPE

SPRING

POWER

ARC

TRANSFORMER

S

A.C.
MAINS

SOLA
CONSTANT VOLTAGE
STABILIZER
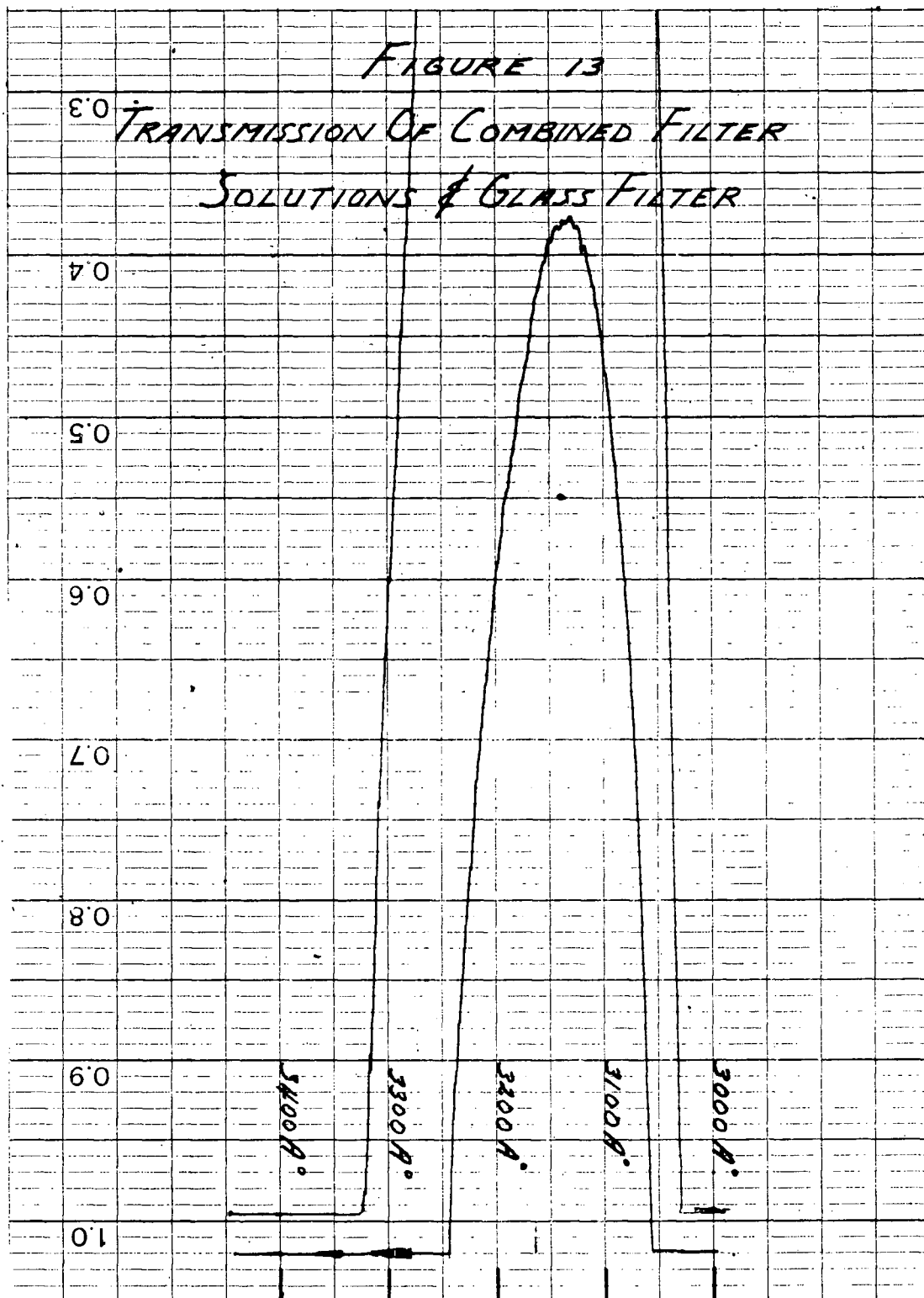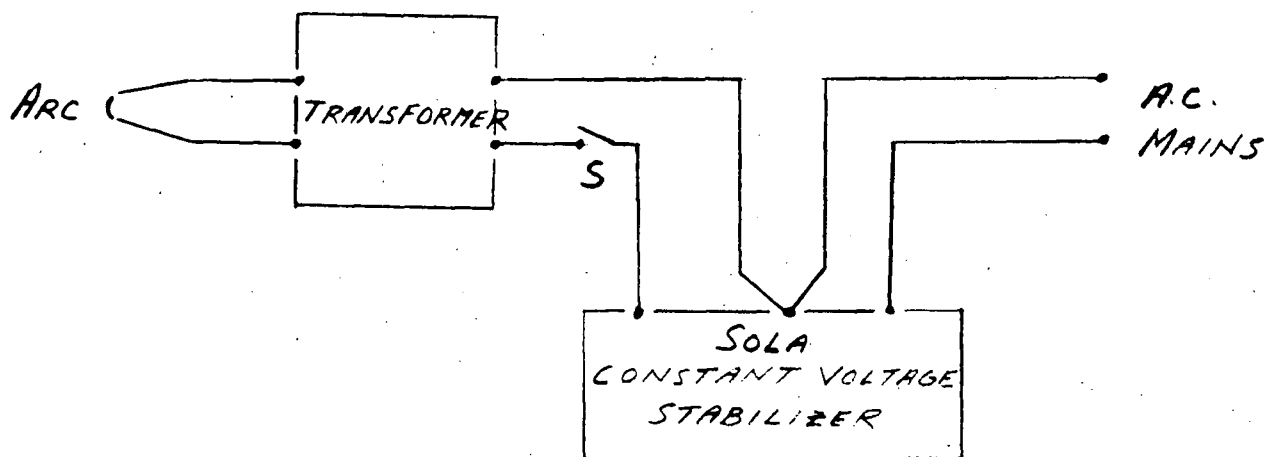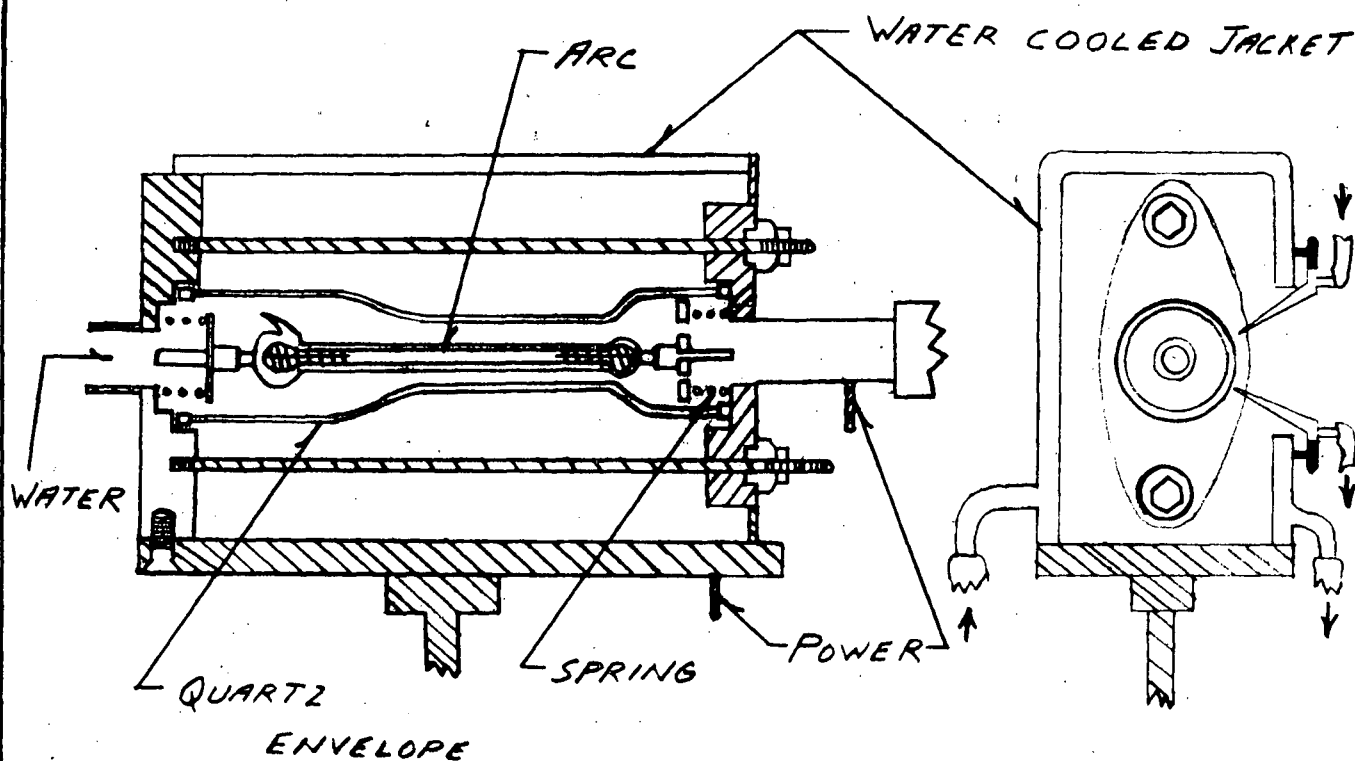
FIGURE 14   MECURY ARC BLOCK &
CIRCUIT DIAGRAM.

When the lamp was running, current was taken from a 1000

volt transformer. The transformer primary was supplied

from 110 volt a.c. mains stabalized by a Sola constant

voltage transformer. The starting current required by

the lamp was 2.5 amps at 1000 volts. The lamp quickly

attained normal operating conditions and the illumination

remained constant to $\pm$ 1% over a period of half an hour.

Over a period of time the intensity from any one arc

decreased. It was estimated that on an average the

intensity dropped to about 80% of its original value after

50 hours operation. The performance of individual arcs

varied in as much as some would start only a few times

and then fail to start, whereas some started up to 50

times before failing.

5. The Photometer Unit

The circuit diagram is shown in Figure 15.

a) Photocell – the photocell was a Cintel QVA39 con-

taining a quartz envelope and designed for ultra violet

light. It is claimed to give an output which is accurately

proportional to the intensity of light shone into it.

b) Operation – the photocell current passed through the

resistor chain R_{1-4} and the required voltage was tapped

off with the selector switch S_1.
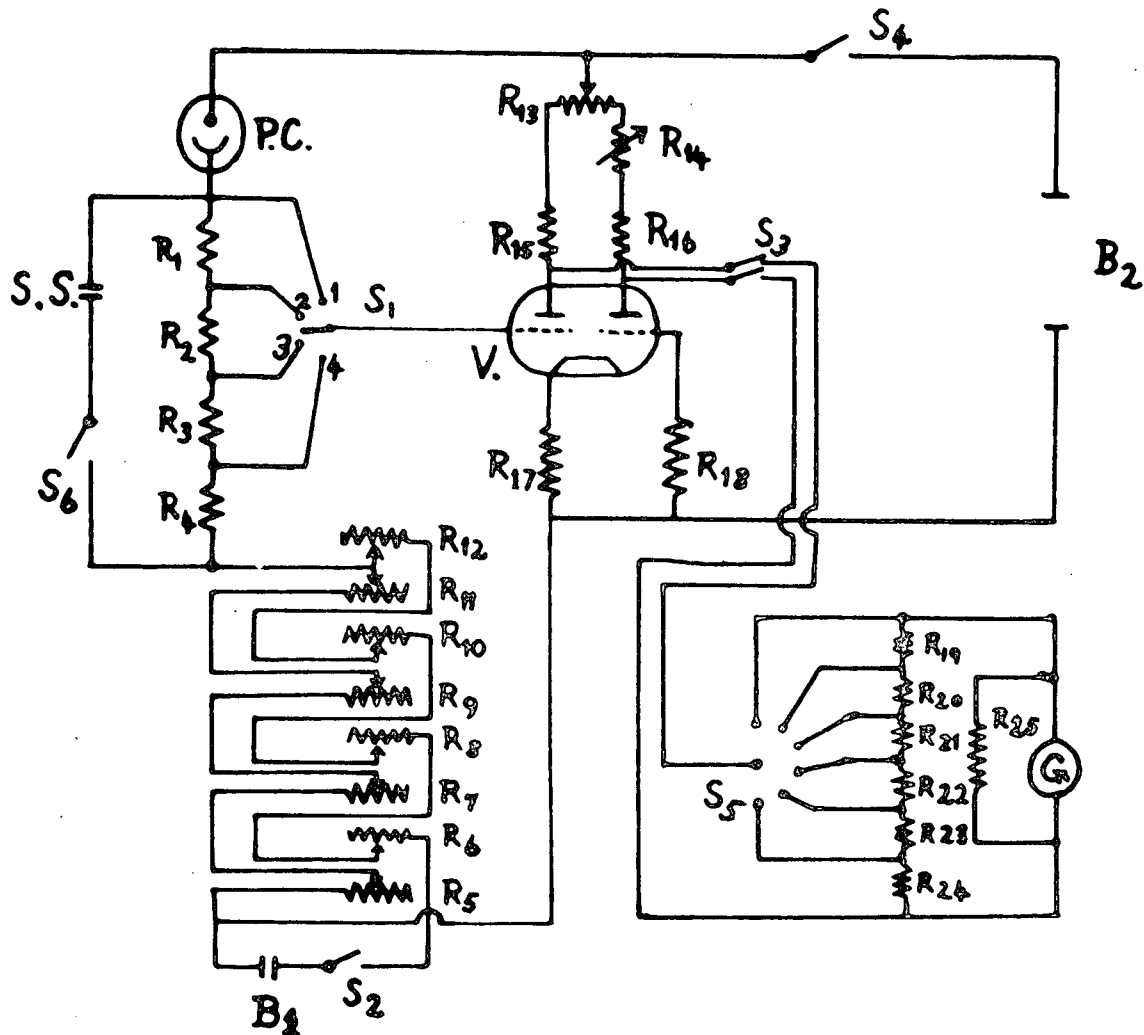
KEY:-

B1	2 volt accumulator.	R_{13}	25k : w.w.
B2	120 volt h.t. battery.	R_{14}	2k : w.w.
G.	Galvanometer.	R_{15}	50k : w.w. : 1W.
P.C.	Photocell: QVA 39.	R_{16}	50k : w.w. :1W.
S.S.	Weston Standard Cell.	R_{17}	2.2k : w.w. : 1W.
V.	6SC7 valve.	R_{18}	1M : $\frac{1}{2}$W.
R_1	5M : h.s.c. : 1W.	R_{19}	100k : w.w. : 1W.
R_2	1.5M : h.s.c. : 1W.	R_{20}	33k : w.w. : 1W.
R_3	500k : h.s.c. : 1W.	R_{21}	10k : w.w. ; 1W.
R_4	150k : h.s.c. : 1W.	R_{22}	3.3k : w.w. : 1W.
$R_{5,6}$	10k : dual decade : Muirhead.	R_{23}	1k : w.w. ; 1W.
$R_{7,8}$	1k : " " : "	R_{24}	330 ohms : w.w. : 1W.
$R_{9,10}$	100 ohms " " : "	R_{25}	10k : w.w. : 1W.
$R_{11,12}$	10 ohms " " : "		

Fig. 15.   Photometer Unit.

An opposing voltage was then applied by the potentiometer circuit consisting of the battery B_1 and the series of dual decades, R_{5-12}. B_1 was normally 2V and the voltage tapped from the potentiometer was adjustable to any value between 0 and 2 volts with an accuracy of 2×10^{-4} volts.

The difference between the voltage tapped from the resistor chain R_{1-4} and the opposing voltage from the potentiometer was applied to the double triode amplifier value V. The second triode unit compensated for supply voltage variation. The output of the amplifier was then fed into the galvonometer G via the attenuator R_{19-24}. The high tension for the unit was derived from a 120 volt battery and the low tension from a 6 volt mains-transformer.

c) <u>Photometric measurements</u> - the instrument was turned on by closing switches S_2, S_3 and S_4 and allowing it to warm up for 15 minutes.

With no light falling on the photocell, and the potentiometer reading zero, the dark current from the photocell was balanced by adjusting R_{13} and R_{14} for zero galvanometer current. The circuit had to be rebalanced for each position of the selector switch S_1.

S_6 was then closed, thus applying a standard voltage

across the resistor chain R_{1-4}. The potentiometer

voltage was then increased until the galvonometer showed

zero deflection. The potentiometer reading was taken.

This operation was carried out to ensure that B_1 gave

a constant voltage.

S_6 was then opened and light allowed to fall on the

photocell. The potentiometer was adjusted so that the

galvonometer showed zero deflection and the potentiometer

reading taken. Assuming that the photocell characteristic

is linear, then this potentiometer reading was proportional

to the light intensity.

The photometer unit was used for monitoring the out-

put of the mercury arc and mearuring the absorption of

light by a sample of formaldehyde in the reaction vessel.

6. **The Gas Admission System to the Perkin - Elmer**
   Model 154-C Vapour Fractometer.

The gas admission system as shown in Figure 16 was

constructed of pyrex and all stopcocks were lubricated

with Apiezon "N" grease. The system was backed by a

cold trap, a conventional mercury diffusion pump and a

rotary "Hyvac" mechanical pump. The refrigerant for the

cold trap was always liquid nitrogen.

FIGURE 16 GAS ADMISSION SYSTEM
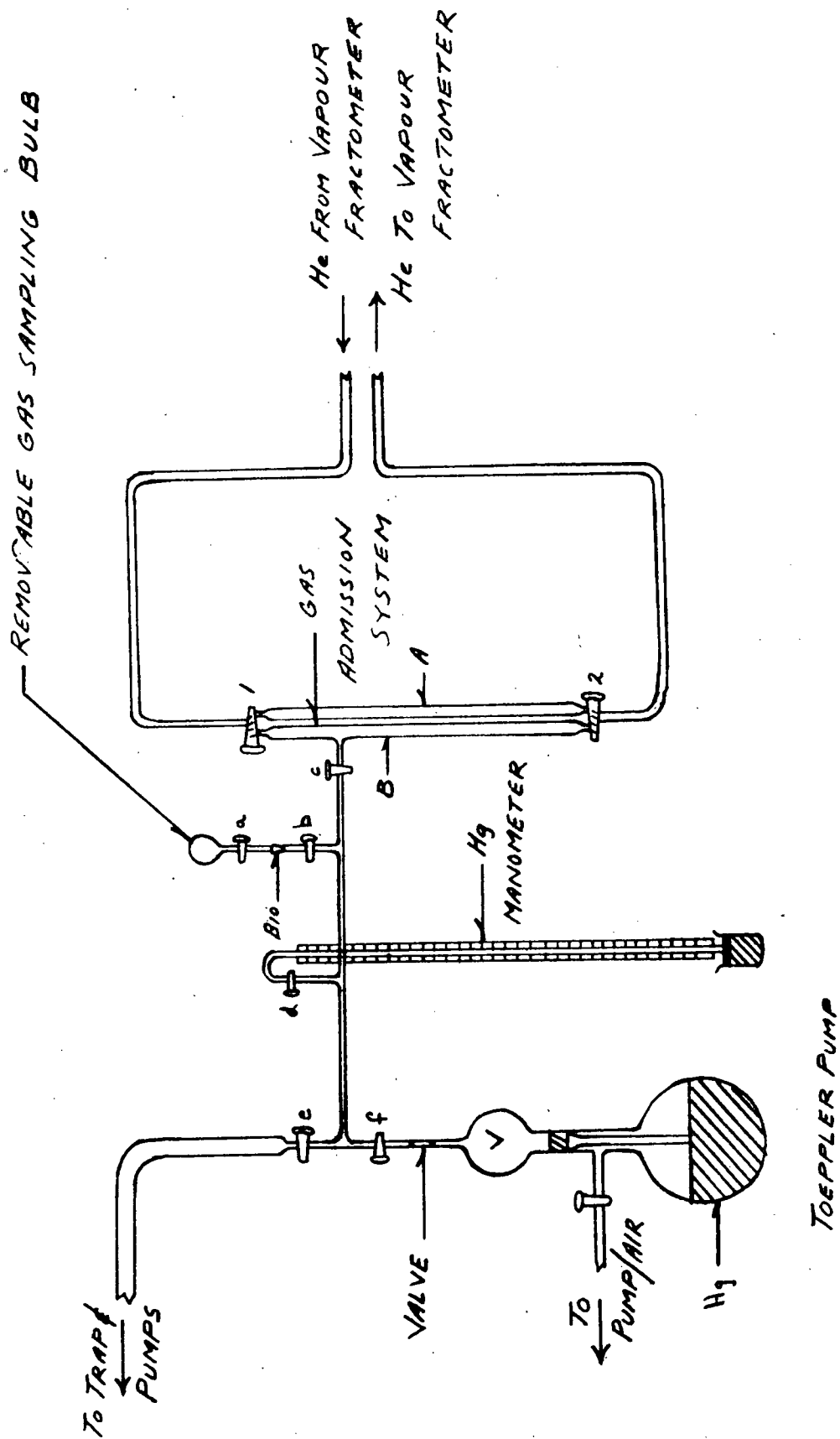
This system was used for the analysis of hydrogen, carbon monoxide and carbon dioxide. The permanent gases (hydrogen and carbon monoxide) were admitted to the system by means of the removable gas sampling bulb as shown in Figure 8-B. The following procedure was employed for analysis.

With helium from the Fractometer flowing through column A, the system was evacuated by opening all the taps except a. The manometer reading was then taken, tap e closed and tap a opened. This allowed the gas to expand into the large volume V. Tap b was then closed and the mercury raised in the Toeppler pump to push most of the gas into column B of the gas admission system. The manometer reading was then taken, tap c closed and taps 1 and 2 simultaneously turned to divert the helium stream through column B thus picking up the gas and carrying it to the Fractometer.

Since the volume of B had been previously calibrated (32.1 ml) it was possible to calculate the number of moles of gas present in any particular sample.

7. <u>Temperature Measurement - The Thermocouple</u>

The thermal couple circuit is shown in Figure 18. The termal couples were used to measure the temperature of the furnace and the electrical heating tapes.

FIGURE 18 THERMO-COUPLE
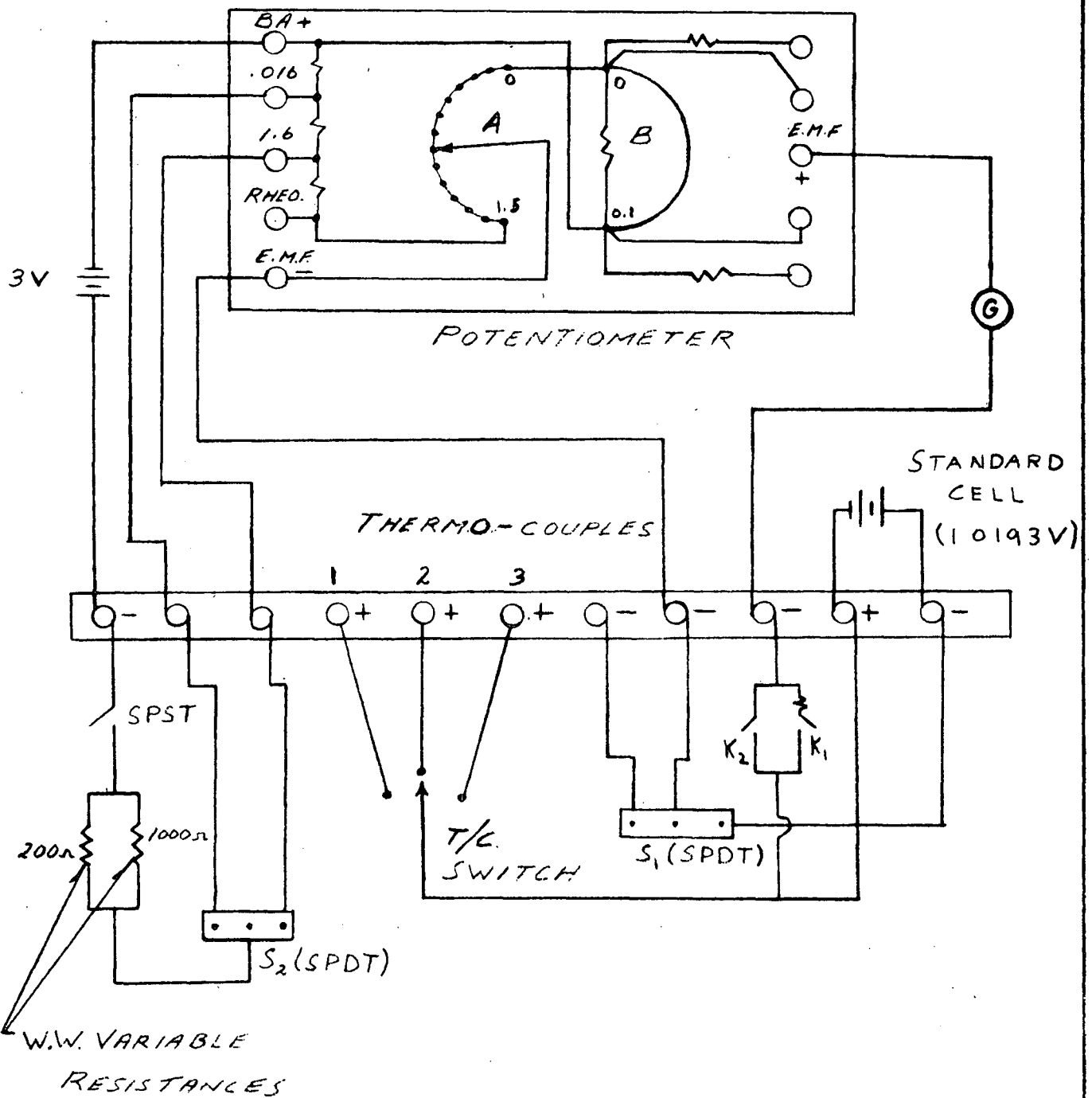
The potentiometer was a Students' Type "S" obtained from the Rubicon Company and was comprised of calibrated resistors. Two ranges were provided, 0 to 1.6 volts and 0 to 16 millivolts. Each range was covered by two measuring dials, the first of which was comprised of a 16 position switch controlling 15 fixed 10 - ohm resistors, and the second of which was comprised of a 14 - inch slidewire with 200 divisions. On the upper range 15 increments of 0.1 volt each were developed across the first dial resistors, the slidewire affording continuous variation throughout a 0.1 volt interval with 0.0005 volt each. On the lower range, the corresponding values were one-hundredth of the foregoing.

Potentiometric measurements were made by connecting the potentiometer to the accessories as shown in Figure 18. To adjust the current in the potentiometric circuit, S_1 was set to the standard cell position, S_2 to the 1.6 volt range and dials A and B set to standard cell value. K_1 was then tapped and the wire wound variable resistances were adjusted until the galvanometer G showed no deflection. K_2 was then tapped and the resistance readjusted until no galvanometer deflection was observed. The thermo-couple switch (T/C) was then turned to the thermo- couple required, S_2 to the required potentiometer range, K_1 tapped and dials A and B adjusted to give no deflection on the galvanometer.

K_2 was then tapped and dials A and B readjusted to give the final potentiometric reading.

The thermo-couples were comprised of copper-constantan wires and a reference junction of $0^{\circ}C$ was used. The temperature corresponding to a measured E.M.F. was taken from the Handbook of Chemistry and Physics (40).

CHAPTER IV

THE MECHANISM OF THE PHOTOCHEMICAL OXIDATION OF GASEOUS FORMALDEHYDE AT 110°C

1. Object of the investigation

2. Experimental Procedure

3. Determination of Formic Acid

4. Determination of Hydrogen and carbon monoxide

5. Determination of Carbon Dioxide

6. The influence of oxygen

7. Tests for Peroxide

8. The Photolysis of Formaldehyde

9. A summary of the Experimental Results

10. Proposed Mechanism

CHAPTER IV

THE MECHANISM OF THE PHOTOCHEMICAL OXIDATION OF
FORMALDEHYDE AT 110°C

1. Object of the Investigation

It is well known that the products of the photochemical
oxidation of formaldehyde are CO, H_2, HCOOH and CO_2. How-
ever, there has been some disagreement on the relative
amounts of these products, the resulting quantum yields
and especially the mechanism of the photochemical oxidation.
Other workers (22) have used light at a wavelength of 2537A°
and 2650A°, and reaction mixtures which contain a rather
high O_2/CH_2O ratio. They found that the reaction was oxygen
dependent to some extent. All workers agree that no peroxides
or only traces of peroxides are found in the reaction pro-
ducts. One of the main problems of the kinetics is to
satisfactorily account for the formic acid produced.

The object of this work was to study the photochemical
oxidation at 110°C using monochromatic light at a wavelength
of 3130A°. In most experiments, the O_2/CH_2O ratio was
1:10 which is much less than that used by other workers.
The reaction products and their quantum yield were obtained
as a function of the formaldehyde pressure. Tests for
peroxides were made and the effect of an increased O_2/CH_2O
ratio was studied.

Experiments were also carried out in order to determine the effect of varying the absorbed light intensity, Ia. The experimental results follow.

2. Experimental Prodedure

The lamp and the photometer unit were turned on and allowed to warm up for 15 minutes. The potentiometer of the photometer unit was then balanced against the standard cell with no light falling on the photocell. Light was then allowed to fall on the photocell and the initial incident intensity, $(I_0)i$, as measured by the photometer unit was recorded. The temperature of the furnace had been adjusted to $110^{\circ}C$ as registered by the thermal couple. During this period, the vacuum system was thoroughly pumped down. Oxygen and formaldehyde were then metered into the reaction vessel by means of the spiral gauge. Oxygen was always admitted first. Light was then shone onto the reaction mixture for an appropriate time as measured by a time clock. The transmitted light intensity, It, was measured at convenient intervals during the reaction. The light was then cut off and the reaction products were led to the "Bell" trap which was cooled in liquid nitrogen. After 10 minutes, the non condensable gases were pumped off by means of the toeppler pump and admitted to the removable gas analysis bulb.

The final incident intensity, $(I_0)f$ was then measured.
The average of $(I_0)i$ and $(Io)f$ was taken as the incident
intensity, I_0. The difference between this value and the
value of the averaged transmitted light intensity value,
It, was the value of the light absorbed during the reaction, Ia.

3. Determination of Formic Acid

After the non - condensible gases had been removed
from the "Bell" trap, air was admitted and the lower
portion of the trap removed while still immersed in the
liquid nitrogen dewar. The trap was then quickly re-
moved from the dewar and 4 or 5 ml of the phenolphthalien
indicator solution were carefully added to the condensed
products. The resulting clear solution was then quickly
titrated in the trap with the standardized N/1000 sodium
hydroxide to the pink end point. Hence, the number of
micro moles of formic acid produced was given directly
as the volume in ml of the base used.

In order to allow for impurities or the effect of
increasing amounts of formaldehyde in the acid titration,
50 mm, 100 mm, 150 mm, 200 mm, 250 mm and 300 mm pressures
of formaldehyde were photolyzed and the amount of formic
acid determined. The results are shown in Table II and
it is evident that, in the absence of oxygen, no appreciable

amount of formic acid was produced. For following determinations, a correction was applied to the titration value depending on the concentration of formaldehyde used.

TABLE II

Blank Titrations for the determination of formic acid

Run	Time of Run	$PCH_2O(mm)$	ml N/1000 NaOH
1	30 min.	50	0.10
2	30 min.	100	0.15
3	30 min.	100	0.15
4	30 min.	150	0.20
5	30 min.	200	0.25
6	30 min.	200	0.25
7	30 min.	250	0.25
8	30 min.	300	0.25

a) Variation with time of irradiation

The variation of formic acid produced during the photooxidation with respect to the time of irradiation is shown in Figure 19. In these runs, the initial pressure of oxygen and formaldehyde were approximately 10 mm and 100 mm respectively. I_O was approximately 8000 Ω . The results are shown in Table III.
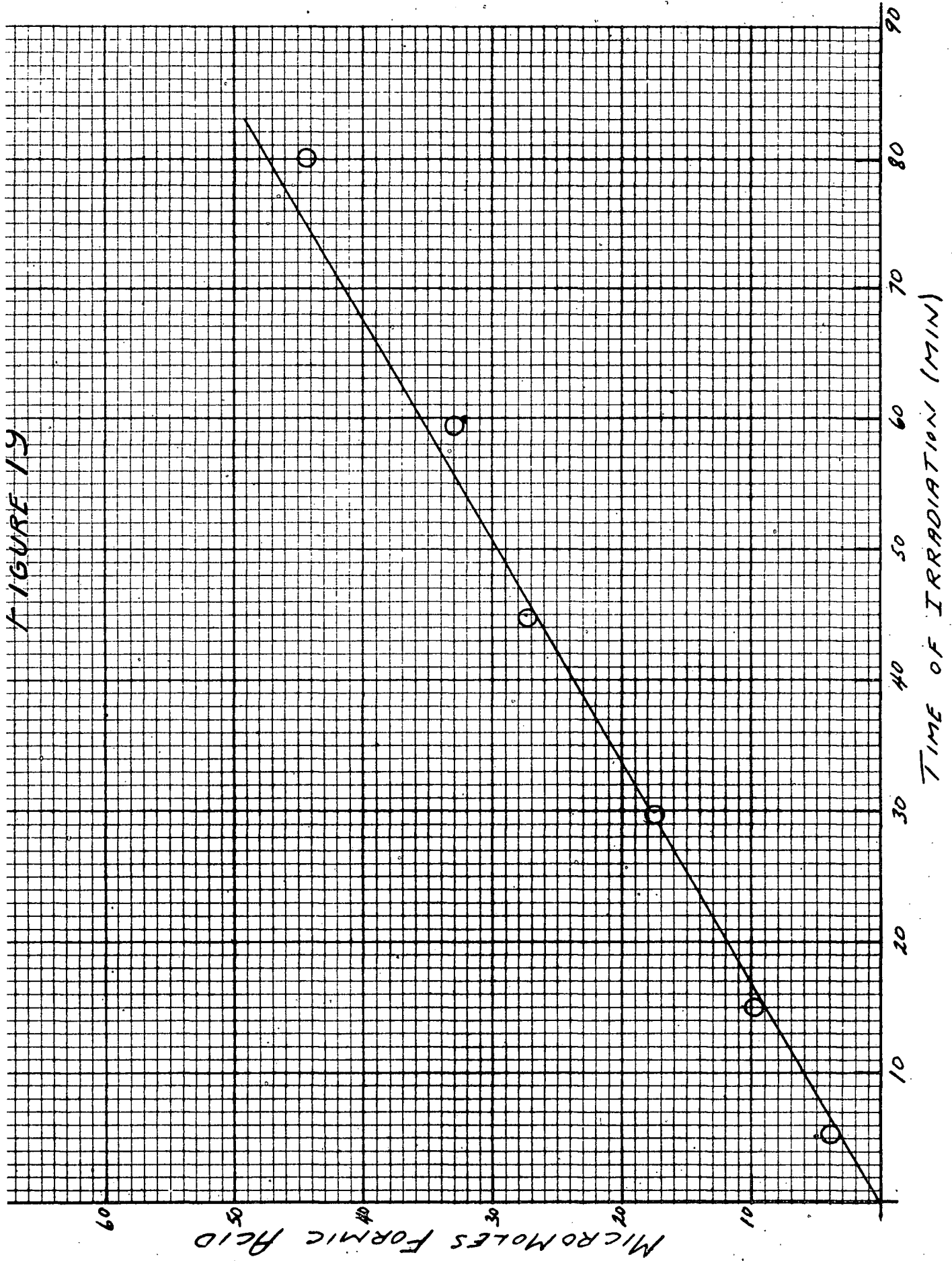
FIGURE 19

MICROMOLES FORMIC ACID

TIME OF IRRADIATION (MIN)

TABLE III

Run	Time of run (min)	ml N/1000 NaOH
9	5	4.20
10	15	9.60
11	30	17.60
12	40	27.50
13	60	33.0
14	80	44.50

b) **Variation with the absorbed light**

The variation of the formic acid produced with the intensity of the absorbed light, Ia, is shown in Figure 20 where the log of the absorbed light, Ia, is plotted against the log of the number of micro moles of formic acid produced. Two sets of data are listed in Table IV; one set for mixtures containing 100 mm Hg of formaldehyde, 10 mm Hg of O_2, and the other set for mixtures containing 50 mm Hg of formaldehyde, 5 mm HgO_2.
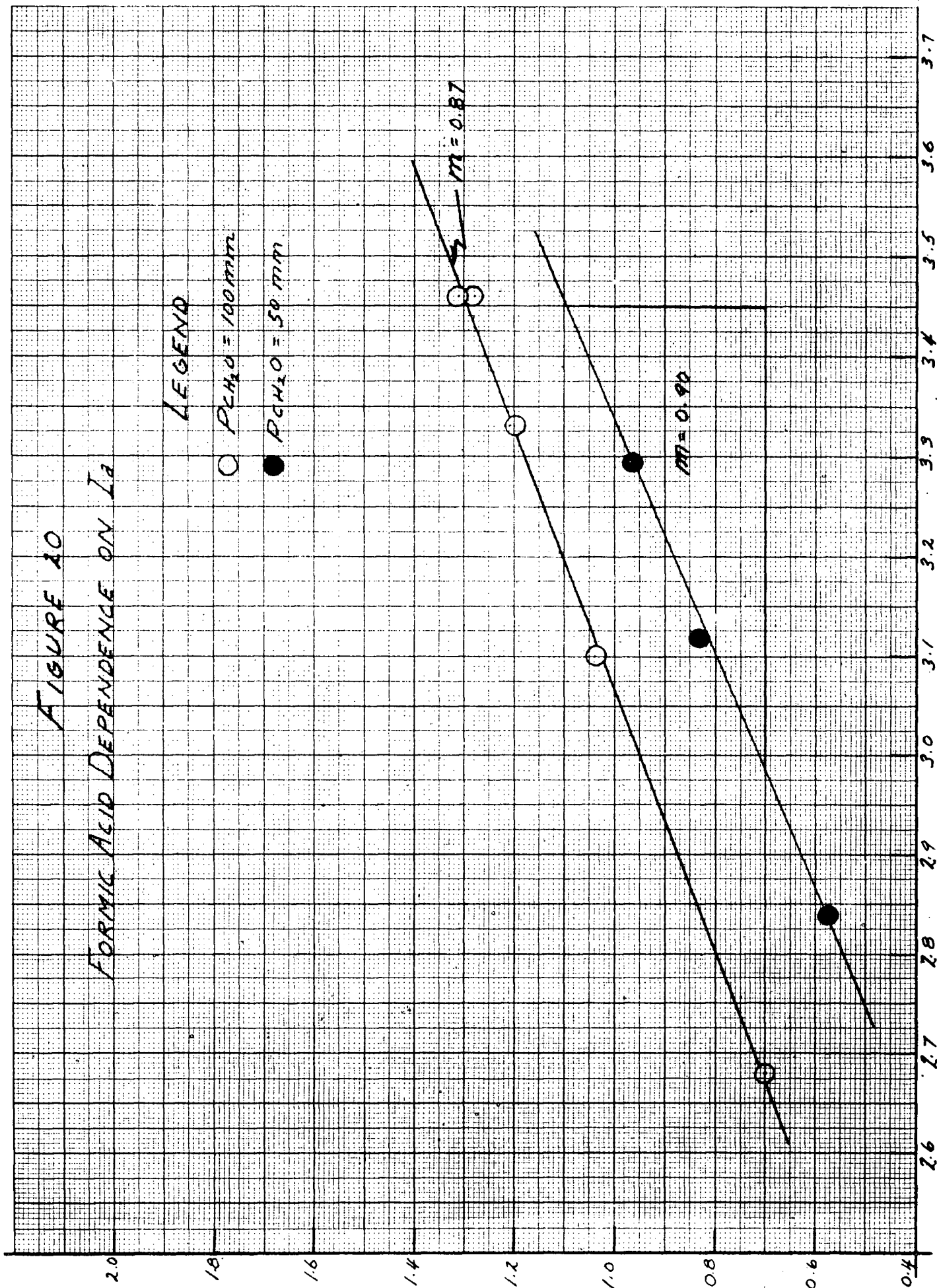
TABLE IV

Run	PCH_2O (mm)	PO_2 (mm)	ml N/1000 NaOH	Ia(Ω)
15	101.1	11.5	18.00	2850
16	104.7	13.5	14.10	2155
17	103.5	11.1	8.32	1260
18	101.9	11.1	4.05	475
19	103.3	12.2	18.50	2840
20	49.5	5.4	3.05	695
21	52.7	5.3	9.15	1920
22	51.5	4.9	5.65	1305

FIGURE 10

FORMIC ACID DEPENDENCE ON Ia

From the resulting plots, it is evident that formic acid is nearly directly proportional to the absorbed light intensity.

c) Variation with the initial formaldehyde pressure

.It was found that the amount of formic acid produced was proportional to the initial pressure of formaldehyde. Data for these runs are shown in Table V. In all cases, PO_2 was approximately 10 per cent of PCH_2O, the incident light intensity, I_0, was 8000 Ω and the time of each run was 30 minutes.

TABLE V

Run	PCH_2O (mm Hg)	ml N/1000 NaOH	Ia(Ω)	$\phi HCOOH$
23	20	2.58	1120	2.70
24	21	2.50	1100	2.68
25	23	2.55	1160	2.58
26	40	4.52	1420	3.74
27	40	5.30	1575	3.98
28	41	5.05	1485	4.1
29	44	5.50	1580	4.07
30	48	7.50	1925	4.57
31	48	6.80	1800	4.44
32	48	6.95	1825	4.47
33	50	7.35	1840	4.78
34	59	9.65	1880	5.74
35	78	12.15	2295	6.27
36	100	16.50	2430	8.02
37	100	18.40	2760	7.88
38	105	16.30	2630	7.40
39	128	21.42	2810	9.00

TABLE V

Run	PCH$_2$O (mm Hg)	ml N/1000 NaOH	Ia(Ω)	ϕHCOOH
40	150	24.90	3030	9.68
41	152	28.50	3570	9.38
42	152	29.75	3610	9.60
43	160	26.00	3380	9.05
44	191	35.62	4010	10.30
45	200	33.50	3760	10.40
46	200	36.60	4240	10.10
47	220	38.00	4190	10.75
48	240	43.20	4320	11.80
49	250	45.00	4400	12.00
50	30	3.05	1200	3.00
51	31	3.15	1100	3.42

Some of the tabulated results are plotted in Figure 21. In Figure 22, the logarithm of the formaldehyde pressure (mm Hg) is plotted against the logarithm of the number of micro moles of formic acid produced. The slope of this line is 1.17 and hence the formic acid produced is nearly directly proportional to the initial formaldehyde concentration.

d) Quantum Yield as a function of formaldehyde pressure

Quantum yields for HCOOH, H$_2$ and CO are plotted in Figure 23. The quantum yield for each of these products increases gradually with increasing formaldehyde pressure. The data for formic acid are found in Table V.

FIGURE 21

DEPENDENCE OF HCOOH, H₂ & CO ON PCH₂O

FIGURE 22

$m = 1.1$

LOG$_{10}$ P$_{CH_2O}$ (mm)

LOG$_{10}$ MICROMOLES HCOOH
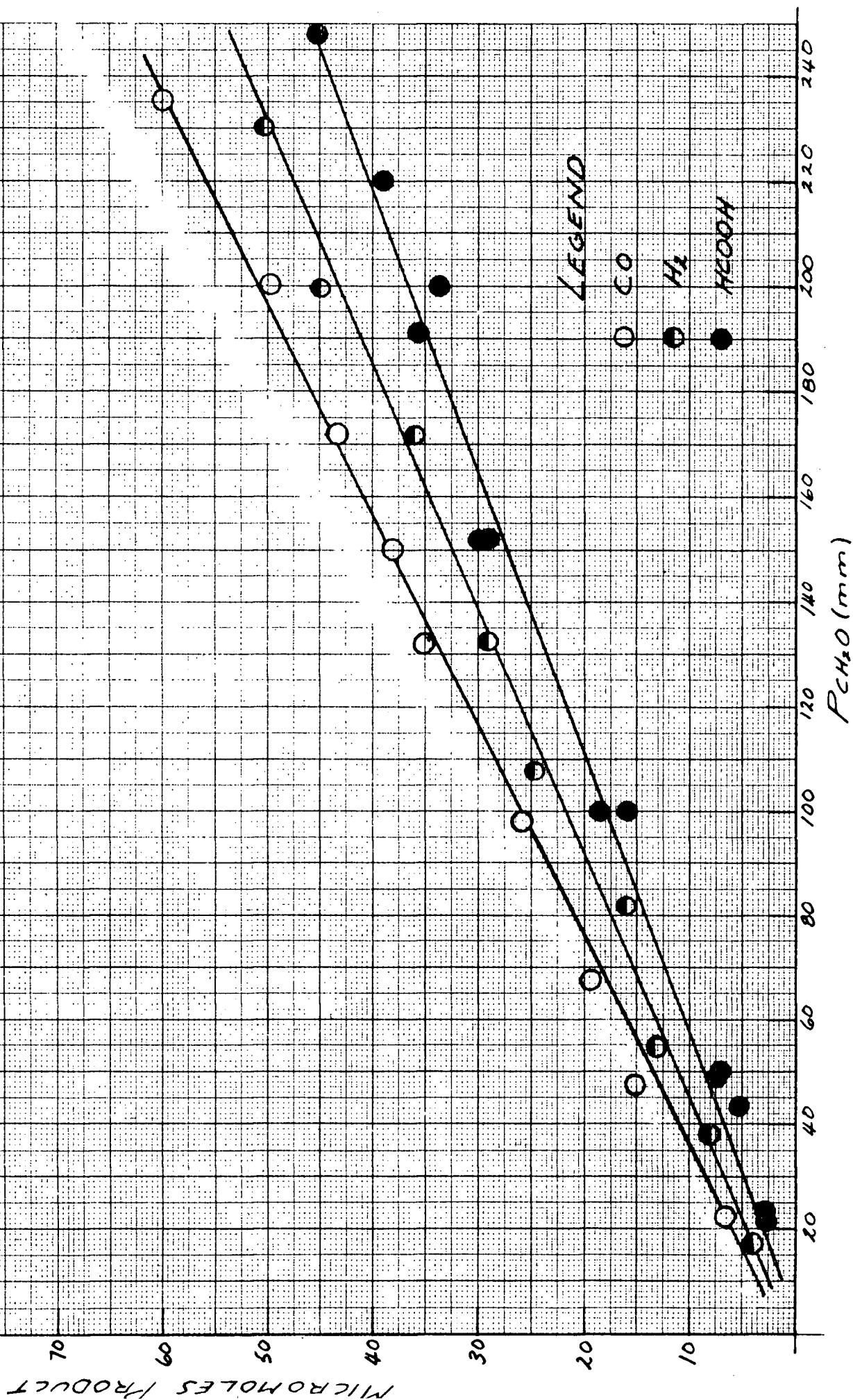
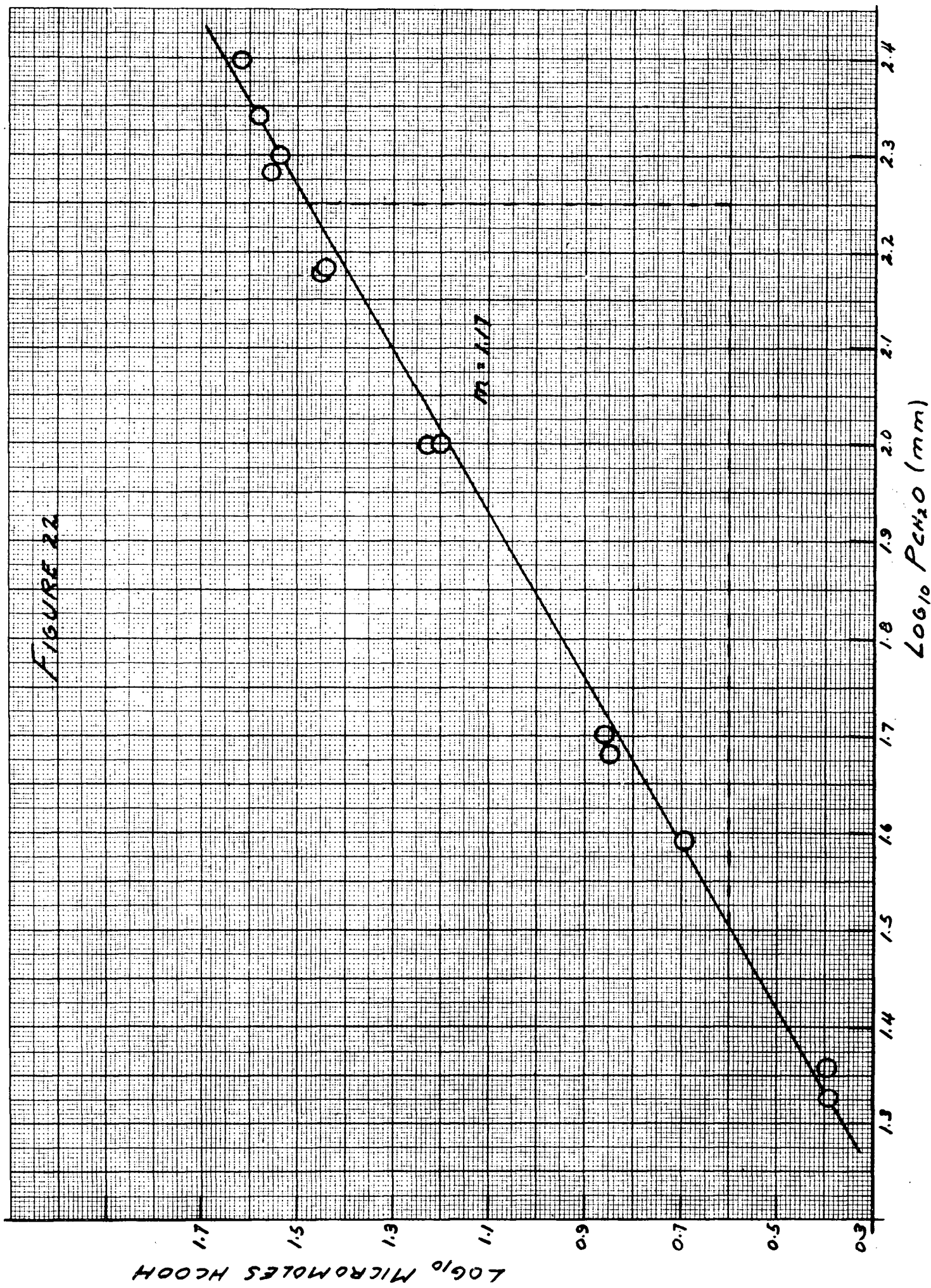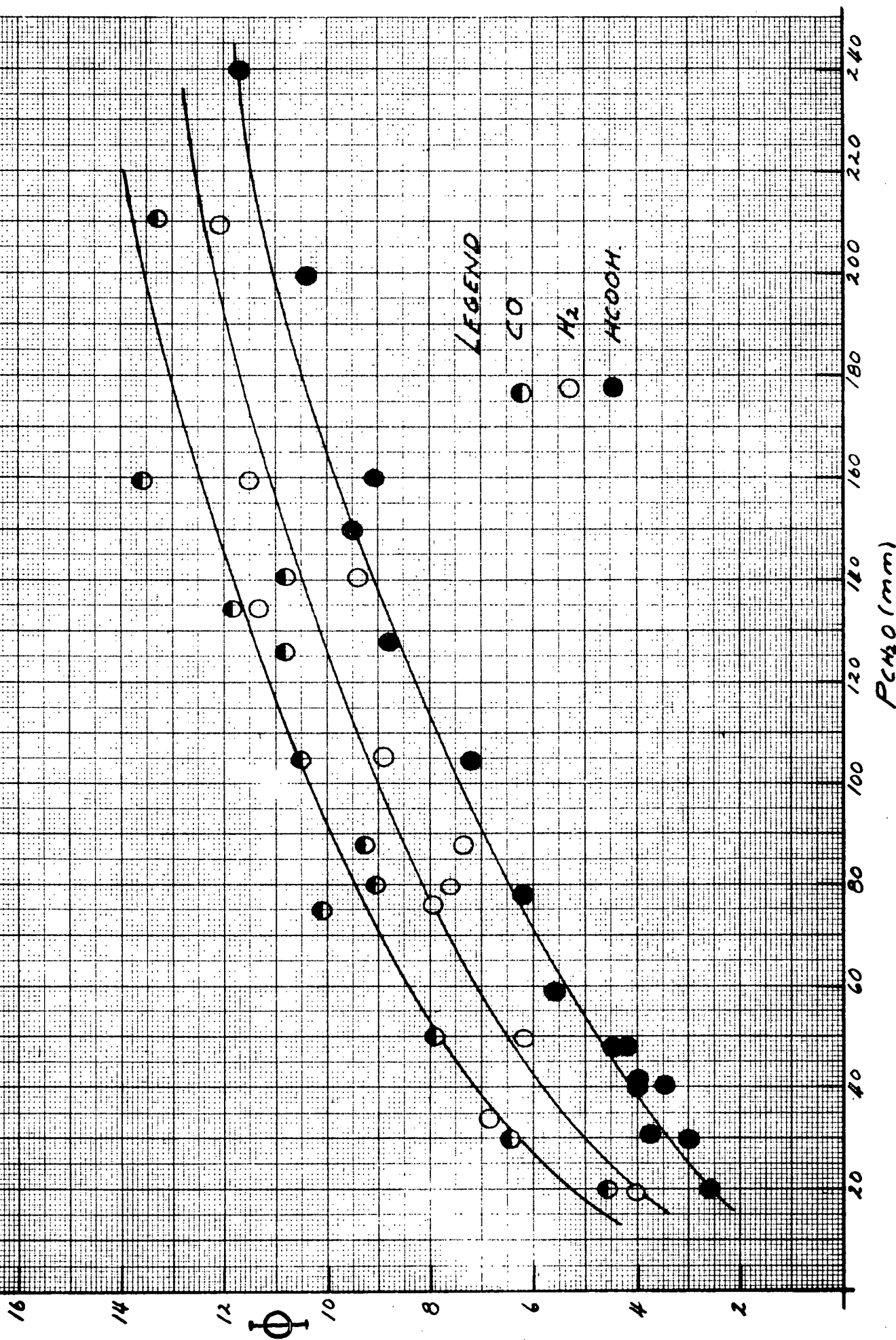Figure 23 Quantum Yields

Sample Calculations for ΦHCOOH

From the actinometric calibrations (see p37) the
number of quanta per ohm per second is 2.85×10^{11}.
Hence, the total quanta absorbed will be given by
the following expression.

$$Q_T = (2.85 \times 10^{11}) \text{ (time in sec.) } (Ia(\Omega))$$

The total number of molecules of formic acid produced
will be

$$N_T = \text{(moles HCOOH) } (6.02 \times 10^{23})$$

The resulting quantum yield is then given by

$$\Phi = \frac{N_T}{Q_T}$$

Example #1 - Run #20

$$Q_T = (2.85 \times 10^{11})(30 \times 60)(1485) = (2.85)(1.8)(1.485) \times 10^{17}$$
$$N_T = (5.05) (6.02) \times 10^{17}$$

Hence, ΦHCOOH $= \dfrac{(5.05)(6.02)}{(2.85)(1.8)(1.485)} = \quad 4.0$

Example #2 - Run #44

$$Q_T = (1.980) (2.85) (1.8) \times 10^{17}$$
$$N_T = (9.65) (6.02) \times 10^{17}$$

$$\Phi \text{ HCOOH} = \frac{N_T}{Q_T} = 5.7$$

4. Determination of Hydrogen and Carbon Monoxide

The non-condensible gases were comprised of hydrogen, carbon monoxide and unreacted oxygen. By means of the Toeppler pump, these gases were pumped into the calibrated burette of the Toeppler pump and the volume and pressure of the gases were recorded. They were then forced up into the removeable gas analysis bulb by means of compressed air. Analysis of these gases was carried out on the Perkin - Elmer, Model 154-C Vapour Fractometer utilizing the molecular sieve column. Since the pressure and volume of the gases being analyzed was known from the reading of the mercury manometer and the calibrated column B of the gas admission system, the number of micro moles of product could be calculated from the calibration graphs for hydrogen and carbon monoxide (see Figures 4-6)

a) Variation with the time of irradiation

Both hydrogen and carbon monoxide were found to be proportional to the time of irradiation. The results shown in Table VI are for mixtures containing 100 mm H_g of formaldehyde and 10 mm H_g of O_2 and an incident intensity, Io, of 8000 Ω.

TABLE VI

| Run	Time of run (min)	micro moles H_2	Micro moles CO
58	5	6.10	7.43
59	5	7.83	8.20
60	15	14.90	16.40
61	15	13.85	15.80
62	30	25.30	34.00
63	30	24.70	34.50
64	45	38.00	41.20
65	60	50.50	66.80

b) Variation with the absorbed light

The variation of hydrogen and carbon monoxide produced with the intensity of the absorbed light is shown in Figure 24 where the logarithm of the absorbed light, Ia, is plotted against the number of micro moles of product formed. The data in Table VII corresponds to mixtures containing 100 mm H_g of formaldehyde, 10 mm H_g of O_2 and to a time of irradiation of 30 minutes.

TABLE VII

Run	micro moles H_2	micro moles CO	Ia (Ω)
67	14.2	14.8	1480
68	15.2	16.5	1632
69	30.4	37.2	3345
70	21.4	24.2	2400
71	32.7	39.8	3185
72	9.8	12.2	1250

FIGURE 24

DEPENDENCE OF H_2, CO ON I_a

$m = 1.07$

LEGEND

○ CO

● H_2

Log_{10} I_a

Log_{10} MICROMOLES PRODUCT
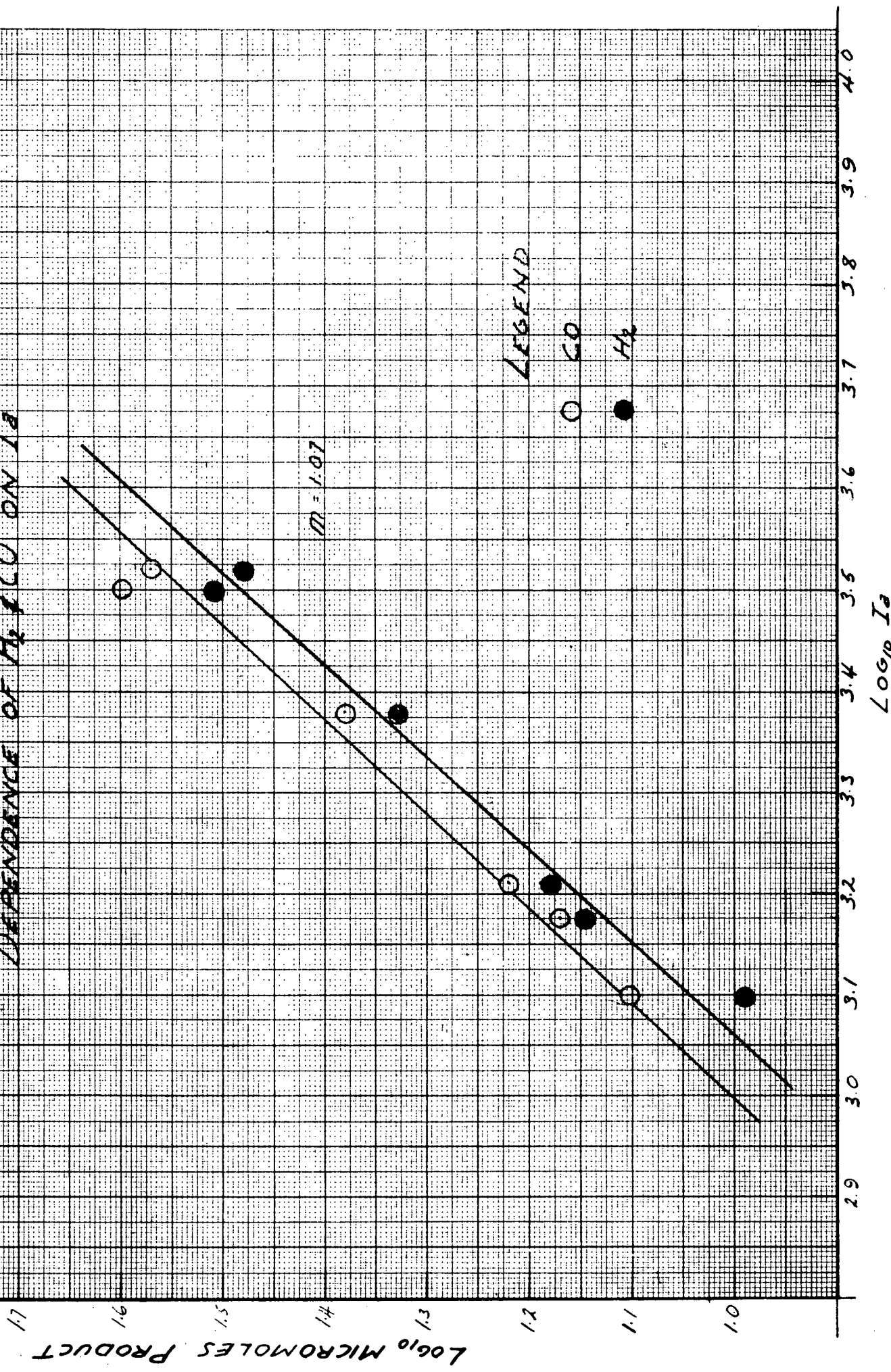
From these plots, it is evident that hydrogen and
carbon monoxide are nearly proportional to the absorbed
light intensity, Ia.

c) Variation with the initial formaldehyde pressure

The amount of hydrogen and carbon monoxide pro-
duced was also found to be proportional to the initial
pressure of formaldehyde. Data for these runs is shown
in Table VIII. All data refers to mixtures where $Po_2 =$
$\dfrac{PCH_2O}{10}$, where $I_0 = 8000\,\Omega$, and where the time of irradiation
was 30 minutes.

<div align="center">TABLE VIII</div>

Run	PCH_2O(mm Hg)	μ moles H_2	μ moles CO	$I_a(\Omega)$	ϕH_2	ϕCO
73	18	4.2	5.3	1350	3.80	4.65
74	22	4.8	6.2	1390	4.05	5.25
75	38	7.2	10.8	1640	5.10	7.70
76	48	11.0	15.2	2140	5.90	8.20
77	55	13.7	15.5	2000	8.05	9.10
78	68	15.1	18.4	2320	7.64	9.30
79	75	15.2	20.0	2570	6.9	9.10
80	82	16.9	20.2	2690	7.26	8.70
81	98	22.3	24.5	2720	9.52	10.50
82	102	21.3	25.0	2740	9.05	10.70
83	107	25.3	27.2	2940	10.20	11.00
84	112	24.8	30.8	2980	9.65	12.00
85	133	29.0	35.0	3420	10.0	12.00
86	148	32.5	38.2	3665	10.30	12.20
87	172	36.2	43.5	4110	10.30	12.40
88	200	45.0	49.8	4260	12.40	13.70

TABLE VIII (Cont..)

Run	PCH$_2$O(mm H$_g$)	μmoles H$_2$	μmoles CO	Ia(n)	ϕH$_2$	ϕCO
89	209	49.2	52.5	4390	13.20	14.10
90	230	50.3	57.0	4570	12.80	14.60
91	235	52.1	60.8	4790	12.80	14.80

Some of the tabulated results are plotted in Figure 21.
In Figure 25, the logarithm of the number of micro moles
of hydrogen and carbon monoxide produced is plotted
against the logarithm of the formaldehyde pressure.

d) Quantum Yield as a function of formaldehyde pressure

Quantum yields are plotted in Figure 23. The data
for hydrogen and carbon monoxide is found in Table VIII.
The calculations are similar to those shown for formic acid.

5. Determination of Carbon Dioxide

After the non-condensible gases had been pumped off,
the liquid nitrogen dewar was removed from the "Bell" trap
and the condensed products allowed to warm up. The dewar
was then placed around the removable trap (Figure 8-B)
and the products re-condensed. Carbon dioxide was then
analyzed on the Vapour Fractometer utilizing column "J".
Since CO$_2$ was a minor product, it was necessary to condense
the CO$_2$ into column B of the gas admission system. This
was done by wrapping a piece of cotton wool around the top
portion of column B and saturating it with liquid nitrogen.

FIGURE 23

DEPENDENCE OF H_2 / CO ON P_{CH_2O}
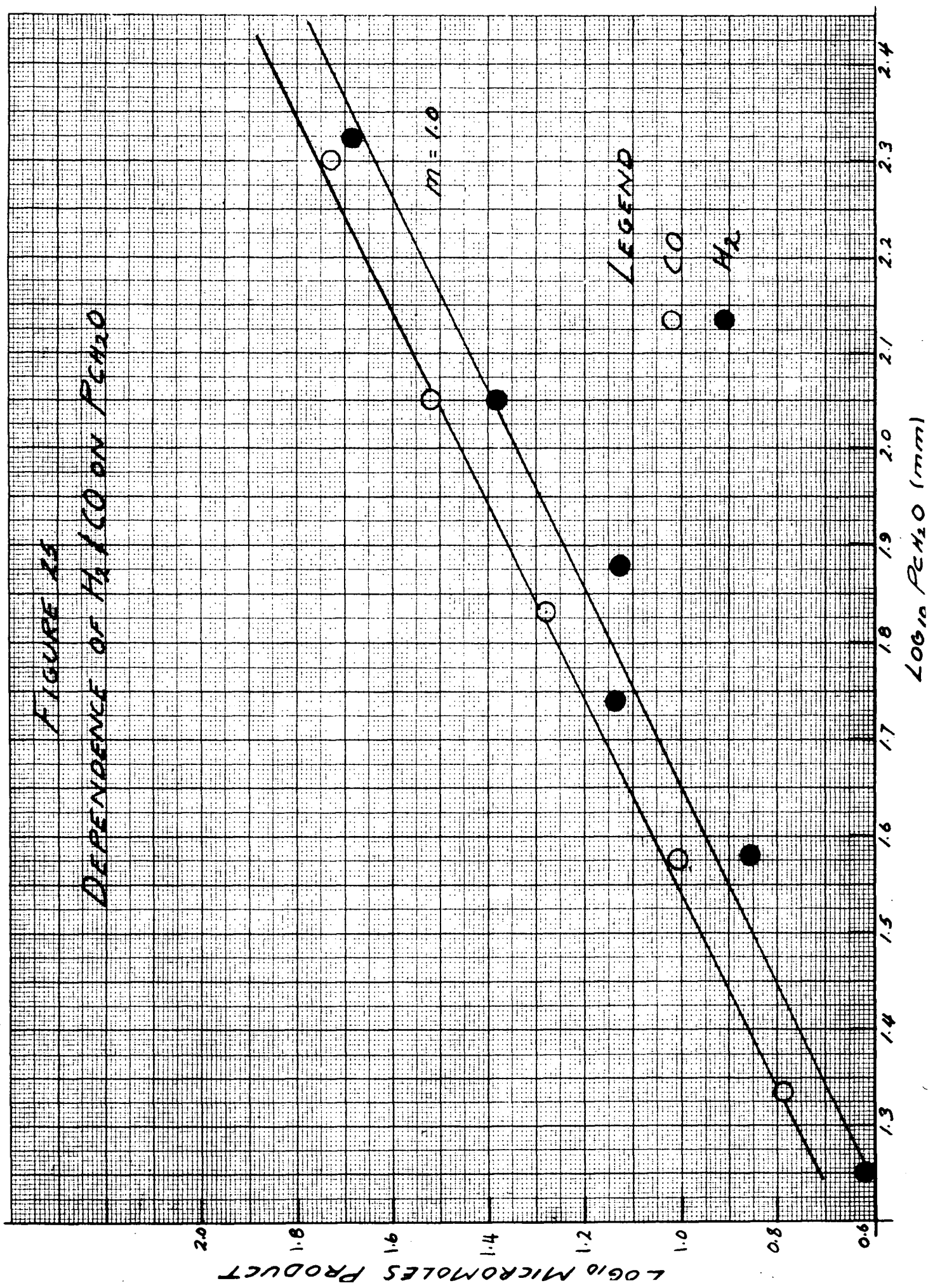
In this way, all the CO_2 was analyzed. Another problem with the CO_2 analysis was the polymerization of unreacted formaldehyde. Each time the condensed products were allowed to warm up, some polymerization occurred with the result that some of the CO_2 was trapped in the polymer. For this reason, the CO_2 analysis are probably low and a rather large error in the determination resulted.

a) <u>Variation with formaldehyde Pressure</u>

CO_2 was found to vary proportionately with the initial pressure of formaldehyde. Some results are listed in Table IX. These runs correspond to mixtures of CH_2O/O_2 in a 10/1 ratio, an initial intensity Io of 8000 Ω , and a time of irradiation of 30 minutes.

<p style="text-align:center"><u>TABLE IX</u></p>

<u>Run</u>	<u>PCH_2O(mm H_g)</u>	<u>micro moles CO_2</u>	$I_a(\Omega)$	ϕCO_2
92	30	0.34	1350	0.31
93	51	0.45	1840	0.31
94	56	0.55	2100	0.31
95	70	0.87	2490	0.405
96	82	0.80	2500	0.375
97	100	1.15	2780	0.48
98	104	1.05	2910	0.42
99	110	1.40	2900	0.57
100	130	1.46	3420	0.505
101	155	1.70	3680	0.54
102	160	1.78	3975	0.53
103	168	1,80	4080	0.52

Some of the tabulated results are plotted in
Figure 26.

b) Quantum Yield as a function of Formaldehyde Pressure

Quantum yields for varying pressures of form-
aldehyde are shown in Figure 27. The experimental results
are shown in Table IX

6. The influence of Oxygen

Although most experimental results were obtained
for reaction mixtures containing a 1:10 ratio of oxygen
to formaldehyde, several runs were carried out in which
this ratio was increased. In general, an increased
proportion of oxygen had little effect on the amount
of reaction products formed. However, at fairly large
oxygen concentration, 3:2 and 2:1 mixtures of oxygen to
formaldehyde, a noticable reduction in the amounts of
reaction products was apparent. This fact was also
observed by Style and Summers (22) who did most of their
work at relatively high ratios of oxygen to formaldehyde.

7. Test for Peroxides.

Peroxides were tested for in the condensed products
by the ferrous thiocyanate method. About 5×10^{-7} mole of
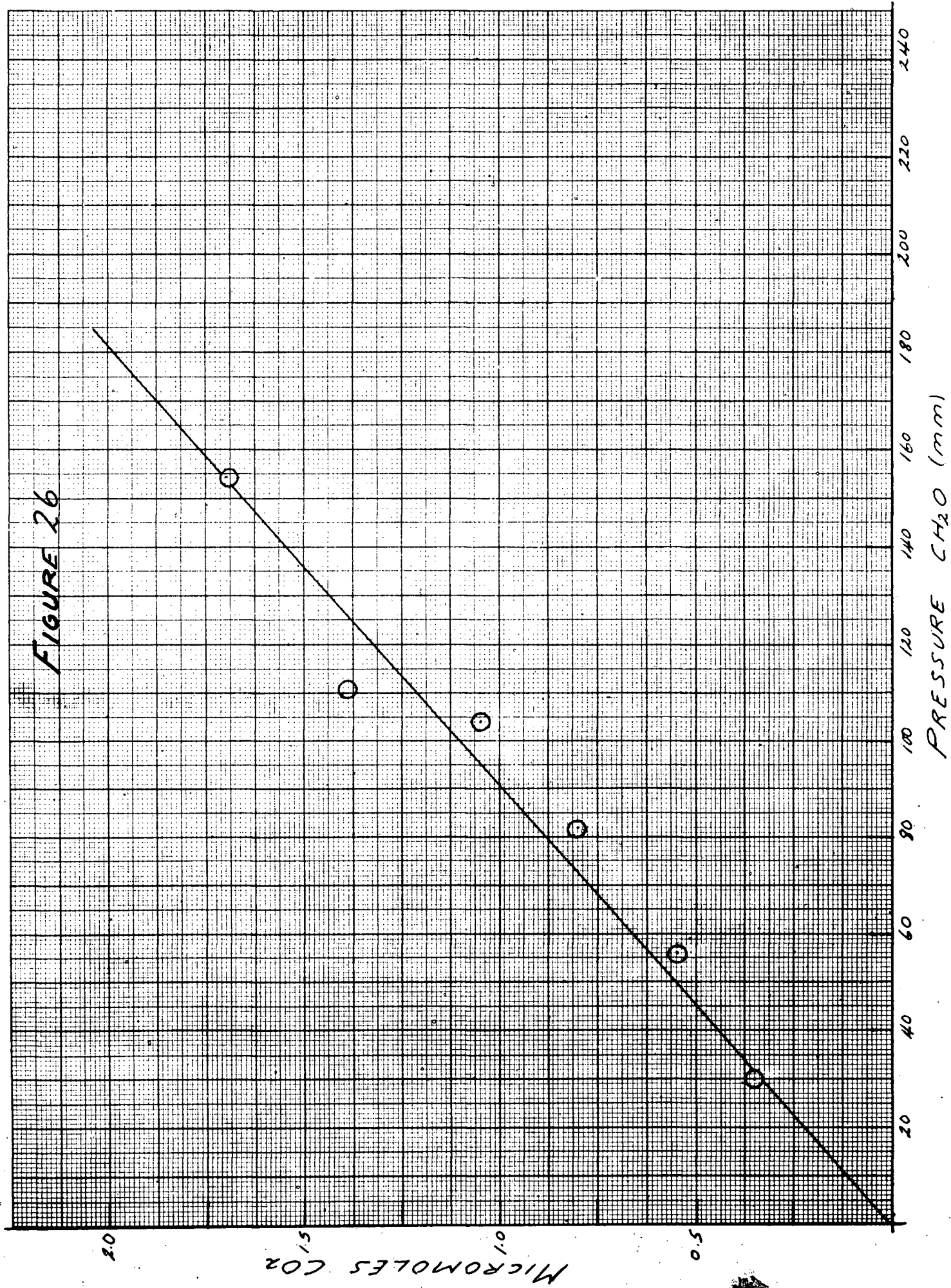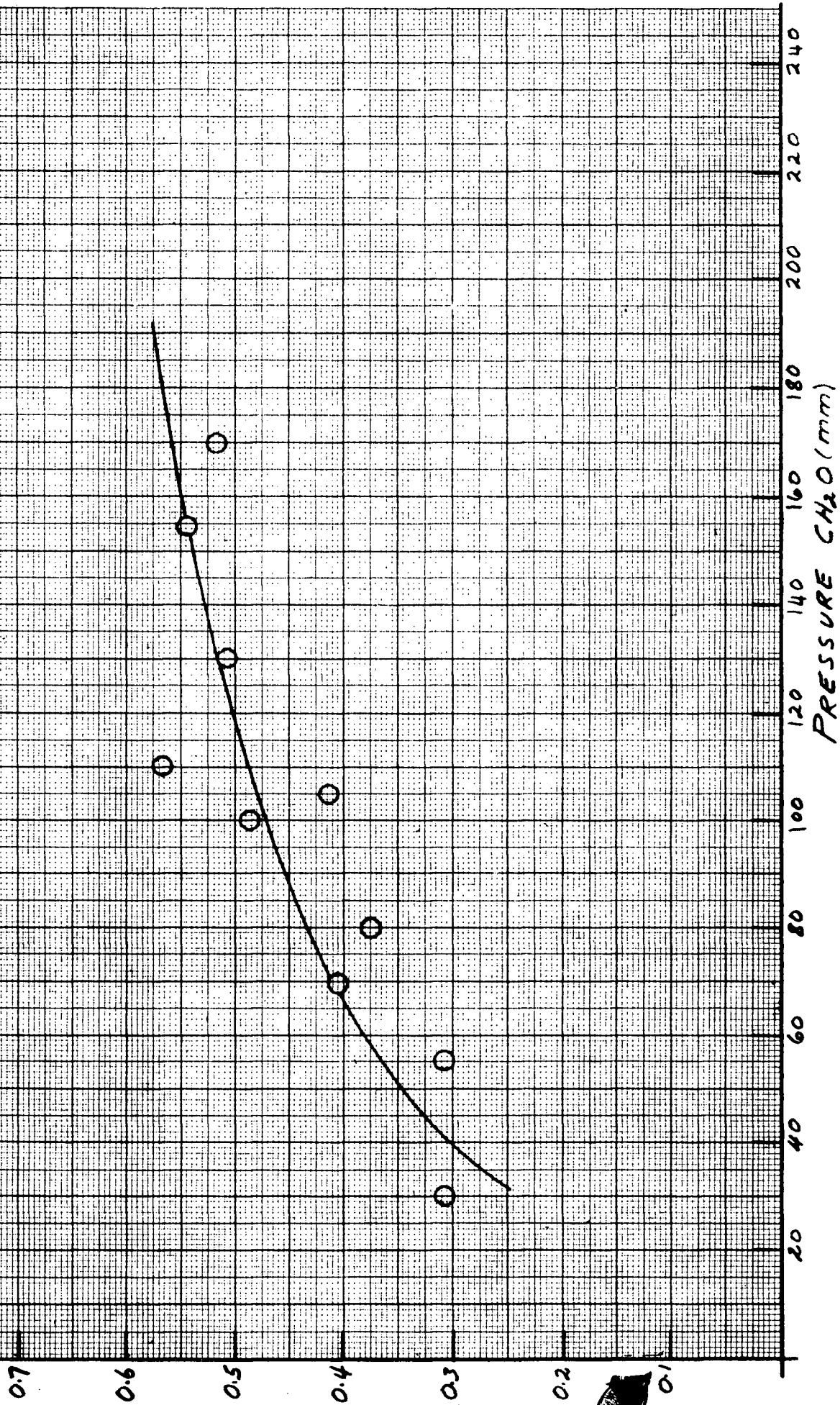peroxide can be estimated with a fair degree of accuracy
by this method.

FIGURE 26

FIGURE 27

QUANTUM YIELD CO₂

It relies on measuring the intensity of the red colour developed (due to the formation of red ferric thiocyanate complex) when a small amount of peroxide is added to a known volume of ferrous thiocyanate solution.

In order to make qualitative tests for peroxide, the "Bell" trap was removed while still immersed in liquid nitrogen. Several ml of the prepared ferrous thiocyanate solution were then added and the resulting solution allowed to warm up. The red colour was then allowed to develop for 10 minutes at room temperature.

In all the tests carried out, only a very pale pink colour resulted indicating that only trace amounts of peroxide were present in the reaction products.

8. The Photolysis of Formaldehyde

Three experiments were carried out in order to determine the quantum yields of hydrogen and carbon monoxide during the photolysis of formaldehyde at $110^\circ C$. An incident irradiation of 8000 Ω was used in each run. The results are summarized in Table X.

TABLE X

(All runs irradiated for 30 minutes)

Run	PCH_2O (mm Hg)	μmoles CO	μmoles H_2	$Ia(\Omega)$	ϕCO	ϕH_2
104	166	4.62	4.70	3960	1.36	1.38
105	163	4.88	4.60	4130	1.38	1.29
106	121	4.02	3.90	3310	1.43	1.39

9. A Summary of the experimental results

Before discussing the mechanism of the photochemical oxidation of formaldehyde at $110^{o}C$, it is advantageous to summarize the facts obtained from the preceding experiments.

a) CO, H_2 and HCOOH are the major products formed; CO_2 is a minor product.

b) The major products produced are directly proportional to the initial formaldehyde pressure.

c) The major products produced are directly proportional to the intensity of the absorbed light, Ia.

d) The quantum yields of these products vary with the initial pressure of formaldehyde; $\phi CO > \phi H_2 > \phi HCOOH$

e) No peroxides were detected in the reaction products.

f) Most of the experimental results were obtained with 1:10 mixture of O_2 to H_2CO; the reaction was independent of O_2 until fairly high ratios of O_2/CH_2O were used.

10. The Proposed Mechanism

The preceding results on the photochemical oxidation of formaldehyde at $110^{o}C$, using light at a wavelength of $3130A^{o}$ and reaction mixtures where the $CH_2O : O_2$ ratio is approximately 10:1, show that the rate of formation of the main products is governed by the following kinetic equations:

(i) $d[CO]/dt = KIa[CH_2O]$

(ii) $d[H_2]/dt = K^1 Ia [CH_2O]$

(iii) $d[HCOOH]/dt = K^{11} Ia [CH_2O]$

Mixtures of formaldehyde and oxygen at $110^{\circ}C$ are known to be unreactive and hence the mechanism of the photochemical oxidation must be dependent on the primary process in the photolysis of formaldehyde. Most workers (21,22,29) agree that the primary process in the photolysis at $3130A^{\circ}$ is the formation of a hydrogen atom and the formyl radical.

Hence,

$$CH_2O + h\gamma \longrightarrow H + HCO$$

Several possibilities exist for the fate of the resulting formyl radical. There is disagreement as to whether or not the formyl radical will decompose since activation energies for its decomposition vary from 13.5 to 26 kilo calories. However, most of the evidence indicates that the formyl radical will be stable at $110^{\circ}C$.

Several reactions of the formyl radical with oxygen are possible. These are outlined below.

$$(1) \quad CHO + O_2 \longrightarrow CO + HO_2$$
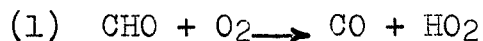
This reaction has been postulated by Chamberlain et al (41) in the oxidation of methane and by Style and Summers(22) in the photooxidation of formaldehyde.

$$(11) \quad CHO + O_2 \longrightarrow CO_2 + OH$$
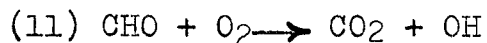
Marcotte and Noyes (42) have postulated this reaction in the photolysis of acetone in the presence of O_2 and it has also been postulated in the oxidation of methane (43).

$$(111) \quad CHO + O_2 \longrightarrow CHO_3$$
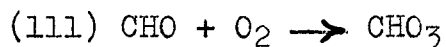
This reaction has been postulated in the oxidation of formaldehyde and methane by Lewis and von Elbe (20)

The first two of these three reactions have been incorporated into the proposed mechanism, and although the third seems to be quite likely, no satisfactory mechanism could be obtained when it was included in the reaction mechanism. Horner, Style and Summers (30) were also unable to incorporate this reaction into their mechanism.

Many workers (21,22,28,30) have proposed the following reaction between hydrogen atoms and formaldehyde.

$$H + HCHO \longrightarrow H_2 + HCO$$
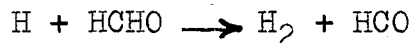
It seems reasonable that this reaction is the main source of the hydrogen produced. It might also be expected that hydrogen atoms will react with O2 to form the HO_2

radical. Hence, the reaction

$$H + O_2 + M \longrightarrow HO_2 + M$$
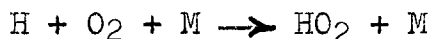
(Where M is a formaldehyde or oxygen molecule) must
also be considered.

The reaction of the hydroxyl radical with form-
maldehyde has been postulated in the oxidation of
methane and formaldehyde (20,44,45). It may be written
as follows,

$$OH + HCHO \longrightarrow CHO + H_2O$$

In order that the high quantum yield of hydrogen
can be accounted for, it is necessary to reproduce
hydrogen atoms. Since the decomposition of the formyl
radical is unlikely at $110^{\circ}C$, hydrogen atoms must be
produced by some other means. Several reactions between
formaldehyde and the HO_2 radical have been postulated,
some of which produce the required hydrogen atoms.
Style and Summers (22) postulated the following reaction,

$$HO_2 + HCHO \longrightarrow CO, CO_2, HCOOH, H$$
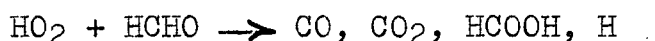
In order to explain the experimental results in
this work, it was necessary to postulate the following
reaction between HO_2 and formaldehyde

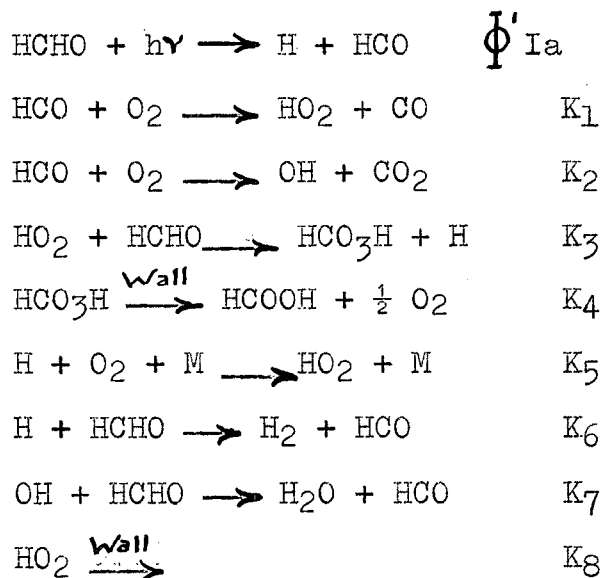$$HO_2 + HCHO \longrightarrow HCO_3H + H$$
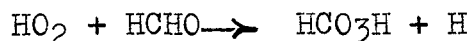
Since peracetic acid is found in the photochemical oxidation of acetaldehyde (48), it is not unreasonable to expect the performic acid in the photooxidation of formaldehyde. However, no peroxides are detected in the reaction products and it must be assumed that the performic acid decomposes to form the normal acid,

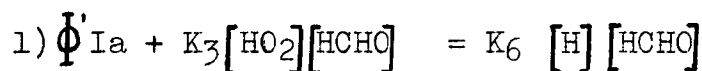$$HCO_3H \longrightarrow HCOOH + \tfrac{1}{2} O_2$$
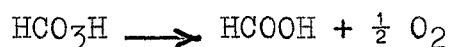
It has been found (47) that performic acid is quite unstable in comparison to peracetic acid and therefore it seems quite reasonable to assume this decomposition.

With these postulates and the experimental facts in mind, it has been possible to propose a mechanism which satisfactorily explains the kinetic results. The following reactions are envisioned.
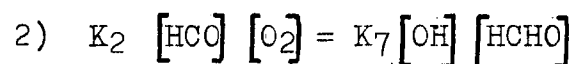
$$HCHO + h\gamma \longrightarrow H + HCO \qquad \phi' I_a$$
$$HCO + O_2 \longrightarrow HO_2 + CO \qquad K_1$$
$$HCO + O_2 \longrightarrow OH + CO_2 \qquad K_2$$
$$HO_2 + HCHO \longrightarrow HCO_3H + H \qquad K_3$$
$$HCO_3H \xrightarrow{Wall} HCOOH + \tfrac{1}{2} O_2 \qquad K_4$$
$$H + O_2 + M \longrightarrow HO_2 + M \qquad K_5$$
$$H + HCHO \longrightarrow H_2 + HCO \qquad K_6$$
$$OH + HCHO \longrightarrow H_2O + HCO \qquad K_7$$
$$HO_2 \xrightarrow{Wall} \qquad K_8$$

Since the ratio of $CH_2O:O_2$ was 10:1 in the reaction
mixtures, it might be argued that K_5 will be small compared
to K_6. If we make this assumption and apply the stationary
state hypothesis to the hydrogen atoms, the OH, HO_2, HCO
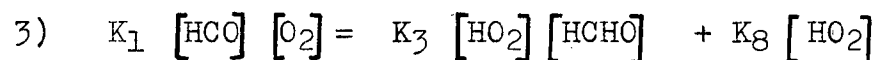radicals and to the performic acid, then we may derive
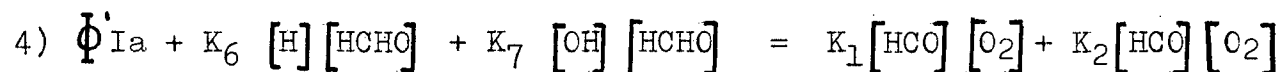the following equations.

H Atoms

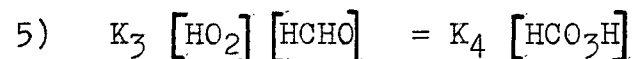1) $\phi' Ia + K_3 [HO_2][HCHO] = K_6 [H][HCHO]$

OH radicals

2) $K_2 [HCO][O_2] = K_7 [OH][HCHO]$

HO2 Radicals

3) $K_1 [HCO][O_2] = K_3 [HO_2][HCHO] + K_8 [HO_2]$

HCO radicals

4) $\phi' Ia + K_6 [H][HCHO] + K_7 [OH][HCHO] = K_1 [HCO][O_2] + K_2 [HCO][O_2]$

HCO3H molecules

5) $K_3 [HO_2][HCHO] = K_4 [HCO_3H]$

Since $K_2 [HCO][O_2] = K_7 [OH][HCHO]$ from 2), reaction
4) becomes $\phi' Ia + K_6 [H][HCHO] = K_1 [HCO][O_2]$

Substituting for $K_1 [HCO][O_2]$ from 3), the above
expression becomes,

$\phi' Ia + K_6 [H][HCHO] = K_3 [HO_2][HCHO] + K_8 [HO_2]$
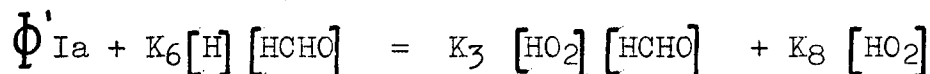
Adding 1) to this expression, we obtain

$$2\Phi' Ia = K_8 HO_2$$

Hence, $\quad HO_2 = 2\Phi' Ia / K_8$

In order to obtain an expression for $[H]$, we can substitute the result for $[HO_2]$ into 1). Upon doing this, we obtain the following expression,

$$[H] = \Phi' \frac{Ia(K_8 + 2K_3 [HCHO])}{K_6 K_8 [HCHO]}$$

From 3) we get the following expression fpr $[HCO]$,

$$[HCO] = 2\Phi' \frac{Ia(K_8 + K_3 [HCHO])}{K_1 K_8 [O_2]}$$

and from 2) we obtain an expression for $[OH]$.

$$[OH] = 2\Phi' \frac{Ia(K_8 + K_3 [HCHO]) K_2}{K_1 K_8 K_7 [HCHO]}$$

We are now able to derive the expressions for the reaction products;

$$d [HCOOH]/dt = K_4 [HCO_3H] = K_3 [HO_2][HCHO]$$
$$d [HCOOH]/dt = 2\Phi' Ia \frac{K_3 [HCHO]}{K_8}$$

$$d [H_2]/dt = K_6 [H][HCHO]$$
$$d [H_2]/dt = \Phi' \frac{Ia(K_8 + 2K_3 [HCHO])}{K_8}$$

Similarily,

$$d [CO]/dt = 2\Phi' \frac{Ia(K_8 + K_3 [HCHO])}{K_8}$$

$$d [CO_2]/dt = \frac{2K_2 \Phi' Ia(K_8 + K_3 [HCHO])}{K_1 K_8}$$

These expressions agree well with the experimental results. Since the ratio of $CO:CO_2$ is found to be about 30:1, then $K_2:K_1$ must also be about 30:1.

Expressions for the quantum yields of the major products can be deduced by dividing by Ia, Hence, we can derive the following expressions for the quantum yields.

$$\phi \text{ HCOOH} = 2\phi' \frac{K_3}{K_8} [\text{HCHO}]$$

$$\phi \text{H}_2 = \frac{\phi'(K_8 + 2K_3 [\text{HCHO}])}{K_8}$$

$$\phi \text{CO} = \frac{2\phi'(K_8 + K_3 [\text{HCHO}])}{K_8}$$

These expressions can be reduced to the following forms if we let $2\phi' \dfrac{K_3}{K_8} [\text{HCHO}] = A$

Hence,
$$\phi \text{ HCOOH} = A$$
$$\phi \text{H}_2 = \phi' + A$$
$$\phi \text{CO} = 2\phi' + A$$
$$\therefore \phi \text{ HCOOH} = \phi \text{H}_2 - \phi' = \phi \text{CO} - 2\phi'$$

From Figure 23, where the quantum yields of these products are shown, we see that the above relation is in fair agreement with the experimental results.

When the ratio of oxygen to formaldehyde was increased, it was found that the amounts of products formed was reduced. This would be expected from the proposed mechanism, since with increasing oxygen concentration, K_5 will begin to compete with K_6. When we include this reaction, we find that the rate equations governing the formation of products become

$$d\,[HCOOH]/dt \;=\; 2\phi'Ia\,\frac{K_3}{K_8}\,[HCHO]$$

$$d\,[H_2]/dt \;=\; \frac{K_6\,\phi'Ia\,(K_8 + 2K_3\,[HCHO])\,[HCHO]}{K_8\,(K_6\,[HCHO] + K_5\,[O_2]\,[M])}$$

$$d\,[CO]/dt \;=\; \frac{2\phi'Ia\,(K_8 + K_3\,[HCHO])}{K_8} \;-\; \frac{\phi'Ia\,K_5\,[M]\,[O_2]\,(K_8 + 2K_3\,[HCHO])}{K_8\,(K_6\,[HCHO] + K_5\,[O_2]\,[M])}$$

$$d\,[CO_2]/dt \;=\; K_2/K_1\,(d\,[CO]/dt)$$

and we see that the products H_2, CO and CO_2 will become less when the oxygen concentration is increased which is in agreement with the experimental results.

Although the above mechanism has been shown to agree satisfactorily with the experimental results, there is a good possibility that the primary step when a formaldehyde molecule absorbs a quantum of light at $3130A^\circ$ is the formation of an activated molecule,

$$HCHO + h\gamma \longrightarrow HCHO *$$

The activated formaldehyde molecule could then react in two ways,

a) $HCHO^* + X \longrightarrow H + HCO + X$

b) $HCHO^* + O_2 \longrightarrow HO_2 + HCO$
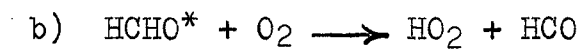
Once again, when the proportion of oxygen in the reaction mixture is low, one would expect a) to predominate. This would lead to the same kinetic expression as before.

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