THE EXTINCTION OF FLAMES

by

David Gardiner Biggar, A.R.T.C., A.I.C..

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It is also the author's pleasant duty to record his sincere gratitude to the Governors of The Royal Technical College for their generous awards throughout the past three years, which enabled him to carry out this research.

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INTRODUCTION.

The object of the work done and recorded herein was to determine extinction points for the common combustible gases when burning freely at a jet, as nearly as possible at atmospheric pressure.

For the purpose of this paper the extinction point (E.P.) has been defined as *The maximum percentage of oxygen, by volume, in any homogeneous gaseous mixture which fails to support the combustion of the combustible body under the conditions of the experiment.*

Very little work of this exact nature appears to have been done, although many investigators have studied closely allied branches of the subject.

In general there are three methods by which the problem may be investigated :-

1. Determination of limiting or extinctive values for flame propagation in gaseous mixtures containing a combustible gas and oxygen in a confined volume.
2. Determination of extinctive conditions for a gas burning at a jet in an enclosed vessel.
3. Determination of the extinction point for a gas burning in an open vessel at constant pressure in an atmosphere of constant composition, which may be altered in composition at will.

In order to elucidate the connection between the foregoing programmes, it will be helpful to review briefly the work done in each.

1. Wheeler and his collaborators have shown by much experimental evidence that combustible gas-air mixtures at normal temperature and pressure have definite "Lower limits" and "Higher limits" of inflammability when subjected to an electric spark discharge and confined in closed vessels.

Burgess and Wheeler(2) found these limits for methane-air mixtures to be 5.6 and 14.8 per cent of methane respectively.

Considering the upper limit for methane, of composition :-

Nitrogen	67.3%
Methane	14.8%
Oxygen	17.9%

we have a true extinction atmosphere in which the diluent is methane, and the extinction point is 17.9 by this method. Wheeler and his collaborators also found(5) that these limits, referred to above, converge to a point as the oxygen content is reduced by means of nitrogen until, at 13.25% of oxygen and lower, no addition of methane gives an inflammable mixture. Thus 13.25 may be regarded as another value for the extinction point, for the given conditions.

Coward and Hartwell(4) have shown that for methane-air mixtures diluted with nitrogen and carbon dioxide respectively, the non-inflammable point (extinction point) is reached at 12.9% and 15.7% of oxygen. The former figure is in reasonable agreement with that of Burgess and Wheeler. The higher extinction point, using carbon dioxide as a diluent, is, according to these workers, due to the greater cooling effect of this gas on account of its higher specific heat.

2. Dollwig, Knolls, and Loevenhardt(1) have investigated extinctive residual atmospheres for the candle and ethyl alcohol flame, and show that the partial pressure of oxygen in the case of a flame burning to extinction in a closed vessel at atmospheric pressure is very much greater than when conducted at reduced pressure, by rapid exhaustion of the combustion chamber. The

figures for ethyl alcohol wick fed flames given are 112.7m.m., and 27m.m. partial pressure of oxygen, respectively. These workers attribute this difference to the cooling effect of nitrogen and its retarding influence on the access of oxygen to the flame.

The results of work done by Clowes and Feilmann(9), Jorissen and Siewertz von Reesema(10), and Harger(11), are given in Table II below, and the results of observations made for The Home Office Explosions in Mines Committee(2) are given in Table I.

3. Very little appears to have been done in this branch of the work. Rhead, in a recent paper(2) gives the results of earlier investigators and contributes the results of his own researches as shown in part in Table II.

TABLE I. - RESIDUAL ATMOSPHERES.

Gas	Oxygen (%) in residual atmosphere in neighbourhood of jet.
Methane	15.5
Propane	15.8
Butane	16.0
Pentane	16.4
Cyanogen	15.1
Carbon monoxide	10.2
Hydrogen	5.6

TABLE II. - RESIDUAL AND EXTINCTIVE ATMOSPHERES.

Observer	Oxygen content in atmosphere %					
	Residual			Extinctive		
	Methane	Hydrogen	Carbon monoxide	Methane	Hydrogen	Carbon monoxide
Clowes & Feilmann.	15.6	5.5	13.35	17.4	6.3	15.1
Jorissen & S. von Reesema.	-	4.0	11.2	-	3.5	10.0
Harger.	17.5	7.5	-	-	-	-
Rhead(1)*	-	-	-	18.2	-	-
Rhead(2)*	-	-	-	16.8	-	-
Rhead(3)*	-	-	-	16.6	-	-

		(1)*	(2)*	(3)*
(a)	Speed of atmosphere Cm. per Min.	195	350	715
(b)	Speed of gas Cm. per Min.	230	514	288
	(b) - (a)	35	164	- 487

It will be apparent that the extinction points determined by each of the above methods for any one gas will vary within wide limits, but the author considers that much may be gained from a joint study of these methods, as they have more in common than may at first be realised.

Combustible gas-air mixtures have definite limits of inflammability for any given temperature and pressure conditions. These limits converge to the point of complete non-inflammability as the percentage of oxygen by volume is progressively reduced by dilution with an inert gas.

A jet of combustible gas when directed into an atmosphere capable of supporting combustion, either in a closed vessel or in a vessel open to the atmosphere, becomes in a very short time, due to its velocity of projection and to diffusion, a combustible mixture not altogether unlike the mechanically stagnant mixture used for flame propagation experiments as in 1. above. This combustible mixture at any instant after the introduction of the jet of combustible gas can be conceived of as strata or zones of mixed gases, ranging from these which are too weak in combustible gas to ignite, to these in the immediate neighbourhood of the jet which contain combustible gas in excess of the higher limit of inflammability. Between these limits we have an inflammable zone which depends on many factors, such as diffusion and relative velocity of the combustible gas to that of the atmosphere. When this zone is ignited, the conditions, due to increased kinetic energy etc., will of course be altered, but in all probability only in degree, and the flame will occupy the the position of the strata whose flame propagation speed is equal to the speed of the same strata away from the jet. It may be deduced from this conception that for low gas speeds the flame will occupy a position near the jet in the zone of slow flame speed mixtures rich in combustible gas. For greater gas speeds the flame may occupy the zone of highest flame speed mixtures and, if this be exceeded, the flame may either be blown out or recede to the slow flame speed zone weak in combustible gas, depending on the speed gradient of the mixture from the jet.

If the assumption, which seems quite unjustifiable to the author, that the composition of the mixed residual gases in methods 1. and 2. above, represents the true composition of the atmosphere enveloping the flame at the instant of extinction, be granted, then perhaps the most significant difference between these methods of arriving at the extinction point for any gas lies in the presence or absence of the products of combustion in the extinctive atmosphere. The only mixing which can take place in a closed vessel is due to convection currents and diffusion. The effect of carbon dioxide, as one of the normal products of combustion, is given by Coward and Hartwell(4) as follows :-

TABLE III.

Diluent	Composition (%) of extinctive atmosphere for methane.		
	Carbon dioxide	Nitrogen	Oxygen
Nitrogen	-	87.1	12.9
Carbon dioxide	25.0	59.3	15.7

from which it is seen that carbon dioxide raises the extinction point considerably.

From the foregoing discussion it will be evident that, in choosing the third method the author's aim has been to arrive at extinction point values under conditions as free as possible from avoidable contributing influences.

PART I.

THE EXTINCTION OF HYDROGEN FLAMES.

PRELIMINARY WORK.

In devising a suitable apparatus the following conditions had to be satisfied :-

(1) A steady flow of atmosphere which could be varied in composition and rate of flow at will, was required.

(2) A combustion chamber of such shape and dimensions that the products of combustion would be immediately swept out by the flow of atmosphere decided upon; and such that the pressure inside would be as nearly as possible atmospheric; and such that there would be no inflow of air from the atmosphere; was required.

(3) A constant steady flow of the combustible gas was necessary.

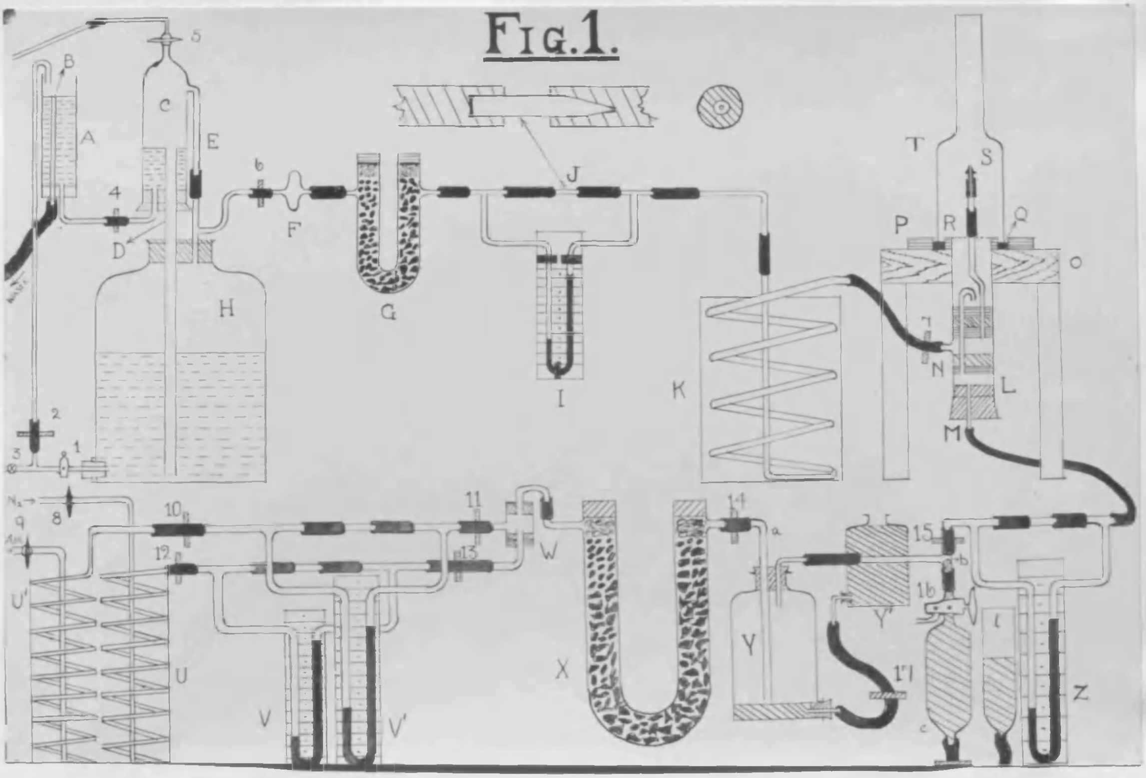
(4) A ready means of access to the jet for lighting purposes was required.

(5) Provision for sampling the gas actually being supplied to the combustion chamber at any instant, was required.

The composition of the atmosphere was made easily variable by passing the constituent gases through differential gauges and altering the pressure according to requirements. Use was made of a third differential gauge for controlling the rate of flow of the atmosphere.

A combustion chamber was selected which by trial satisfied the conditions laid down in (2) above.

FIG.1.


B
A
C
5
E
4
D
H
6
F
G
J
I
K
T
S
P
R
Q
O
7
N
L
M
2
3
1
N₂→
8
9
AIR
10
12
11
13
W
14
a
X
Y
Y'
15
b
16
17
c
l
Z
U'
U
V
V'

Use was made of a mercury seal to satisfy condition (4) above.

The sampling arrangements made use of were changed several times in the course of the work, and are treated fully in the Appendix.

DESCRIPTION OF APPARATUS.

The apparatus used for the preparation of hydrogen, sampling, and analyses, are described in the Appendix.

Figure 1 shows the general lay out of the apparatus employed to obtain extinctive conditions. In this sketch all stopcocks screw clips etc. are designated, for ease in reference, by numbers, the other parts being referred to by letters as follows :-

A. A weir, 10" in height, internal diameter 2½".

B. A sliding tube whereby the water level in "A" may be adjusted.

C. A closed weir, the pressure inside being always the same as in "H" due to the connection "E".

D. A wide tube, about ¾" internal diameter, chosen to take the maximum flow of water from "A" without running full bore.

F. A water trap to prevent the accidental admission of water, lodged in the connections, to "H", from entering "G".

G. A 4" calcium chloride tube for drying the gas.

H. A 10 litre aspirator bottle for the storage of gas.

I. A differential gauge, graduated in m.m., a detailed section of the jet being shown above.

J. A suitable glass jet.

K. A spiral of ⅛" bore copper tubing immersed in a beaker of water at room temperature.

L. Virtually an annular tube, internal diameter 1½", length 6". Air is led in at "M" and the combustible gas at "N".

O. A block of wood, 6" x 6" x 1½", through the centre of which a hole is bored to hold "L" tightly in position.

P. A circular slab of paraffin wax securely moulded on to "O" by means of oblique channels bored into the wood, with an annular grove, ⅛" in width, cut in it to form a mercury seal.

Q. A mercury seal.

R. A perforated cardboard disc securely attached to the top of "L" to distribute the air entering "T".

S. A suitable metal jet cemented into the glass tube with asbestos-silicate cement, to prevent conduction of heat as far as possible.

T. A glass combustion chamber of dimensions and shape to suit the particular gas being burned at "S".

The nitrogen used was stored in a 12 c. ft. gas holder over water and passed through a soda-lime tower on its way to the control cock 8.

The air used was stored in a 2 c. ft. balanced gas holder over water, connected to the cock 9.

U and U'. Lead pipe coils ¼" bore immersed in water at room temperature.

V and V'. Differential gauges similar to "I", for the control of nitrogen and air respectively.

W. A mixing chamber for air and nitrogen.

X. A calcium chloride U-tube, to effect drying and further

	mixing of the gases.
Y and Y'.	A sampling arrangement.
Z.	A differential gauge similar to "I" graduated in tenths of an inch.
"a"	A glass tube terminating about ½" from the bottom of "Y".
"b"	A 50 c.c. sampling tube.
"d"	A levelling tube connected to "c" by means of rubber tubing.

CALIBRATIONS.

1. The jet "J" for delivery of hydrogen.

The desired size of flame, 1 cm. in height, was first obtained by trial of various jets in "I" and different levels in "A". With this jet in position, screw clips 4 and 6 were closed, 1 opened to waste, and 5 opened to gas supply -See Fig. 4 Appendix - Gas was passed in till no more water was displaced through 1 which was then closed. 4, 6, and 7 were then opened and 5 closed, the time being simultaneously noted, and the gas burned for a noted time at "S", during which the steady reading on "I" was noted.

4, 6, and 7 were then closed and the water which had collected in "H" was displaced with a fresh charge of gas and weighed, thus giving the volume of gas consumed per hour under the conditions of the experiment.

2. The corresponding theoretical volume of oxygen required for the complete combustion of the gas was calculated, a chosen excess added, and an approximation to the volume of the extinctive atmos-

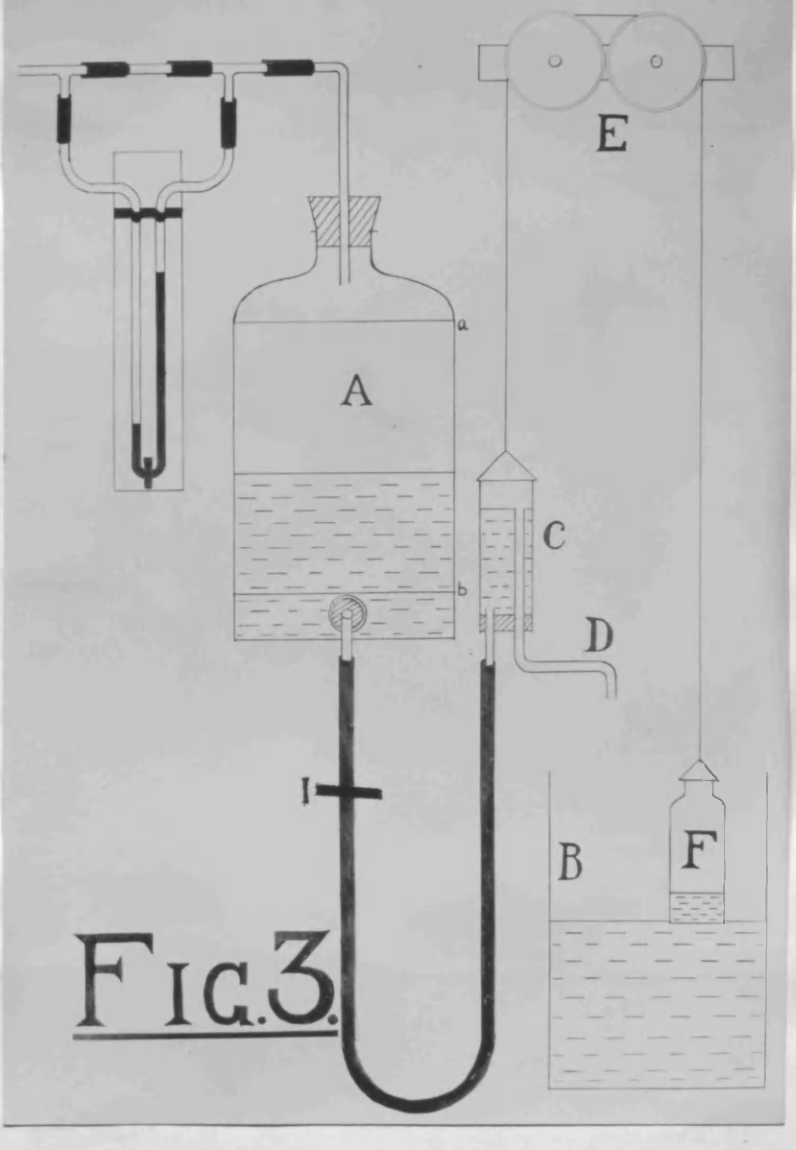


FIG.3.

phere which would contain the calculated volume of oxygen was arrived at by assuming a likely extinction point as shown later in actual examples.

The jet in "Z" was then set , after selection by trial and error, to deliver the required volume of atmosphere per hour for a convenient gauge reading. "Z" was then calibrated according to the method of Gray(13) the apparatus used being sketched in Fig. 3.

In Fig. 3. :-

A. represents a 10 litre aspirator bottle,

B. a parallel walled vessel of exactly the same cross sectional area as "A",

C. a weir connected by means of rubber tubing to "A",

E. a smooth running double pulley,

F. a bottle which can be weighted so as to balance "C".

The level in "B" rises at the same rate as the level in "A" falls, so that a constant head of water is maintained between "A" and "C" and hence a constant flow of gas through the differential gauge is effected.

The method of procedure is as follows :-

"A" is filled up to the mark 'a' with water, then connected to the gauge "Z" to the side nearest the constricted end of the jet. "C" and "F" were arranged so that with a tared quantity of water in "B" , "F" just floated on the surface. The head of water between "A" and "C" may be adjusted by means of the sliding tube

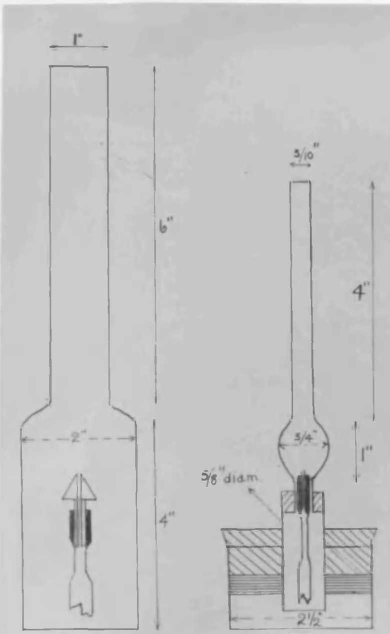
"D" or by altering the length of the string connecting "C" and "F", this being done in different estimations in order to obtain various gauge readings, so that a graph may be plotted (Gauge reading x Delivery)

Before the above method was adopted, differential gauges V and V' Fig. 1. were calibrated by means of an ordinary bellows type gas meter in order to compute the composition of the atmosphere passing, from the gauge readings, and vice versa. It was found however that the introduction of a third differential gauge "Z" made this a very difficult proposition in view of the fact that an alteration in either of the auxiliary gauges V and V' mutually influenced the other two gauges in the system. Prior to the introduction of "Z" the bellows gas meter method of calibrating V and V' was found to be inaccurate, due, most probably, to the uneven motion of the bellows at the end of each stroke. Another very probable reason for the discrepancy between the results computed from gauge readings and these obtained from analyses is the probable inconstant admixture of oxygen with the nitrogen supplied.

It was finally decided to make the jets in V and V' variable by means of the screw clips 10, 11, 12, and 13, as shown in Fig. 1., and as described under " Method of Procedure ".

PREPARATION AND STORAGE OF HYDROGEN.

The hydrogen was prepared from pure zinc and dilute hydrochloric acid as described on p. 141. and stored in "H" -Fig. 1. - as follows :-



(A) (B)

FIG. 2.

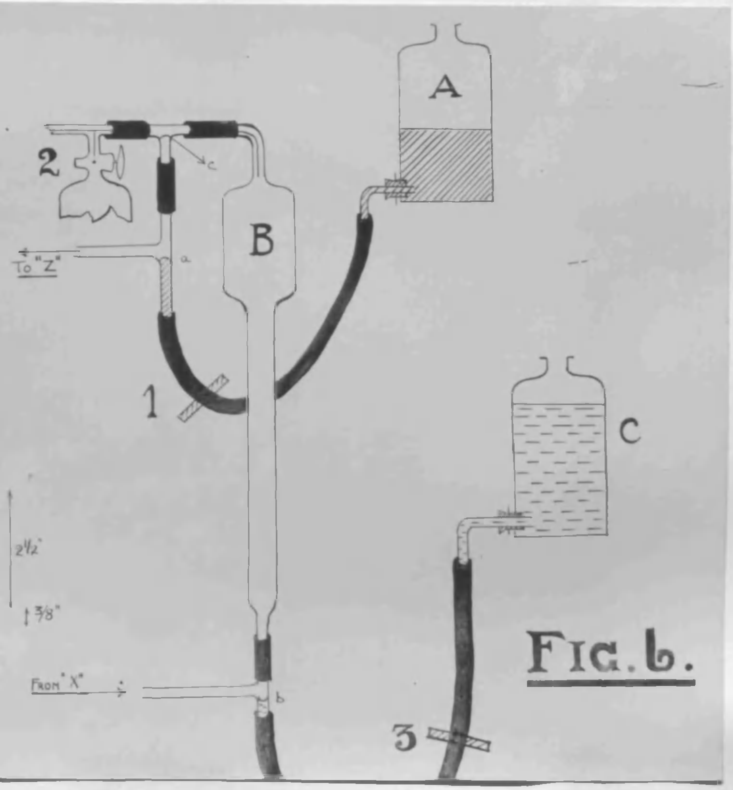


FIG. 6.

Referring to Fig. 1. Cocks 2, 4, and 6 were closed, and 1, 3, and 5 opened until "H", "C". and the connecting tube from 5 were completely filled with water. 3 was then closed and 5 connected to the hydrogen generator. 1 was opened to waste and a full charge of gas allowed to flow into "H" by displacement of water through 1, which was then closed.

SELECTION OF COMBUSTION CHAMBER.

The conditions laid down in "Preliminary Work" - page 2. - were satisfied by the combustion chamber shown in Fig. 2A. for a 10% excess of the extinctive atmosphere.

SELECTION OF BURNER JET.

An ordinary mouth-blow-pipe jet with an orifice of 0.01" diameter was found to be the most satisfactory of the various jets tried in so far as it did not set up any appreciable back pressure - as shown on the gauge "I" - (Fig. 1.) and gave a flame 1 cm. in height for a suitable reading on "I". Glass jets were previously tried but were found to be unsatisfactory because of the tendency of the glass to soften with the high local temperature of the flame.

The jet was cemented into the glass tube by means of asbestos-silicate cement which proved to be quite satisfactory.

RATE OF COMBUSTION.

The jet "J" was selected so as to give a suitable range of readings on "I" for different readings on "A" (Fig. 1.), and to

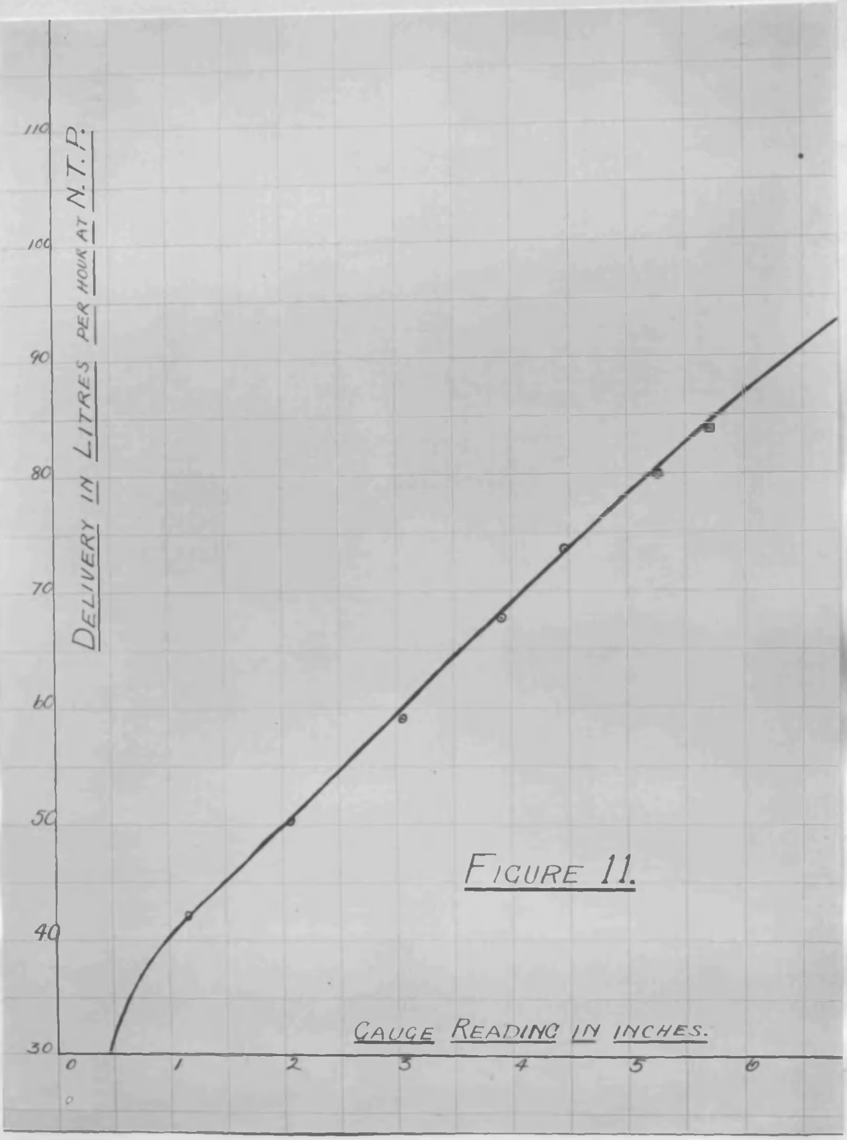

DELIVERY IN LITRES PER HOUR AT N.T.P.
110
100
90
80
70
60
50
40
30
GAUGE READING IN INCHES.
0
1
2
3
4
5
6

FIGURE 11.

deliver the requisite volume of hydrogen to maintain a flame 1 cm. in height at "S" when "T" was removed.

The rate of combustion was then determined in triplicate as described on page 6., of which determinations the following represents the mean.

Duration of test. (minutes)	75
Height of flame. (cms.)	1
Gauge reading on "I" (cms.)	5.0
Atmospheric pressure (cms.)	75.4
Atmospheric temperature (°C)	16.0
Volume of water displaced (litres)	9.95
Volume of hydrogen burned (litres at N.T.P.)	9.33
Rate of combustion of hydrogen (litres per hour at N.T.P.)	7.46

RATE OF FLOW OF ATMOSPHERE.

As a first approximation the extinction point for hydrogen was assumed to be 5.0, and on this basis the rate of flow of atmosphere required was calculated thus :-

7.46 litres of hydrogen require for complete combustion 3.73 litres of oxygen.

Allowing a 10% excess, oxygen required = 4.10 litres.

Hence atmosphere (containing 5.0% of oxygen) required

$$= \frac{100 \times 4.1}{5.0} = 82 \text{ litres.}$$

A jet capable of delivering 82 litres of atmosphere per hour for a convenient gauge reading was selected for "Z" - Fig.1 - and calibrated with the help of an apparatus designed by Gray(13) The results shown in Table IV. were obtained, and the graph obtained by plotting delivery x scale readings, is shown in Fig. 11.

TABLE IV.

Gauge reading (inches)	Delivery (litres per hour at N.T.P.)
5.7	84.1
5.25	80.0
4.55	73.7
3.9	67.8
3.05	59.3
2.05	50.4
1.15	42.2

PRELIMINARY ESTIMATION.

At this stage of the work the method of manipulating the apparatus, sampling, analysis, etc. varied considerably from that in use in later work. See "Sampling" and "Analysis" in Appendix.

In order to have a more accurate basis for calculating the rate of flow of atmosphere required to give a 10% excess of oxygen at the extinction point than that of an assumed extinction point, (5.0) as above, the following series of results was obtained using the above quantities of hydrogen and atmosphere. Sampling by method 2. (appendix), and analysing by means of Orsatt's apparatus.

TABLE V.

Flame	Oxygen (%) in atmosphere.
Extinguished	5.3
"	5.6
"	5.8
"	5.8
Persisted	5.9
"	6.0
"	6.0
"	6.2

THE FINAL ESTIMATION.

From the results shown in Table V. the extinction point appears to be approximately 5.8. On the assumption that the extinctive atmosphere contains 6.0 per cent of oxygen, when the volume of the atmosphere is 10 per cent in excess of that required theoretically for the complete combustion of the hydrogen, the required volume of the extinctive atmosphere was found by calculation to be 68.3 litres per hour. = 4.0" on gauge from graph (Fig. 11.)

METHOD OF PROCEDURE.

The hydrogen storage bottle "H" - Fig. 1. - and the nitrogen and air holders are all charged with the respective gases.

Water is turned on by means of the cock 3 and allowed to overflow freely in "A" to waste. 4, 6, and 7 are then opened and the reading on "I" adjusted by means of "B" to 5.0 cms.. "T" is then removed, the hydrogen at "S" ignited, and "T" replaced.

Y' is now lowered and the clip 17 opened so as to adjust the level in Y, to allow a free passage for air through it, as shown in Fig. 1. Clip 17 is then closed and Y' raised. By opening 16 and raising *l* the mercury in 'c' is raised to the mark 'b', 16 is then closed.

8, 9, 14, and 15 are thes successively opened and, after a lapse of about two minutes, to allow the composition of the atmosphere to become constant, the hydrogen at "S" is relighted if necessary. The composition of the atmosphere is then altered at three-minute intervals, according to the behaviour of the flame, by means of the screw clips 10, 11, 12, and 13. Eg. Closing 10 reduces the reading in V' and Z, and gives less air, whereas closing 11 increases the reading in V', lowers the reading in Z, and gives less air.

The reading in Z is maintained at 4.0" so that an increment in either the nitrogen or the air supply must be followed by a corresponding decrement in the supply of the other gas. The approximate extinctive atmosphere is arrived at in this way and then fine adjustment is made by the removal or addition of small weights from or to the nitrogen and air holders.

When the point is reached where a slight alteration of the weights causes the flame to persist or to be extinguished, as the case may be, 14 is quickly closed and then 15, the sample being thus confined in "Y" . 4, 3, 6, 7, 8, and 9 are then closed in the order given. Sampling is effected by opening 16 and 17 until the required volume of the sample is obtained in "C", 16 and 17 are then closed and air admitted to "C" by means of the three-way cock 16. "C" and "L" are then detached and connected to the Haldane gas analysis apparatus (Fig. 7.) as described in the Appendix, and the gas analysed.

RESULTS.

A series of estimations was carried out as described above, each analysis being conducted in duplicate, and the results are given in Table VI.

TABLE VI.

Flame	Oxygen per cent in atmosphere.		
	(1)	(2)	(Mean)
Persisted	6.24	6.18	6.22
"	6.22	6.19	6.20
"	6.25	6.11	6.18
"	6.10	6.18	6.14
"	6.07	6.15	6.11
"	6.10	6.03	6.07
"	6.08	6.06	6.07
"	6.02	6.08	6.05
Extinguished	6.05	6.05	6.05
"	5.95	6.09	6.02
"	5.94	6.09	6.02
"	5.94	6.07	6.01
"	5.96	6.04	6.00
"	6.01	5.95	5.98
"	5.96	5.99	5.97
"	5.89	6.03	5.96

From the results given in Table VI above the extinction point for hydrogen flames, as determined by the foregoing method, is 6.0.

OBSERVATIONS AND NOTES.

In the foregoing work the effect of varying atmospheric conditions on the masses of the respective gases was neglected, it being taken that the effect would be much the same for each gas, and the ratio fairly constant.

The effect of admixture of air with the hydrogen on the nature and behaviour of the flame was tried. Quantities of air, varying from 0.5 to 20 per cent were found to cause the flame to become progressively smaller and more sharply defined as the proportion of air increased.

An insufficiency of atmosphere which, in excess, was known to support steady combustion, caused the flame to elongate very noticeably, and to flicker or pulsate. The flickering was thought to be due to a back draught of air from the surrounding atmosphere down the interior walls of the combustion chamber.

Near the extinction point the hydrogen flame is somewhat difficult to see even in a darkened room. Its linear dimensions increase about 2½ times in all directions, so that the volume of the flame at the extinction point is probably about ten times as great as its volume would be if burning under the same conditions in atmospheric air. The flame does not leave the jet until almost at the extinction point.

While maintaining the same volumes of hydrogen and atmosphere from day to day, no detectable variation in the extinction point, due to altering atmospheric conditions (temperature and pressure), could be detected.

SUMMARY. - PART I. -

In order to determine the maximum proportion of oxygen, in an atmosphere of oxygen and nitrogen, which just fails to support the combustion of hydrogen burning at a jet as nearly as possible at atmospheric pressure, the apparatus shown in Fig. 1. (p. 3.) was assembled.

By means of this apparatus a supply of hydrogen at constant pressure was available. Air and nitrogen could be readily mixed in any desired proportions while being continuously delivered, almost at atmospheric pressure, to a combustion chamber part of which could be easily removed for lighting purposes.

The rate of flow of atmosphere was arranged by trial and error so that the volume of the atmosphere was 10 per cent in excess of that theoretically necessary to effect complete combustion of the hydrogen.

The extinction point for hydrogen was found to be 6.0.

GENERAL CONCLUSIONS.

The apparatus used and shown in Fig. 1. has been found to be capable of very fine adjustment, easy manipulation, and to give very satisfactory results in duplicate estimations of the extinction point of hydrogen flames.

The extinction point determined for hydrogen, viz. 6.0 , is in reasonable agreement with the figure 6.3 given by Clowes and Feilmann(9), but vastly different from the result (3.5) given by Jorissen and Siewertz von Reesema(10), as shown in Table II.

Although, in the light of information gleaned from subsequent work with carbon monoxide flames, the author feels that the above result is open to objections on the the grounds that no cognizance has been taken of the humidity of the reacting gases, their respective speeds, and the temperature of the combustion chamber walls, he considers that, since water vapour is formed by combustion in this case, the slight variations due to atmospheric changes are not likely to have any influence on the value obtained. From the comparison shown in Table VII. the speed of the reacting gases will have much less effect on flame maintenance in the case of hydrogen than in the case of carbon monoxide. In view of the fact that the hydrogen flame shows very little tendency to rise from the jet the combustion chamber walls will, in all probability, have a lower temperature than is the case with carbon monoxide flames.

The author therefore considers that the influences referred to above will not, in the case of hydrogen flames, materially affect the value obtained for the extinction point.

PART II.

THE EXTINCTION OF CARBON MONOXIDE FLAMES.

PREPARATION OF CARBON MONOXIDE.

The carbon monoxide used in much of the earlier work was prepared from sodium formate by the action of concentrated sulphuric acid. Subsequently, due to the presence of small quantities of nitrogen in the gas, derived from air mechanically or physically entrapped in the sodium formate crystals, it was decided to use formic acid in place of the sodium salt. Both methods are fully described in the Appendix.

SELECTION OF BURNER JET.

It was found experimentally that the jet used to give a flame 1 cm. in height, in the case of hydrogen, could only be used to maintain flames of a very much smaller order in the case of carbon monoxide. The carbon monoxide flame was extinguished, even in air, long before this gas, supplied at a gradually increasing rate, could be passed in sufficient quantity to give a flame 1 cm. in height with the above jet.

As this phenomenon of carbon monoxide has a direct bearing on some of the difficulties encountered in the course of the following work, as well as for the purpose of reference, a brief discussion may not be out of place here.

When pure combustible gas is continuously projected from a jet into the atmosphere, the gas, due to diffusion and its velocity of projection, mixes with the air. Zones of gas-air mixtures are thus established varying from pure gas at the jet to pure air at some distance from the jet. Within these limits are the narrower limits of gas-air mixtures which are inflammable. Within these narrower limits there is one definite mixture, depending on the gas, in which the speed of propagation of flame is a maximum; and two mixtures, represented by the limits themselves, in which the flame propagation speeds are minima for rich and weak mixtures respectively.

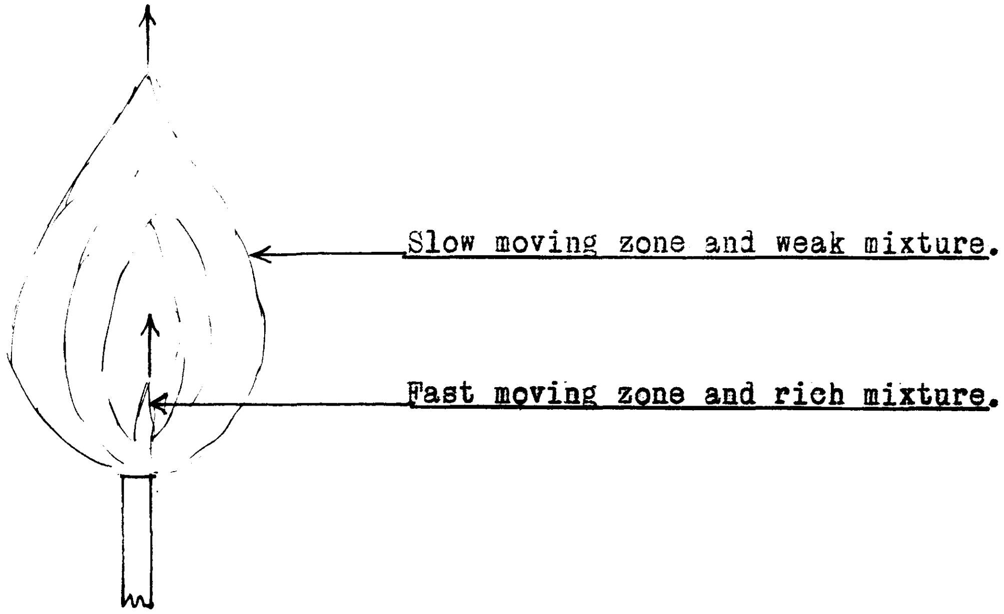
It is well known that the maintenance of a flame at, or near, a jet is only possible when the speed of movement of the combustible mixture away from the jet is exactly balanced by the flame propagation speed, which it has been shown is strictly finite. Hence the velocities of the combustible mixtures have limiting values for flame maintenance.

These limiting values will depend on, (1) the velocity of projection of the gas from the jet, (2) the rate of diffusion of the gas in air, (3) the oxygen requirements for complete combustion of the gas, (4) the speed of flame propagation of its mixtures with air, and (5) the range between the limits of inflammability of mixtures of the gas and air.

TABLE VII.

Combustible gas	Relative rates of diffusion	Oxygen required to burn 1 mol.	Limits of inflamm-ability	Maxm. flame speed cm/sec	Mol. Ht. of products of combustn.
Hydrogen	1.00	½ mol.	6.2 to 71.4	484	8.44
Carbon monoxide	0.27	½ mol.	16.3 to 71.2	60	10.30

From the foregoing table of miscellaneous collected data it is seen (1) that hydrogen has a much greater rate of diffusion than carbon monoxide, hence inflammable mixtures will be more quickly established in the slow velocity zones some distance from the jet - See sketch -



(2) the oxygen requirements are the same. (3) Hydrogen forms an inflammable mixture much weaker in gas than in the case of carbon monoxide and therefore further removed from the influence of the velocity of projection of the gas, i. e. in the slower moving zone. (4) The maximum speed of flame propagation for hydrogen is much greater than for carbon monoxide.

Summing these contributing factors it is evident, from what has been said, that it is possible to maintain a flame with hydrogen projected from a jet at a much greater velocity than is possible in the case of carbon monoxide.

Various jets were tried, and finally one was selected which gave a flame 1 cm. in height. This was a short piece of 1/16" bore brass tubing and was cemented into the glass delivery tube with asbestos-silicate cement. Subsequently, in view of the much lower local temperature at the jet in the case of carbon monoxide flames than was found by trial with hydrogen flames, it was possible, and was deemed advisable, to minimize conduction losses by using a glass jet of the same bore.

RATE OF COMBUSTION.

(Referring to Fig. 1.) It was found that the jet "J", as used for hydrogen, delivered, with suitable adjustment of the water level in "A", sufficient carbon monoxide to maintain a flame 1 cm. in height, when burning freely in air, with a gauge reading of 4.4" on "I". With this gauge setting the rate of combustion was determined in triplicate as described on p.p. 6, 7, 11, 12, and 13, and found to be 4.1 litres per hour at N.T.P.

RATE OF FLOW OF ATMOSPHERE.

Assuming as a speculative approximation that the extinction point for carbon monoxide would be about 15; the amount of atmosphere, containing this extinctive proportion of oxygen, which would contain 10 per cent in excess of the theoretical oxygen for the complete combustion of 4.1 litres of carbon monoxide, was calculated, and found to be 15.1 litres per hour at N.T.P.

A jet capable of delivering at this rate was selected and

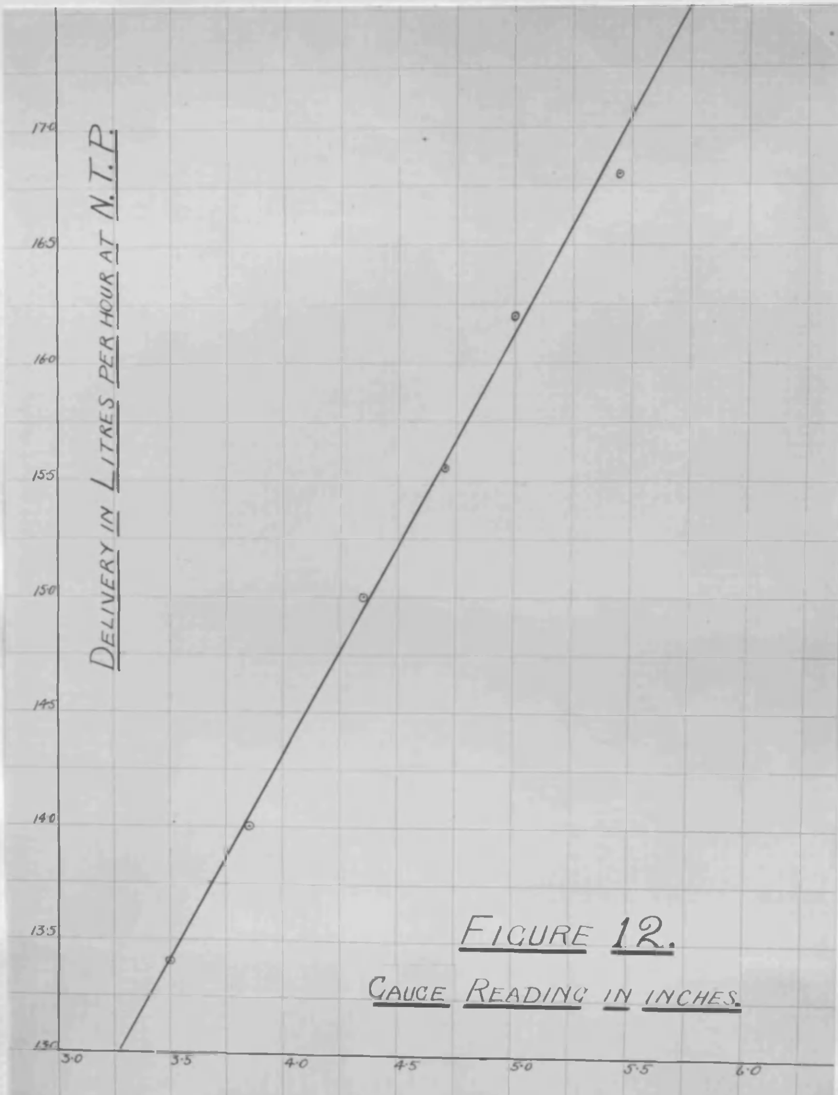


FIGURE 12.

DELIVERY IN LITRES PER HOUR AT N.T.P.
17·0
16·5
16·0
15·5
15·0
14·5
14·0
13·5
13·0
3·0
3·5
4·0
4·5
5·0
5·5
6·0
GAUGE READING IN INCHES.

calibrated as already described in the case of hydrogen (p.2.) with results as shown below in Table VIII.

TABLE VIII.

Gauge reading (inches)	Delivery of air at N.T.P. (litres per hour)
3.5	13.4
3.85	14.0
4.35	15.0
4.7	15.55
5.0	16.2
5.45	16.8

In Fig. 12. the graph obtained by plotting gauge readings against delivery in litres per hour at N.T.P. is shown, and from this, by interpolation, the gauge reading corresponding to 15 litres per hour was found to be 4.35".

SELECTION OF COMBUSTION CHAMBER.

At this stage of the work the author was not familiar with the explanation of the phenomenon exhibited by the flame floating some distance above the jet in atmospheres slightly richer in oxygen than the extinctive atmosphere, and, as will be shown, a considerable amount of time was spent investigating this 'unnatural' condition with a view to correcting it. As this investigation however has a very direct influence on the gradual evolution of the apparatus finally used, it is considered to have justified its inclusion in this thesis, and will be discussed more fully throughout the following record of experimental work.

EXPERIMENTAL WORK.

It was found that when the necessary amount of atmosphere , in this case air, to give a 10 per cent excess of oxygen over the theoretical amount required for the complete combustion of the carbon monoxide (delivered at the rate of 4.1 litres per hour) was supplied to the flame, and the combustion chamber (Fig.1) placed in position, that the flame rose from the jet to a height of about 2 cms. in which position it hovered unsteadily for a brief space of time before it was extinguished.

This behaviour of the flame was considered to be due to the accumulation of a heavy layer of the products of combustion, and accordingly rates of air representing 20, 30, 50, and 100% excess of oxygen were tried. The flame was found to persist with the 50% excess but it was extinguished when the chimney was constricted to ⅜" diam. by means of an extension tube. This was also found to be the case with 100% excess oxygen in the form of air.

From this it was concluded that combustion was maintained in the case of 50% excess air due to convection currents of air entering the top of the chimney, and that even with 100% excess air i.e. about 20 litres per hour through a tube 1" in diameter, (see Fig. 2A) or approximately a linear speed of 1 cm. per second, combustion was only maintained with the unconstricted chimney, due to the inadvertent admission of air from the atmosphere.

The extinction of the flame by restriction of the width of the chimney suggested that even 100% excess air was insufficient to prevent comparatively stagnant conditions inside the combustion chamber, somewhat analagous to a jet burning in a confined space.

50% excess air was next passed from the top of the chimney in a converse direction to the flow of carbon monoxide, and this was also found to extinguish the flame.

A parallel walled glass combustion chamber 3/4" internal diameter was tried but did not give satisfactory results. Finally the arrangement shown in Fig, 2 B. was tried, and this appeared to function satisfactorily.

PRELIMINARY ESTIMATION.

In order to obtain a nearer approximation to the extinction point than the conjectured one, viz. 15, upon which to base calculations for a 10% excess of oxygen in the extinctive atmosphere, a series of estimations was carried out in which the excess atmosphere was based upon the conjectured extinction point, thus :-

$$2CO + O = 2CO_2$$

4.1 + 2.05 . . . . . . litres

10 % excess oxygen .205 "

Total oxygen 2.255 "

Corresponding volume of an atmosphere containing 15 % of oxygen = 15.0 litres.

Hence rate of flow of atmosphere is 15 litres per hour.

The results of this series are given in Table IX. below.

TABLE IX.

Flame	Oxygen (%) in atmosphere		
	(1)	(2)	(mean)
Extinguished	15.44	15.37	15.41
"	15.49	15.59	15.54
"	15.52	15.56	15.54
"	15.59	15.55	15.57
Persisted	15.60	15.68	15.64
"	15.75	15.67	15.71
"	15.69	15.73	15.71
"	15.91	15.97	15.94

From Table IX the extinction point would appear to be 15.6.

In all of the above estimations where the flame was extinguished, the flame started pulsating some little time before extinction, and this phenomenon became progressively more pronounced as the extinction point was approached. Before the extinctive atmosphere had been reached in all of the above estimations the flame started to rise from the jet, rising higher and higher as the proportion of oxygen in the atmosphere was gradually reduced until, immed-

-iately before extinction there was a space of about ½ " between the top of the jet and the base of the flame.

From experience gained with hydrogen - See " Notes and Observations " page 20. - the author concluded that a 10 % excess of atmosphere was, in the case of carbon monoxide burning under the prevailing conditions, insufficient.

INVESTIGATION INTO THE BEHAVIOUR OF THE CARBON MONOXIDE FLAME.

The phenomenon exhibited by the carbon monoxide flame in floating at some distance above the jet was considered to be irregular, and due to some external influence other than the composition of the atmosphere being supplied, and the following suggestions were tabulated for investigation.

(1) The products of combustion form a heavy stagnant layer in the combustion chamber which totally inhibits combustion in this region.

(2) The combustion chamber exerts a confining influence on the flame, thus preventing its normal extinction which, as in the case of hydrogen flames, takes place in a very short, though observable, space of time starting at the base of the flame and finishing at the vertex.

(3) The walls of the combustion chamber facilitate combustion either catalytically or because of their higher temperature than the atmosphere at the jet.

These suggestions were investigated in order as follows :-

(1) The amount of carbon dioxide in the combustion chamber surrounding the jet will vary, for any particular combustion chamber, directly as some function of the rate of flow of atmosphere through it. It was accordingly decided to demonstrate the effect of increased rate of flow of atmosphere on the behaviour of the flame, and on the extinction point.

Mean values of a few estimations carried out using 10, 20, and 30 per cent excess of atmosphere are given below in Table X. These excesses are based on the assumption that the extinctive atmosphere would contain 15.6 % of oxygen.

TABLE X.

Excess atmosphere (%)	10	20	30
Extinction point	15.6	11.3	11.3
Oxygen (litres per hour)	2.35	1.71	2.01

Comparing the excess atmosphere with the extinction point it would appear that a small increase (20 % to 30 %) in the volume of atmosphere being supplied has no influence on the extinction point. The large difference between the results for a 10 % excess and the other two, corroborates the suggestion that the products of combustion are not completely swept out by a 10 % excess of atmosphere. No change was observed in the behaviour of the flame.

When the calculated volume of oxygen being supplied per hour, as shown in Table X., is taken into account, it is evident that the assumption, that small increases in the rate of flow of atmos-

-phere do not influence the extinction point, is not justifiable. The theoretical rate of flow of oxygen required for complete combustion is 2.05 litres per hour, and it seems reasonable to assume that the greater the deficiency of oxygen the higher the extinction point will be. This will be more fully discussed later.

(2) A combustion chamber was constructed as shown in Fig.8. in which the flame was free to rise a much greater distance from the jet without impinging on the confining walls. Observations were made using this and the original combustion chamber consecutively, and it was found that confinement of the flame maintained combustion beyond the point of extinction when less confined. This fact was also simply demonstrated by allowing the flame to impinge on a small glass bead which was suspended by means of a fine glass thread and lowered to any desired position from the top of the combustion chamber. By this means the flame, floating at some distance above the jet, could be pushed down by the glass bead so that it burned steadily at the jet so long as the bead was kept in position.

(3) Before proceeding to investigate the effect of the temperature of the combustion chamber walls on the extinction point, advantage was taken of the information obtained in (1) and (2) above, and a combustion chamber of more suitable shape and dimensions was constructed. The one selected, as shown in Fig. 9, is a modification of the one shown in Fig. 8, as used in previous work, in which care was taken to avoid any shoulders on the bulb,

FIG. 8.

FIG. 9.

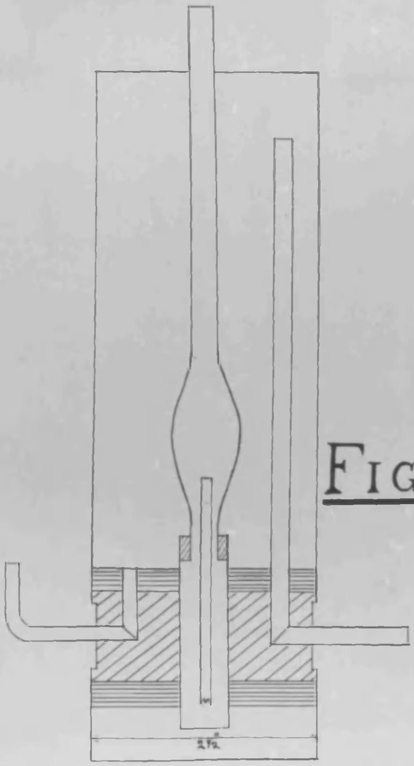


FIG. 10.

which would tend to cause convection currents.

EXPERIMENTAL.

In order to determine the efficiency of the new combustion chamber, with particular reference to (1) and (2), above, the following work was carried out :-

(a) Confinement of Flame.

The relative position of the top of the jet 'a' -now a glass tube - and the widest part of the combustion chamber, 'b', was varied, and the distance between the base of the flame, 'c', and the top of the jet, was measured for each setting. An atmosphere of constant composition, slightly richer in oxygen than would be required for extinction, and at a constant rate of flow, was used throughout. The observations are shown in Table XI.

TABLE XI.

Position of jet.	Distance between 'a' and 'b' (m.m.)	Flame rises 'a' to 'c' (m.m.)
1	7	9
2	10	5
3	13	5

From the foregoing results it was assumed that the walls of the combustion chamber exert a decided attraction on the flame when the latter comes within the necessary distance from the walls for this attraction to manifest itself. The attraction thus appeared to be due to the temperature of the walls of the chimney.

When the distance 'a' to 'b' is increased, as in positions (2) and (3), the flame only rises about half of the distance which it rises in position (1) and it remains floating in this position perfectly steadily, and is presumably quite unconfined. There thus appears to be a critical distance between the walls of the combustion chamber and the position which the flame would occupy if unconfined. This seeming attraction of the flame was considered to be due to a surface combustion effect.

Position (3) was adopted in subsequent work.

(b) Effect of Various Excesses of Atmosphere.

The approximate extinction point was determined for 10, and 20 per cent excesses of atmosphere as shown in Table XII.

TABLE XII.

Excess atmosphere per cent.	Flame	Oxygen in atmosphere		
		(1)	(2)	(mean)
10	Extinguished	11.78	11.94	11.86
"	"	11.95	11.91	11.93
"	Persisted	12.14	12.17	12.16
"	"	12.05	12.11	12.08
20	Extinguished	11.79	11.87	11.83
"	"	11.90	11.99	11.94
"	Persisted	11.88	11.98	11.93
"	"	12.03	11.98	12.00

Approximate Extinction Point = 11.9 .

The results shown above in Table XII., although not accurately obtained, serve sufficiently to indicate that the narrower combustion chamber employed has effected the complete removal of the products of combustion with a 10 % excess of atmosphere. The excesses in each case were based on the extinction point (15.6) as obtained in earlier work - p. 33. -.

Assuming from the above results a nearer approximation to the extinction point to be 12.0, the requisite rate of flow of atmosphere to give a 10 % excess of oxygen was calculated and found to be 18.75 litres per hour = 6.55 " from graph (Fig 12.) With this new rate of flow the following results were obtained :-

TABLE XIII .

Flame	Oxygen (%) in atmosphere		
	(1)	(2)	(mean)
Extinguished	8.41	8.49	8.45
"	8.50	8.58	8.54
"	8.58	8.54	8.56
Persisted	8.60	8.60	8.60
"	8.69	8.65	8.67
"	8.67	8.77	8.72

Approximate Extinction Point = 8.6 .

EFFECT OF MAINTAINING WALLS OF COMBUSTION CHAMBER AT A REDUCED TEMPERATURE.

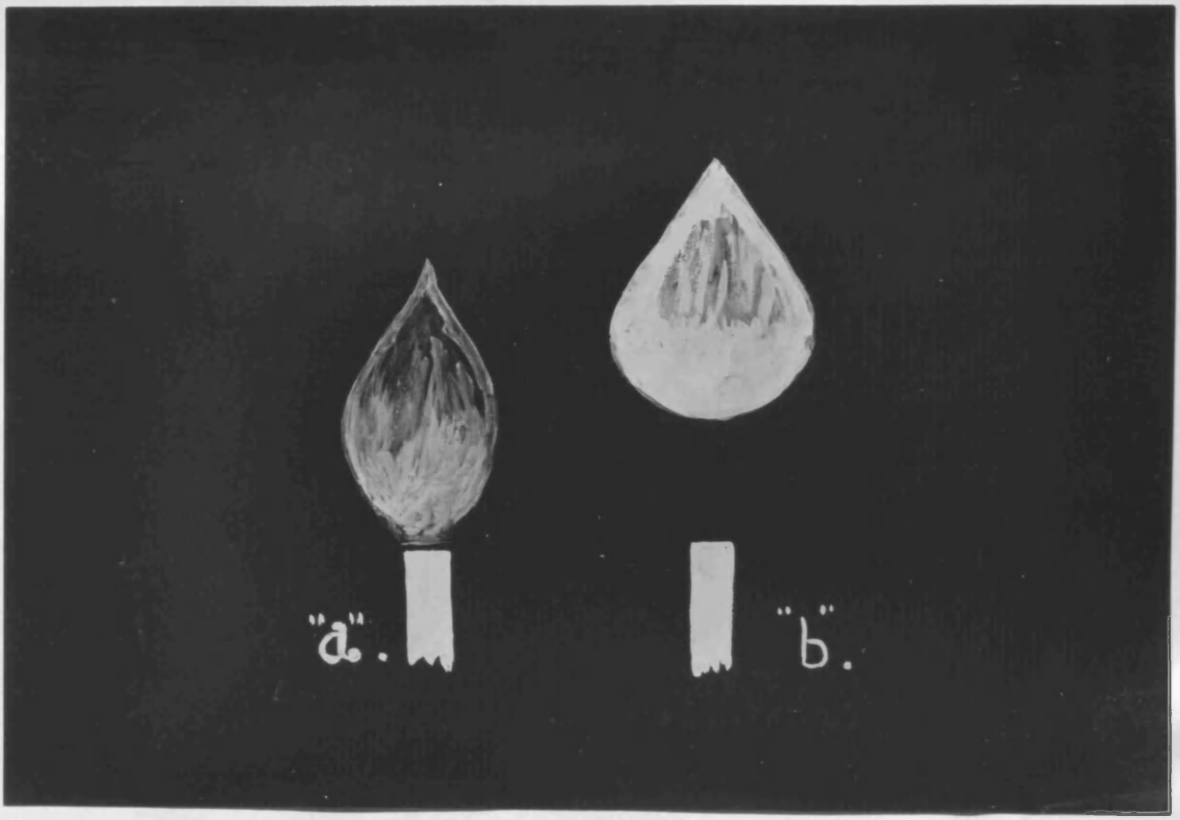
In view of the enormous variations in the extinction points 15.6, 11.9, and 8.6 as shown in tables IX, XII, and XIII respectively, it was deemed necessary to gain some indication of the effect of the heated walls of the combustion chamber before pursuing the main investigation any further.

The combustion chamber was enclosed in a water cooled jacket, or weir, as shown in Fig. 10, through which tap water was circulated. One estimation , carried out in the same manner as the estimations shown in Table XIII., was made. The extinction point in this case was 9.5. The cooling of the combustion chamber walls had thus raised the extinction point from 8.6 to 9.5.

Although the effect of heat, as shown above, is very appreciable, it does not account for the widely divergent results hitherto obtained and given in Tables IX, XII, and XIII.

OBSERVATIONS AND NOTES.

(1) In the foregoing work the carbon monoxide flame when burning freely in air was 1 cm. in height and bright blue in colour. Burning under the conditions prevailing in an estimation of the extinction point, the flame was generally immediately extinguished when the cold combustion chamber, which had to be removed in order to ignite the gas, was placed in position while an atmosphere, which was known to support combustion in a heated combustion


"a".
"b".

chamber was being supplied. After repeated extinctions and re-ignitions, with consequent increments of heat to the combustion chamber, the flame persisted for progressively longer periods and finally remained in indefinitely.

(2) At, or near, the extinction point the flame, when first enclosed by the replacement of the combustion chamber, became pronouncedly less luminous and enlarged considerably, still maintaining its original form although the apex was only faintly visible -fig. "a" - The flame next became suddenly more luminous, and of a paler and brighter blue than the original unconfined flame, and simultaneously slowly floated upwards from the jet. At this point it was found necessary to control the motion of the flame by steady movement of the combustion chamber in a horizontal plane in order to prevent it from clinging to the walls. The flame, as shown in fig. "b", rose to a height of 9 m.m. from the jet at the extinction point, and to corresponding lesser heights for greater proportions of oxygen in the atmosphere.

Immediately prior to extinction the flame pulsated for a second or two with increasing amplitude.

(3) Admixture of 3 % of air with the carbon monoxide caused the flame to contract very considerably, and lowered the extinction point from 11.6 to 9.0 , for the particular conditions under which this was tried. The presence of air was also found to prevent the flame from rising from the jet.

(4) In reviewing the extinction points so far obtained for

carbon monoxide with particular reference to the oxygen supplied per hour, as calculated from the known rate of flow and composition (from analysis) of the atmosphere, it is found that the lower the extinction point is,the lower also is the rate of supply of oxygen,and vice versa. Referring to Table X. (p. 35.) it is seen that an increase in the rate of flow of oxygen from 1.71 to 2.01 litres per hour, with a pro rata increase in nitrogen, has no apparent influence on the extinction point. Viewed however in the light of what precedes, the extinction point corresponding to 1.71 litres of oxygen per hour should be lower than that corresponding to 2.01 litres per hour and vice versa. i.e. on the basis of oxygen supplied, the extinction point for a 30 % excess of atmosphere should be higher than that for a 20 % excess. This however was not experimentally upheld; hence it was inferred that an increase in the rate of flow of atmosphere corresponding to an increase in the rate of flow of oxygen nullifies this effect by lowering the extinction point.

TABLE XIV.

Calculated excess of atmosphere (%)	10	10	10	20	20
Extinction point	8.6	12.0	15.6	11.3	11.9
Oxygen (litres/hour)	1.62	1.73	2.35	1.71	1.95

From the above table of collected data it is seen that, since the theoretical rate of flow of oxygen for complete combustion is 2.05 litres per hour, there is, in every case but one, incomplete combustion. Hence the conclusions deduced from experimental evidence, as given in (1) and (2) above, are rendered invalid.

DISCUSSION.

The extinction point of carbon monoxide at this stage of the work appeared to be influenced by many unavoidable conditions which mutually influenced one another.

The author , in endeavouring to make the conditions parallel to those which existed in the case of hydrogen, did not find it possible :-

(1) to maintain a 10 % excess of the extinctive atmosphere,
(2) to entirely sweep out the products of combustion, and
(3) to prevent a greater transference of heat to the walls of the combustion chamber than in the case of hydrogen, simultaneously.

The extinction point appears to be influenced as follows :-

(a) Lowered by,

(1) Increase in the rate of flow of atmosphere.
(2) Proximity of the flame to the walls of the combustion chamber.
(3) Presence of air in the carbon monoxide.
(4) Elevated temperature of the combustion chamber walls.

(b) Raised by,

(1) The presence of products of combustion.

Due to the smaller rate of flow of carbon monoxide than hydrogen to give a flame 1 cm. in height, to the denser and more extinctive nature of the products of combustion, and to the smaller volume of extinctive atmosphere necessary to contain the chosen 10 % excess of oxygen, a very small combustion chamber is necessary. The confinement of the flame due to this small combustion chamber produces external influences which materially affect the value obtained for the extinction point and facilitates combustion in atmospheres containing less oxygen than is theoretically required for complete combustion.

It was thus evident that no dependable value could be obtained for the extinction point of carbon monoxide burning in an atmosphere containing 10 % of excess oxygen, and it was thus decided at this juncture to use a much larger combustion chamber and a rate of flow of atmosphere sufficient to expel the products of combustion.

CALIBRATION OF JET FOR RATE OF FLOW OF ATMOSPHERE.

It was found necessary to calibrate a jet to deliver more atmosphere than had been previously required. The same method of calibration was adopted and the results are given in Table XV. The graph obtained by plotting delivery x gauge reading is shown in Fig. 13.

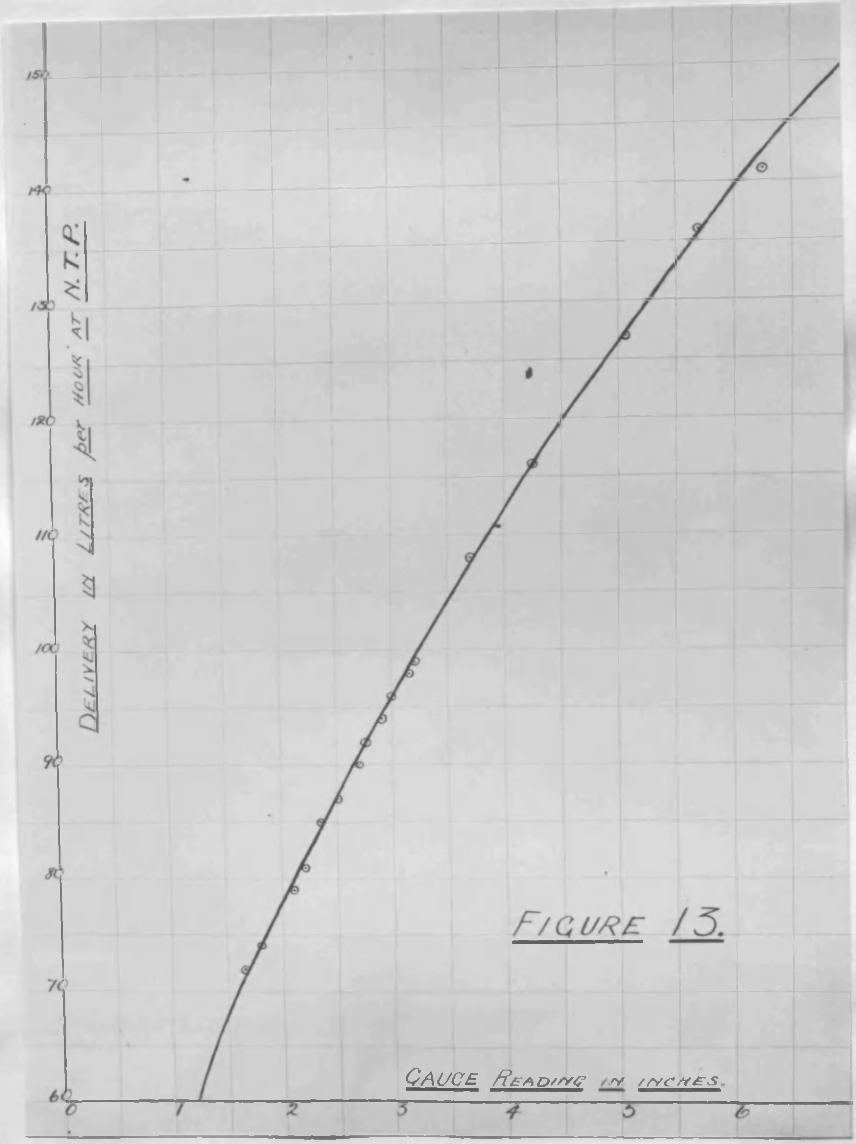


FIGURE 13.

DELIVERY IN LITRES per HOUR AT N.T.P.
150
140
130
120
110
100
90
80
70
60
0
1
2
3
4
5
6
GAUGE READING IN INCHES.

TABLE XV.

Time (mins.)	Volume (litres)	Gauge (ins.)	Barometer (m.m.)	Temperature °C	Delivery (litres)	
					A.T.P.	N.T.P.
2	5.00	6.25	758	16.0	150	141
2.5	6.00	5.70	758	16.0	144	136
2.5	5.70	5.05	750	18.0	137	127
2.5	5.20	4.25	750	18.0	125	116
3	5.85	3.70	750	18.0	117	108
3.5	6.25	3.20	748	18.0	107	99
3.5	6.15	3.15	748	18.0	106	98
3.5	5.95	3.00	762	18.5	102	96
3.5	5.95	2.90	749	18.0	102	94
3.5	5.80	2.75	749	18.0	100	92
3.5	5.70	2.70	749	18.0	98	90
3.5	5.50	2.50	749	18.0	94	87
3.5	5.40	2.35	749	18.0	92	85
4	5.85	2.20	749	18.0	88	81
4	5.70	2.10	762	20.5	85	79
4	5.25	1.80	762	20.5	79	74
4	5.20	1.70	749	18.0	78	72

CALIBRATION OF JET FOR DELIVERY OF CARBON MONOXIDE.

It was considered wise at this juncture to re-calibrate the carbon monoxide jet in case of probable alteration in the course of its use.

Height of flame - - - - 1 cm.

Head of water - - - - 15 cm.

Temperature - - - - - 16°C.

Duration of test - - - - 141½ min.

Gauge reading - - - - 12 cm.

Volume of CO burned - - - 9.95 litres.

" " " " at N.T.P. - - 9.44 litres.

Hence volume of CO burned per hour at N.T.P. = 4.00 litres.

RATE OF FLOW OF ATMOSPHERE REQUIRED TO DRIVE OUT PRODUCTS OF COMBUSTION.

As already stated it was decided to revert to a wider combustion chamber and to use sufficient atmosphere to sweep out the products of combustion. The combustion chamber shown in Fig. 2A, as used for hydrogen flames, was used.

It has already been found that a rate of flow of atmosphere of 15 litres per hour was effective in sweeping out the products of combustion from a combustion chamber of maximum diameter = ¾" . On this basis of litres per hour per sq. inch of maximum cross sectional area, the rate of flow required to sweep out the products of combustion from the new combustion chamber was calculated and found to be 106 litres/hour = 3.6 " on gauge from Fig. 13.

With the arrangement shown in Fig. 16 and using atmospheric air supplied at the rate of 106 litres/hour the flame rose from the jet and was extinguished.

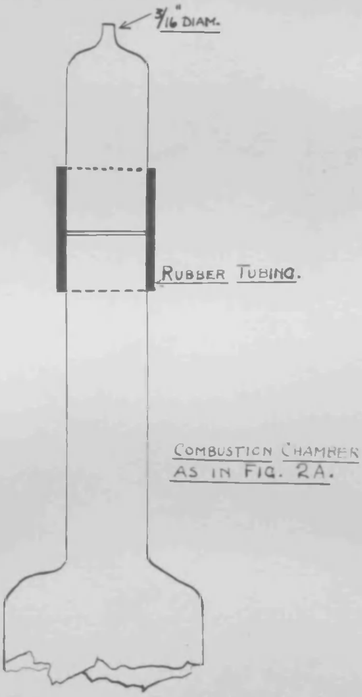

3/16" DIAM.
RUBBER TUBING.
COMBUSTION CHAMBER AS IN FIG. 2A.

FIG. 15.

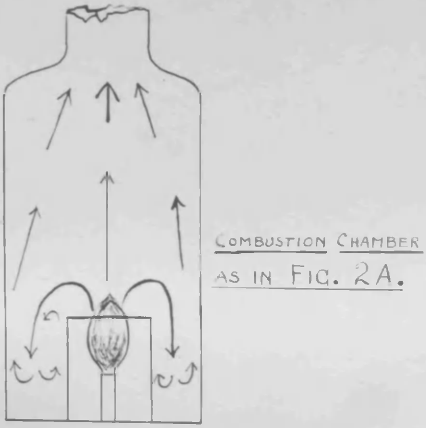

COMBUSTION CHAMBER AS IN FIG. 2A.

FIG. 14.

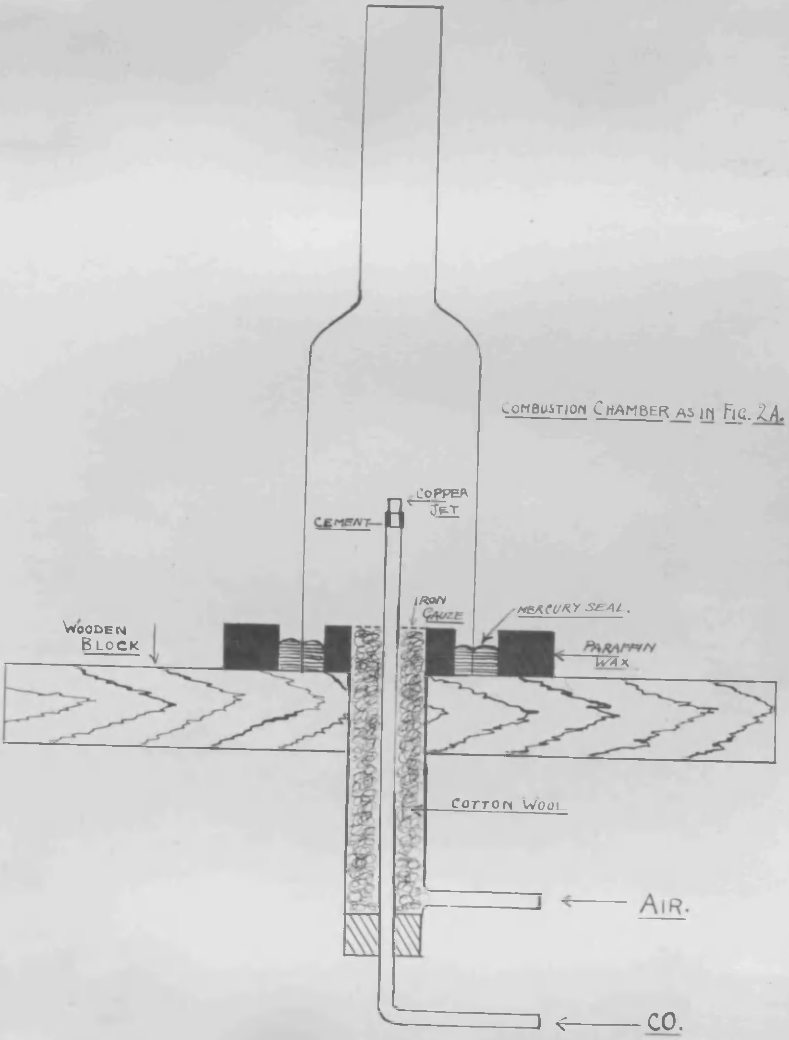

COMBUSTION CHAMBER AS IN FIG. 2A.
COPPER JET
CEMENT
IRON GAUZE
MERCURY SEAL.
WOODEN BLOCK
PARAFFIN WAX
COTTON WOOL
AIR.
CO.

FIGURE 1b.

Various rates of flow of atmospheric air were tried with results as shown in Table XVI.

TABLE XVI.

Air (litres per hour)	Behaviour of flame.
0	Burns steadily
30	" "
45	Flickers and elongates but continues to burn.
60	Flickers and elongates prior to extinction.
120	" " " " "
150	" " " " "

It is thus seen that for atmosphere speeds up to 45 litres per hour the flame continues to burn, but behaves in a manner which suggests the inflow of air as a back draught causing the flame to elongate and flicker. Greater speeds than 60 litres per hour on the other hand would appear to cause the inflammable mixtures rising from the jet to exceed their respective maximum flame propagation speeds (See Introduction p.p. xii and xiii.)

A constricted extension was fitted to the top of the combustion chamber as shown in Fig. 15. When this was tried it was found that an air speed of 12 litres per hour, representing a 20 % excess of atmosphere over the amount theoretically required for complete combustion, extinguished the flame. Greater air speeds up to 150 litres per hour also caused extinction.

Comparing these observations with Table XVI. it would appear

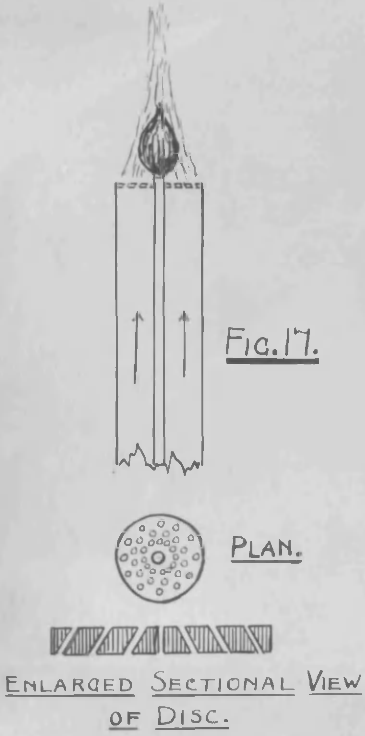


FIG. 17.

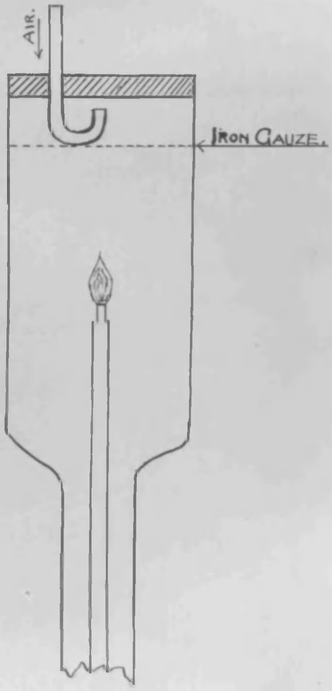


FIG. 18.

that back draughts had been eliminated and the atmosphere speed effect accentuated.

In order to protect the flame from the possible influence of the products of combustion, the burner jet was enclosed in a glass tube of about $\frac{5}{8}$ " diameter which extended to about 2 cms. above the top of it. An annular space was thus formed immediately below the flame through which the air was supplied, as shown in Fig. 14. The arrows, representing the products of combustion, indicate the anticipated mechanism of this arrangement.

It was found on trial with various speeds of air that the foregoing arrangement did not have any noticeable influence on the behaviour of the flame as previously recorded.

From what has been said it will be seen that the maintenance of a carbon monoxide flame in a current of air flowing in the same direction as the projected gas, and at sufficient speed to sweep out the products of combustion from a combustion chamber of sufficient cross sectional area to prevent surface combustion effects, has not been found possible.

A perforated disc was fitted to the top of the air tube as shown in Fig, 17. with a view to producing a conical zone of atmosphere in the neighbourhood of the jet. This effect was achieved as demonstrated by means of ammonium chloride 'smoke', but, although the tendency of the flame to rise from the jet was not so pronounced, it still existed.

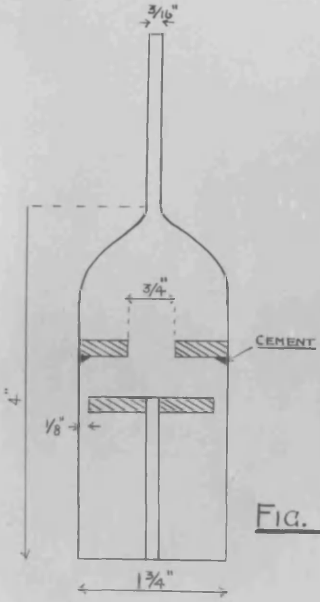
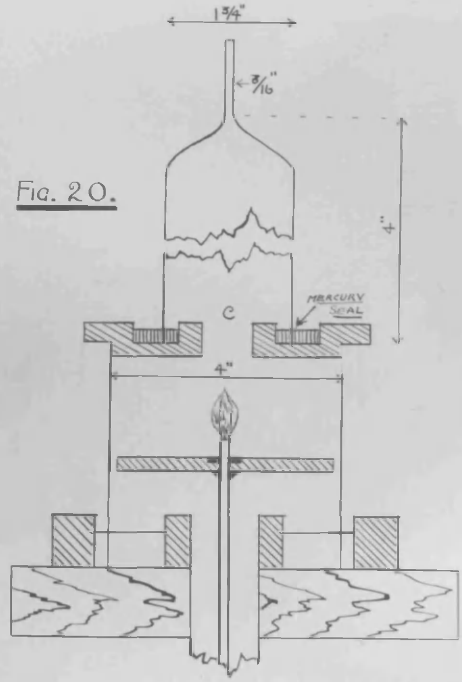


FIG. 19.

FIG. 20.



A converse current of air was next tried and the flame burned steadily for air speeds ranging from 100 to 150 litres per hour, but was extinguished at lower speeds. The principle in an apparatus of this design (See Fig. 18.) is necessarily faulty, as it is impossible to prevent the products of combustion from continuously mixing with the air taking part in the combustion. This experiment was tried prior to arranging for the flow of atmosphere at the jet to take place in a horizontal plane, as described in the following experiment.

The arrangement shown in Fig. 19. was tried using various speeds of air up to 150 litres per hour, and found to be quite satisfactory for air, but, as the tendency of the flame to rise from the jet increases as the partial pressure of the oxygen in the atmosphere approaches the extinctive limit, the flame still rose from the jet when the oxygen content of the atmosphere was reduced by dilution with nitrogen.

In order to still further minimize the ' blowing out ' effect of the atmosphere, a modification of the above combustion chamber was constructed as shown in Fig. 20. by means of which it was hoped to produce a flow of atmosphere converging to a point at the jet in the form of a very flat inverted cone and then rising in a vortex. So far as it could be demonstrated by means of smoke this desired effect was achieved with the arrangement shown. At this point the combustion chamber was made in two sections so that the glass chimney could be easily removed for lighting purposes.

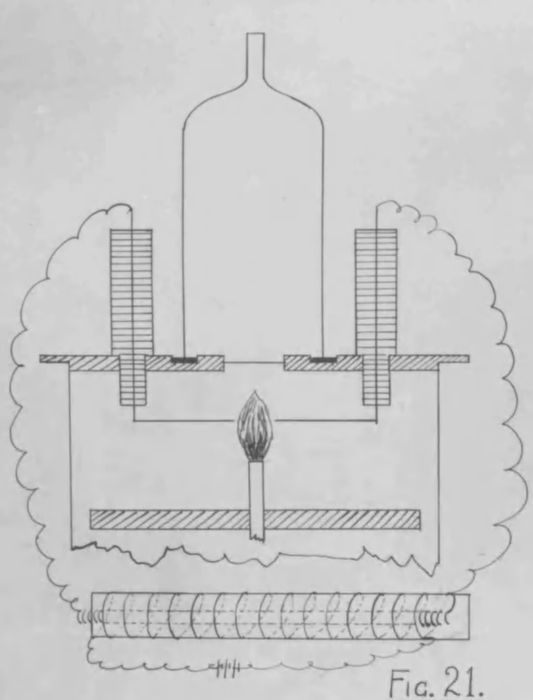
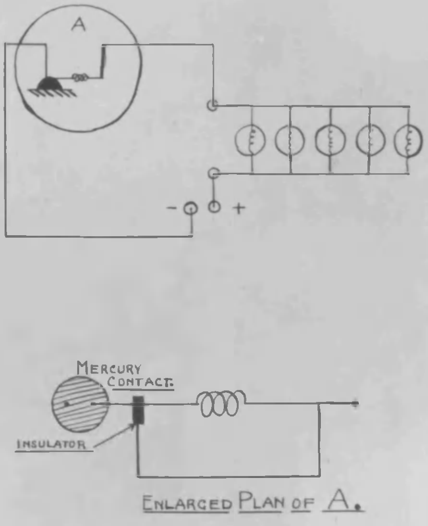


FIG. 21.



ENLARGED PLAN OF A.

FIG. 22.

The following experiments were conducted using atmospheric air.

TABLE XVII.

Air		Behaviour of flame.
Excess (%)	litres per hour	
20	12	Extinguished
80	18.5	Flickers before extinction
500	60	Burns steadily.

When it was attempted to determine the extinction point using 60 litres per hour of an atmosphere which was being progressively diluted with nitrogen, the flame, after rising to " C " - Fig. 20 -, was extinguished, and a very considerable increase in the proportion of oxygen present was necessary before the gas could be re-ignited, although a relatively small decrement of oxygen had caused the extinction of the flame. This was considered to be due to some disturbing influence caused by the removal of the chimney and application of a small lighted jet of coal gas.

The difficulty mentioned above made each determination very laborious and slow, because sufficient time must be allowed after each small decrement of oxygen to allow the change to communicate itself to the combustion chamber - a period of a few minutes.

INTERNAL IGNITION.

A high tension electric spark was tried in the following manner.

A six volt storage cell and induction coil were used to obtain the high potential current used. This was adjusted to give a spark between insulated copper poles near the top of the jet as shown in Fig. 21.

This arrangement was found to ignite the gas in atmospheres somewhat richer in oxygen than the extinctive atmosphere, but failed in atmospheres only slightly richer, so the method had to be abandoned.

The next method tried was an electrically heated platinum wire which could be removed from the flame zone after ignition. 3 " of 0.008 " diameter platinum wire was used and 4 loops of 5 m.m. diameter were made on it. The length of the spiral so formed was about 5 m.m.

At first the heating current was obtained from a 6 volt storage cell and controlled by means of a resistance. Subsequently the current was taken from the main and controlled by means of carbon filament lamps wired in parallel as shown in Fig. 22.

PRELIMINARY ESTIMATION OF EXTINCTION POINT.

Several estimations were carried out using 140 litres per hour of atmosphere, in order to test the efficiency of the apparatus and method, the results of which are given in Table XVIII.

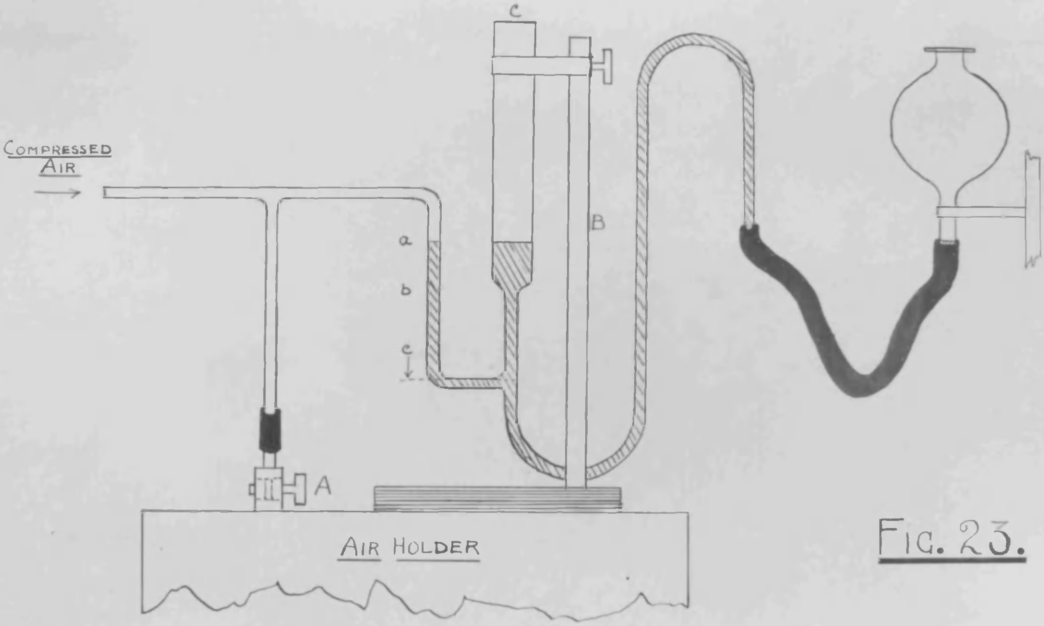


Fig. 23.

TABLE XVIII.

Flame	Oxygen per cent in atmosphere		
	(1)	(2)	(mean)
Extinguished	13.51	13.55	13.53
"	13.52	13.52	13.52
"	13.67	13.60	13.63
"	13.92	13.97	13.95
"	14.49	14.46	14.47
"	15.17	15.21	15.19
"	15.44	15.52	15.48
"	15.68	15.70	15.69
"	15.26	15.41	15.33
Persisted	14.51	14.53	14.52
"	14.38	14.32	14.35
"	14.44	14.29	14.36

The above figures show very wide limits and conflicting results and it was thought that this insensitivity in the estimation was occasioned by variations in the pressure of the balanced gas holder used for air, which was continuously supplied from a compressed air main at fluctuating pressure, the balance for displacement corrections on the holder being rendered unreliable because of the necessary variations in the loading of the tank (or bell) to give different pressures.

In order to maintain the air holder at constant level and so avoid errors due to displacement changes, the arrangement shown in Fig. 23. was attached to it. The levelling bottle is clamped to a rigid stand, the rest of the apparatus is clamped by means of " B " which rests on the bell of the holder and is thus free to move with the bell. The apparatus is filled with mercury to the level 'a' . When "A" is opened the mercury level falls to some position 'b' due to the pressure of air in the holder. When compressed air is turned on, the bell rises until the mercury level falls to 'c' and any excess air over the amount required to maintain the bell at any arranged level, escapes to the atmosphere. Hence, so long as air is escaping through the wide tube C, the bell remains at a constant level.

With the foregoing arrangement fitted to the air holder the series of estimations tabulated in Table XVIII was repeated with results as shown in Table XIX.

TABLE XIX.

Oxygen per cent in atmosphere (mean of two analyses)	
Flame extinguished	Flame persisted.
18.35 18.68 17.91 18.11 17.65	17.81 18.42 18.58 18.68 18.14
Range :- 17.65 to 18.68	17.81 to 18.68

The results shown in Table XIX are again very unsatisfactory, and very much higher than the results of parallel estimations as given in Table XVIII.

The carbon monoxide was analysed in the Hempel gas analysis apparatus and although there was a perceptible fume in contact with phosphorus no absorbtion could be detected. In order, however, to minimize the presence of traces of oxygen in the gas, all possible joints in the apparatus were sealed in the blowpipe and the series again repeated as shown below.

TABLE XX.

No.	Oxygen per cent in atmosphere (mean of 2 analyses)	
	Flame extinguished	Flame persisted
1	15.51	16.43
2	15.69	17.13
3	16.42	16.31
4	17.65	17.50
5	11.52	11.37
6	11.14	11.56

The enormous lowering of the extinction point in Table XX., numbers 5 and 6, coincided with the admission of a fresh charge of carbon monoxide into the storage bottle "H" - Fig. 1. - and, although analysis of the gas in Haldane's apparatus only showed the presence of 0.01 % of oxygen, the author was led to assume that the inconsistent results so far obtained were due to traces of oxygen, present in varying amounts, in the carbon monoxide.

The method of preparation of the carbon monoxide was changed at this juncture, and in all subsequent work formic acid (80 %) was used in place of the sodium salt, and the gas stored in the presence of phosphorus as described in the Appendix, and shown in Fig. 24.

Carbon monoxide thus prepared was found to give a green tinged flame which was considered to be due to the phosphorus pentoxide. A cotton wool scrubber moistened with glycerine effectively removed the phosphorus pentoxide so far as could be detected by the eye, but the flame still remained tinged with green, due very probably to the presence of phosphorus vapour. This was momentarily overlooked and the series shown in Table XX. was repeated with results as shown in Table XXI.

TABLE XXI.

Oxygen per cent in Atmosphere	
Flame extinguished	Flame persisted
12.15	14.96
12.75	15.21
13.22	15.56
14.71	15.64
14.80	15.66
14.91	16.40
15.00	16.70
15.16	16.73

Although the overlapping in the two columns of results in the foregoing table is not so pronounced as in previous attempts, the limits are very wide and suggest great variation due to some unknown influence.

In the foregoing work much difficulty was experienced by the frequent fusing of the platinum spiral due to the action of traces of phosphorus vapour, forming the brittle compound Pt_3P_5.(6) When a spiral of nichrome wire was tried, constant flashes, due to poor contact with the mercury, were obtained which very soon melted the end of the wire and rendered it too short to make contact with the mercury. A suitable spiral was eventually made from nichrome wire to which a short piece of stout copper wire was firmly attached, to form the pole which made contact with the mercury. The effect of phosphorus on the platinum and the colour of the flame suggested that no dependable results could be assumed until this had been removed from the gas.

Removal of Phosphorus from the Carbon Monoxide.

Various metallic salt solutions of copper, silver, mercury, and lead were prepared and the effect of passing through these a stream of carbon monoxide containing phosphorus vapour was visually estimated. Of the solutions tried, silver nitrate appeared to be the most efficient. On passing the gas through a scrubber containing a strong solution of silver nitrate on cotton wool, there was no trace of green when the gas was ignited. (See Fig. 25.)

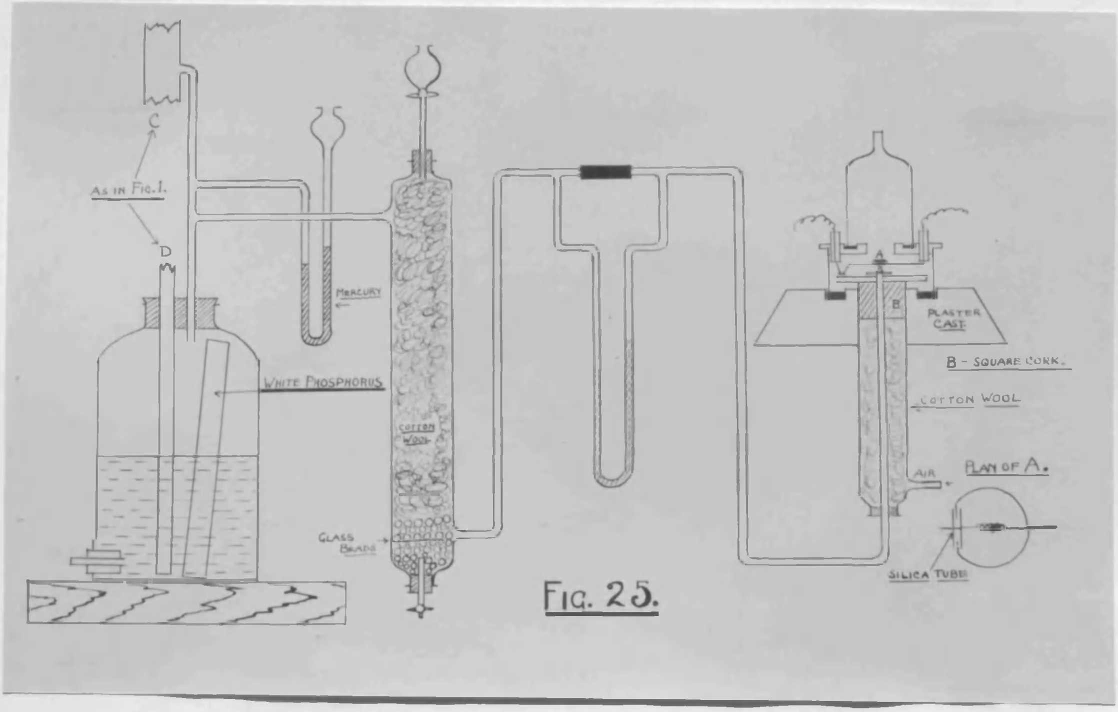

C
AS IN FIG. 1.
D
MERCURY
WHITE PHOSPHORUS
COTTON WOOL
GLASS BEADS
A
B
PLASTER CAST
B - SQUARE CORK.
COTTON WOOL
AIR
PLAN OF A.
SILICA TUBE

FIG. 25.

EFFECT OF RATE OF FLOW OF ATMOSPHERE ON THE EXTINCTION POINT.

The results shown in Table XXII. were determined to show the effect of the rate of flow of atmosphere on the extinction point. In each case the extinction point was arrived at from the results of five duplicate analyses of atmospheres which just supported combustion and five in which the flame was extinguished.

TABLE XXII.

Gauge reading	1.2"	2.2"	3.3"	6.1"
Rate of flow of atmosphere in litres/hour.	60	80	100	140
Flame persisted (oxygen % - limits)	10.64 to 10.86	10.93 to 11.20	11.00 to 11.10	11.00 to 11.08
Flame extinguished (oxygen % - limits)	10.63 to 10.75	10.92 to 11.16	10.88 to 11.10	10.95 to 11.04
Extinction point (oxygen %)	10.8	11.0	11.0	11.0

In these estimations it was observed that the slower the rate of flow of atmosphere, the greater was the tendency of the flame to rise from the jet, and experience has shown that this causes inconsistent results, probably due to some influence of the heated surroundings on the flame. It was further observed that when the oxygen in the atmosphere was gradually reduced till the extinction point was reached that the flame could be relit on slightly increasing the oxygen, only if the attempt was made immediately after extinction, and that a considerable increase in oxygen was required if some time was allowed to elapse before the attempted reignition was made. This difference was attributed to the cooling of the combustion chamber walls. The above effect was not so marked with the greatest speed of atmosphere tried, (140 litres/hour), and the tendency decreased as the rate of flow of atmosphere increased.

It would appear from Table XXII. that the rate of flow of atmosphere has no decided effect on the extinction point, within the limits tried.

EFFECT OF SIZE OF FLAME ON THE EXTINCTION POINT.

The carbon monoxide jet was set to deliver 2.8 litres per hour, and atmosphere speeds from 60 to 140 litres per hour were again tried. The flame was found to rise from the jet as before, and in addition pulsated very noticeably in each case. The results are given in Table XXIII below.

TABLE XXIII .

Gauge reading	2.2"	6.1"
Rate of flow of atmosphere in litres/hour.	60	140
Flame persisted (oxygen % - limits)	10.75 to 10.86	11.24 to 11.34
Flame extinguished (oxygen % - limits)	10.77 to 10.90	11.19 to 11.25
Extinction point (oxygen %)	11.2	10.8

In the foregoing table, 5 estimations were carried out at each gauge reading, and each analysis was conducted in duplicate.

In view of the behaviour of the flame, no justifiable conclusions could be drawn from the work, and in order to make any progress it was considered necessary to investigate fully these peculiar phenomena and, if possible, eradicate the cause.

The wash bottles containing alkaline pyrogallate solution were recharged, but this had no effect.

The carbon monoxide generator at this stage of the work was found to require much greater heating than when it was originally charged, due to the dilution of the sulphuric acid according to the equation :-

$$HCOOH = CO + H_2O$$

it was therefore recharged to prevent the formation of any gaseous product which, if not entirely absorbed, would cause the flame to rise and pulsate. This however had no effect.

The silver nitrate tower, used for scrubbing the carbon monoxide free from phosphorus vapour, was re-impregnated with fresh silver nitrate solution in order to ensure that traces of phosphorus were not causing the trouble. This had no effect on the behaviour of the flame.

The soda-lime U-tube in the air circuit was recharged and this was found to cause the flame to remain at the jet, and conversely, when the 'Sindanyo' disc carrying the jet was moistened with water the flame again rose from the jet, an atmosphere of the same composition being used throughout these experiments.

EFFECT OF MOISTURE ON THE EXTINCTION POINT.

The foregoing discovery led the author to investigate more fully the effect of moisture on the flame and on the extinction point before proceeding with other work, as it was considered at this point that many of the difficulties and unsatisfactory duplicate estimations of the extinction point might, conceivably, have been due to slight variations in the humidity of the gases used; thus necessitating rigid control of this factor in future work.

The 'Sindanyo' disc was thoroughly dried in an air bath and desiccated till cool. A $CaCl_2$ drying tube was placed in the atmosphere circuit, on the jet side of the soda-lime U-tube (X - Fig. 1). One estimation of the extinction point with this addition to the apparatus gave the surprising result 16.6 % oxygen, whereas reasonably consistent results of the order 11 % had previously been obtained over a long series of experiments.

It was therefore concluded that traces of moisture play a vital part in the value of the extinction point.

A calcium chloride drying tube was fused into the carbon monoxide circuit near the jet and it was found that the flame was now extinguished in atmospheric air supplied at the rate of 60 litres per hour through the drying system referred to above.

The following day this could not be repeated until a phosphorus pentoxide tube was added to the jet side of the drying battery in the air circuit. It was found necessary to progressively add P_2O_5 drying tubes (freshly charged) to both the air and carbon monoxide circuits in order to maintain atmospheric air an extinctive atmosphere.

The foregoing observations recall H.B.Dixon's classical discovery in 1880(16) and the extreme precautions of his collaborator H.B.Baker to obtain a carbon monoxide-oxygen mixture of such a degree of dryness, Bakerian dryness, that it failed to ignite with the passage of an electric spark which easily caused ignition if a slight trace of moisture was present.

It would appear from what precedes that calcium chloride, when freshly used, is a very efficient dehydrating agent but quickly loses its initial high efficiency. The author considers this to be due to the enormous surface exposed by the calcium chloride dust which very soon loses its activity.

The drying batteries shown in Figs. 26 and 27 were included in the air and carbon monoxide circuits respectively, and it was found impossible to burn carbon monoxide in air thus dried. The U-tubes shown were 6" in height and ¾" in diam. The P_2O_5 tubes 8" long and 1" in diam., and the filtration flask (Fig. 26) was 100 c.c. in capacity.

When first lit, the flame burned steadily at the jet for a few seconds after replacement of the glass chimney, which it was

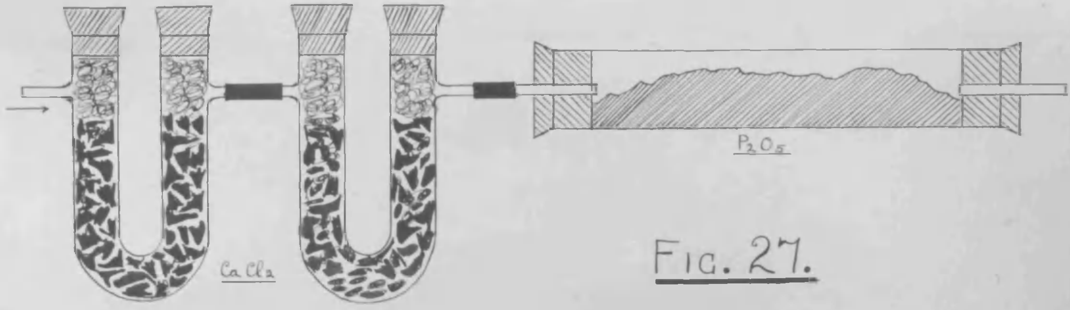

Ca Cl2
P2O5

FIG. 27.

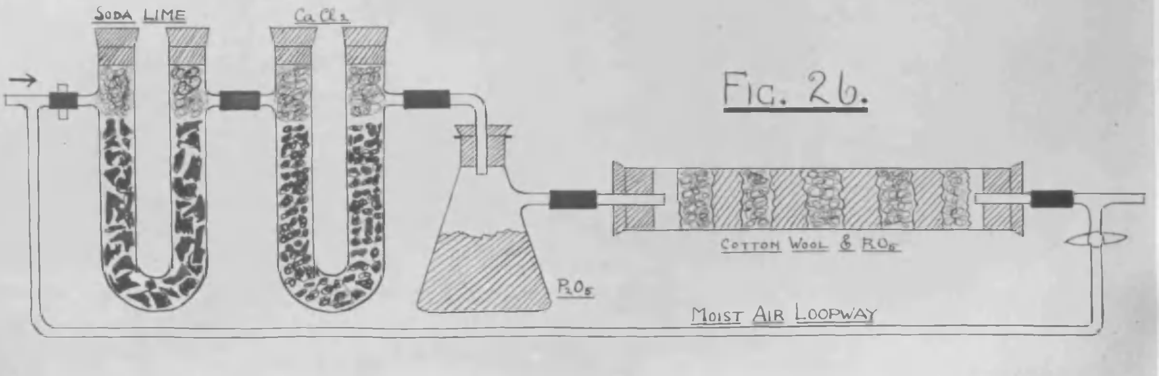

SODA LIME
Ca Cl2
P2O5
COTTON WOOL & P2O5
MOIST AIR LOOPWAY

FIG. 26.

found necessary to remove before the flame could be lit, and then rose steadily to a height of about 4 m.m. from the jet before extinction. When moist air was admitted, by means of the loopway shortcircuiting the air drying battery as shown in Fig. 26, the flame burned steadily at the jet.

It was noted that, with the highest temperature of spiral tried, the gas could not be ignited till (1) moisture from the atmosphere was admitted by removal of the glass chimney, (2) a moistened glass thread was slowly lowered through the chimney - ignition in this case took place when the thread was about three inches from the jet - , (3) by means of a loopway, moist air was admitted to the combustion chamber.

In the foregoing work it was observed that after the passage of moist air it was necessary to pass the dried air in some instances for over an hour before it extinguished the flame. This was corrected by removing the cotton wool, impregnating the cork with paraffin wax, and varnishing the 'Sindanyo' discs in the combustion chamber with collodion. (See Fig. 25.) It was also found that fitting the differential gauges "J" and "Z" - Fig. 1. - with rubber tubing and screw clips, so that water vapour from this source could be excluded, facilitated extinction.

Extinction point using ' Chemically dried ' Atmosphere.

One estimation was carried out to determine the extinction point of carbon monoxide in an atmosphere dried in the manner described above. Oxygen and nitrogen were used in place of air and nitrogen as heretofore. It was not considered necessary to attempt an estimation of the humidity of such an atmospmere. The flame was extinguished by an atmosphere containing 25.5 % of oxygen.

It is highly probable that the flame would be extinguished by the passage of pure oxygen of Bakerian dryness, but this is a problem of no easy fulfilment and was not attempted.

The above work clearly demonstrates the marked quantitative effect of water vapour on the value obtained for the extinction point and, in view of the fact that no cognisance has been taken of this effect in all the work done up to this point, the value of such work lies only in the experience gained and the evolution of a method, and not in the results.

HUMIDITY EXPERIMENTS.

In order to obtain a continuous flow of atmosphere containing a definite quantity of water vapour, the author tried several methods, the best and simplest of which is shown in Fig. 31.When this was assembled it was found to be entirely satisfactory in supplying atmosphere saturated with water vapour for the range 0° to 60°C. in quantities up to 140 litres per hour.

The atmosphere, after passing through "Z" - Fig. 1. - enters at the top side tube of tower No.1. (Fig. 31.),which is an ordinary Liebig's condenser jacket of suitable dimensions, and traverses the battery of towers as shown in plans by means of small

Fig. 30.

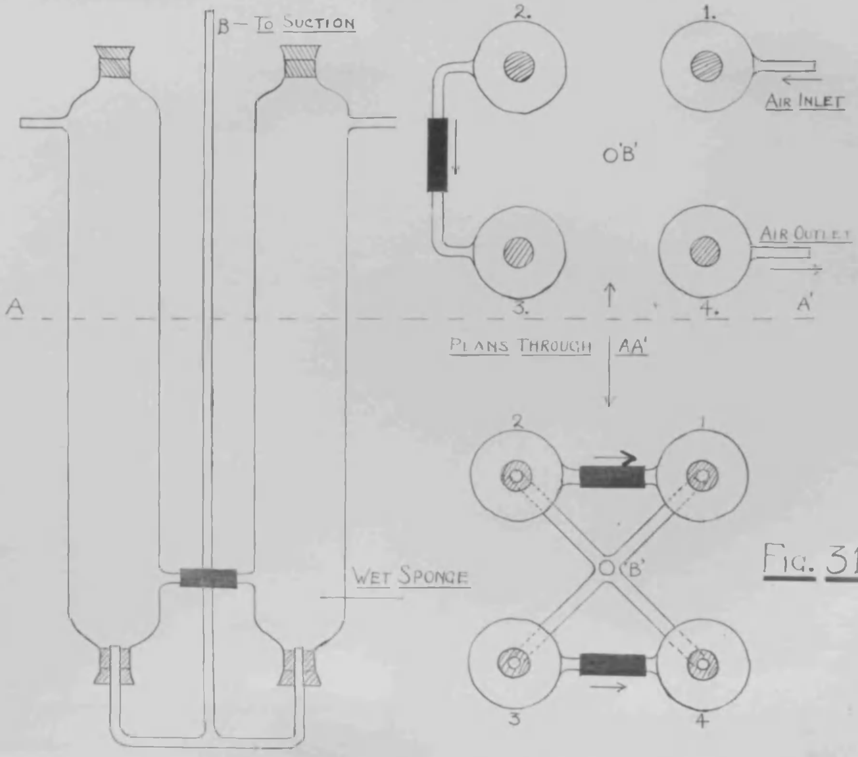

B – To Suction
2.
1.
Air Inlet
O'B'
Air Outlet
A
3.
4.
A'
Plans Through AA'
Wet Sponge
2
1
B'
3
4

Fig. 31.

arrows. The towers are packed with wetted sponge and then filled with water through the top of each. The stoppers are then replaced and the excess water sucked off by means of the central tube "B" which is in connection with the bottom of each tower. Sufficient water is left in the towers to form a seal to prevent the shortcircuiting of air through the draining tube "B".

The whole battery of towers, bound together by means of cork clamps, is weighted and submerged in an electrically controlled thermostat. - Fig. 47. -

The outlet is connected to a steam jacketed pipe leading to the combustion chamber as shown in Fig, 32 and this was found to satisfactorily prevent condensation. By means of the heating lamp, enclosed in the asbestos cylinder, and the damper, which is a circular slab of asbestos board mounted on a horizontal axis through its centre, the temperature in the combustion chamber compartment could be regulated; this temperature was arranged to be higher than the saturation temperature of the atmosphere and thus prevented condensation in the combustion chamber.

Estimation of Saturation at 50°C.

The thermostat was set to maintain itself at 50°C. and air at the rate of 140 litres per hour was passed through. The steam jacket was heated and disconnected from the combustion chamber. An empty U-tube, which was immersed in a beaker containing a freezing mixture of ice and salt, was connected

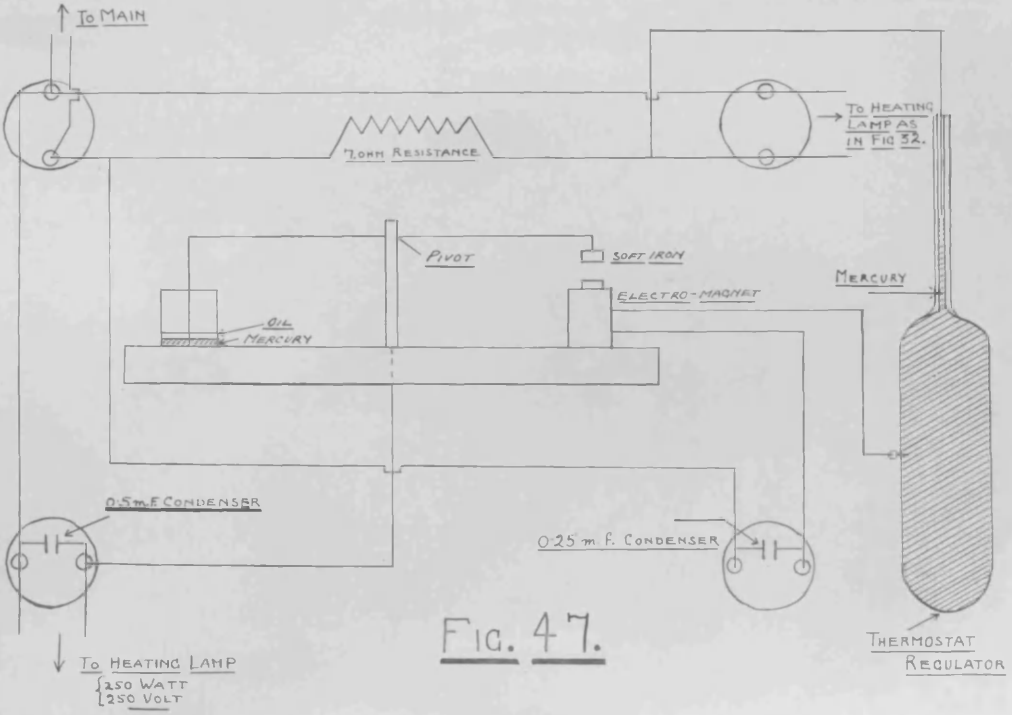

To Main
To Heating Lamp as in Fig 32.
7 ohm Resistance
Pivot
Soft Iron
Electro-Magnet
Mercury
Oil
Mercury
0.5 m.F. Condenser
0.25 m. f. Condenser
To Heating Lamp
{250 Watt
{250 Volt
Thermostat Regulator

Fig. 47.

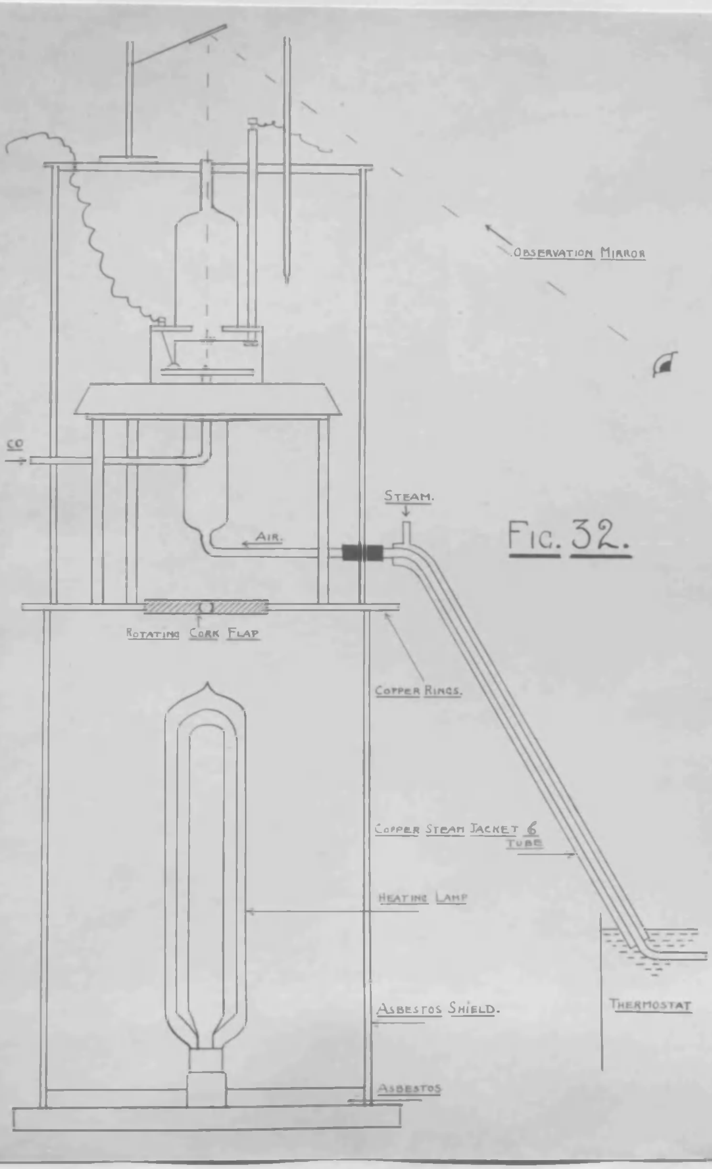

Observation Mirror
CO
Steam.
Air.
Rotating Cork Flap
Copper Rings.
Copper Steam Jacket & Tube
Heating Lamp
Asbestos Shield.
Thermostat
Asbestos

Fig. 32.

to the exit air tube of the steam jacket. Two calcium chloride drying tubes were then connected to this U-tube and at a noted time the air was turned on. The air required to be hastily adjusted to the required rate of flow (140 litres/hour) due to the increased resistance caused by the drying tubes.

The estimation was run for a noted time, barometric and temperature readings taken, and the water collected was weighed by difference. The calculation and result are given below.

Water collected in 1st. tube	6.262 grammes.
" " " "	1.419 "
" " " "	0.006 "
Total water collected	7.687 "
Duration of test	36 minutes
Rate of flow of atmosphere (A.T.P.)	140 litres per hour
Temperature of saturation	50°C
Barometric pressure	769 m.m.
Room temperature	15°C

Calculation :-

140 litres at 769 m.m. and 15 °C

$$= \frac{769 \times 140 \times 273}{288 \times 760} = 132.4 \text{ litres per hour at N.T.P.}$$

$$= \frac{760 \times 132.4 \times 323}{273 \times 769} = 155 \text{ litres per hour at atmospheric pressure and } 50°\text{C.}$$

$\therefore$ Grammes water per litre of air at 50°C

$$= \frac{7.687 \times 60}{155 \times 36} = 0.0827$$

From tables(14) Grammes water per litre at 50°C = 0.0823

As a further confirmation that air passing through the battery of sponge towers was saturated at the temperature of the thermostat, it was noted that when the temperature of the combustion chamber compartment inadvertently fell to 57°C. when air saturated at 60°C. was passing through there was condensation in the combustion chamber.

It was accordingly assumed in all subsequent work that the atmosphere was saturated at the temperature of the thermostat, and care was taken to remoisten the towers frequently as already described.

EFFECT OF WATER VAPOUR ON THE EXTINCTION POINT.

A series of estimations of the extinction point was carried out at each of various saturation temperatures. In each case the rate of flow of atmosphere was 140 litres per hour, and of carbon monoxide 4 litres per hour, measured at atmospheric temperature and pressure. The temperature in the combustion chamber compartment was 65°C throughout, and the steam jacketed tube was heated.

Ten estimations were performed at each saturation temperature and each analysis was conducted in duplicate. For the sake

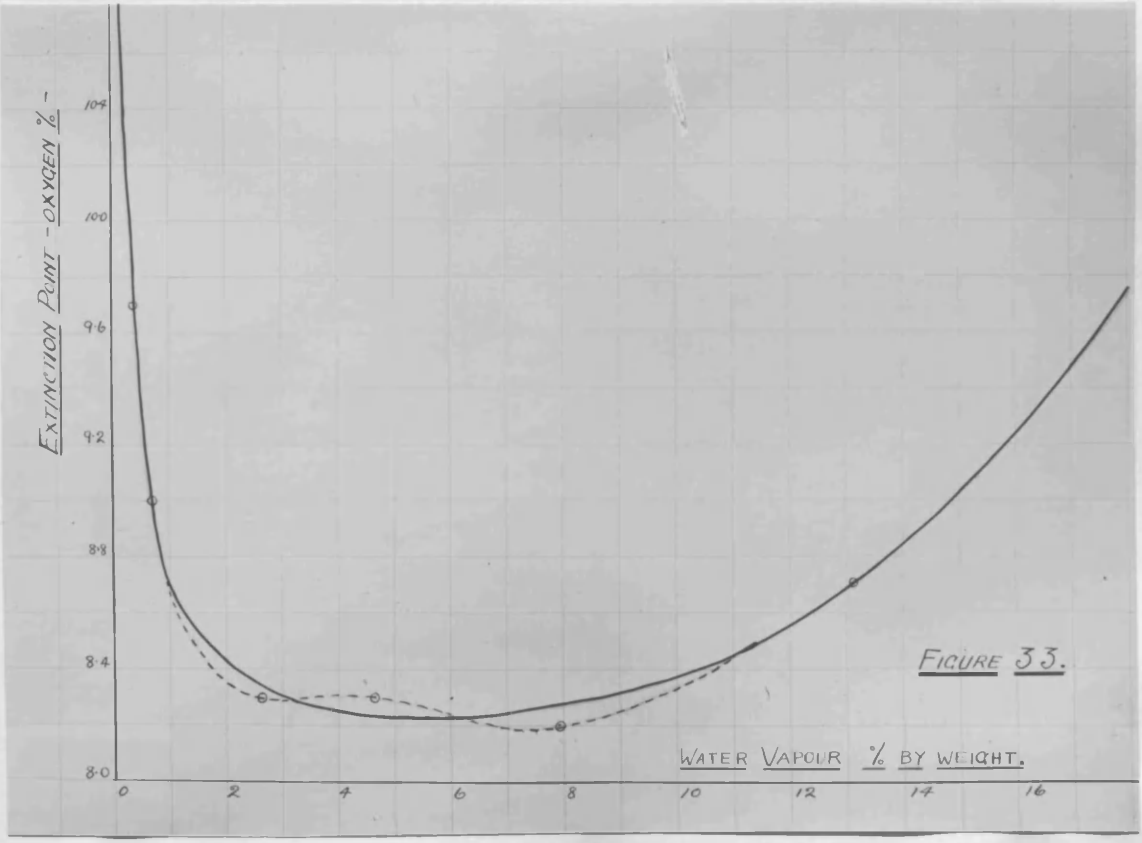


FIGURE 33.

EXTINCTION POINT - OXYGEN % -
10·4
10·0
9·6
9·2
8·8
8·4
8·0
WATER VAPOUR % BY WEIGHT.
0
2
4
6
8
10
12
14
16

of simplicity only the limits and the estimated extinction points are given in Table XXV. below.

TABLE XXV.

Saturation temperature (°C)	Flame		Extinction point (oxygen %)	Water Vapour % by weight
	Extinguished (oxygen %)	Persisted (oxygen %)		
0	9.64 to 9.71	9.74 to 9.82	9.7	0.380
10	8.91 to 9.02	9.04 to 9.10	9.0	0.757
20	8.40 to 8.50	8.51 to 8.63	8.5	1.432
30	8.21 to 8.29	8.27 to 8.37	8.3	2.625
40	8.18 to 8.27	8.29 to 8.35	8.3	4.622
50	7.93 to 8.16	8.28 to 8.43	8.2	7.893
60	8.50 to 8.64	8.66 to 8.73	8.7	13.133

At the higher saturation temperatures, and particularly at 60°C, the flame rose at the extinction point to about 1 " above the jet, and was entirely located in the upper section of the combustion chamber. It was also noted that the flame became evanescent, and very similar to the hydrogen flame, at high water vapour saturations.

In Fig. 33 the extinction points are plotted against the water vapour in the respective atmospheres per cent by weight. From this graph it will be seen that water vapour, up to a certain degree of saturation, facilitates combustion, but that when this saturation, about 6 % by weight, is exceeded, the

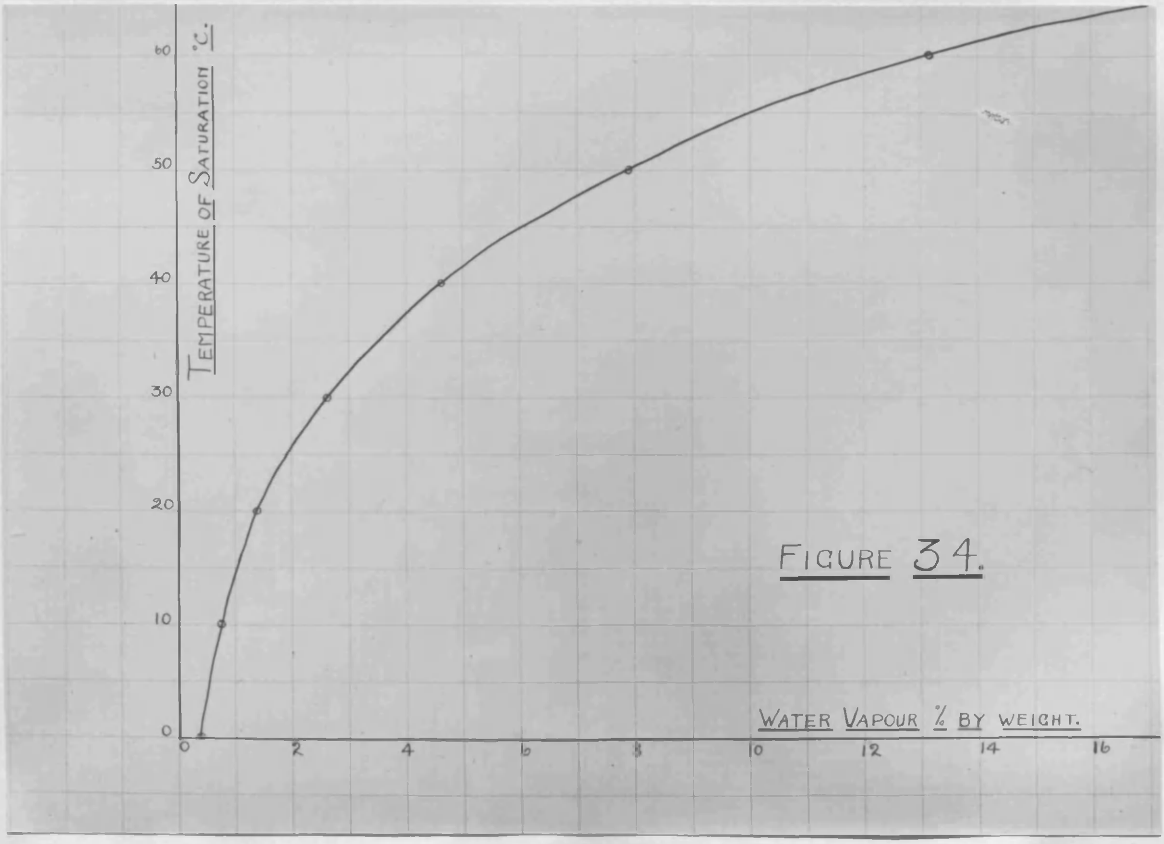

TEMPERATURE OF SATURATION °C.
60
50
40
30
20
10
0
WATER VAPOUR % BY WEIGHT.
0
2
4
6
8
10
12
14
16

FIGURE 34.

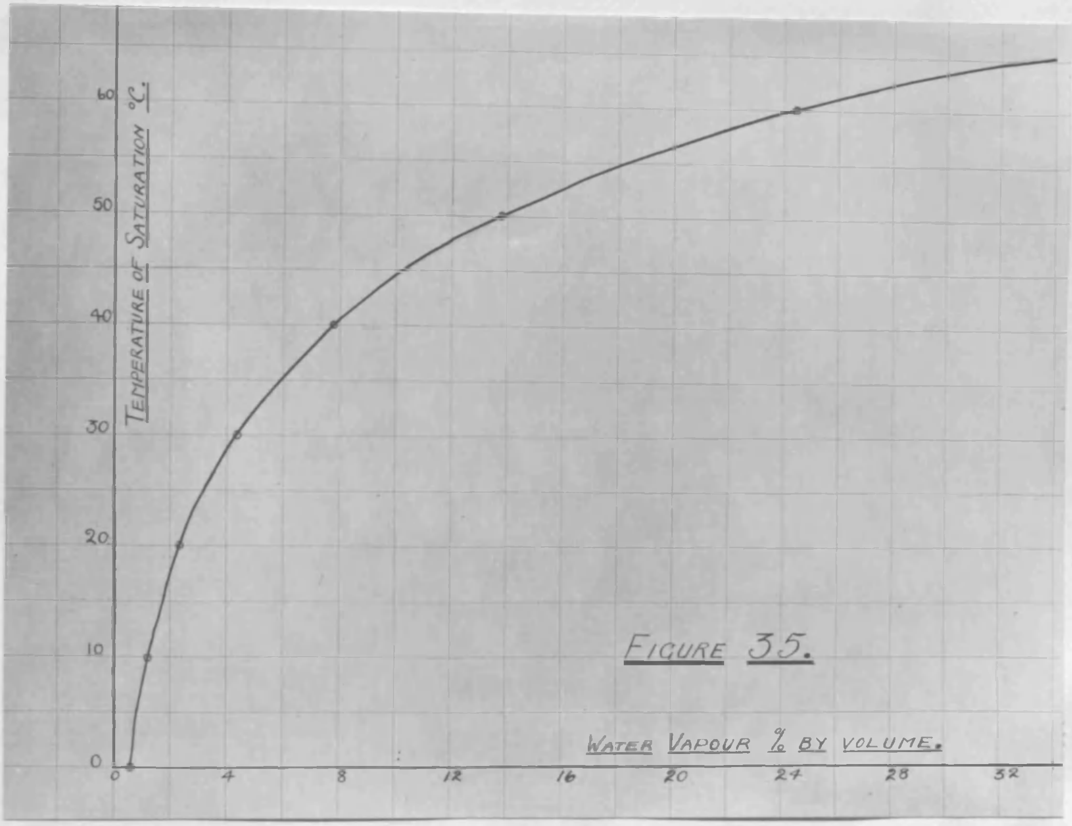

TEMPERATURE OF SATURATION °C.
60
50
40
30
20
10
0
0
4
8
12
16
20
24
28
32
WATER VAPOUR % BY VOLUME.

FIGURE 35.

further addition of water vapour inhibits combustion, very probably due to its diluent action and cooling effect on account of its relatively high specific heat.

In Fig. 33 the graph drawn through the actual points is also shown in the region of the turning value of the extinction point, this will be discussed later.

For convenience in reference and interpolation of saturation temperature from water per cent by weight and by volume, figures by Castell-Evans are given in Table XXVI. , and the graphs obtained by plotting water % by weight and by volume respectively, against saturation temperatures in degrees Centigrade,are shown in Figs. 34 and 35.

TABLE XXVI .

Temperature of saturation (°C)	Water vapour (% by weight)	Water vapour (% by volume)
0	0.380	0.60
10	0.757	1.23
20	1.432	2.35
30	2.625	4.32
40	4.622	7.80
50	7.893	13.77
60	13.133	24.39

From Fig. 34 the temperature of saturation corresponding to 6 % of water vapour by weight, as obtained for the minimum extinction point value in Fig. 33., is 45°C. but it is worthy of note that the turning point of this graph is very flat and, within the limits of apparent experimental inaccuracy, the temperature of saturation which gives a minimum extinction point could quite readily, it would appear, lie between 25° and 50°C., corresponding to 2 and 8 per cent by weight of water vapour, respectively.

EFFECT OF TEMPERATURE ON THE EXTINCTION POINT.

In order to determine whether the heating of the combustion chamber compartment and the steam jacketed tube had any influence on the extinction point value, a series of six estimations was carried out at saturation temperature 20°C. and all else at room temperature - this being possible of achievement, without condensation, at this temperature of saturation. The results so obtained are compared with those obtained with the combustion chamber compartment and steam jacketed tube heated, as given in Table XXV.

As a matter of comparison and interest, the extinction point for both gases dried by means of calcium chloride and all else at atmospheric temperature, was repeated, and the results compared in Table XXVII with the previous results, taken from Table 22. Six estimations were carried out and duplicate analyses conducted on each sample.

TABLE XXVII .

No.	Conditions	Flame		Extinction point (oxygen %)
		Extinguished oxygen % (limits)	Persisted oxygen % (limits)	
I.	Heated compartment and steam jacket. Saturd. 20 ° C.	8.40 to 8.50	8.51 to 8.63	8.5
II.	Compartment and steam jacket at atmos. temp. Sat. 20 ° C.	9.20 to 9.29	9.27 to 9.33	9.3
III.	As in II. but dried, as in earlier work, with $CaCl_2$	11.34 to 11.46	11.49 to 11.56	11.5
IV.	As in III. results taken from Table XX.	10.95 to 11.04	11.00 to 11.08	11.0

As will be seen from Table XXVII. above, the effect of temperature plays a very significant part in the value obtained for the extinction point, and this would suggest that the series of results given in Table XXV, and purporting to demonstrate the influence of water vapour, is not strictly valid in so far as the temperature of the atmosphere entering the steam jacketed tube varies from 0°C to 60°C., and will most probably vary, although within considerably narrower limits, at the jet after having passed through the heated system, in which, it is reasonable to suppose, the air entering at the lower temperature will be raised through a greater range of temperature. This question is more fully dealt with later.

Another aspect of the influence of temperature is the very probable fluctuation in the temperature of the combustion chamber walls, according to the length of time during which the flame has been burning prior to extinctive conditions being reached. This also is dealt with later.

INFLUENCE OF SPEED OF ATMOSPHERE ON THE EXTINCTION POINT.

In order to demonstrate the effect of rate of flow of atmosphere on the extinction point at different humidities, a parallel series to that recorded in Table XXV. was conducted, in which the rate of flow of atmosphere was the only factor which was altered, this being maintained at 60 litres per hour instead of 140, as in Table XXV.

The object in repeating the whole Humidity Series with the altered rate of flow of atmosphere, was primarily to compare the graphs obtained in each series by plotting water saturation against extinction point, with a view to verifying the efficiency of the saturating device for different loads - rates of flow - .

The results shown in Table XXVIII show the limits, in each case, of five estimations, the analyses being conducted in duplicate for each sample.

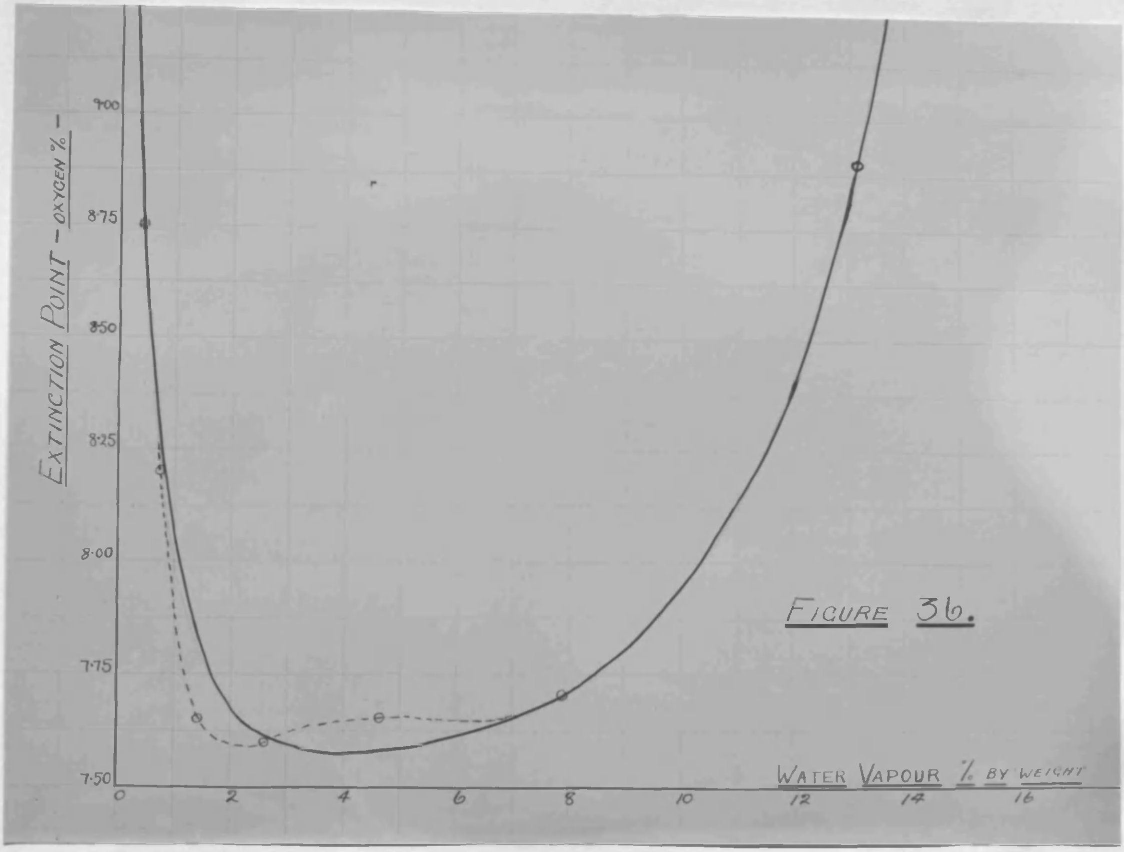

EXTINCTION POINT - OXYGEN % -
9·00
8·75
8·50
8·25
8·00
7·75
7·50
WATER VAPOUR % BY WEIGHT
0
2
4
6
8
10
12
14
16

FIGURE 36.

TABLE XXVIII .

Saturation temperature (°C.)	Flame		Extinction point (oxygen %)	Water vapour % by weight
	Extinguished (oxygen %)	Persisted (oxygen %)		
0	8.69 - 8.75	8.77 - 8.85	8.75	0.380
10	8.15 - 8.20	8.24 - 8.34	8.2	0.757
20	7.56 - 7.65	7.67 - 7.75	7.65	1.432
30	7.51 - 7.61	7.60 - 7.69	7.6	2.625
40	7.61 - 7.67	7.68 - 7.74	7.65	4.622
50	7.65 - 7.74	7.70 - 7.80	7.7	7.893
60	8.81 - 8.91	8.88 - 9.01	8.9	13.138

Taking 8.0 as a representative extinction point in the foregoing table, then 60 litres per hour of atmosphere is equivalent to 4.8 litres per hour of oxygen, i.e. 140 % excess. Similarily 140 litres of atmosphere per hour, for the same extinction point, is equivalent to 460 % excess oxygen.

In Fig. 36 the extinction points are plotted against water vapour per cent by weight.

Comparing the graphs obtained, as shown in Figs. 33 and 36, by joining each point, the author was impressed with their similarity in character in the region of minimum extinction values, despite the possibility that a smooth curve only deviates from the curve connecting the points by amounts within the limits of accuracy of their determination. Several repeat estimations of what were considered to be 'vagrant' points, helped to confirm the author's opinion that the true curve passed through each of the actual plotted points - shown in graphs by a dotted line -, and it was accordingly decided to repeat the series for 140 litres per hour and to take all known precautions to obtain accurate results, more particularly in exploring the region represented by low extinction points, as shown later.

In further comparison of Figs. 33. and 36., it is seen that, contrary to the author's previous observations, as shown in Table XXII., it would now appear that the rate of flow of atmosphere has a very decided influence on the value obtained for the extinction point. This is of considerable importance in so far as it shows the presence of a third variable factor of which no cognizance has been taken in the Humidity Series, the results of which appear in Table XXV. The presence of the second variable has already been alluded to on p.p. 87 and 88.

From Fig. 35., it is seen that air saturated with water vapour at 60° C. contains about 25 % of water vapour by volume, so that air saturated with water vapour at atmospheric temperature, say 20° C, passing into the saturator at 60° C. at the rate of 140 litres per hour will increase in volume due to ordinary expansion in accordance with Charles' Law, and further due to the addition of water vapour.

$$\frac{V}{T} = \frac{V'}{T'} \quad \therefore \quad \frac{140}{293} = \frac{V'}{333} \quad \therefore \quad V' = 160.$$

From Fig. 35, at 60° C. three volumes of air are associated with one volume of water vapour.

∴ 160 volumes of air will be associated with 53 volumes of water vapour. i.e. the rate of flow of air through the combustion chamber is of the order 210 litres per hour instead of 140, as will be approximately the case at 20° C. saturation in the same series.

It is thus evident that, in order to apply a correction for this influence, it will be necessary to explore the effect of rate of flow of atmosphere, plot the extinction point values against the respective atmosphere rates, and then find the correction by interpolation from the graph so obtained. - See Fig. 40. -

EFFECT OF WATER VAPOUR - REPEAT SERIES.

As has already been mentioned, the flame near the extinction point progressively rose to a greater height from the jet as the proportion of water vapour in the atmosphere was increased. At 60° C. water vapour saturation the flame, immediately prior to extinction, was entirely located in the upper section of the combustion chamber, and was therefore no longer subject to the horizontal flow of atmosphere for which the combustion chamber was designed. The lower section of the combustion chamber was accordingly replaced by a cylinder 3 " in internal diameter and 2 " in height; the one used up to this point was only 1.3 " in height.

With this alteration the effect of water vapour was redetermined with results as shown in Table XXIX. At each saturation temperature ten estimations of the extinctive atmosphere were made. Each analysis was carried out in duplicate, the extinction point given being the mean of 20 analyses in each instance. For comparison the extinction points obtained with the original combustion chamber (taken from Table XXV.) are also given in Table XXIX.

TABLE XXIX.

Saturation temperature (° C.)	Water % by weight	Extinction point (oxygen %)		Previous results from Table XXV.
		Limits	Mean	
20	1.43	7.39 to 7.62	7.52	8.5
25	1.95	7.19 to 7.27	7.22	-
30	2.62	7.08 to 7.19	7.14	8.3
35	3.50	7.19 to 7.27	7.23	-
40	4.62	7.46 to 7.56	7.50	8.3
45	6.05	7.61 to 7.74	7.68	-
50	7.89	7.79 to 7.85	7.80	8.2
55	10.21	8.27 to 8.40	8.35	-
60	13.13	8.82 to 8.92	8.86	8.7

The extinction points in Table XXIX above are plotted against water vapour (% by weight) in their respective atmospheres, as shown in Fig. 37. It will be seen that the limits are reasonably narrow in every case except for saturation

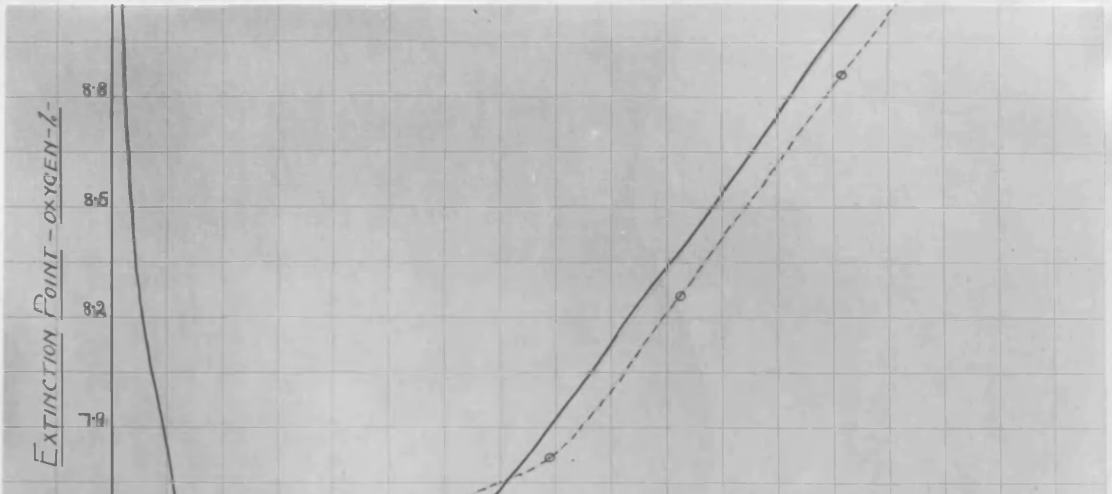


FIGURE 37.

EXTINCTION POINT - OXYGEN - %
8·8
8·5
8·2
7·9
7·6
7·3
7·0
0
2
4
6
8
10
12
14
16
WATER VAPOUR % BY WEIGHT.

temperature 20° C., to justify the statement of results to the second decimal place. The reason for the exception at 20° C. will be discussed later. Even with the greater accuracy in the results, the graph (Fig. 37) has the same general form as the earlier ones shown in Figs. 33 and 36. In this case the deviations from a smooth curve can not reasonably be explained on the basis of experimental inaccuracy, and the author was disposed to consider that the influence of varying speed of atmosphere, occasioned by varying temperature and amounts of water vapour taken up, might cause the apparent distortion of the curve.

Comparing the extinction point values in Table XXIX, with earlier results obtained when the shallower combustion chamber was used, it is seen that the value has been considerably lowered. This, it was considered, could not be due to any temperature effect of the walls of the combustion chamber, since a larger combustion chamber would be at a lower temperature and so give higher results. It was accordingly assumed that the earlier results were high due to the fact that the flame, near the extinction point, had risen above the zone of horizontal flow of atmosphere into the zone of vertical flow.

The tendency of the two series of extinction points shown in Table XXIX. to converge as the water vapour saturation increases, would indicate that the lower section of the combustion chamber was still too shallow, and that for high water vapour saturations, where the flame rises to greater heights from the jet, it is still in the zone of vertical flow of atmosphere.

Reference has been made to the relatively wide limits obtained for saturation temperature 20° C.(Table XXIX.) During the course of a long series of 60 estimations at this saturation very inconsistent results were obtained and trouble was experienced by the behaviour of the flame. The trouble was brought to a climax when it was found that the flame could not be kept alight even in atmospheric air, saturated at 20° C. and flowing at the rate of 140 litres per hour.

Even when the spiral (Fig. 22.) was maintained at a bright red heat, the combustion was entirely confined to the locus of the heated surface of the spiral.

After much investigation it was found that when the carbon monoxide control stopcock (No. 7. Fig. 1.) was only very slightly closed so that practically no change could be detected in the gauge reading, and therefore in the rate of flow of the gas, the flame burned steadily at the jet. Exactly the same behaviour of the flame was observed for greater and lesser rates of flow of carbon monoxide and for various atmosphere speeds. In each instance the behaviour of the flame was found to depend on the baffling of the carbon monoxide gas by means of the tubulure of the stopcock.

In the course of earlier work a plug of loosely packed cotton wool was placed in the carbon monoxide system, between the stopcock (No. 7. Fig. 1.) and the jet, as a precautionary measure to remove any very fine particles of phosphorus pentoxide which might have escaped absorbtion in the silver nitrate scrubber.. It was found that when this plug of cotton wool was replaced by a new one, the flame burned normally again.

From these observations it would appear that the cotton wool plug had, in the course of extended use, become disarranged in such a way to produce the reverse effect obtained by partially closing the stopcock without observable change in the rate of flow of the gas, as read on the gauge.

The linear speed of a gas through the tubulure of a stopcock could conceivably be very materially altered by a slight change in the angle which the tubulure makes with its axis when full open. For small rates of flow (litres/hour) of gas relative to the diameter of the tubulure,small changes from the full open position will not greatly affect the volume of gas passing in a given time. It is thus seen that the local linear speed of the gas can vary without much change in the volume of gas passing in a given time, i.e. the gauge reading.

Recalling the observations of Osborne Reynolds(8) and others, on streamline and turbulent flow, the author considers that this has some significance in regard to the noted behaviour of the flame.

The author suggests the following explanation :-

Referring to Fig. 1.

Gas passing through the jet "J" at relatively high velocity, is in turbulent motion but before reaching stopcock No. 7. it falls below the critical velocity and assumes streamline flow. In the absence of a cotton wool plug the tubulure of the stopcock is of great enough diameter, when full open, to maintain the velocity of the gas below the critical velocity at which streamline flow would become turbulent flow under the prevailing conditions.

When the effective bore of the stopcock is reduced, by partially closing it, the local velocity of the gas is increased to a point exceeding the critical velocity, and turbulent flow is again established, and apparently maintained up to the jet where the gas is burned.

According to the foregoing reasoning and experimental observations, the function of the cotton wool plug would appear to be that of locally increasing the linear speed of the gas to a point exceeding its critical velocity, and its efficiency in this respect could quite conceivably be radically affected by very slight disarrangement or disturbance.

On the assumption of the validity and correctness of the above explanation, it is still necessary to discuss why streamline flow should prevent the maintenance of a flame at the jet under conditions where turbulent flow does maintain steady combustion.

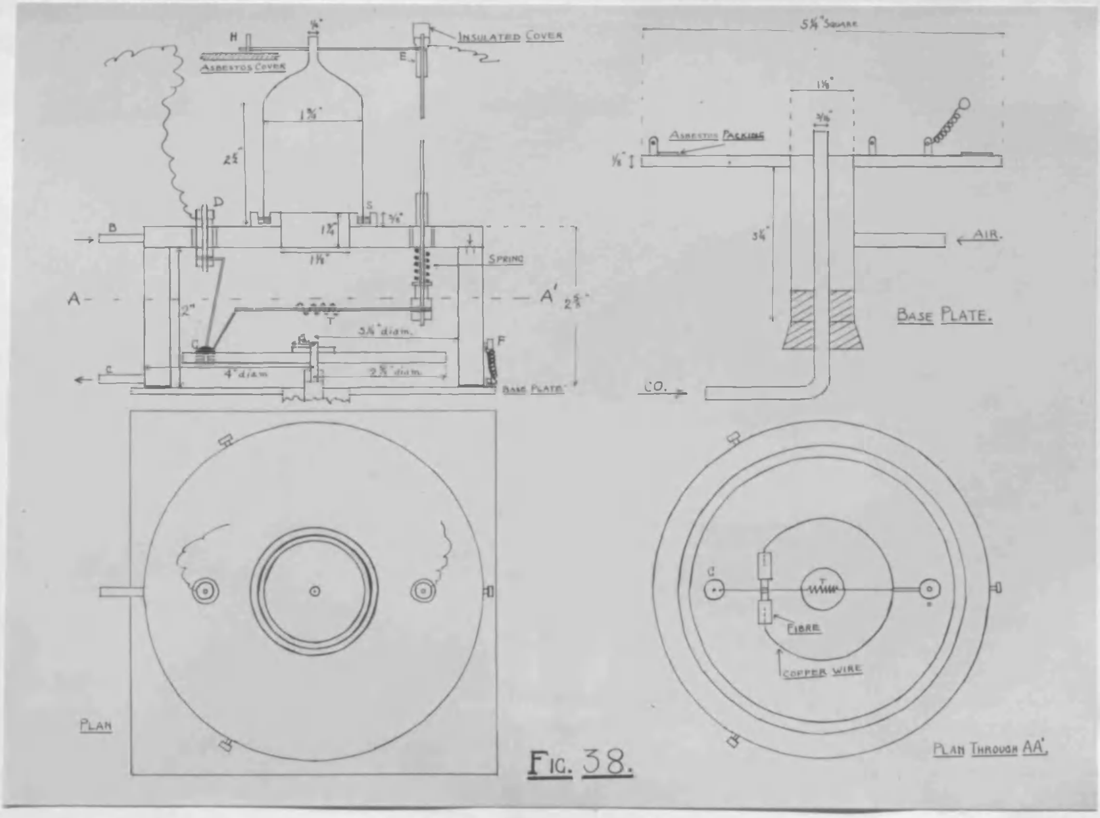

H
Asbestos Cover
Insulated Cover
E
1⅜"
2½"
D
S
B
1¾"
1⅜"
Spring
A
A'
2⅝"
2"
T
3¼" diam.
C
F
C
4" diam
2⅞" diam
Base Plate
5¼" Square
Asbestos Packing
Air.
3¼"
Base Plate.
CO.
Plan
C
Fibre
Copper Wire
Plan Through AA'

Fig. 38.

In this respect it has been pointed out on p.p. 25 to 27 that the establishment of inflammable mixtures at, or near, a jet depends on many factors, two of which are the velocity of projection of the gas from the jet and its rate of diffusion. The former condition, being constant, may be overlooked here; but the second, viz. the rate of diffusion, may reasonably be considered to vary directly as the state of turbulence of the gas as it is projected from the jet. Thus a gas in turbulent flow will more readily form inflammable mixtures near the jet than it would if in streamline flow. The author considers this to be a satisfactory explanation of the observed phenomena.

CONSTRUCTION OF JACKETED COMBUSTION CHAMBER.

In view of the effect which, it has been demonstrated, the temperature of the combustion chamber walls has on the value obtained for the extinction point, the combustion chamber shown in Fig. 38. was constructed so that the temperature of the walls could be controlled by the passage of some fluid between them.

In a few unsuccessful trial estimations with this apparatus, prior to the construction of the base plate shown in Fig. 38., it was set into a plaster of Paris cast by means of Wood's alloy. The objections to this method were (1) action between the alloy and the metal of the combustion chamber, and (2) fracturing of the plaster cast by the repeated melting and setting of the alloy.

In Fig. 38., B and C are inlet and outlet pipes for the heating or cooling fluid, by means of which the fluid may be circulated through the spaces between the vertical and horizontal walls of the combustion chamber as indicated by small arrows.

The walls of the combustion chamber were made from thin brass tubes and rings soldered together.

S is an annular space formed by two brass rings which were soldered on to the combustion chamber. This space was filled with plaster of Paris, allowed to set, and an annular grove then cut in it to act as a mercury seal.

D and E are insulated terminals which are connected to the source of electric current used for heating the nichrome spiral T. G is a metallic contact to act as a switch. The combustion chamber was clamped to the base plate by means of the three equidistant studs F and strong detachable springs, and a ring of asbestos paper was used as a packing between the two to ensure a reasonably tight joint.

EFFECT OF STEAM HEATING AND WATER COOLING THE WALLS OF THE COMBUSTION CHAMBER.

Steam was passed through the combustion chamber at a pressure slightly greater than atmospheric and allowed to escape freely at B - Fig. 38. -to which a long piece of rubber tubing was attached to carry the steam away from the combustion chamber surrounds. The steam jacketed tube and combustion chamber

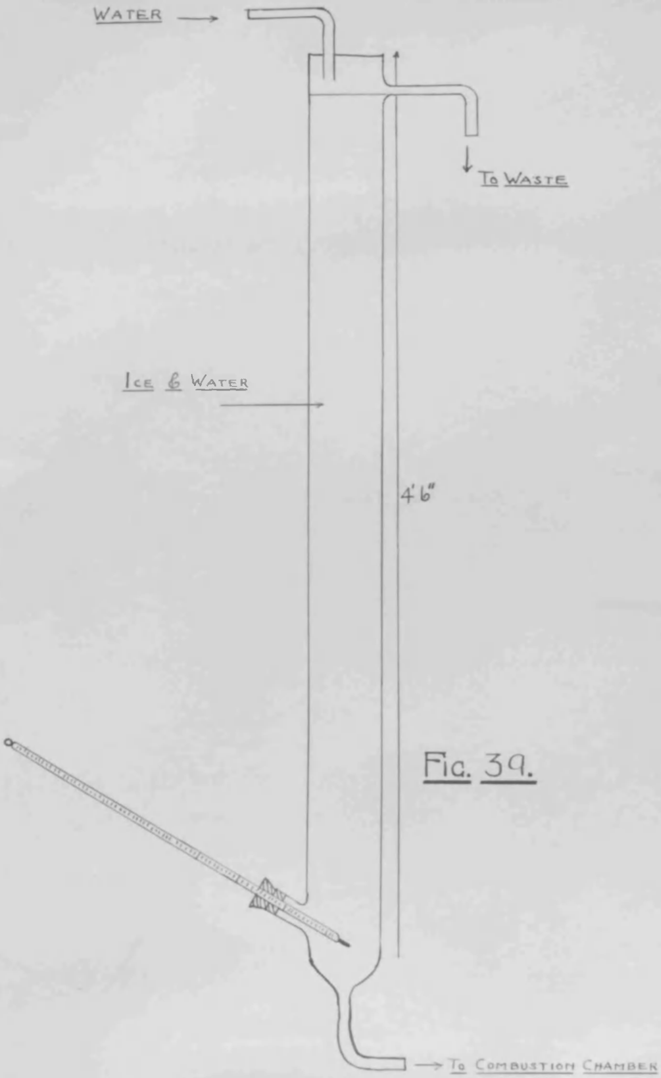


Fig. 39.

compartment were not heated, and air saturated at 0° C. was supplied at the rate of 140 litres per hour.

A series of ten estimations was carried out and each analysis conducted in duplicate. The limits for the ten estimations were -

7.99 to 8.16 % oxygen

and the mean extinction point was -

8.05 % oxygen.

Water Cooling.

Water at 0° C. was passed through the combustion chamber at the measured rate of 140 c.cms. per minute and all other conditions were kept the same as in the foregoing experiment. The arrangement used for the supply of water at 0° C. is shown in Fig. 39.

The limits for ten estimations were -

9.29 to 9.44 % oxygen

and the mean extinction point was -

9.35 % oxygen.

Thus we have -

TABLE XXX.

Combustion chamber	Mean extinction point (oxygen %)
Steam heated (100° C.)	8.05
Water cooled (0° C.)	9.35

REDETERMINATION OF THE EFFECT OF WATER VAPOUR ON THE EXTINCTION POINT.

It was decided to repeat the Humidity Series now that the temperature of the combustion chamber walls could be controlled.

Atmosphere, saturated at different temperatures with water vapour, was supplied at the rate of 140 litres per hour in each case. Throughout each series the combustion chamber and steam jacket were steam heated, and the combustion chamber surrounds were heated by means of the 250 Watt lamp shown in Fig. 32.

During the course of this work a very considerable amount of trouble was experienced in so far as long sequences of very inconsistent results were obtained, and much time was spent searching for the cause of the trouble, which was ultimately traced to the intermittent leaking of water from the rubber connection at "A" Fig. 38., on to the base plate, and thence, by way of the asbestos paper packing between the combustion chamber and the base plate, into the interior of the combustion chamber. The short life of rubber tubing through which steam is passing, suggests that the tubes "A" and "B" should be of sufficient length to reach the exterior of the asbestos cylinder forming the combustion chamber compartment, and that they should be bent downwards at their ends.

A further difficulty was encountered in the course of subsequent estimations. A faulty contact between the moving pole and the mercury contact inside the combustion chamber caused a vivid flash and dispersion of volatilized mercury which could be seen as a film of minute beads adhering to the glass chimney of the combustion chamber.

Prior to this, the extinction point value - Table XXXI. No. 1 - was in close agreement with the mean result of some earlier estimations, viz. 6.91., but immediately following this mishap the value dropped to 6.34 (No. 2.).

Coincident with this occurrence the pyrogallate solution in the Haldane gas analysis apparatus was renewed; this having been prepared as usual from equal volumes of 50 % potassium hydroxide solution and 20 % pyrogallic acid solution.

For convenience in reference the results obtained are given below .

(3) and (4) represent repeat estimations carried out under the same conditions as (2). The rise in (4) was attributed to the volatilization of some of the mercury, and before carrying out any further estimations,the mercury was entirely removed from the glass chimney of the combustion chamber. (6) was then carried out. The result being still low, it was thought that mercury adhering to the lower, or jet, portion of the combustion chamber was the cause. This was accordingly removed and thoroughly wiped, but it was impossible to ascertain whether or not the mercury was being retained in solution with solder, with which the interior walls of the combustion chamber had been partially coated in the process of construction. The

TABLE XXXI.

No.	Oxygen (per cent) in extinctive atmosphere.		
	(1)	(2)	(mean)
1	6.92	7.08	7.00
2	6.28	6.40	6.34
3	6.20	6.36	6.28
4	6.48	6.63	6.55
5	6.38	6.48	6.43
6	6.50	6.60	6.55
7	6.59	6.73	6.66
8	6.55	6.73	6.64
9	6.55	6.71	6.63
10	6.48	6.60	6.54
11	6.47	6.53	6.50
12	6.50	6.62	6.56
13	6.79	6.77	6.78
14	7.26	7.21	7.23
15	6.92	7.09	7.00
16	6.53	6.80	6.66
17	6.61	6.46	6.53
18	6.78	6.82	6.80
19	6.96	7.01	6.98
20	6.92	6.96	6.94
21	6.94	7.06	7.00
22	6.95	6.90	6.92
23	6.84	6.99	6.91
24	6.90	6.81	6.85

only feasible method for removing such mercury was by volatilization, and accordingly a current of air was passed through the heated chamber for long periods. (6) gives the result after two days' heating, and (7), (8), and (9) for further periods of several hours' heating.

As continued heating appeared to have no further effect, it was thought that the discrepancy from the original figure (6.91) was now being caused by volatilization of mercury from the mercury contact, which had been very much enlarged in area in order to prevent a recurrence of the faulty contact which gave rise to this investigation.

It was therefore decided at this juncture to substitute some other form of interior switch or contact for the one in use. The one chosen is shown in Fig. 38. A recess was cut in each side of the 'Sindanyo' disc to carry the small brass rivet as shown, and a pool of solder then fused on to the top side of the rivet. The switch arm "E" was rendered capable of vertical motion in addition to its rotational movement, so that it could be raised then rotated into position, as determined by the stop pin "H", and then lowered so as to make contact with "G" -See Fig. 38. - "H" was mounted on the asbestos cover of the combustion chamber compartment.

(10),(11),(~~and~~ 12), carried out with this new arrangement, showed no improvement. (13), the analysis of which was conducted using pyrogallate solution which had previously been used to absorb in all somewhat less than its own volume of oxygen, was considered to be a false value. (14), (15), and (16) were analysed with fresh pyrogallate solution.

In this connection it is worthy of note that standard authorities confer a very much longer life on alkaline pyrogallate solution in gas analysis than the author has found possible of achievement for experiments of the accuracy aimed at in this work.

The marked rise in the extinction point shown in (14) et. seq., coincident with the renewal of the potassium pyrogallate solution in the Haldane gas analysis apparatus, caused the author to use phosphorus for the absorbtion of oxygen in the later experiments.

The Haldane pipette "L" (Fig. 7.), was accordingly filled with straight sticks of white phosphorus, packed vertically, and the length of the sticks chosen such that they would not reach the shoulder of the pipette - this having been found necessary to prevent entrapment of small bubbles of gas in the pipette.

(17) was now carried out. At this point the Haldane burette and the mercury in it required to be cleaned, after which (18) to (24) were obtained. These last seven estimations are in reasonable agreement, showing limits 6.8 to 7.0, and the mean extinction point (6.91) is in exact agreement with the original figure referred to on p. 104.

During the course of analyses conducted since the introduction of phosphorus as an oxygen absorbent, great difficulty was experienced through the occurrence of dirt in the Haldane measuring burette. Every conceivable precaution was taken to exclude probable sources of dirt and to clean the mercury, culminating in the distillation of the mercury,(after cleaning by means of acids, organic solvents, filtering etc.); varnishing all rubber in contact with the mercury; and lubrication of stopcocks with phosphoric acid instead of vaseline. Dirt however still continued to appear in the burette..

As dirt in the burette, and more particularly moveable dirt, makes the duplication of results to the desired degree of accuracy quite impossible, as evidenced in (17) and (18) of Table XXXI. and in the following example :-

	(1)	(2)
Volume of sample taken	19.227	19.165 c.cs.
Volume after absorbtion of oxygen	17.859	17.859 c.cs.
Volume of oxygen	1.368	1.306 c.cs.
Extinction point (oxygen %)	7.11	6.82

it is seen that some method had to be devised whereby the dirt was either removed or avoided. In the example given above an error of 0.062 c.cm. in one reading of the burette, causes an error of about 0.3 % in the extinction point.

The author has found that errors of this magnitude due to (1) dirt, (2) dirt associated with minute globules of mercury,

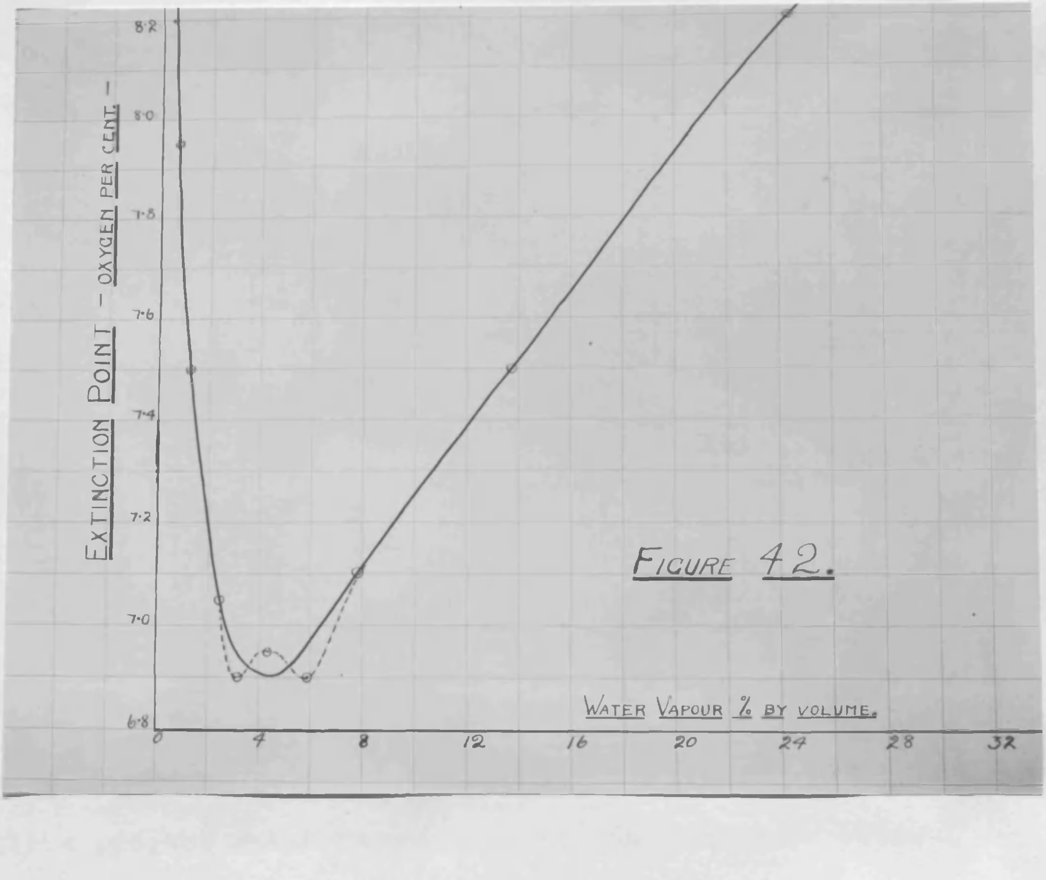


FIGURE 42.

EXTINCTION POINT - OXYGEN PER CENT. -
8·2
8·0
7·8
7·6
7·4
7·2
7·0
6·8
WATER VAPOUR % BY VOLUME.
0
4
8
12
16
20
24
28
32

and (3) the dilute sulphuric acid kept in the burette for the purpose of maintaining the volume of aqueous vapour in the gas constant; can arise, unless scrupulous care is taken to avoid their occurrence. A considerable amount of time was therefore devoted to the evolution of a method of analysis to correspond in degree of accuracy with the method by which extinctive atmospheres were obtained. This investigation and the method adopted are described fully in the Appendix p.p.152 et seq..

In reviewing the past work it will be seen that several attempts have been made, with some measure of success, to demonstrate the influence of water vapour on the extinction point. The author now considers that, with the experience gained from difficulties overcome, the results set forth in Table XXXII. represent a true statement of the effect of water vapour, provided allowance is made for the possible temperature effect (p. 87.), and the rate of flow of atmosphere effect (p.p. 91 and 92), referred to earlier, and subsequently estimated (p.p. 112 and 118).

The results of the series, as described on p. 103, are given in Table XXXII., and the graph obtained by plotting extinction points against water vapour per cent by volume is given in Fig. 42., p. 109.

TABLE XXXII.

Saturation temperature (° C.)	Extinction point (% oxygen)		Water vapour % by vol.
	Limits	Mean	
0	7.90 to 7.99	7.95	0.60
10	7.43 to 7.56	7.50	1.23
20	6.97 to 7.07	7.05	2.35
25	6.89 to 6.98	6.90	3.16
30	6.91 to 7.03	6.95	4.32
35	6.86 to 6.96	6.90	5.90
40	7.04 to 7.16	7.10	7.80
50	7.44 to 7.53	7.50	13.77
60	8.13 to 8.25	8.20	24.39

It will again be seen that the plotted points for minimum values of the extinction point do not lie on a smooth curve, and that the graph connecting these points has the same general form as in each of the three previous determinations, as shown in Figs. 33, 36, and 37. Apart from the consistency with which this has occurred, however, the deviations from a smooth curve lie within the extreme limits of experimental error, so no definite conclusions can be made.

EFFECT OF TEMPERATURE

GENERAL.

The effect of the temperature of the combustion chamber walls has already been referred to on several occasions, and in some instances demonstrated, p.p. 87, and 102. Reference has also been made (p. 87.) to the possible influence on the extinction point of the varying temperatures at which the water-vapour-saturated atmospheres leave the saturating towers, in determinations of the effect of water vapour on the extinction point. No reliable data have so far been given to show the relative and individual influence on the ultimate temperature of the atmosphere, and on the extinction point, of the various heating elements, viz. the steam jacketed tube, the heated combustion chamber compartment, and the steam heated combustion chamber walls.

The following investigation was therefore carried out.

(1) Effect of the temperature of the heated combustion chamber walls.

This effect was tried at 0°C. and 20°C. water vapour saturations. Atmosphere at the rate of 140 litres per hour was supplied, and the steam jacket and combustion chamber compartment were heated in each case. Water at 0° and 14° C. respectively was passed through the combustion chamber. The mean results of five estimations, carried out at each saturation

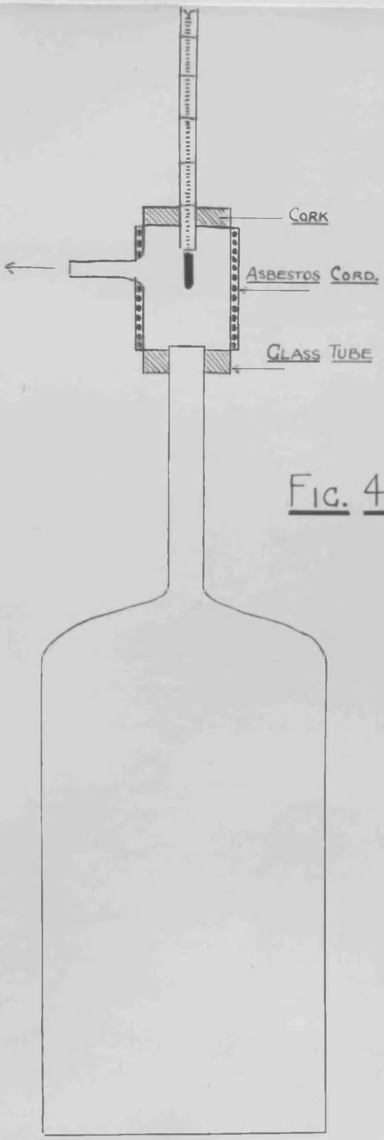


FIG. 43.

temperature are given in Table XXXIII. together with corresponding figures taken from Table XXXII., in which the combustion chamber was steam heated.

TABLE XXXIII.

Saturation temperature (° C.)	Extinction point (oxygen % mean)	Temp. of Comb. Ch. walls °C.	'a' Temp. raised (°C.)	'b' Ext. Pt. lowered (°C.)	Ratio b/a
0	10.00	0	-	-	-
0	7.95	100	100	100	.0205
20	8.80	14	-	-	-
20	7.05	100	100	86	.0204

From the foregoing results it is seen that the temperature of the combustion chamber walls has a very marked influence on the value of the extinction point. It is also of interest to note that the ratio of the change in temperature of the walls to the change in the extinction point value, within the narrow limits investigated, is constant.

(2) Effect of various heating units on the extinction point, and on the resultant temperature of the atmosphere.

In this series of estimations the individual and collective influence of the three heating units, viz. steam jacket, combustion chamber walls, and the combustion chamber compartment, on the extinction point, and on the temperature of the atmosphere as measured at the top of the combustion chamber chimney, was measured. The temperatures were measured by means of the device shown in Fig. 43., the flame being extinguished, and time allowed for the reading to become constant.

In all these estimations, the results of which are given in Table XXXIV., atmosphere saturated with water vapour at 20° C. was supplied at the rate of 140 litres per hour. Five estimations were carried out in each case, and the mean extinction point only is given.

TABLE XXXIV.

No.	Temperature in ° C. of -				Extinction Point (oxygen %)
	Combustion chamber walls	Steam jacketed tube	Combustion chamber compartment	Atmosphere at chimney	
1	15	17	17	20	8.80
2	15	100	17	22	8.79
3	15	17	65	31	8.77
4	100	17	39 *	59	7.14
5	100	100	65	63	7.05
6	15	100	65	33	8.77

* Temperature raised due to steam heated combustion chamber only.

It is apparent from Nos. 1, 2, 3, and 6, above that the heated combustion chamber compartment and steam jacketed tube have no measurable influence on the extinction point, individually or jointly. The heated steam jacket only causes a rise of 2° C. in the temperature of the atmosphere, (1), and the heated combustion chamber compartment (3) causes a rise of 11° C. This latter measurement being made in the mixed, hot and cold, strata of gases at the top of the chimney is, in all probability, much higher than the actual temperature in the neighbourhood of the jet.

(4) and (5) show the relatively large influence of the steam heated combustion chamber walls on the extinction point and on the ultimate temperature of the atmosphere, which again may be assumed to be considerably higher than the actual temperature at the jet. These experiments also show the very small joint influence of the heated steam jacket and combustion chamber compartment.

(3) Effect of pre-heating the atmosphere.

In discussing the influence of water vapour on the extinction point, reference has been made (p.p. 87 and 110.) to the influence which the varying temperatures of the atmosphere leaving the saturating towers may have on the estimation, thus possibly masking the true influence of water vapour.

It will be seen from Table XXXIV No. 5 that the resultant temperature, at the chimney, of air which entered the steam jacket at 20° C. is 63° C. i.e. air saturated at 20° C., is raised through 43° C. and that it is impossible under the conditions of the method for air saturated at 60° C. to be raised the same amount. It is reasonable however to assume that air saturated at 60° C. will be raised to some higher temperature than air saturated at 20° C. It was decided to determine this higher temperature, and to conduct a series of estimations at 20° C. saturation, in which the saturated atmosphere was pre-heated by an amount necessary to maintain the temperature T at the top of the chimney.

T was found to be 67° C.

Pre-heating. A double surface condenser was chosen such that when heated by the passage of steam through it, and when substituted for the steam jacketed tube, saturated air entering the condenser at 20° C. was raised to 67° C. at the chimney.

Five estimations were carried out and the results, compared with data taken from Table XXXII and elsewhere, are given in Table XXXV, below.

TABLE XXXV.

No.	Saturation temperature (°C.)	Temperature of atmosphere at chimney (°C.)	Extinction point (oxygen %)	
			Limits	Mean
1	20	63	6.97 to 7.07	7.05
2	60	67	8.13 to 8.25	8.20
3 *	20	67	6.99to 7.12	7.04

* Atmosphere pre-heated.

It will be seen from Table XXXV. that, within the limits of variation in temperature which prevail in the series of estimations demonstrating the influence of water vapour on the extinction point as given in Table XXXII. , the influence of temperature is not measurable.

EFFECT OF RATE OF FLOW OF ATMOSPHERE.

The determination of the effect of speed of atmosphere has already been attempted, Tables XXV. and XXVIII. (p.p. 82 and 90.) prior to the introduction of several refinements in the apparatus and general method of procedure.

In the following series of estimations, the results of which are given in Table XXXVI., atmosphere saturated with water vapour at 20° C. was used in each case. The combustion chamber and steam jacketed tube were steam heated, and the combustion chamber compartment was heated.

Atmosphere, varying in rate of flow from 50 to 170 litres per hour, was passed through the combustion chamber, and five estimations of the extinction point were carried out at each speed. The limits of these estimations, and the mean extinction points are given below.

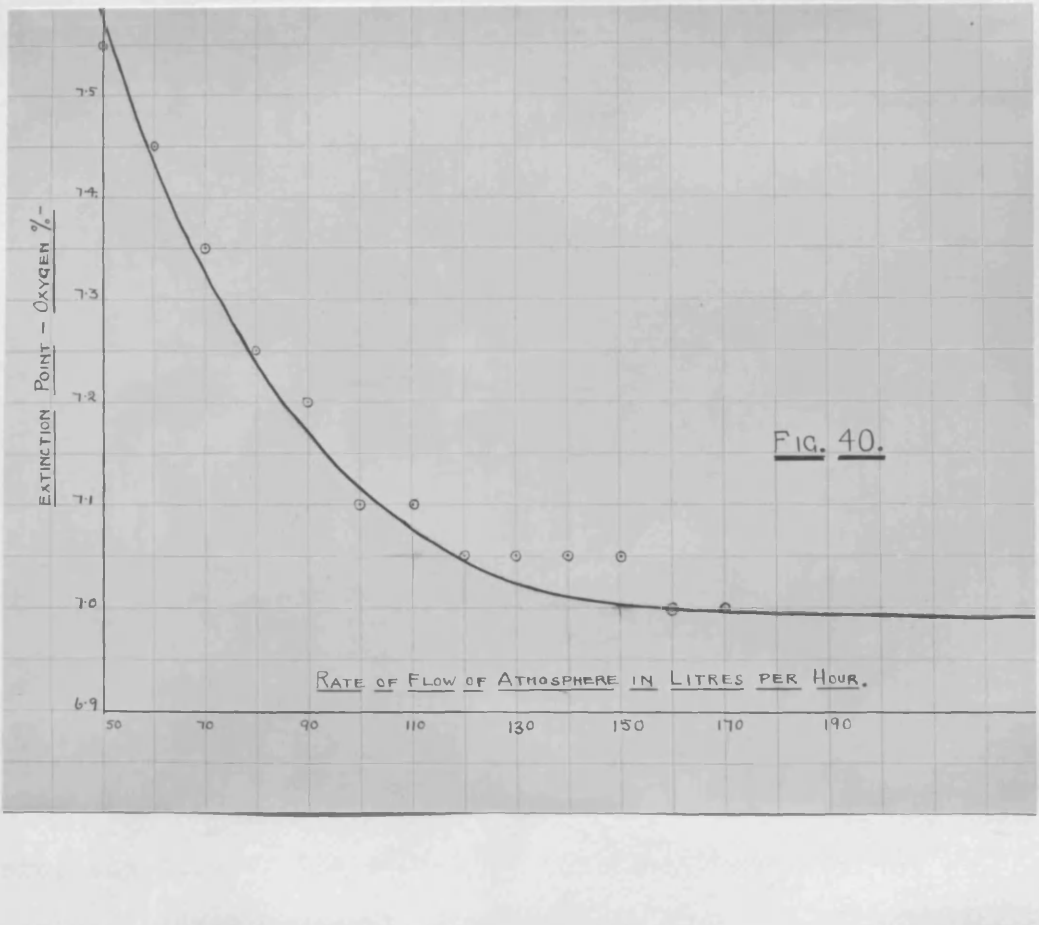

EXTINCTION POINT - OXYGEN %.
7·5
7·4
7·3
7·2
7·1
7·0
6·9
50
70
90
110
130
150
170
190
RATE OF FLOW OF ATMOSPHERE IN LITRES PER HOUR.

FIG. 40.

TABLE XXXVI.

Rate of flow of atmosphere in litres per hour.	Extinction point (oxygen %)	
	Limits	Mean
50	7.50 to 7.60	7.55
60	7.38 to 7.51	7.45
70	7.27 to 7.41	7.35
80	7.19 to 7.30	7.25
90	7.07 to 7.25	7.2
100	7.08 to 7.16	7.1
110	7.04 to 7.16	7.1
120	6.99 to 7.10	7.05
130	7.02 to 7.08	7.05
140	6.98 to 7.09	7.05
150	7.00 to 7.08	7.05
160	6.90 to 7.07	7.0
170	6.93 to 7.05	7.0

The rate of flow of atmosphere is plotted against the extinction point in Fig. 40., from which it is seen that, within the limits investigated, the greater the speed of atmosphere, the smaller the effect on the extinction point. This is of particular interest in connection with the results given in Table XXXII. in which variations in speed due to increase in volume by heating and by addition of water vapour were not taken cognizance of. (See p.p. 91, 92, and 110.) Time did not permit of calibrating a jet in order to explore the effect of atmosphere speeds for speeds greater than 170 litres per hour, but the nature of the graph, (Fig. 40.), suggests that greater speeds than 170 litres per hour, such as will be caused by heating, and the addition of water vapour, will have a negligible effect on the character of the curve shown in Fig. 42.

The effect of rate of flow of atmosphere given above is at variance with the results given in Tables XXV. and XXVIII. (p.p. 82 and 90.), but in view of the imperfection of the apparatus and method in this earlier work, the author attaches no importance to this apparent contradiction, and accepts the more recently demonstrated effect, as given in Table XXXVI.

Rhead(2) refers to the effect of speed of atmosphere on extinction points, but no definite conclusions can be drawn from his published results.

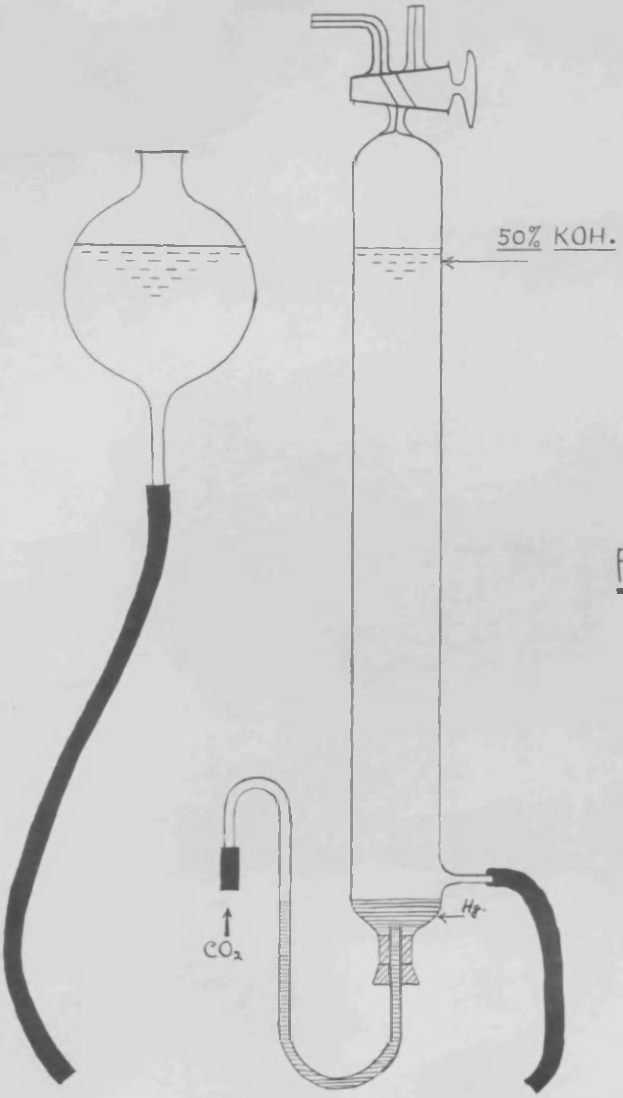


FIG. 44.

EFFECT OF CARBON DIOXIDE AS A DILUENT.

Work done for The Safety in Mines Research Board(4) shows the greater effect of carbon dioxide than nitrogen in inhibiting combustion. Coward and Hartwell, in continuing this work, state that the greater effect is due to the greater specific heat of carbon dioxide and, incidentally, its greater cooling effect.

The carbon dioxide used was stored in a balanced gas holder and was the ordinary commercial product supplied in cylinders. This gas on analysis was found to contain 1.1 % of foreign gaseous bodies of the composition :-

Oxygen	16.25 %
Inert gases	83.75 %

Sufficient of the foreign gases in the carbon dioxide to conduct an analysis in duplicate was collected by means of the nitrometer shown in Fig. 44. This was filled with 50 % potassium hydroxide solution and had the usual mercury valve as shown.

APPROXIMATE ESTIMATION.

An approximate estimation in which the gauge reading corresponding to 140 litres per hour of extinctive atmosphere containing carbon dioxide, was guessed, was carried out in order to

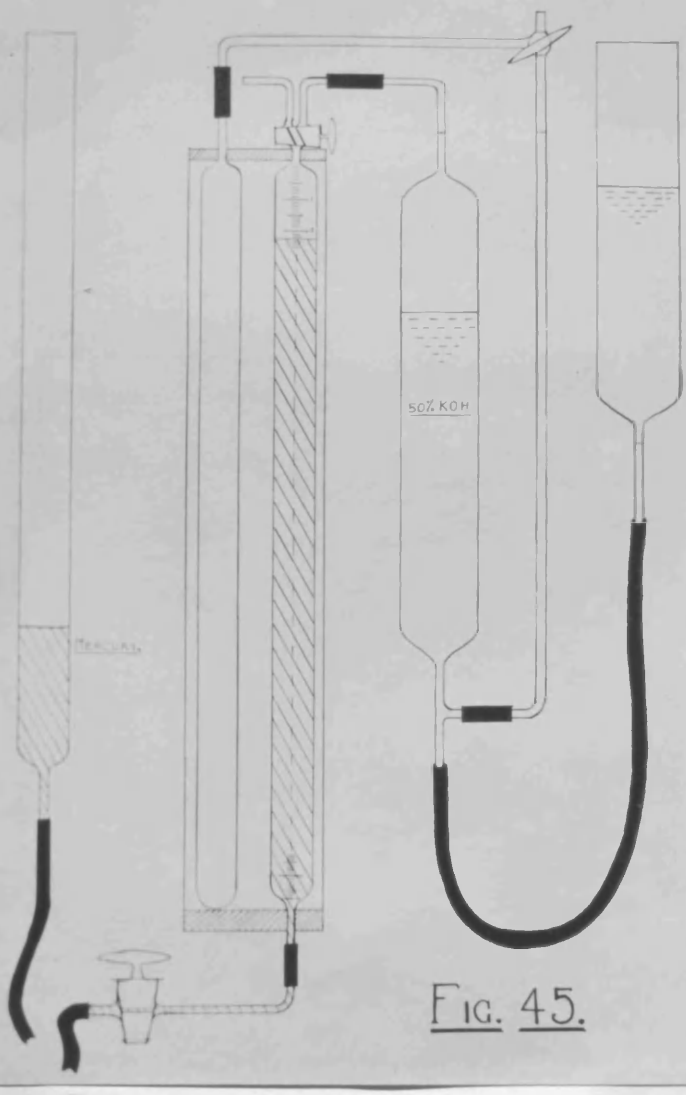


FIG. 45.

have some basis on which to calibrate a jet for the delivery of 140 litres per hour. The result of this estimation was :-

Carbon dioxide	47.5 %
Oxygen	11.0 %
Nitrogen	41.5 %

CALIBRATION OF ATMOSPHERE JET.

As it was only intended to use one rate of flow of this carbon dioxide-air atmosphere, viz. 140 litres per hour, the gauge reading corresponding to this rate of flow only, was found by trial and error by the method of Gray(13). This was found to be 8.8 " using the jet for which the calibration for nitrogen-air mixtures is shown in Fig. 13.

METHOD OF ANALYSIS.

The composition of the extinctive atmosphere shown above rendered the conduction of its analysis impossible by the method used up to this point.

Various methods were tried and the following found to be the most satisfactory. An improvised Haldane's apparatus, as shown in Fig. 45., was constructed using a Hempel burette and compensator tube and a CO_2 absorbtion pipette of sufficient capacity to take a 100 c.cm. sample; this pipette was filled with 50 % KOH solution. As the composition of the original gases were both known, and periodically determined, it was not considered necessary to estimate both carbon dioxide and oxygen in each sample. The former, and preponderating, constituent only was estimated, and the oxygen in each case calculated as in the following example :-

Analysis of Extinctive Atmosphere.

Carbon dioxide in sample (estimated)	50.00 %
Foreign gases in original CO_2 used	1.1 %
Air + foreign gas in sample	50.00 %
Foreign gas in sample (approx.)	0.55 %
$\therefore$ air in sample	49.55 %

Oxygen in foreign gas (estimated)	16.25 %
Oxygen in air used (estimated)	20.87 %

Hence oxygen in sample

= (16.25 % of 0.55 %) + (20.87 % of 49.45 %)

= 0.09 % + 10.32 %

= 10.41 %

EFFECT OF CARBON DIOXIDE AND WATER VAPOUR ON THE EXTINCTION POINT.

Using carbon dioxide instead of nitrogen as a diluent for air, the effect of water vapour was again demonstrated, as shown in Table XXXVII. The duplicate estimations and analyses agreed so closely that only five estimations were carried out

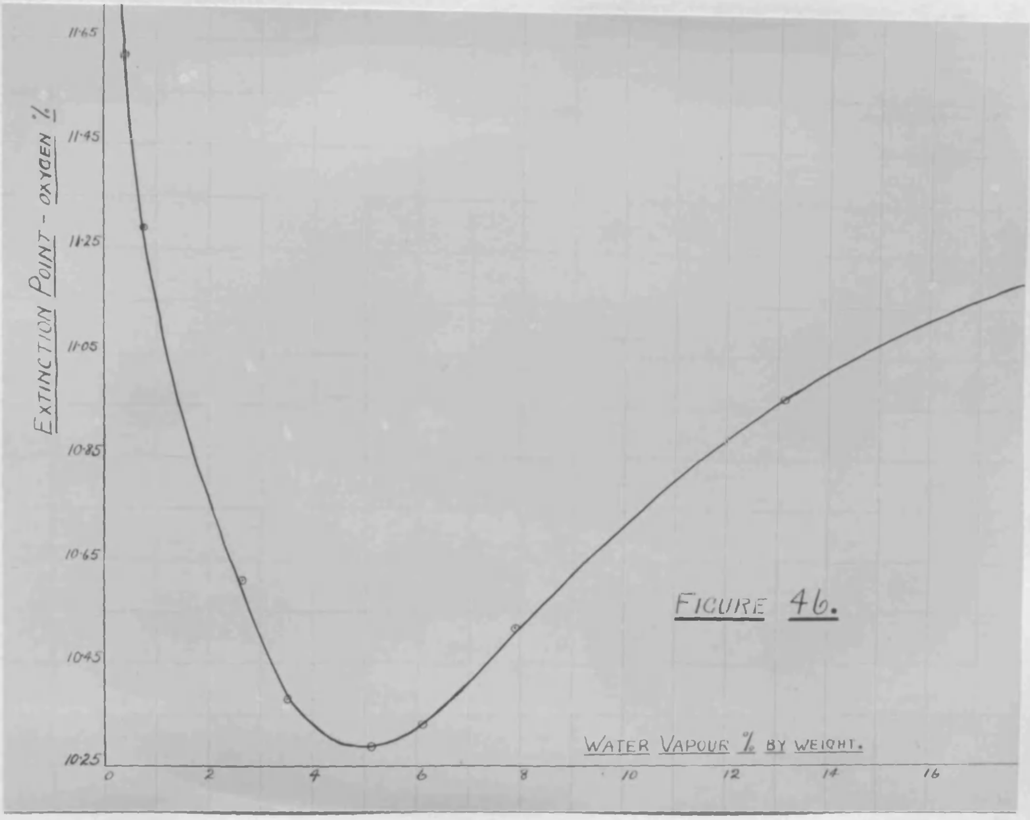

EXTINCTION POINT - OXYGEN %
11·65
11·45
11·25
11·05
10·85
10·65
10·45
10·25
WATER VAPOUR % BY WEIGHT.
0
2
4
6
8
10
12
14
16

FIGURE 46.

at each saturation temperature, the limits and mean extinction points only being given. Where possible the parallel results, taken from Table XXXII., as obtained for nitrogen-air atmospheres, are given for comparison. Extinction points are plotted against water vapour, per cent by weight, in Fig. 46.

TABLE XXXVII.

Saturation temperature (°C.)	Water vapour % by weight	Extinction Point (oxygen %)			'a'-'b'
		Limits	Mean ' a '	Nitrogen-air mixtures.'b'	
0*°	0.38	11.44-11.83	11.62	7.95	3.67
10 *	0.76	-	11.29	7.50	3.79
20	1.43	10.90-11.03	10.96	7.05	3.91
30	2.62	10.57-10.64	10.61	6.95	3.66
35	3.50	10.34-10.47	10.38	6.90	3.48
40	4.62	10.25-10.33	10.29	7.10	3.19
41 *	5.00	-	10.29	-	-
45	6.10	10.29-10.38	10.33	-	-
50	7.89	10.50-10.54	10.52	7.50	3.02
60	13.13	10.93-11.01	10.97	8.20	2.77

*° 10 estimations - poorer duplicates.

* Not estimated - results interpolated from graph.

It will be seen from the foregoing table that carbon dioxide has a much greater extinctive power than nitrogen.

This is in agreement with the observations of Coward and Hartwell (4).

Although the estimations are by no means parallel, it is of interest to note that (See Table XXXVIII.) the ratio $\frac{a - b}{b}$, where 'a' is the extinction point for carbon dioxide-air atmospheres, and 'b' the extinction point for nitrogen-air atmospheres, bears some relationship to the amount of carbon dioxide present.

TABLE XXXVIII.

Combustible gas	In Extinctive Atmosphere (%)		$\frac{a - b}{b}$
	Carbon dioxide	Oxygen	
Methane	Nil.	b. 12.9*	.217
"	25	a. 15.7*	
Carbon monoxide	Nil.	b. 7.5	.506
" "	50	a. 11.3	

* Coward and Hartwell.

Referring again to Table XXXVII., it is of interest to note that the difference a-b has a minimum turning value at the saturation temperature 20° C.

SUMMARY - PART II.

The apparatus used to determine the extinction point of hydrogen flames was found to be quite unsuitable in the case of carbon monoxide flames.

The author has not found it possible, (a) to maintain a ten per cent excess of atmosphere, (b) to entirely sweep out the products of combustion, and (c) to prevent a greater transference of heat to the combustion chamber walls than in the case of hydrogen flames, simultaneously.

It was found necessary to select a relatively much larger combustion jet for this gas than for hydrogen, thus lowering the velocity of projection of the gas from the jet in order to maintain a flame.

The rate of flow of atmosphere was found to greatly exceed the 10 % excess originally aimed at in order to effectively sweep out the products of combustion and prevent the inflow of air from the external atmosphere to the combustion chamber. (p.p. 39, 49, 67, 88, and 122.)

The relatively low flame propagation speed of carbon monoxide-air mixtures rendered it necessary, in order to maintain a flame, to reduce the velocity of the gas-air mixture from the jet by means of a horizontal air flow. (p.p. 56, and 92.)

The temperature of the combustion chamber walls was found to have a very marked effect on the value of the extinction point; the higher temperature giving the lower extinction point. (p.p. 41, 86, 101, and 112 et seq.)

The effect of water vapour is very considerable and has been fully investigated. (p.p. 70, 80, 92, and 103 to 111.) The effect of drying the gases has also been demonstrated. (p.p. 70 to 74.)

The influence of the rate of flow of atmosphere has been investigated. (p.p. 88, and 118.)

The state of flow of the carbon monoxide, turbulent or streamline, was found to have a marked influence on flame maintenance. (p.p. 96 to 100.)

Carbon dioxide, when used in place of nitrogen as a diluent, was found to have a much greater inhibiting effect on combustion. (p.p. 124 to 130.)

The tendency of carbon monoxide flames to rise from, and float above, a jet, has been found to vary directly as the degree of saturation of the atmosphere with water vapour. (p.p. 82, 95, and 96.)

The optimum water vapour saturation temperature for air-nitrogen, and air-CO_2 atmospheres has been found to be 30° C. and 41° C., respectively. (p.p. 111, and 129.)

An interesting reaction between mercury and phosphorus was observed,; this is discussed in the Appendix. p.p. 154-156.

GENERAL CONCLUSIONS.

The determination of the extinction point of carbon monoxide has proved to be very much more difficult of achievement than that of hydrogen flames.

The influence of the temperature of the combustion chamber walls on the extinction point, together with the phenomenon exhibited by the carbon monoxide flame of floating upwards from the jet, necessitates a relatively large combustion chamber.

The heavy nature of the products of combustion, their effect on the extinction point value, and the necessity of having a large combustion chamber necessitate a relatively great supply, and speed, of atmosphere in order to sweep out these products.

From data given in Table VII., the velocity of combustible mixtures rising from the jet requires to be relatively low for flame maintenance in the case of carbon monoxide. The velocity of projection was reduced by using a wide jet, but it was found necessary in order to have the large rate of flow of atmosphere mentioned above, and the low atmosphere speed required for flame maintenance, to construct a combustion chamber in which the atmosphere flowed in a horizontal plane and converged to a point at the jet.

It was found necessary to fit an electrically heated spiral inside the combustion chamber in order to ignite the gas without otherwise disturbing the system.

The carbon monoxide used in later work was prepared from formic acid and sulphuric acid then stored over phosphorus. Phosphorus vapour was removed by passing the gas , on its way to the jet, through a scrubber containing cotton wool impregnated with a concentrated solution of silver nitrate.

The state of humidity of the reacting gases has been found to play a very important part in the value of the extinction point. In a somewhat parallel experiment to that of Traube$^{(3)}$ in 1895, the author has found that passing the reacting gases through single U-tubes freshly charged with $CaCl_2$, rendered the carbon monoxide noninflammable, even when atmospheric air, thus treated, was used. An estimation of the extinction point for gases thus dried gave the result 25.5 % of oxygen.

The effect of water vapour has been very fully investigated, and several attempts have been made to estimate it. The final estimation, using the apparatus shown in full in Fig. 48., and in sections in other Figures throughout this report, shows 4.6 % of water vapour, by volume, as giving the minimum value for the extinction point; this corresponds to the saturation temperature 31° C.

The temperature of the combustion chamber walls also greatly influences the value of the extinction point, as shown in

Table XXXIII., this necessitated the construction of a jacketed combustion chamber as shown in Fig. 38.

The influence of water vapour on combustion has, since Dixon's classical researches(16), proved a matter of great interest, and in recent years much attention has been devoted to this question, notably by Wheeler and his collaborators, in the various aspects of combustion. Dixon(18) investigated the influence of water vapour on the mean rate of flame propagation for CO-air mixtures, but did not explore the turning value, where water vapour in excess acts as a diluent. Later(20), Dixon showed that the maximum speed of detonation wave in a 2-1 CO-air mixture contained 6 % of water vapour by volume. Payman(19) has referred to, and gives examples of, the effect which water vapour has on the speed of uniform movement of flames for 50-50 CO-air mixtures. Dixon and Walls(21) give the maximum rate of explosion for a $CO-O_2$ mixture containing 5.5 % water vapour by volume. Payman and Wheeler(5) and (17) give the optimum condition for flame propagation in " Speed of uniform movement " experiments for CO-air mixtures as 6 % water vapour by volume, and in " Rate of developement of pressure " experiments for CO-air, 48-52, mixtures as 5.5 %.

The author has found the minimum extinction point for air-nitrogen atmospheres saturated with water vapour at 31° C., corresponding to 4.6 % water vapour by volume, and for CO2-air atmospheres 41° C., or 8.5 % water vapour by volume. These results are not comparable with the results given above for combustion in confined spaces with varying amounts of carbon dioxide present in the residual atmospheres, but the agreement between them is interesting.

The method of procedure and the apparatus used had to be continuously revised and altered as the work proceeded, due to the unfoldment of various influences which affect the value of the extinction piont. Much work has consequently been done which has no absolute value apart from its interest in illustrating the evolution of a method, and perfecting of an apparatus, with which the author feels assured the extinction point for any of the common combustible gases could be easily and accurately determined, as has been done in the case of carbon monoxide, which is very probably the most difficult extinction point to determine.

The apparatus used is fully illustrated throughout this thesis by means of sketches. The general assembly of the final apparatus used is shown in Fig. 48., the main parts of which are lettered as follows :-

A. and B.	CO generator (see Fig. 24.)
C.	CO wash bottles (see Fig. 24.)
D.	CO storage bottle (see Fig. 25.)
E.	Gray's constant pressure gas supply apparatus(12).
F.	Steam generator.
G. and H.	Combustion chamber (see Figs. 32 and 38.)

I.	Silver nitrate scrubber for removing phosphorus from CO (see Fig. 25.)
J.	Differential gauge for measuring CO.
K. and L.	Differential gauges for air and nitrogen.
M.	Mixing chamber for air and nitrogen.
N. and O.	Sampling device.
P.	Differential gauge for control of atmosphere supply.
Q.	Thermostat containing saturating towers, regulator, heating lamp, and stirrer (see Figs. 31, 32, and 47.)
R.	Thermostat electrical control diagram (see Fig. 47.)

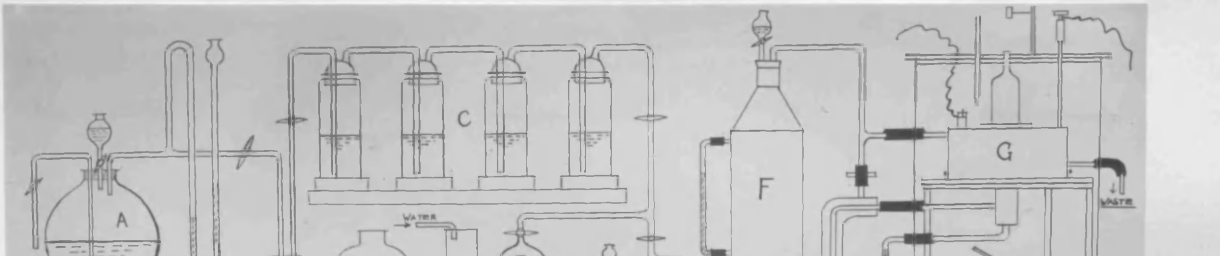


FIG. 48.

APPENDIX.

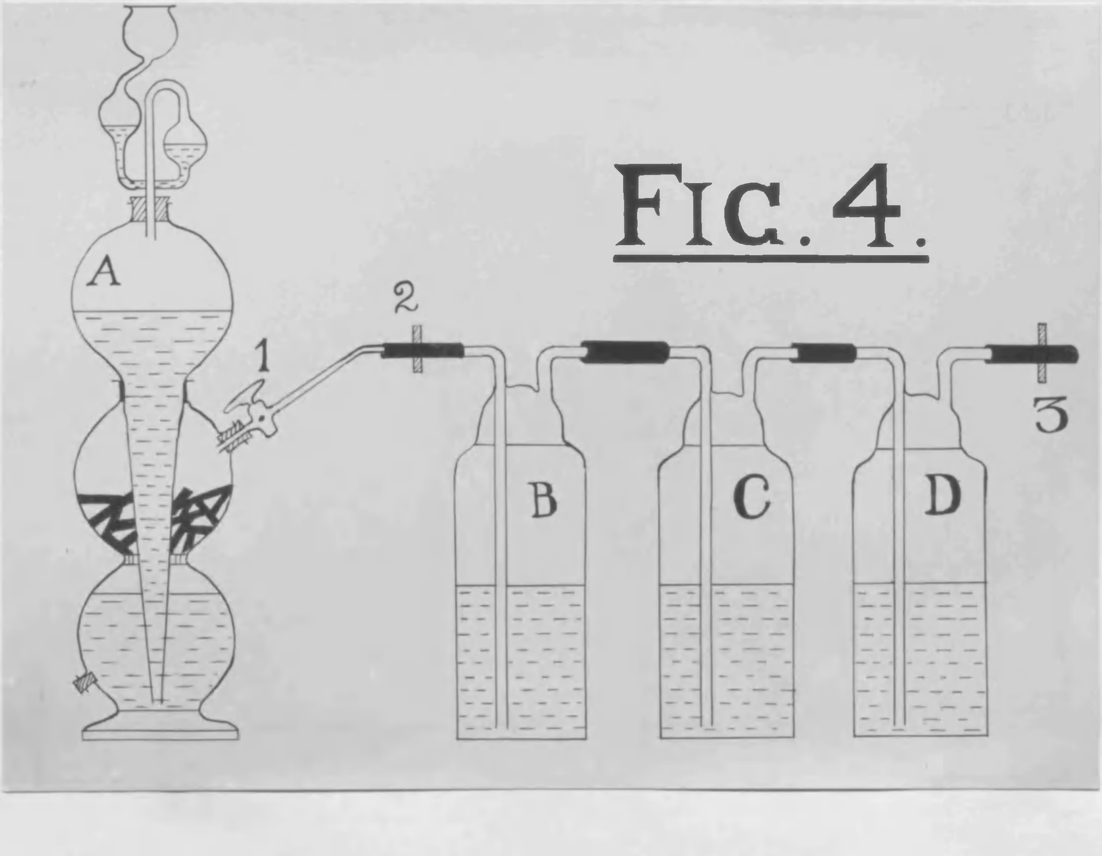


FIG. 4.

APPENDIX.

PREPARATION OF HYDROGEN.

The hydrogen used in all work with this gas was prepared from pure zinc and hydrochloric acid in a Kipp's apparatus, as shown in Fig. 4., in which :-

A is a 2 litre capacity Kipp's apparatus.

B is a wash bottle containing a 50 % solution of KOH.

C is a wash bottle containing a saturated solution of $KMnO_4$.

D is a wash bottle containing equal parts of 50 % KOH solution and 20 % pyrogallic acid solution.

"A" was charged with pure cast zinc rods and 15 % hydrochloric acid solution, the air thoroughly displaced with hydrogen, and then connected to the wash bottles from which the air was dispelled by a rapid stream of hydrogen. The screw clips (2) and (3) are provided so that the generator may be detached for recharging purposes without admitting air to the wash bottles.

PREPARATION OF CARBON MONOXIDE.

(a) From potassium ferrocyanide and concentrated sulphuric acid.

It was found that this required to be heated very strongly and that it caked very badly on cooling, thus introducing considerable risk of breaking the container on re-heating,

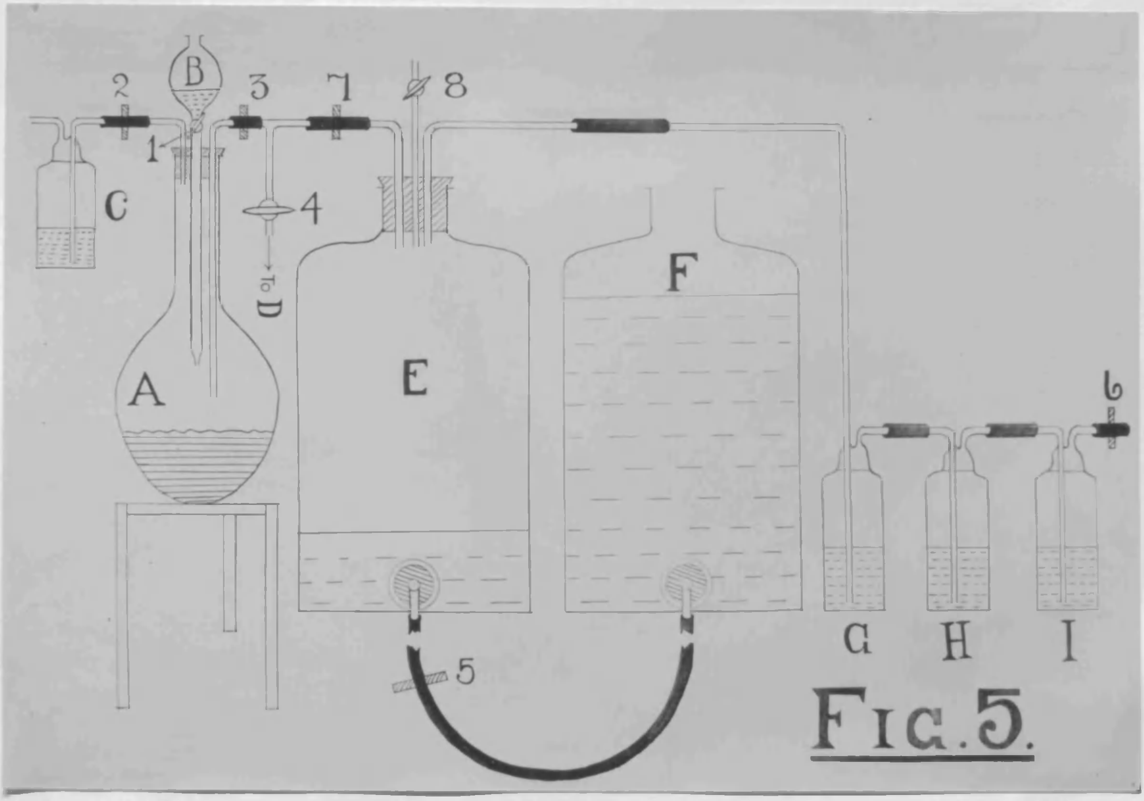


FIG. 5.

each time a fresh supply of gas was required. A further objection to this method is the formation of HCN with dilute H_2SO_4.

(b) <u>From potassium cyanide and sulphuric acic.</u>

This method proved quite satisfactory but was not adopted because of the evolution of HCN gas, which is generated almost quantitatively with dilute sulphuric acid.

(c) <u>From sodium formate and concentrated sulphuric acid.</u>

This method was at first considered to be very satisfactory but was finally abandoned because of the risk of air, associated with the sodium formate crystals, contaminating the gas. This method however was used in much of the earlier work and merits description.

The reaction appears to take place in three distinct stages, and is somewhat difficult to control, which necessitated ample provision being made for the storage of a sudden evolution of the gas.

Referring to Fig. 5, which shows the apparatus employed :-

A	is a 1 litre capacity Kjeldahl flask fitted with a three holed rubber stopper.
B	is a wash bottle containing water.
C	is a Kipp's apparatus charged with marble chips and 15 % hydrochloric acid solution for the generation of CO_2.
E	is a 5 litre capacity aspirator bottle connected at the bottom to a similar bottle "F" which may be raised or lowered according to requirements.

C. and H. are wash bottles containing a 50 % solution of KOH.

I. is a wash bottle containing equal parts of 50 % KOH solution and 20 % pyrogallic acid solution.

The numbers indicate stopcocks and screw clips.

Method of Procedure.

One pound of anhydrous sodium formate crystals is placed in "A" and the stopper, with fittings, tightly inserted, connections are then made as shown in Fig. 5.

(1) and (7) are closed and (2), (3), and (4) opened so that a stream of carbon dioxide, which can be visually observed in "C" and controlled by means of (4), is allowed to pass through the apparatus for some time till all air is judged to have been expelled. (2) is then closed and (1) opened to expel the air in "B". (1) and (4) are then closed and "B" filled with 98 % sulphuric acid.

(3), (5), and (7) are then opened and small quantities of sulphuric acid admitted until "E" is about half filled with gas, when (6) is partially opened and the gas allowed to impinge on a flame for some time until it is considered to be free from nitrogen (derived from air displaced from the wash bottles) (6) is then closed and connection is made with (5) -Fig. 1. - and a charge of gas thus obtained.

When "H" - Fig. 1. - is filled "E" acts as an auxiliary storage chamber for the gas evolved until the reaction stops. By raising "F" a pressure greater than atmospheric may be maintained in "A" during cooling, thus preventing any tendency toward an in-leak of air.

Freeing the apparatus from air by means of carbon dioxide which is subsequently absorbed in "G", "H", and "I" has two advantages :-

(1) It dispenses with the necessity of destroying, or otherwise disposing of, explosive mixtures of carbon monoxide and air during the expulsion of air from the apparatus.

(2) Economy in carbon monoxide each time the apparatus requires to be recharged.

This method, apart from the objection of air associated with the sodium formate crystals already cited, was found to be very satisfactory and easy to work.

(d) From formic acid and concentrated sulphuric acid.

Reference has already been made to this method. The apparatus used is sketched in Fig. 24, to which reference is made in the following description and method of manipulation.

Description of Apparatus, and Method of Manipulation.

Cocks (2), (8), and (4) are closed and (1) and (3) opened. The apparatus up to the cock (4) is then evacuated by means of an electric pump connected to "F" until the water in "H" has been boiling for some considerable time so that the water vapour displaces the last traces of air. (1) is then closed and the pump attached to "B".

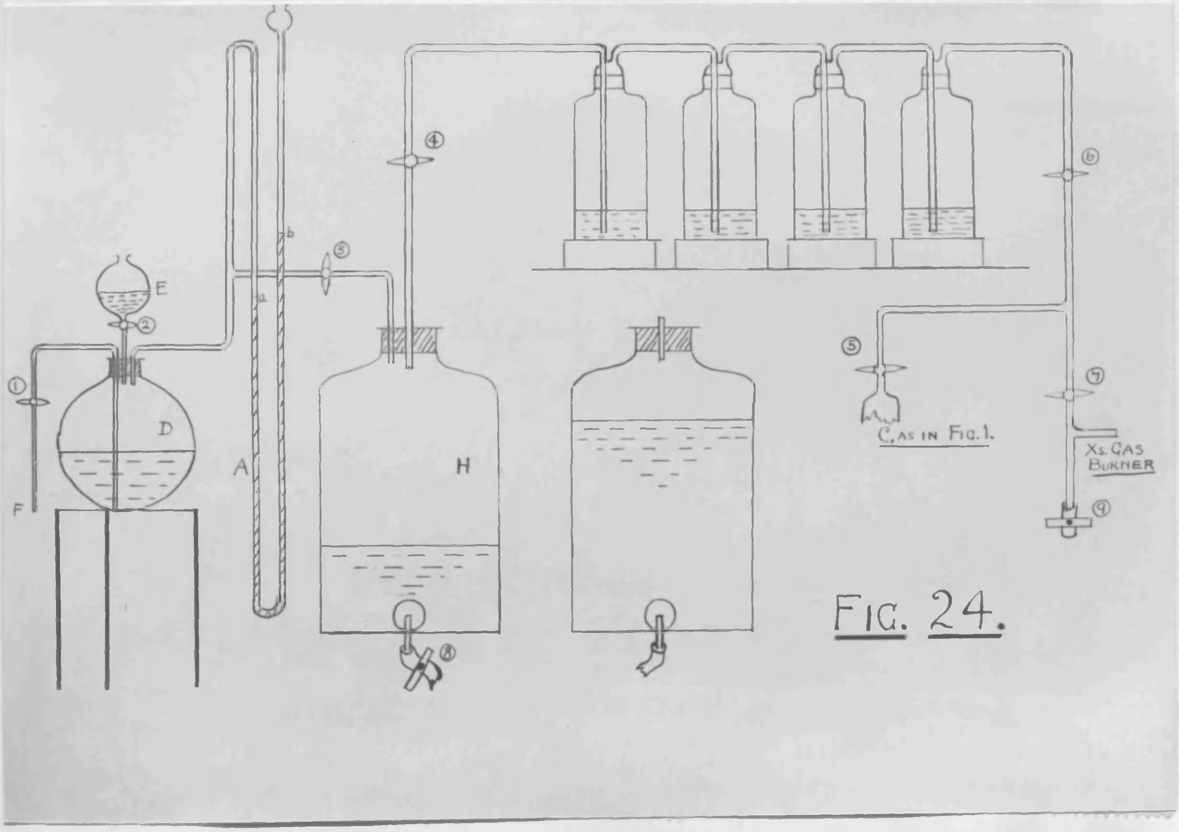


FIG. 24.

The cocks (4), (5), and (9) being closed, and (6) and (7) open, the other section of the system up to the cock (4) is evacuated for some time. (4) is then cautiously opened and evacuation continued for a time so that the water vapour displaces the last traces of air from the apparatus as before. (7) is then closed after which (2) is cautiously opened and "D" half filled with concentrated sulphuric acid.

"E" is then filled with 80 % formic acid and very small quantities periodically admitted to "D". When the pressure in the system exceeds atmospheric, as shown by the mercury in "A", (5) and (8) are opened and a charge of gas admitted to "H" - Fig. 1. - where it is stored over phosphorus (white sticks) contained in a tall vertical cylinder made from copper gauze.

Apart from the advantage this method has over (c), in which sodium formate is used, in using air free liquids, it has the very important advantage of being continuous since spent, or diluted, sulphuric acid in "D" can be discharged through "F" by raising the pressure in the system. In practice it has been found to operate continuously over a period of two years of almost constant daily use.

This method was found to be highly satisfactory.

PREPARATION OF NITROGEN.

As the nitrogen used did not require to be free from oxygen it was obtained from the suppliers in cylinders, discharged as required into a balanced gas holder, and used without purification.

METHODS OF SAMPLING EXTINCTIVE ATMOSPHERES.

The following methods of sampling were used at successive stages of the work in the order given.

(1) The sample was drawn into Orsatt's apparatus by means of a T-piece at (14) -Fig. 1. -, the combustion chamber circuit being first closed. This method was found to give very inconsistent results due to the fact that the altered conditions of pressure under which the sample was taken affected the relative amounts of air and nitrogen passing their respective jets in V and V' (Fig. 1.), so that the sample was neither representative of the extinctive atmosphere nor was the method consistent.

(2) In this method the gas from "X" (Fig. 1.) was continuously passed through the Orsatt measuring burette on its way to the combustion chamber, as shown in Fig. 6. p. 10. It was found that the gas could not be passed through the whole of the capillary branch arm because of the great resistance this offered to the gas, and the consequent increase in pressure which this would necessitate.

In Fig. 6. (See page 10) :-

A is a 250 c.cm. levelling bottle containing mercury.

B is the Orsatt measuring burette.

C is the Orsatt levelling bottle containing water.

During the course of an estimation of the extinction point the water level is maintained at 'b', so that there is a free passage for the gas through "B", which is placed in the circuit between "X" and "Z" (Fig. 1.) in place of the arrangement shown. When it is required to take a sample the connection to "X" is closed then (1) is opened and the mercury level raised to 'c'. (3) is then opened and the level of the water raised from 'b' to the zero graduation on the Orsatt burette, thus enclosing the sample at atmospheric pressure in the usual way.

Apart from the objections of not being able to duplicate an analysis, and the limits of accuracy of the Orsatt method of analysis, this method proved quite satisfactory.

(3) When greater accuracy was considered to be legitimate, it was necessary to devise some other method of sampling whereby the sample could be obtained in the usual form of sampling tube, for use in conjunction with Haldane's gas analysis apparatus, which was selected for more accurate work.

The straight passage of the gas through the capillary connections of a sampling tube presented the same difficulty as was experienced in (2), above, and had to be discarded on this account.

(4) This method is described on p. 18., and the sketch of the apparatus used is incorporated in Fig. 1.

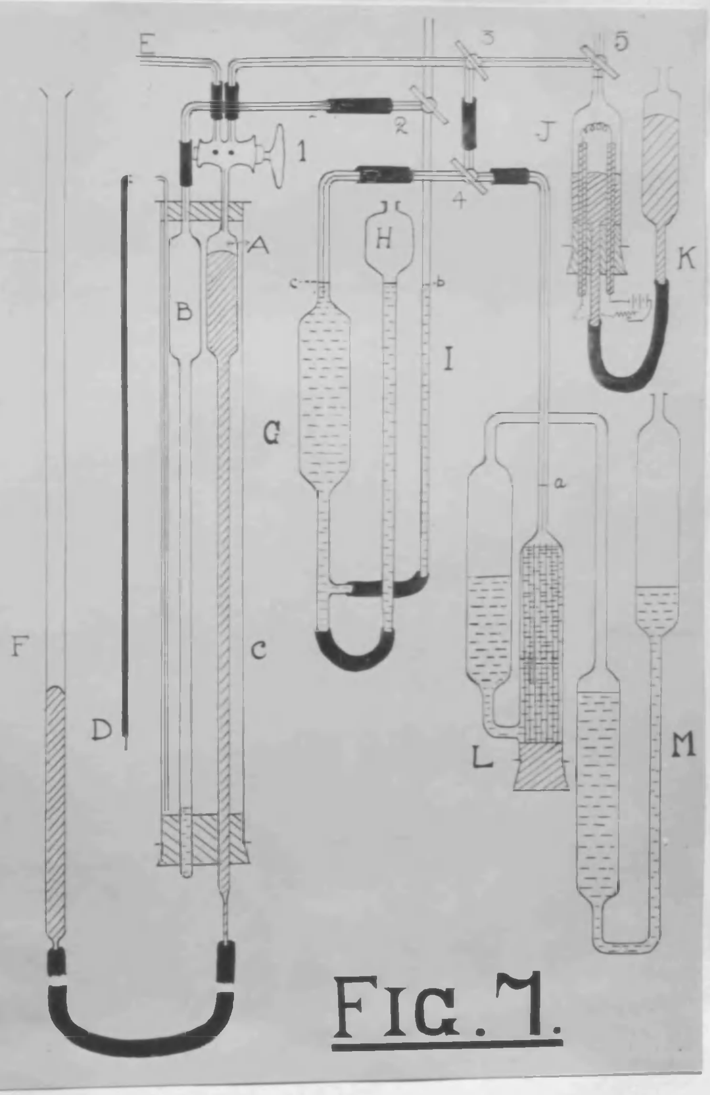


FIG. 7.

METHODS OF ANALYSIS.

The preliminary analyses in the case of hydrogen extinctive atmospheres were carried out by means of Orsatt's apparatus. In all subsequent work Haldane's apparatus, or necessary modifications of it to suit prevailing conditions, has been used.

For convenience in reference a diagramatic sketch of this apparatus is shown in Fig. 7., the stopcocks being numbered and the individual parts lettered as follows :-

A is a measuring burette of 20 c.cm. capacity, the volume of the bulb being 15 c.cm. and that of the stem 5 c.cm. The latter is graduated in 0.01 c.cm. divisions, and readable by means of a lens to 0.001 c.cm.

B is a similar tube to "A" but is not graduated. This acts as a compensating tube to correct for temperature changes during the course of an analysis.

C is a water jacket surrounding "A" and "B" through which air may be blown for mixing purposes by means of "D".

E is the connection for attaching the sampling tube to.

F is a levelling tube connected to "A" through a stopcock, not shown, and is partially filled with mercury.

G is an absorbtion pipette containing a 50 % solution of KOH.

H is a levelling tube connected to G.

I is a capillary tube which, by means of the three way T-stopcock (2) may either be connected to "B", or to "B" and the atmosphere at the same time.

J is a combustion pipette containing a spiral of fine gauge platinum wire which may be heated by means of the external electrical circuit shown.

K is a levelling tube connected to "J" and containing mercury.

L is the absorbtion pipette for oxygen containing (1) equal volumes of 50 % KOH solution and 20 % pyrogallic acid solution or (2), straight vertical sticks of white phosphorus in water.

M is a water seal for "L".

METHOD OF CONDUCTING AN ANALYSIS.

(1) Using alkaline pyrogallate solution.

Connection is established between "A" and "L", and "F" is adjusted to bring the liquid in "L" to the mark 'a'. Connection is then made, by means of (4), between "A" and "G", (2) is then opened to the atmosphere and the level in "I" is brought to the mark 'b' by means of "H". "I" is then connected to "B" by means of (2). The liquid in "G" is brought to the mark 'c' by adjustment of "F". (1) is then opened to "E", and "F" is raised till the connections up to and including the sampling tube, not shown, are filled with mercury.

The sampling tube cock is now opened to "A", "F" lowered, and the desired volume of gas admitted to "A". (1) is then closed.

The level in "A" and "F" is made as nearly as possible the same, and (1) is then opened to "G". Air is blown through "C" for a short time and the level 'c' adjusted, the volume of gas in "A" is then read and noted.

By means of (4) and by manipulation of "F" the gas is passed ten times between "A" and "G", three times into "L", and five times into "G" successively to remove any oxygen in "L" which may have been inadvertently admitted during the process of adjusting the level 'c' immediately prior to taking the volume reading. The gas is now retained in "A", the water in "C" mixed by means of a current of air as before, and after a short lapse of time the levels 'a', 'b', and 'c' are adjusted as before and the volume of gas in "A" read and noted.

The above process is repeated until constant readings are obtained, and the analysis is conducted in duplicate.

(2) Using white phosphorus.

Reference has been made to this method (p. 110.), and to the circumstances which led to its adoption.

Investigation :- (1) Foreign matter in Haldane burette.

The ease with which mercury when treated with impure ether (containing sulphur compounds) formed a black compound, as observed in an earlier attempt to wash the mercury free from grease etc., suggested that the sulphur in the vulcanized rubber

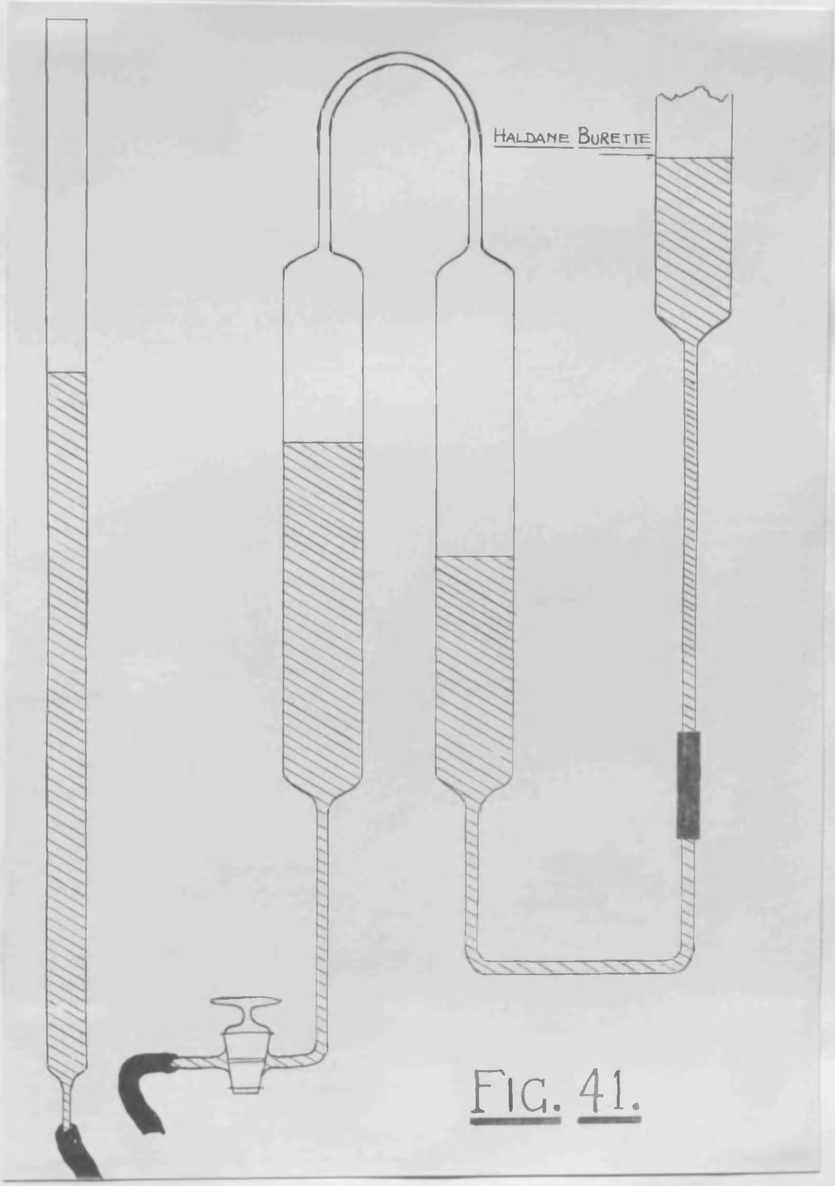


FIG. 41.

between the levelling tube and the burette of the Haldane apparatus, was forming mercuric sulphide with the mercury. The interior walls of this tube were varnished with collodion and allowed to dry, but this did not prevent the formation of foreign matter in the burette.

Finally, in order to prevent the occurrence of foreign matter, derived either from the mercury or from the rubber tube, the air cushion arrangement shown in Fig. 41. was fitted between the levelling tube and the burette by means of the butt-end connection "A", and freshly distilled mercury was placed in the burette.

Foreign matter was again observed after a few analyses had been carried out, thus definitely proving that the dirt was being formed by the interaction of phosphorus vapour, P_2O_5, phosphorus, mercury, water vapour, and dilute sulphuric acid, or some combination of these.

Phosphorus pentoxide when allowed to stand in contact with mercury in an open vessel appeared to have no effect. A small piece of phosphorus added to this system produced no visible effect. When however a quantity of clean mercury and phosphorus were placed in separate containers in a desiccator containing water the following observations were made.

(1) After 2 hours a faint fume of phosphorus pentoxide filled the desiccator, and the surface of the mercury was dimmed.

(2) After 24 hours the surface of the mercury was bright and covered with very small water white beads of liquid (phosphoric acid).

(3) After 72 hours the surface of the mercury was quite dry and a heavy film of a solid substance with a metallic lustre was observed.

Subsequently, in conducting an analysis in a darkened room, phosphorescent flashes were observed in the Haldane measuring burette and in tha capillary connections to the phosphorus pipette, and particularly vivid phosphorescent flashes were observed at the surface of the mercury and at the surface of particles of foreign matter in the burette.

It was further noted that, after complete removal of oxygen from the Haldane apparatus and the introduction of a fresh sample, containing oxygen, to the burette, there was a slight fume formed at the surface of the mercury. When this experiment was conducted in the dark a bright glow was observed in the immediate locus of the mercury surface, and at the surface of particles of foreign matter adhering to the walls of the burette.

From what has been said it is apparent that the cause of the dirt observed in the Haldane burette is a reaction between mercury and phosphorus vapour in which phosphorus pentoxide and dilute sulphuric acid may or may not take part, and that the compound so formed can react with oxygen in much the same way as phosphorus, to give a solid body which is incapable, under normal conditions, of further reaction with oxygen. No published reference to this compound could be found.

(2) <u>Water (dilute H_2SO_4) in Haldane burette.</u>

Apart from the effect which small amounts of aqueous liquids were found to have in congregating particles of dirt into small lumps, and the capillary forces of such liquids which cause these lumps to adhere to the walls of the burette, there are two important considerations :-

(a) The influence of water on the formation of the solid phosphorus-mercury compound, of which little was known.

(b) The error introduced in measuring, as gas, the small quantities of liquid in the burette.

The minimum volume of dilute sulphuric acid necessary to wet the walls of the burette was found to be of the order 0.03 c.cm. If this volume remained constant, the error due to its presence would only be 0.03 in 20, or 0.15 %, and in an estimation of an extinction point of say 10 % oxygen, would only represent an error of 0.01 in the result (9.99 instead of 10.00). If however, and this is easily possible, the liquid, measured as gas, in the first reading is 0.06 c.cm., and in the second, due to wetting of the surface of the burette below the surface of the mercury etc., the liquid measured as gas is 0.03 c.cm., this will give an additional error of 0.03 c.cm.

in a total contraction of 2 c.cm. i.e. an error in the result of 0.10.

In all probability errors of even greater magnitude could have been attributed to this cause, but unless some other means of maintaining the water vapour in the gas constant could be found, errors of a much greater order would be introduced by the exclusion of water vapour from the burette. A compromise was made as described in the following method.

Method of Conducting an Analysis.

Referring to Fig. 7. :- The sample is taken into "A" which is thoroughly dry, and immediately passed into "G" which is filled with water, and retained there for a few minutes, then passed backwards and forwards between "A" and "G" several times to ensure its saturation with water vapour at the temperature of "G", which is always slightly higher than the temperature of "A". The sample is then retained in "A" for a few minutes to allow it to assume the temperature of the water in "C", then the level at 'c' is adjusted and the volume read.

The water in "G" is next raised from the level 'c' so as to just fill the tubulure of the stopcock (4) which is then connected to "L" and the sample passed over to "L" and allowed to remain till most of the phosphorus pentoxide fume is dissolved. The sample is then taken back to "A" in order to sweep out the capillary connections, then passed to "L" and again allowed to remain till the fume has dissolved. This process is repeated until no further fume is observed.

The sample is next saturated with water vapour in "G" as already described, and finally measured in "A". When a fresh sample is to be analysed the burette "A" is rinsed out with atmospheric air in order to render inactive any of the phosphorus-mercury compound which reacts with oxygen.

When the above method was strictly adhered to, splendid duplicate analyses were obtained, and no difficulty was experienced in keeping the walls of the burette clean; whether this is due to the avoidance of the surface tension and congregating effects of the moisture on the phosphorus-mercury compound, or to the inhibiting action of the absence of moisture on this compound's formation, has not been definitely ascertained.

The foregoing method was used in all later work with carbon monoxide flames.

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