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PRESENTED BY JOHN MACFIE HOLM B.Sc.,

RESEARCH STUDENT IN THE NATURAL PHILOSOPHY DEPARTMENT.

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On the Ignition of Explosive Gaseous Mixtures by Small Flames.

By John M. Holm. B.Sc., Carnegie Scholar in the Natural Philosophy Department of the University of Glasgow.

Introduction.

Since 1815 it has been known that the flame of an explosive gaseous mixture will not travel along a tube containing the mixture when the diameter of the tube is small, but nevertheless finite. This fact, which was discovered by Sir Humphrey Davy, was the starting point of the invention of the safety lamp which bears his name.

Davy[1] found that with methane-air mixtures, no flame would propagate along a metal tube less than 1/7 inch in diameter and that metal tubes were more effective than glass ones in preventing flame propagation. He also observed that the addition of an inert gas, such as carbon dioxide or nitrogen, reduced the explosibility of the mixture. From these and similar experiments, he deduced that the effect of the tubes and the inert gases in preventing propagation depended on their cooling powers, ie. on their thermal conductivity. Hence it was easy to explain why the metal tubes extinguished the flame more readily than the glass ones.

The idea that the limiting diameter of tube just sufficient to prevent flame propagation, depends to a

considerable extent upon the thermal conductivity of the tube, is, the writer believes, fairly widely accepted. It must be admitted that, at first sight, it is a very reasonable assumption to make. Thus Messrs W. Payman and R.V. Wheeler[2], when investigating the increase of uniform flame speed with diameter of tube, came to the conclusion . . . "that the higher the coefficient of conductibility of the material of which tubes of small diameter are made . . . the larger is the diameter of tube capable of preventing the spread of flame in any mixture."

Although Mallard and Le Chatelier[3] found that the velocity of uniform flame propagation in a tube of given diameter was independent of the material of which the tube was made and therefore of the thermal conductivity or cooling effect of the walls, yet they came to the rather paradoxical conclusion that the decrease in flame speed observed with a decrease in diameter of tube, was caused by the increased cooling effect of the walls. They showed however, that the diameter of tube necessary to extinguish the flame of a given mixture was smaller, the greater the flame velocity in the mixture.

It would appear from the experiments described in Part II, that the above assumption was not justified, ie. that the limiting diameter of tube just great enough to allow

flame propagation to take place, is determined primarily by the thermal conductivity of the walls of the tube. In these experiments it has been found that, for every explosive mixture examined, the limiting diameter for copper and glass tubes is the same, with a maximum error of 2.5% . Thus it is difficult to believe that the extinction of the flame depends largely upon the cooling effect of the walls, since altering their thermal conductivity in the ratio of about 460 : 1 does not change the limiting diameter for a given mixture by more than 2.5 %.

A similar phenomenon arises in the case of spark ignition. The theory of this has been successfully developed by Professor E. Taylor Jones, Dr. J.D. Morgan and Professor R.V. Wheeler[4] upon the assumption that general ignition of the mixture depends on the volume of gas which the spark, by its own heat, can raise to the ignition temperature of the mixture. The underlying idea[5] is that when the radius of the spherical flame starting out from the spark is very small, the ratio of the rate at which heat is being lost by conduction from the flame surface, to the rate at which heat is being produced inside the flame by the chemical combination, is very large. Hence unless the radius of the sphere exceeds a certain minimum value, the small flame will fail to spread throughout the gas and produce general ignition, since it will be extinguished by too rapid conduction from its surface.

The energy of the minimum spark required for ignition is thus the balance of heat which is necessary to keep the surface of the flame at the ignition temperature as the flame spreads out to the minimum radius where it becomes self-supporting and can propagate indefinitely by its own heat. The actual value of the radius of the maximum sphere which can be raised to the ignition temperature by a condenser spark without producing general ignition, has been determined experimentally by Messrs Coward and Meiter[6] and found to be about .62 mm. for an 11.2% methane-air mixture. The value of the radius as calculated by Messrs Jones, Morgan and Wheeler[4] was about .91 mm., which is of the same order of magnitude.

A similar explanation could be applied to the popular form of petrol lighter. If the spark from the flint and steel does not contain sufficient heat to enable the flame to propagate out to the limiting diameter, no general ignition of the petrol vapour is produced. It is exceedingly interesting to note that, previous to the introduction of the Davy and similar safety lamps, a glimmering light was obtained in dangerous coal mines from flint and steel mills[7]. By pressing a piece of flint against the periphery of a rapidly rotating steel disc, a stream of glowing particles in quick succession was produced. The success of the method was due to the comparatively high ignition temperature and low flame speeds of methane-air mixtures. The mills were known to be dangerous

to use in atmospheres containing hydrogen.

From these phenomena it is evident that the cooling effect of the unburnt gas in contact with the outer flame surface is sufficient to extinguish the flame when its radius is small, and it is suggested that the same effect is the primary cause in preventing propagation along narrow tubes, or through small apertures in thin plates.

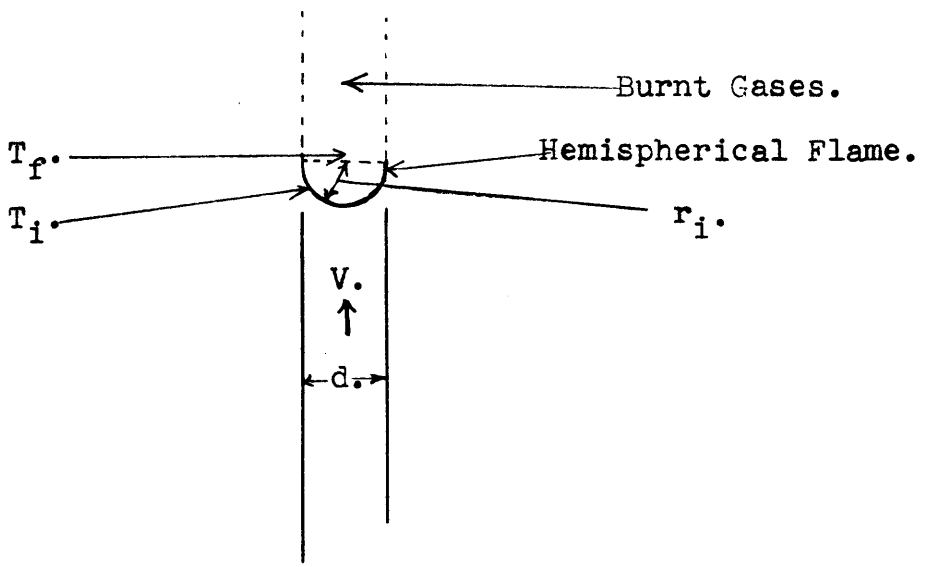
When a flame is travelling along a tube of diameter slightly greater than that necessary for propagation, the flame is, with the exception of those in mixtures approaching the usual lower limit of inflammability, practically a hemisphere of radius slightly less than that of the tubes. See Plate I, (d), page 36 . It is evident that the flame can never actually touch the surface of the cold tube, as that would involve an infinite temperature gradient. Thus the flame is not cooled by the material of the tube directly, as it is always separated from its surface by a layer of usually unburnt gas. The chief effect of reducing the diameter of the tube is to force the flame to burn as a smaller hemisphere, which is therefore more effectively cooled by the gas in contact with its external surface. The presence of the tube will affect the distribution of temperature from the flame surface, not primarily on account of its thermal conductivity, but because it presents a finite boundary which is maintained at practically the temperature of the cold unburnt mixture.

A formula connecting the limiting diameter for

propagation along tubes with various constants of the gaseous mixture can be derived in the following manner from the above hypothesis. While it is not claimed to be anything more than a first approximation, it certainly indicates correctly the manner in which the limiting diameter changes with the constants involved and on calculation yields a result which is of the required order of magnitude.

Suppose we have a vertical tube of diameter d, up which a steady stream of explosive mixture is passing with velocity V. Let the velocity be such that it will permit a self-supporting flame to burn at the top of the tube. If the velocity V, is just slightly greater than v, the velocity of the flame down the tube through the stationary mixture, then this flame is approximately a hemisphere of radius r_i, slightly greater than that of the tube. When V is reduced, the flame contracts and travels slowly down the tube when V is just less than v and r_i is slightly less than d/2.

Fig. I.



If d is just less than the limiting diameter for propagation, then the hemispherical flame goes out abruptly when the rate of flow is still finite[+] and the radius of the flame is approximately equal to that of the tube. In this case , if the concentration of the mixture is not greater than that for theoretically complete combustion, the lowest point of the flame does not sink below the level of the top of the tube.

Let T_o be the temperature of the unburnt gaseous mixture and T_i its ignition temperature, which must therefore be the temperature of the surface of the hemispherical flame. Let Q be the total quantity of heat evolved when 1 cc. of the mixture at temperature T_o and atmospheric pressure is burnt at constant (atmospheric) pressure and let $\bar{C}_p$ be the mean specific heat of the products of combustion between T_o and T_f, the mean temperature of the burnt gases escaping through the plane surface of the hemisphere. Let k be the thermal conductivity of the gaseous mixture at T^oC.

Consider the heat produced inside this hemispherical flame in a short interval of time dt. Assuming that all the gas escaping from the tube is burnt inside the flame, which is probably true for the small rates of flow employed and for mixtures not too rich in combustible gas, the heat produced from this source is

$$\pi \frac{d^2}{4} V Q \, dt.$$

+ See proof on page 68

The quantity carried out of the hemisphere by the upward flow of the burnt gases through the circle of radius r_i, is

$$\pi \frac{d^2}{4} V \, dt \, \bar{C}_p \, (T_f - T_o).$$

The quantity lost by conduction through the spherical surface of the flame is

$$- 2 \pi r_i^2 \left[k \frac{\partial T}{\partial r} \right]_{r=r_i} .dt,$$

where T is the temperature at a distance r from the centre of the hemisphere. This assumes that the distribution of T is spherically symmetrical.

There will be practically no conduction of heat through the plane surface of the hemisphere, since the temperature gradient will be almsot zero there.

It is obvious that the flame cannot continue to exist if the rate at which heat is being produced inside its volume is less than the rate at which it is being lost through its external surface. If the rate of generation is greater, then the flame is easily self-supporting and the limiting condition when the flame is on the point of being extinguished is given by

$$d^2 V Q = d^2 V \bar{C}_p (T_f - T_o) - 8 r_i^2 \left[k \frac{\partial T}{\partial r} \right]_{r=r_i} \quad . . . (1).$$

The exact determination of the heat lost by conductio from the hemispherical flame is decidedly difficult and rather

ideal conditions have to be assumed. These assumptions make it impossible to obtain the exact numerical value of the limiting diameter in any particular case, but still give a formula which is substantially correct.

To calculate the temperature gradient $\frac{\partial T}{\partial r}$, consider the flame to be a sphere of radius r_i maintained at the constant temperature T_i. The equation for the spherically symmetrical conduction of heat in the steadily state is

$$\frac{\partial}{\partial r} k r^2 \frac{\partial T}{\partial r} = 0 \quad \ldots\ldots\ldots\ldots\ldots (2).$$

Let k, the thermal conductivity of the mixture at temperature T, be f(T) and let

$$\int f(T)\, dT = F(T) \quad \ldots\ldots\ldots\ldots\ldots (3).$$

Integrating (2) twice with respect to r and eliminating the constants of integration by substituting

$T = T_i$ when $r = r_i$

and $T = T_o$ when $r = \infty$,

we obtain

$$F(T) = \frac{r_i}{r}\left\{F(T_i) - F(T_o)\right\} + F(T_o) \ldots (4)$$

Therefore on differentiating,

$$k \frac{\partial T}{\partial r} = -\frac{r_i}{r^2}\left\{F(T_i) - F(T_o)\right\} \ldots\ldots\ldots (5)$$

Let $\bar{k}$ be the average value of the thermal conductivity of the mixture between the temperatures T_o and T_i.

Therefore $$\bar{k} = \frac{F(T_i) - F(T_o)}{T_i - T_o} \quad \ldots\ldots\ldots (6).$$

Substituting in (5),

$$\overline{k \frac{\partial T}{\partial r}}_{r=r_i} = - \frac{\bar{k} (T_i - T_o)}{r_i} \quad \ldots\ldots\ldots (7).$$

Hence we have on substituting from (7) in (1),

$$d^2 V \left\{ Q - \bar{C}_p (T_f - T_o) \right\} = 8 r_i \bar{k} (T_i - T_o)$$

If V is reduced to v, the velocity of propagation along the tube, the radius of the flame falls to practically that of the tube and will travel down the tube if

$$d > \frac{4 \bar{k} (T_i - T_o)}{v (Q - \bar{C}_p (T_f - T_o))} \quad \ldots\ldots\ldots (8)$$

When the right hand side of (8) is greater than the left, the flame is not self-supporting and therefore is extinguished. Thus the limiting diameter necessary for propagation is given by

$$d = \frac{4 \bar{k} (T_i - T_o)}{v (Q - \bar{C}_p (T_f - T_o))} \quad \ldots\ldots\ldots (9)$$

where v is the limiting value to which the velocity of propagation approaches as the diameter of tube tend to the limiting diameter. See page 68.

The formula indicates the manner of variation of the limiting diameter fairly successfully. Thus d decreases with increase of velocity of propagation, which is in agreement with Mallard and Le Chateliers' observations and also with those described in Part II. Also d will increase if the thermal conductivity of the mixture increases, which is necessary since the efficiency of the cooling by conduction will then be greater. It also indicates that gases having low ignition temperatures, will, ceteris paribus, pass through tubes of smaller diameter.

The limiting diameter is infinite if

$$Q = \bar{C}_p(T_f - T_o) \quad \ldots\ldots\ldots\ldots (10)$$

that is, if all the heat from the chemical reaction is contained in the burnt gases. Provided the average flame temperature is known, this gives a method of calculating the usual limits of inflammability, which are determined in tubes of large diameter. Alternatively, if the concentration of the inflammable gas at the usual limits of inflammability are known, the average flame temperature at these limits can be found.

In some mixture, probably those in which the thermal conductivities of the components are practically identical, the maximum flame speed occurs at nearly the same concentration as the maximum of Q, ie. at c_o , the concentration for theoretically complete combustion. Thus with methane-air

mixtures, the maximum flame speed is obtained at a concentration between 9.5 and 10.0 %, whereas the mixture for maximum Q is

$$CH_4 + 2\,O_2 + 7.52\,N_2 ,$$

or 9.51% methane by volume. The minimum limiting diameter for propagation in these mixtures is obtained at 9.63 %.

When we start to calculate the absolute value of the limiting diameter given by equation (9), in any particular case, we are faced with the problem of obtaining the correct values of the constants at the high temperatures involved. The greatest difficulty is experienced with $\bar{k}$, the mean thermal conductivity of the mixture between room temperature and its ignition temperature. It would appear that, up to the present, all measurements of k have been made at temperatures below 100°C. The usual way of expressing the result is

$$k = k_o(1 + \alpha T) \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

where k is the thermal conductivity at T°C. Thus Gregory and Archer[8] give for air,

$$k_o = .0000583$$

and $\alpha = .00297$ in C.G.S. units over the range from 7 to 12°C, while Schneider[9] finds

$$k_o = .00059$$

and $\alpha = .00395$ over the range from 8 to 40°C.

As will readily be observed, there is a considerable discrepancy between the two values of α, which suggests

that α increases fairly rapidly with temperature. If this is true then the following calculation will give values of d which are too small. For lack of a better value at present, the thermal conductivity of methane will be assumed to be the same as that of air.

The values of the mean specific heats of the gases involved have been found from the tables given by Messrs J.R. Partington and W.G. Shilling[10]. These tables extend up to about 2000°C in most cases.

In order to calculate the limiting diameter for the theoretical methane-air mixture

$$CH_4 + 2O_2 + 7.52N_2 = CO_2 + 2H_2O + 7.52\ N_2 \quad . \ . \ .(12)$$

the following values have been used,

T_i = Ignition Temperature = 750°C.[11]

T_f = Average Flame " = 1670°C.[12]

T_o = Room " = 1670°C. ~~C.~~ °C.

= 18°C.

Heat of combustion of 1 gm. mol. of methane = 212.10^3 cal.[13] when burnt completely to carbon dioxide and water at 18°C.

Therefore for this 9.51 methane-air mixture,

$$Q = Q_o = \frac{212.10^3 . 273 . 9.51}{22.4 10^3 . 291 . 100}$$

$$= .844 \text{ cal./ cc. of mixture at } 18^\circ\text{C.. (13}$$

From the specific heat tables, the amount of heat evolved when the gases on the right hand side of (12) are

cooled down from T_f to T_o is found to be 164,300 cal., ie. for 10.52 gm. mol. of unburnt mixture.

$$\text{Therefore } \bar{C}_p(T_f - T_o) = \frac{164,300. 273}{22,400. 291. 10.52}$$

$$= .654 \text{ cal./ cc.}$$

Assuming that the formula

$$k = k_o(1 + \alpha T)$$

can be extrapolated up to 750°C, which is rather doubtful, we have,

$$\bar{k} = k_o(1 + \alpha/2(T_i + T_o)$$

$$= .0001248 \quad \text{using Gregory and Archers' value}$$

$$= .0001483 \quad \text{using Schneider's value.}$$

The limiting value, v, to which the velocity of propagation tends as the diameter of the tube approaches the limiting diameter has been determined by Bunsen's method. A detailed description of the experiments is given in Part II, page 68. The results show that the velocity of propagation tends to a finite value at the limiting diameter, and that the velocity of the mixture which is just sufficient to maintain a self-supporting flame at the top of tubes whose diameter is less than the limiting diameter, also tends to this value at the limiting diameter. For a 9.5% methane-air mixture, this value was found to be 14.0 cm/sec..

Hence we have from equation (9),

$$d = 1.37 \text{ mm. using Gregory and Archers' value for } k$$

A more reliable formula for the calculation of $\bar{k}$ is given in the International Critical Tables and is

$$k_\theta = \frac{k_{273}(273 + C)\ \theta^{\frac{3}{2}}}{(\theta + C)\ 273^{\frac{3}{2}}}$$

where k_θ is the thermal conductivity at θ°Abs., and C is a constant which has the value of 125 for air.

Using Gregory and Archer's value for k_{273}, this reduces to

$$k_\theta = .000005144\frac{\theta^{\frac{3}{2}}}{125 + \theta} = A\frac{\theta^{\frac{3}{2}}}{125 + \theta} \quad \text{say.}$$

In order to find $\bar{k}$ we must calculate the value of

$$\int k_\theta d\theta \quad \text{over the range for } \theta_1 = 273 + T_o$$
$$\text{to } \theta_2 = 273 + T_i.$$

By substituting $\theta = C\psi^2$ we obtain

$$\int k_\theta d\theta = 2AC^{\frac{3}{2}} \int \frac{\psi^4}{1 + \psi^2} d\psi$$
$$= 2AC^{\frac{3}{2}} \int \left\{\psi^2 - 1 + \frac{1}{1 + \psi^2}\right\} d\psi$$
$$= 2AC^{\frac{3}{2}} \left\{\frac{\psi^3}{3} - \psi + \tan^{-1}\psi\right\}$$

Hence on substituting $T_o = 18^\circ C$ and $T_i = 750^\circ C$, we have for $\bar{k}$

$$\bar{k} = \frac{\int_{\theta_1}^{\theta_2} k_\theta d\theta}{\theta_2 - \theta_1}$$

$$= .0001084 \text{ C.G.S.U.},$$

against $\bar{k} = .0001248$ as calculated from

$$k = k_o(1 + \alpha T).$$

This new value of $\bar{k}$ gives

$$d = 1.19 \text{ mm.}$$

and $d = 1.64$ mm. using Schneider's value for k.

The actual limiting diameter for a 9.5% methane-air mixture has been found to be 3.80 mm..

Thus the formula gives the correct order of magnitude for the diameter but the actual value is too small. The uncertainty of the value of k at high temperatures and the ideal conditions assumed for the calculation of the cooling by conduction from the flame surface would probably account for this discrepancy.

Let us apply equation (10), ie

$$Q = \bar{C}_p (T_f - T_o) \quad \ldots\ldots\ldots\ldots\ldots (10)$$

to calculate the percentage of methane in the methane-air mixture at the usual lower limit of inflammability.

If c is the percentage by volume of methane in the mixture, then one gm. mol. can be represented by

$$\frac{c}{100} CH_4 + \frac{100-c}{476} \{ O_2 + 3.76 N_2 \} \quad \ldots\ldots\ldots (14).$$

which gives on combustion,

$$\frac{3.76}{4.76} N_2 + \frac{1}{4.76} O_2 + \frac{c}{100} \{ CO_2 + 2H_2O - \frac{10.52}{4.76} O_2 - \frac{3.76}{4.76} N_2 \} \quad (15).$$

The calculation of the amount of heat evolved when this latter quantity of burnt gas is cooled down from T_f to T_o is simplified by the fact that the specific heats of

nitrogen and oxygen are identical. See Partington and Shilling[12]

Let $\bar{C}_{pn}$ and $\bar{C}_{pc}$ be the mean specific heats per gm. mol. of nitrogen and oxygen between T_f and T_o and let $\bar{C}_{ps}$ be the mean specific heat of steam between T_f and 100^oC.

Since (15) are the products of combustion of 1 gm. mol. of the mixture, we have

$$\bar{C}_p(T_f - T_o) = \frac{1}{V}\left\{\left[\bar{C}_{pn} + \frac{c}{100}\left(\bar{C}_{pc} - \frac{14.28}{4.76}\bar{C}_{pn}\right)\right](T_f - T_o) + \frac{2c}{100}\left[\bar{C}_{ps}(T_f - 100^o) + L + 18(100 - T_o)\right]\right. \quad \ldots\ldots (16)$$

where V is the volume of 1 gm. mol. at T_o and normal pressure and L is the latent heat of steam per gm. mol..

For given values of T_f and T_o we can evaluate the right hand side of (16) from the specific heat tables referred to above.

If we assume as before, $T_f = 1670^oC$ and $T_o = 18^oC$, then we obtain,

$$\bar{C}_p(T_f - T_o) = .5111 + .0151\,c \text{ , cal./cc..} \quad \ldots\ldots (17)$$

Equation (17) of course gives,

$$\bar{C}_p(T_f - T_o) = .654 \text{ cal./ cc.}$$

when $c = 9.51\%$ cf. p 14 above

Let Q_o and c_o be the values of Q and c for the theoretical mixture for complete combustion, then , if c is less than c_o

$$Q = \frac{c}{c_o} Q_o = \frac{.8441}{9.506} c = .08876\, c \quad \ldots\ldots (18)$$

for methane-air mixtures.

Hence assuming that the average flame temperature at the usual lower limit of inflammability is 1670°C, we have for c', the percentage concentration at that limit

$$.08876\, c' = .5111 + .0151\, c'$$

or
$$c' = 6.93\,\% \quad \ldots\ldots\ldots\ldots\ldots (19)$$

If the average flame temperature at the usual lower limit is only the ignition temperature, ie. $T_f = T_i = 750°C$, we obtain

$$\bar{C}_p(T_f - T_o) = .2175 + .0108\, c \quad \ldots\ldots (20)$$

giving
$$c' = 2.79\,\% \quad \ldots\ldots\ldots\ldots (21)$$

The average of 28 values of c' under normal conditions given by Bone[14] is 5.66 %. Hence the average flame temperature at the lower limit lies between 750 and 1670°C and by successive approximation we can deduce the value of T_f which will give c' equal to 5.66 % .

In this way, we find that if $T_f = 1425°C$, then

$$\bar{C}_p(T_f - T_o) = .4305 + .01323\, c \quad \ldots\ldots (22)$$

which gives
$$c' = 5.67\,\%.$$

On making similar calculations for hydrogen-air mixtures, further evidence is obtained to show that the formula for the limiting diameter is substantially correct.

Starting with the theoretical mixture for complete combustion,

$$2H_2 + O_2 + 3.76N_2 = 2H_2O + 3.76N_2 \quad , \ . \ . \ (23)$$

or 29.6% hydrogen, the following values have been used.

T_f = Average Flame Temperature = $1900^{\circ}C.$[12]

T_i = Ignition " = $600^{\circ}C.$[11]

Heat of combustion of 1 gm.mol. of hydrogen when burnt completely to water at $18^{\circ}C$ = $68.4 \ .10^3$ cal..[13]

k_h = the thermal conductivity of hydrogen

$= .0004043 \ (1 + .00265 \ T)$[9]

From these values we deduce for the above mixture,

$Q = Q_o = .848$ cal./cc. of unburnt mixture,

and $\bar{C}_p(T_f - T_o) = .699$ cal./ cc..of " " .

Assuming that the thermal conductivity of the hydrogen-air mixture can be calculated from

$$k = \frac{c}{100} k_h + \frac{100-c}{100} k_a \quad , \ . \ . \ . \ . \ . \ . \ . \ . \ . \ (24)$$

where c is the percentage, by volume, of hydrogen in the mixture and k_a is the thermal conductivity of air, we find

$$k = .0001608(1 + .00273 \ T) \ . \ . \ . \ . \ . \ . \ . \ (25).$$

which gives $\bar{k} = .0002965$. C.G.S.U.

Hence on substituting in equation (9), we obtain

$$d = \frac{4.64}{v} \text{ cm.} \quad \ldots\ldots\ldots\ldots\ldots (26).$$

The value of v for the 29.6 hydrogen-air mixture has been found to be 67.1 cm./ sec., which gives

$$d = .691 \text{ mm..}$$

The actual experimental value of the limiting diameter for this mixture is .93 mm.. See Part II.

On applying equation (11) as above to calculate the percentage concentration of hydrogen at the usual lower limit of inflammability, we find that if the average flame temperature is only the ignition temperature, ie $T_f = T_i = 600^{\circ}C$, then

$$\bar{C}_p(T_f - T_o) = .1719 + .003933\ c \text{ cal./ cc.}$$

which, when solved along with

$$Q = .02865\ c \text{ cal./ cc.}$$

gives $c' = 6.95\%$ . . . . . (27).

If, however, T_f is equal to $1900^{\circ}C$, then

$$\bar{C}_p(T_f - T_o) = .5905 + .003674\ c \text{ cal./ cc.}$$

which yields $c' = 23.6\%$ . . . . . (28).

The average of eight value given by Bone[14] for c' for vertically downward propagation is 9.23%. Hence the average flame temperature at the usual lower limit of inflammability lies between 600 and 1900°C, and by successive approximation we find that if $T_f = 790°C$, then

$$\bar{C}_p(T_f - T_o) = .2293 + .003790\ c \quad \text{cal./ cc.}$$

giving $$c' = 9.22\% \quad \ldots\ldots\ldots\ldots (29).$$

It is interesting to note that the value of c' for vertically upward propagation is only about 4.39%[14], which means that the average flame temperature at that limit is less than the normally accepted ignition temperature. See equation (27) above. Attention has already been drawn to this fact by Dr. A.G. White[15].

To calculate the value of T_f at the latter limit, if we assume $T_f = 385°C$, then

$$\bar{C}_p(T_f - T_o) = .1077 + .004108\ c \text{ cal./ cc.}$$

which gives $$c' = 4.39\% \quad \ldots\ldots\ldots\ldots (30).$$

The limiting conditions for the propagation of flame along a tube, the section of which is a rectangle whose length is large compared with its breadth, b, can be treated in a similar manner. If such a tube is arranged as previously described for the cylindrical ones, then, when the velocity of flow, V, is just sufficient to prevent the flame from travelling down, the shape of the flame is that of the lower half of a horizontal cylinder cut by a horizontal plane through its axis.

Let the radius of this semicylindrical flame be R_i , then, with the same notation as before, we must have, on considering unit length of the flame

$$b\,V\,(Q - \bar{C}_p(T_f - T_o)) \quad = \quad -\pi\,R_i\overline{k\frac{\partial T}{\partial R}}_{R=R_i} \quad . \quad . \quad . \quad . \quad (31).$$

where T is now the temperature at a distance R from the axis of the flame.

Assuming as before that the distribution of T can be represented with sufficient accuracy by that from a complete cylinder, we have if the length of the flame is large compared with its breadth,

$$\frac{\partial}{\partial R}\,k\,R\,\frac{\partial T}{\partial R} = 0 ,$$

which when integrated twice gives,

$$F(T) = \frac{F(T_i) - F(T_o)}{\log R_i - \log R_o} \log R + \frac{F(T_o)\log R_i - F(T_i)\log R_o}{\log R_i - \log R_o} \quad \ldots\ldots (32).$$

where $T = T_o$ when $R = R_o$

and $T = T_i$ when $R = R_i$.

On differentiating equation (32) with respect to R we obtain

$$\left[k \frac{\partial T}{\partial R}\right]_{R=R_i} = \frac{\bar{k}\,(T_i - T_o)}{R_i(\log R_i - \log R_o)}$$

On substituting in (31) we have finally,

$$b = \frac{\pi \bar{k}\,(T_i - T_o)}{v'(Q - \bar{C}_p(T_f - T_o))(\log R_o - \log R_i)} \quad .(33)$$

where v' is the limiting velocity for propagation along the long rectangular tubes.

From equations (9) and (33) we can find the ratio of the limiting diameter for propagation along a cylindrical tube to the limiting breadth for propagation a tube of the above description. It is

$$\frac{d}{b} = \frac{4 v' (\log R_o - \log R_i)}{\pi v} \quad \ldots\ldots\ldots (34).$$

R_o is of the same order of magnitude as the length of the flame and R_i is practically equal to b/2. In the actual slots used the length was about ten times the breadth,

so that the value $\log R_o - \log R_i$ would be about $\log_e 20$ or 3.0.

Hence in this case

$$\frac{d}{b} = \frac{12\ v'}{\pi\ v} .$$

The actual values of b and d for the 20% coal gas air mixture were found to be 1.05 and 1.80 mm., which gives

$$\frac{d}{b} = 1.71 .$$

This suggests that v' is less than v in the ratio of about

$$\frac{v'}{v} = .446 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (35).$$

Experimental Work.

Part I.

Times of Contact for Failure of Ignition.

The initial experiments on the limiting conditions for the ignition of an explosive gaseous mixture by flames, were based upon the assumption that there existed a definite, measurable interval of time, during which a given flame could remain in contact with the mixture without producing general ignition. The object was to obtain a curve showing the variation of the maximum time of contact for failure of ignition with the percentage of inflammable gas in the mixture, and then to determine how the curve changed for various flames having different rates of generation of heat, size, and temperature. It was not found possible to carry out this programme, as, using coal gas air mixtures ignited by small coal gas flames, no definite and repeatable ignition curve of the above description could be obtained. It is doubtful, however, if the results would be of much value, since they would be obtained under conditions in which it would be difficult to interpret exactly what was taking place.

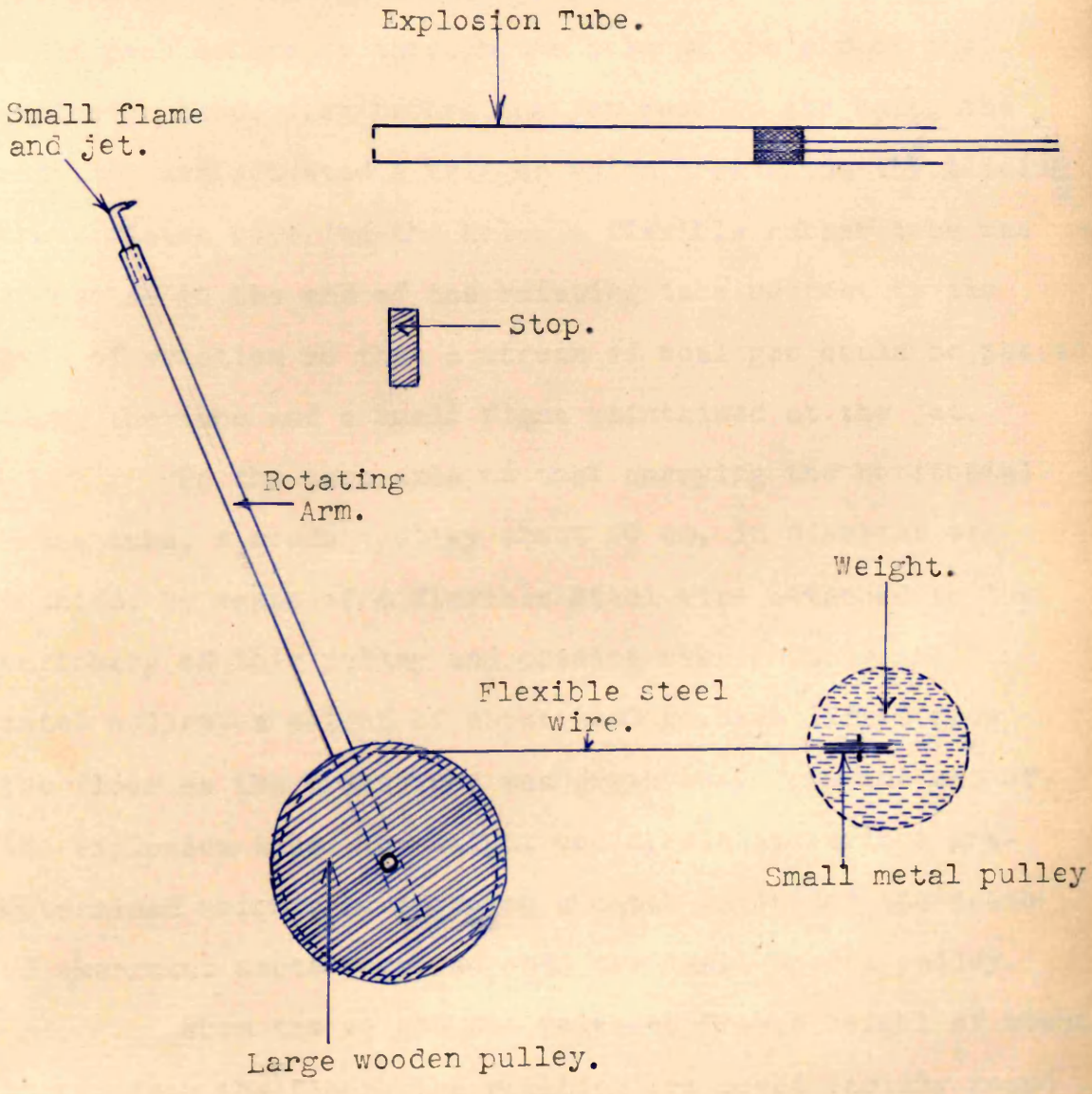
The experiments involve bringing a small flame burning in air into contact, for a very short interval of time, with a volume of the explosive mixture contained in a closed vessel. Hence the flame and the mixture must be in rapid relative motion at the time of contact, or else a rapidly

moving partition separating the two, uncovers an aperture which allows them to come into contact. One of the main difficulties in the experiments is to make certain that what is taken as failure of ignition is not really failure of the surface of the flame to come into contact with the mixture. Another inherent difficulty is encountered with mixtures too rich in combustible gas. When such a mixture comes into contact first with the air surrounding the flame, it forms a layer of the strongest mixture possible between the flame and the mixture being investigated. The matter is much more complicated than the corresponding problem of spark ignition, since a very small spark, lasting for a very short interval of time, can readily be produced inside a closed vessel containing a homogeneous quiescent mixture of known and definite composition.

In the first type of apparatus tried, a horizontal explosion tube, 40 cm. long and 3.0 cm. in internal diameter, was used. At one end of the explosion tube, there was a brass plate pierced by a circular hole, 1 cm. in diameter and concentric with the tube. This opening could be closed by a thin brass plate acting as a slide valve. The mixture could be drawn into the explosion tube from the gas container through the hollow stem of a piston which closed the other end of the tube. A piece of strong brass tubing (about 5/8 inch external diameter and about 40 cm. long) was mounted so that it could rotate freely in the horizontal plane containing

Fig. II.

Plan.


Explosion Tube.
Small flame and jet.
Stop.
Rotating Arm.
Weight.
Flexible steel wire.
Small metal pulley
Large wooden pulley.

the axis of the explosion tube. Into the outer end of this tube, a glass jet, which was bent at right angles to the tube, could be inserted be means of a long rubber stopper. The jet and rotating arm were adjusted so that the jet would pass centrally through the hole at the end of the explosion tube. Just before the jet reached the hole, the rotating arm actuated a trigger which drew aside the sliding brass plates covering the hole. A flexible rubber tube was connected to the end of the rotating tube nearest to the axis of rotation so that a stream of coal gas could be passed along the tube and a small flame maintained at the jet.

On the same axle as that carrying the horizontal brass tube, a wooden pulley about 20 cm. in diameter was mounted. By means of a flexible steel wire attached to the periphery of this pulley and passing over another small metal pulley, a weight of about 2640 gm. was lifted from the floor as the brass tube was drawn away from the end of the explosion tube. The weight could be held at various predetermined heights by engaging a catch in one of the teeth of a serrated sector screwed onto the large wooden pulley.

When the weight was released from a height of about 20 cm. from the floor, the rotating arm moved rapidly round towards the explosion tube and the small flame burning at the jet went out at the instant when the arm struck against a rigid stop, which was adjusted so that the jet could only

travel about 5 mm. into the explosion tube. By varying the height through which the weight dropped and also the distance which the jet entered the explosion tube, it was hoped that it would be possible to bring the small flame into the mixture for a sufficiently short time to fail to give general ignition of the rest of the mixture in the tube.

The linear speed, v , of the jet at the moment of entering the explosion tube, as calculated from the dynamics of the system, was given by

$$v = 147.8\sqrt{h} \text{ cm./ sec.}$$

where h was the distance in cm. through which the weight dropped.

The apparatus did not however prove successful, as no reliable and consistent results could be obtained.

The greatest difficulty was experienced in obtaining a small flame which would remain lit at very high speeds. With the usual type of flame, the inner blue cone being about 3.5 mm. long and the total length visible in the dark about 7 mm., the maximum velocity attainable was about 5.7 metres per second, giving a minimum time of contact of about 1.6 milliseconds.

A considerable number of experiments were made at this time to determine the optimum conditions of producing a small flame which would remain lit at high speeds.

To this end experiments were made on the variation of maximum speed attainable with a given jet, with the pressure of the coal gas supplied to it. The graphs showed that the limiting speed attainable was a maximum for a certain pressure but that for the small flames used (total length about 6 to 10 mm. and diameter about 2 or 3 mm.) the optimum pressure was practically that of the supply mains, ie. about 12 cm. of water. The jets used were made by partially sealing up the end of a piece of thick walled glass tubing (about 6 mm. in external diameter) so as to give a fairly blunt jet. The flame from the jet pointed as nearly as possible along the direction of motion.

The next type of experiment was on the variation of the maximum speed with the direction in which the flame was pointing with respect to the direction of motion, the jet being supplied with coal gas at constant pressure.

The apparatus (described on page 30) which was used in these experiments enabled the flame to be rotated continuously in a horizontal circle, 50 cm. in radius, at any linear speed up to 35 metres per second. The jet could be turned so that the flame pointed in any direction in the vertical plane containing the direction of motion.

From the results it was evident that the optimum direction for the flame was not along the direction of motion but one making an angle of from 45 to 90°, either upwards

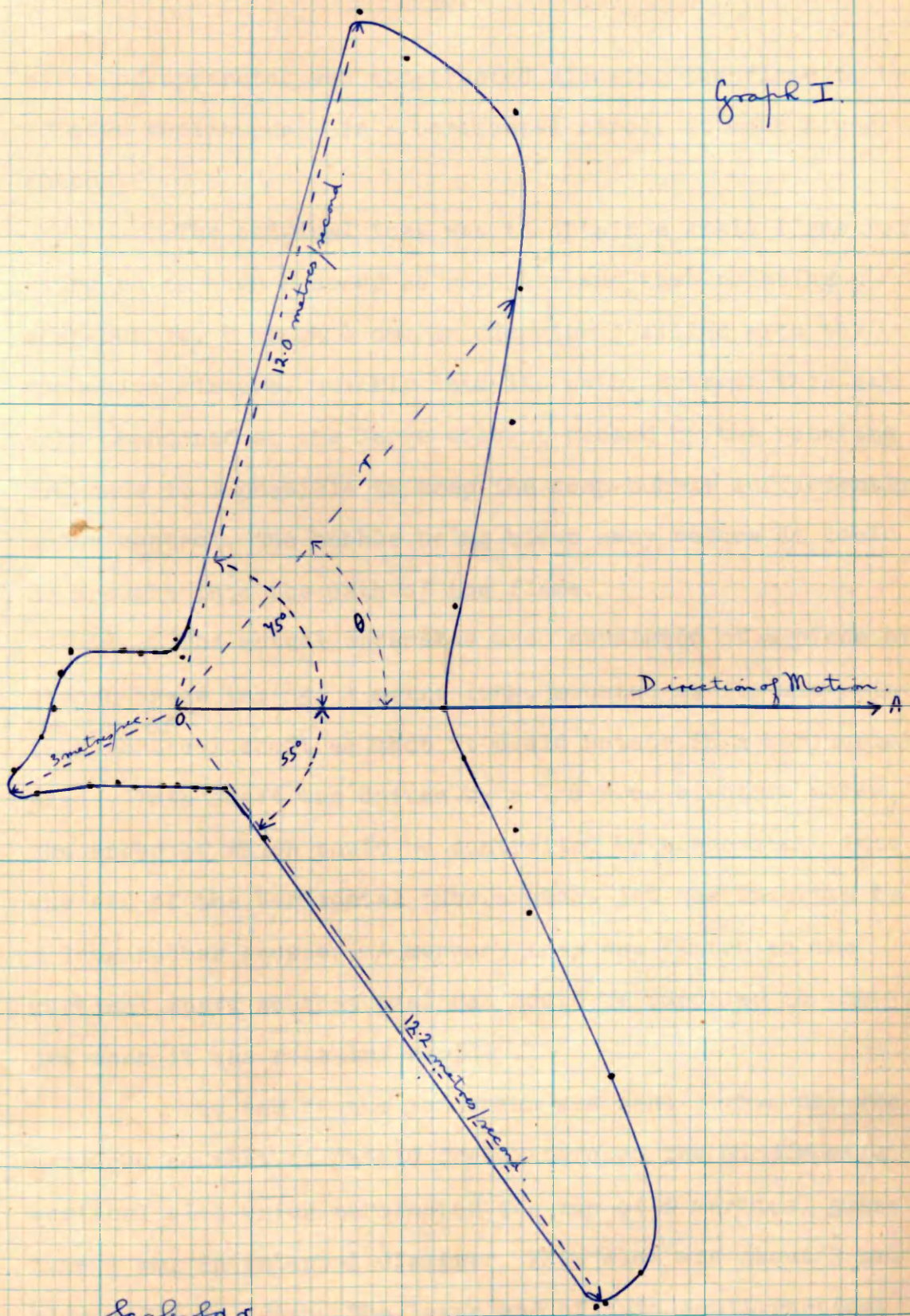
or downwards with it, the speed in this direction being from 2.5 to 3.5 times greater. A typical graph of the results is shown in Graph I, where θ is the angle between the flame and the direction of motion and r is the limiting velocity in metres per second with the flame pointing in this direction. Probably the reason for the small value of r when θ is zero is that when the flame is pointing straight into the direction of motion, the burnt gases are swept past the base of the flame where they prevent the necessary fresh oxygen being drawn in and so extinguish the flame. When the flame is pointing either upwards or downwards, the burnt gases are carried away clear of the base of the flame.

The highest speed obtained with this apparatus was about 30.8 metres per second, or 68.8 miles per hour. The dimensions of this flame were:- Total length = 6 cm., length of inner blue cone = 3 cm., while the cross-section at 1.5 cm. from the base was approximately an ellipse having a major axis of 6 mm. and a minor axis of 4 mm.

The maximum speed at which a flame would remain lit appeared to be fairly consistent and definite.

In the first type of apparatus it was impossible to use with safety speeds much greater than about 10 metres per second, as the large impulse developed when the rotating arm was suddenly stopped, produced a severe strain in the whole rotating system. To overcome this difficulty a new

Graph I.



Scale for r.

1 cm = 1 metre/second.

piece of apparatus was constructed allowing the flame to be rotated continuously in a horizontal circle at much higher speeds.

The original idea was to obtain a small flame rotating at as high a speed as possible and then to bring a soap-bubble, (about 1 cm. in diameter) filled with the explosive mixture, quickly into its path. However this was soon abandoned as the large draught caused by the rotating arm made it impossible to keep the soap-bubble sufficiently under control, the bubble being blown away before it could be brought into the path of the flame.

The actual apparatus used consisted of a piece of strong brass tubing, 1 metre long, mounted at its mid-point to the top of a vertical shaft so that it could rotate in a horizontal plane. This shaft was driven by a 1/6 h.p. electric motor, the speed of which could be controlled by a rheostat. Into one end of the horizontal tube, a glass jet was inserted by a long rubber stopper. A mercury trap was fitted to the vertical shaft so that coal gas could be supplied to the jet when it was rotating rapidly.

The end of the jet, which was bent downwards, was arranged so that it passed freely through the middle of a vertical slot which terminated the top of a vertical glass tube 3 mm. in internal diameter. This slot was about 3 mm. wide and 5 mm. deep. The lower end of this small vertical

tube was connected through a needle valve, a"safety tube" packed with long strips of copper foil and a glass stop-cock, to a glass gas container filled with a 20% coal gas air mixture.

By opening the needle valve and the stop-cock, this mixture was allowed to escape slowly up the small vertical tube and at the same time the horizontal arm was set in motion by the electric motor. The glass tap was closed regularly for half a second every 5 seconds and the number of times which a flame travelled down the small vertical tube in a given time counted. It was found ~~that~~ for a given rate of flow that this number was independent of the speed of the rotating flame, from very small velocities up to 30 metres per second. The actual horizontal length of the flame at these high speeds was certainly less than 2 cm. and we thus had ignition with a time of contact of about .0007 second.

Following these experiments, the tube was replaced by a horizontal sheet of copper foil pierced by a hole 2.06 mm. in diameter. The copper foil was arranged to close the top end of a vertical glass tube 1 cm. in diameter and was .085 mm. thick.

Similar experiments were tried with the flame from the jet passing right over this hole and when the tap was closed the mixture in the 1 cm. tube was ignited although the flame was travelling at 30 metres per second.

However, when this experiment was tried with a hole 1.51 mm. in diameter, it was almost impossible to get ignition at all even if the flame was played against the surface of the hole, as in FigIIa,for 2 minutes. If, however, the jet was held vertically, as in Fig. IIb,so that the end of the flame shot through the hole, then ignition was produced almost immediately.

These experiments, while not actually disproving the existence of a maximum time of contact for failure of ignition, show that the size of the flame exposed to the mixture is of considerable importance in determining whether ignition does or does not take place.

Fig. IIa.

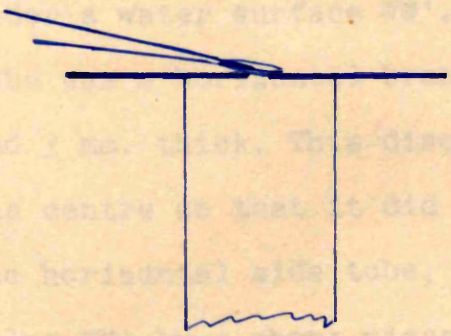
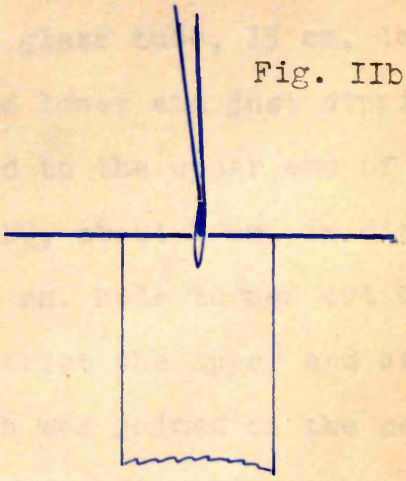


Fig. IIb.



Part II.

Measurements of Limiting Diameters.

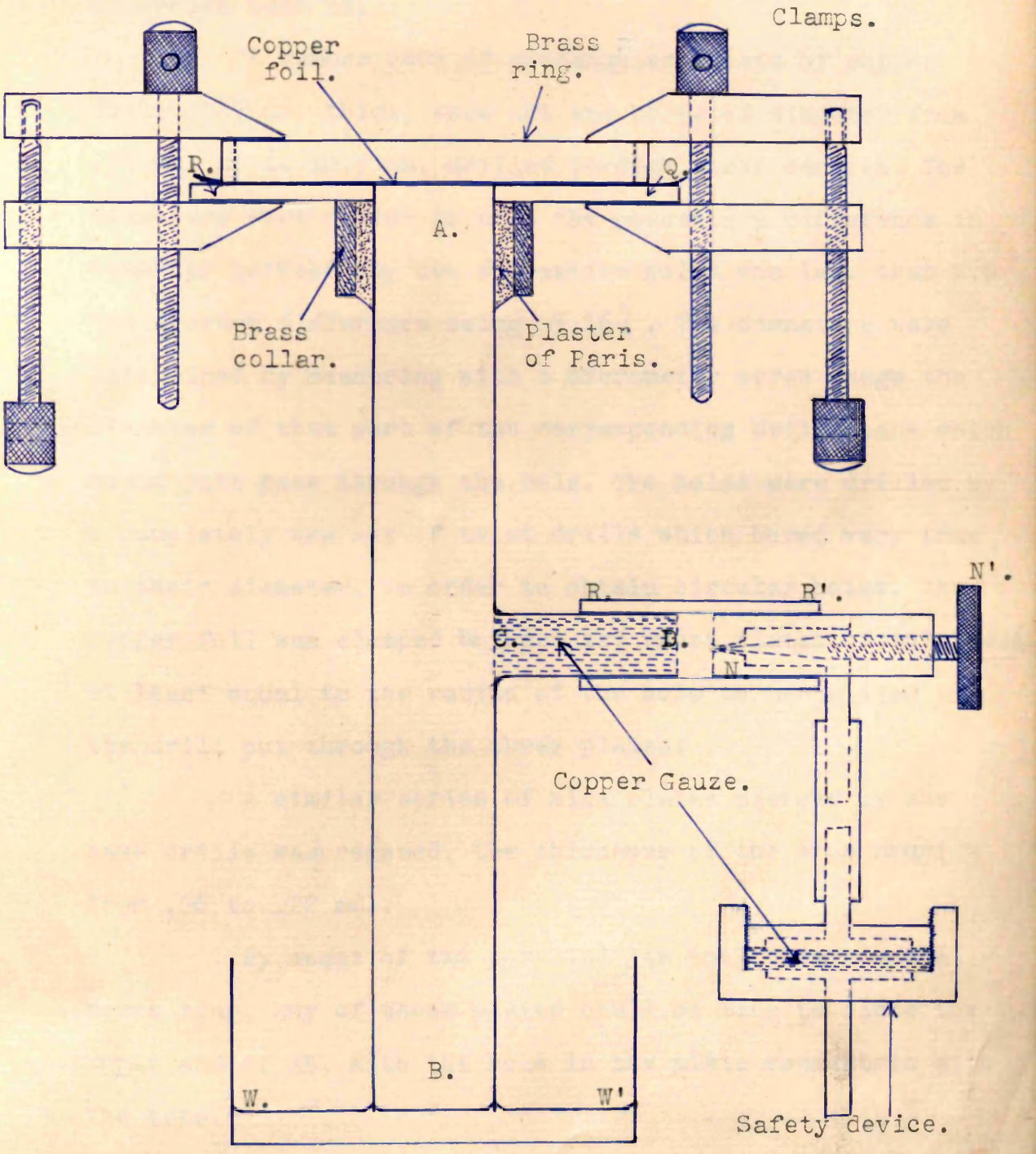
Following the above work, the experiments were changed from the measurements of times of contact to measurements of maximum diameters for failure of ignition or propagation. These experiments have been characterised by their remarkable consistency and definiteness, in marked distinction to those just described. At the same time several interesting and, it is believed, new phenomena have been observed.

The apparatus used was exceedingly simple and is shown in Fig.III. AB was a vertical glass tube, 15 cm, long and 2 cm. in internal diameter, the lower end just dipping under a water surface WW'. Attached to the upper end of this tube was a horizontal brass disc, PQ, about 8 cm. in diameter and 3 mm. thick. This disc had a 2 cm. hole turned out of the centre so that it did not constrict the upper end of AB. The horizontal side tube, CD, which was joined to the needle valve NN' by a short piece of rubber tubing RR', was packed with a roll of copper gauze to prevent the explosion, taking place in AB, from travelling along to the needle valve. Between this valve and the tap of a 10.7 litre glass container, a safety device was inserted. This consisted of nine discs of fine copper gauze, 2.5 cm. in diameter, pressed close

Fig. III.

Elevation.

Full Size.



together in a suitable holder so as to form a flame proof partition in the tube joining the gas container to the explosion tube AB.

A number (40) of rectangular sheets of copper foil, .085 mm. thick, were cut and holes of diameter from .78 mm. up to 10.5 mm. drilled through their centres. The diameters were chosen so that the percentage difference in diameter between any two successive holes was less than 7.0 , the average difference being 5.16% . The diameters were determined by measuring with a micrometer screw gauge the diameter of that part of the corresponding drill shank which would just pass through the hole. The holes were drilled by a completely new set of twist drills which bored very true to their diameter. In order to obtain circular holes, the copper foil was clamped between two brass plates, of thickness at least equal to the radius of the hole to be drilled, and the drill put through the three plates.

A similar series of mica plates pierced by the same drills was prepared, the thickness of the mica ranging from .06 to .22 mm..

By means of two parallel jaw tool clamps and a brass ring, any of these plates could be made to close the upper end of AB, with the hole in the plate concentric with the tube.

A series of copper tubes was made by drilling copper rod with the same drills as were used for making

the copper foil and mica series. The length of each tube was made to be exactly ten times its internal diameter. For diameters up to 3.78 mm. 1/4 inch copper rod was used, from 3.98 to 5.62 mm. 3/8 inch and from 5.95 to 9.50 mm. 1/2 inch rod was used.

A collection of glass tubing was procured, the pieces being selected to be as near as possible to the diameters of the drills used for the other series . From each piece of tubing selected, two lengths were cut, one about ten times the internal diameter and another about twenty five times, thus giving rise to two sets of glass tubes, referred to as A and B.

Any of the tubes could be inserted into the upper end of AB by means of a suitable rubber stopper.

Coal Gas Air Mixtures.+

The method of experimenting with the plates was as follows:- Having made up a coal gas air mixture of known concentration (say 20 %) in the gas container, a copper foil plate was fixed over the upper end of AB and the mixture

+ I am indebted to the Glasgow Corporation Gas Department for supplying the analyses from which the following average is compiled.

H_2	CH_4	CO	N_2	CO_2	C_nH_m	O_2	
51.4	19.1	17.7	5.7	3.5	2.3	.3	% by Volume.

allowed to flow through the hole in the foil and to bubble through the water surface WW' so as to fill the tube AB completely with the mixture.

A small coal gas flame (inner blue cone 1.5 mm. long and total length 3 mm.) was then brought into contact with the mixture escaping from the hole and the needle valve adjusted till a self-supporting flame was obtained. The shape of this flame was conical for high rates of flow, for medium rates it took the form of a flat disc, while for very low rates it was almost hemispherical. See Plate I, (b), (c), and (d). The diameter of the circular disc was slightly greater, while that of the hemisphere was practically the same as that of the hole below it.

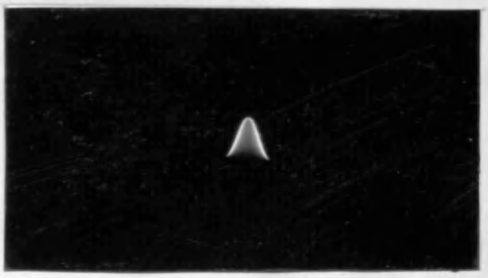
When the rate of flow was slightly increased from that giving a conical flame, an unstable type of flame, shown in (a), Plate I, was formed. This flame was practically elliptical in shape, the centre of the ellipse lying on the axis of the orifice, while its plane was inclined to the vertical at an angle between 20 and 70°. For greater rates of flow it was not possible to maintain a self-supporting flame as this latter flame was carried upward by the flow of the mixture.

In Plate I, the first four photographs represent flames burning at the top of a copper tube 4.76mm. in internal diameter. For (a) and (b) a 9.5% methane-air mixture was

Plate I.

(a).

(b).



(c).

(d).

(e).

(f).

used, while for (c) and (d) the concentration was reduced to 7.85 %, which is very near the lower limiting concentration for that diameter, ie. 4.76 mm.. In (d) the lowest part of the hemisphere is obscured as it lay just below the level of the top of the tube. When these photographs were taken, the axis of the camera lay in the horizontal plane passing through the top of the tube.

Method I.

By closing the needle valve very slowly, this hemispherical flame either passed down through the hole and gave immediate ignition (ie. in less than 1/5 second) of the mixture contained in the tube AB, or went out abruptly on the top side of the plate without giving ignition, according as the diameter of the hole was greater or less than a certain limiting value. For example, with the 20% mixture the hemispherical flame went out on the top side of the plate for diameters up to 1.78 mm. but travelled down and gave ignition, which at this concentration was fairly violent, for diameters of 1.85 mm. and greater.

This criterion, to be referred to as Method I, of determining a limiting diameter for failure of ignition was found to be applicable without change for coal gas air mixtures containing more than 12.5% of coal gas.

In this method, the rate of flow of the explosive mixture was adjusted so that when the escaping mixture was lit, the flame which formed was of the flat disc type shown in (c), Plate I, and within a few seconds the rate of flow was reduced so as to give the hemispherical type of flame. If the diameter of the orifice was considerably greater than the limiting diameter for the mixture being investigated, the disc flame might propagate through the hole and give ignition without first changing into the hemispherical form, when the rate of flow was reduced.

Method II.

For concentrations less than 12.5%, it was not possible to maintain a self-supporting flame above the holes in the thin plates so that the method of experimenting had to be changed slightly. If, say an 11.5% mixture was escaping through a 3.95 mm. hole in copper foil and the small coal gas flame held horizontally about 4 or 5 mm. above it, then a bluish aureole formed on the under side of the flame. When the needle valve was closed slowly, the aureole separated from the flame and, passing down through the hole, ignited the rest of the mixture in AB. The aureole was obviously in unstable equilibrium above the hole for small rates of flow. If, however, the plate was changed for one having a hole 3.80 mm. in diameter, then the aureole was in stable equilibrium above the plate, showing no tendency to travel down

through the hole and give ignition when the needle valve was closed slowly.

As may be seen from the graphs, the curve obtained by this method gave a good continuation of that from 31.5 to 12.5 % obtained by Method I.

With concentrations greater than 24% an exceedingly interesting, though fairly complicated phenomenon was observed. This was virtually an almost spherical flame formed by the mixture burning under the hole in the thin plate and which might in some circumstances last for 20 seconds without producing general ignition. Sometimes the flame expanded, vibrated at an audible frequency and gave ignition of the rest of the mixture in AB, and sometimes it did not. The flame was not perfectly spherical, as a small cap cut off by the plane of the hole was missing and it usually expanded to a diameter about double that of the hole above it.

(e) in Plate I shows a disc flame burning above a 3.25 mm. hole in copper foil, while (f) is a photograph of the almost spherical flame burning below a circular aperture in a mica plate, the diameter of the aperture being 2.78 mm.. In both cases a 29.5% coal gas air mixture was used. The photographs were taken looking down on the top side of the plate, so that in (f), the spherical flame is viewed partly through the mica itself and partly through the actual aperture which appears as a small ellipse above the lower part of the

flame. The duration of this spherical flame below the plate was about 16 seconds and yet no general ignition of the mixture in the vertical tube AB was produced.

It should be explained that this spherical flame was produced when Method I was applied to concentrations greater than 24% . When the rate of flow was reduced, the disc flame burning above the plate, instead of giving immediate ignition of the mixture in AB, merely sank down through the hole and formed this peculiar spherical flame.

The phenomena obtained were very consistent, though they varied considerably with the concentration of the mixture, the diameter of the hole and the method of closing the needle valve, ie. either quickly or slowly. The variation with diameter at a fixed concentration is shown in Table I, which referrs to a 28.5 % coal gas air mixture.

With stronger mixtures such as 25 % , the phenomena corresponding to those found with holes of diameters from 2.64 to 3.44 mm. were missing, while with concentrations greater than 28.5 % their range was extended and that of ignition from a singing expanding flame curtailed. In general as the concentration changed from 24 towards 32 % the time of duration of the various flames below the plates increased and the probability of ignition from them decreased.

It was sometimes possible by opening the needle slowly, to cause the spherical flame burning below the plate

to rise up through the hole and give a disc flame burning as previously on the top side of the plate. This process, if possible once, could be repeated indefinitely and took place most readily with concentrations greater than 28% .

As may be seen from Table I, there are no less than four limiting diameters for the 28.5% mixture. These are bracketed together. The limiting diameters corresponding to the largest two have been determined for holes in copper foil and are shown in the accompanying graphs. It is believed that the curve given by the smaller one is the correct continuation of the curve from 13 to 23 % obtained by Method I.

Method III.

This is applicable between 23 and 32% and is the determination of the maximum diameter which does not give immediate ignition when the disc flame burning above the hole is reduced by closing the needle valve smartly, ie. corresponding to the largest limiting diameter in Table I.

Method IV.

Perhaps it might not be inappropriate to point out here that there is yet another limiting diameter referring to the flames burning above the apertures in the thin plates, or at the tops of the tubes. This is the minimum diameter of hole which will just allow a self-supporting flame to be maintained on the top side of the plate, or at the top of the tube, independently of the rate of flow of the mixture. Thus

Table I.

28.5% Coal Gas Air Mixture. and Copper Foil.

Diameter of hole.	Needle valve closed slowly.	Needle valve closed quickly.
1.67 mm.	Disc flame out above plate. No ignition.	The same.
1.78	As above.	Non-singing, non-expanding flame under plate.
1.85		No ign.. Duration 1.2 sec..
1.93 1.96 2.06	Singing, non-expanding flame under plate. No ign.. Dur. 3 sec..	The same.
2.16 2.26 2.36 2.47	Ignition from singing, expanding flame under the plate. Duration 2.5 sec..	
2.64	No ign. Singing, expanding flame under plate. Dur. 17 sec..	The same.
2.77	No ign. Non singing non expanding flame under plate. Duration 20 seconds.	The same.
2.94 3.17 3.25 3.44	Immediate ignition. No spherical flame under the plate.	No ignition from a non-singing, non expanding flame under plate. Dur. 20 sec..
3.59 and greater	Immediate ignition.	The same.

with an 18% mixture no flame could be maintained above a 1.67 mm. hole in copper foil for any rate of flow whatever, but a self-supporting disc flame could be maintained above a 1.78 mm. hole by suitably adjusting the rate of flow by means of the needle valve. Part of the curve showing the variation of this limiting diameter with concentration is shown in Graph III.

Tubes.

The method of experimenting with the tubes was similar to that for the copper foil and mica plates. Having fitted one of the tubes into the upper end of Ab by means of a suitable rubber stopper, a hemispherical flame was produced at its upper end by following Method I. When the needle valve was closed slowly, it was always found possible to obtain two tubes of neighbouring diameter such that this flame would travel down the tube of greater diameter for a distance at least equal to half its length but would not propagate at all down that of smaller diameter for a distance greater than the diameter.

When the diameter of the tube was just slightly greater than that required for propagation, the surface of the flame which travelled down the tube was approximately hemispherical. The radius of this hemisphere was very slightly less than that of the tube for concentrations greater than 16% , but with weaker mixtures, such as 12% it might

only be about 3/4 that of the tube.

With concentrations between 14 and 26 % , the rest of the mixture in AB was ignited immediately by the flame travelling down the tube of larger diameter. This was true for all three sets of tubes, ie. copper and glass A and B. Outside these limits, the diameter of tube required to produce ignition of the mixture in AB was greater than that for propagation alone, although the exact value was not determined in each case.

With the tubes it was possible to maintain a self-supporting flame down to 11.5 % , but for lower concentrations Method II had to be employed.

The phenomenon of a spherical flame inside AB, corresponding to that observed with the plates, was not obtained with the tubes, indicating that the latter was due to the mixture in the vicinity of the hole not being homogeneous.

With concentrations greater than 25 % , the well kown phenomenon of flame separation took place. This could be observed most readily with the glass tubes. When the flame burning at the top of the tube (assumed greater in diameter than the minimum for propagation) was slowly reduced in size by decreasing the rate of flow, a bright green,hemispherical flame travelled steadily down the tube, leaving a pale blue cone burning at the top. When the

diameter was less than the minimum for propagation, the green flame sank down the tube for a distance not greater than the diameter, started to oscillate with a very low frequency and an amplitude about equal to the radius of the tube and then went out abruptly.

With concentrations less than 24% , the flame burning at the top of the tube was bright blue in colour and went out abruptly without sinking down below the level of the top of the tube, if the diameter was less than that required for propagation. If the diameter was greater, then the flame travelled steadily down the tube without any flame separation.

It should be pointed out here that the spherical flames burning under the plates were always blue in colour. Usually however, the under surface of the disc flames burning above the plate was bright green in colour for concentrations greater than 25% . This green part disappeared as the flame travelled down through the hole when the needle valve was closed.

Provided the folowing precautions were taken, the limiting diameters determined by Methods I, II, III, and IV, were very sharply defined and consistent.

(1)

To make sure that exactly the same criterion of failure of ignition (or propagation) was employed each time

(2).

To clear away all the burnt gas from the previous explosion in the vertical tube AB by allowing the mixture to flow through for a sufficient length of time.

(3).

To avoid heating up the edges of the holes or the tops of the tubes unduly by successive trials, or by allowing the disc flame to burn too long before it was reduced to a hemispherical flame.

(4).

To wait till the surface of the water at the lower end of AB was perfectly still before closing the needle valve. This was necessary, since if the surface was oscillating due to the mixture bubbling through it just previously, the hemispherical flame was given a vertical vibration which might carry it through a smaller diameter than usual.

(5) To have a reliable method of ascertaining the concentration of the mixture. Since the coal gas used in the experiments was drawn direct from the supply mains each time, the small changes occurring in its composition from day to day undoubtedly affected the results. As a rule however the changes produced in the limiting diameter were less than the experimental error (ie. about 2.5%) and passed unobserved.

Altogether about 500 observations of limiting diameters for coal gas air mixtures have been made. The most consistent and reliable are given in the accompanying graphs and tables. The limiting diameter was usually taken to be the mean of the experimental upper and lower limiting diameters, but in some cases it was obvious from the behaviour of the flames that the correct limiting diameter was nearer to that of one hole than it was to that of the other. In these cases the limiting diameter was taken to be the average between the mean diameter and the diameter considered to be nearer to the correct value. If two concentrations had the same experimental upper and lower limiting diameters, say d and d', the actual values were taken to be,

$$d + \frac{d' - d}{4} \quad \text{and} \quad d + \frac{3(d' - d)}{4},$$

and if three concentrations had the same limits, the values were taken as,

$$d + \frac{d' - d}{6}, \quad d + \frac{d' - d}{2} \quad \text{and} \quad d + \frac{5(d' - d)}{6}.$$

Results for Coal Gas Air Mixtures.

Copper Foil.

The complete curve showing the variation with concentration of the limiting diameter obtained by Method I and II is drawn in Graph II. The curve is definitely not symmetrical about the minimum at 20.5% , at which concentration the explosion, as judged roughly by its sound, was the most violent. Above part of this curve, that obtained by Method III from 23 to 31.5% is inserted. It is almost, but not exactly, symmetrical about 20.5% with the other half of the curve for copper foil.

Mica Plates.

From 9.75 to 16% the curve for the mica plates was identical, (ie. within 2.5%) with the corresponding part of the curve for copper foil. The curve lay definitely below that for copper foil from 16 to 26% , as may be seen from Table II. For concentrations greater than 26% the limiting diameter given by Method I has not been determined on account of the ease with which the edges of the holes became red hot. The curve obtained by Method III from 23 to 29% was the same as the corresponding curve for copper foil.

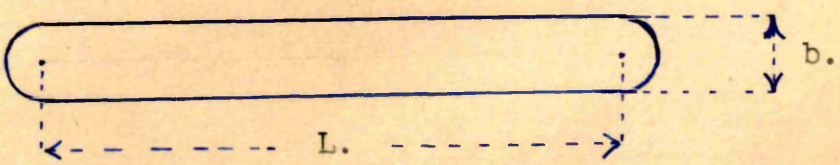
Tubes.

The limiting diameters, determined as described on page 42 above, were identical (ie. within 2.5%) for the copper and glass tubes for all concentrations between 9.75

and 31.5 %. The curve, shown in Graph II , lies slightly, but definitely above that for copper foil from 9.75 to 20.5% . From the latter concentration onwards, the curve rises more steeply than that for the plates and lies distinctly above it.

The minimum diameter occurs at the same concentration as that on the curve for the plates, ie. 20.5 %. From the analysis of the coal gas given on page 35, the theoretical mixture for complete combustion has been calculated to contain 19.0% of coal gas, assuming n = m = 6.

Fig. IV.



$$\frac{L + b}{b} = 9.0$$

Graph II.

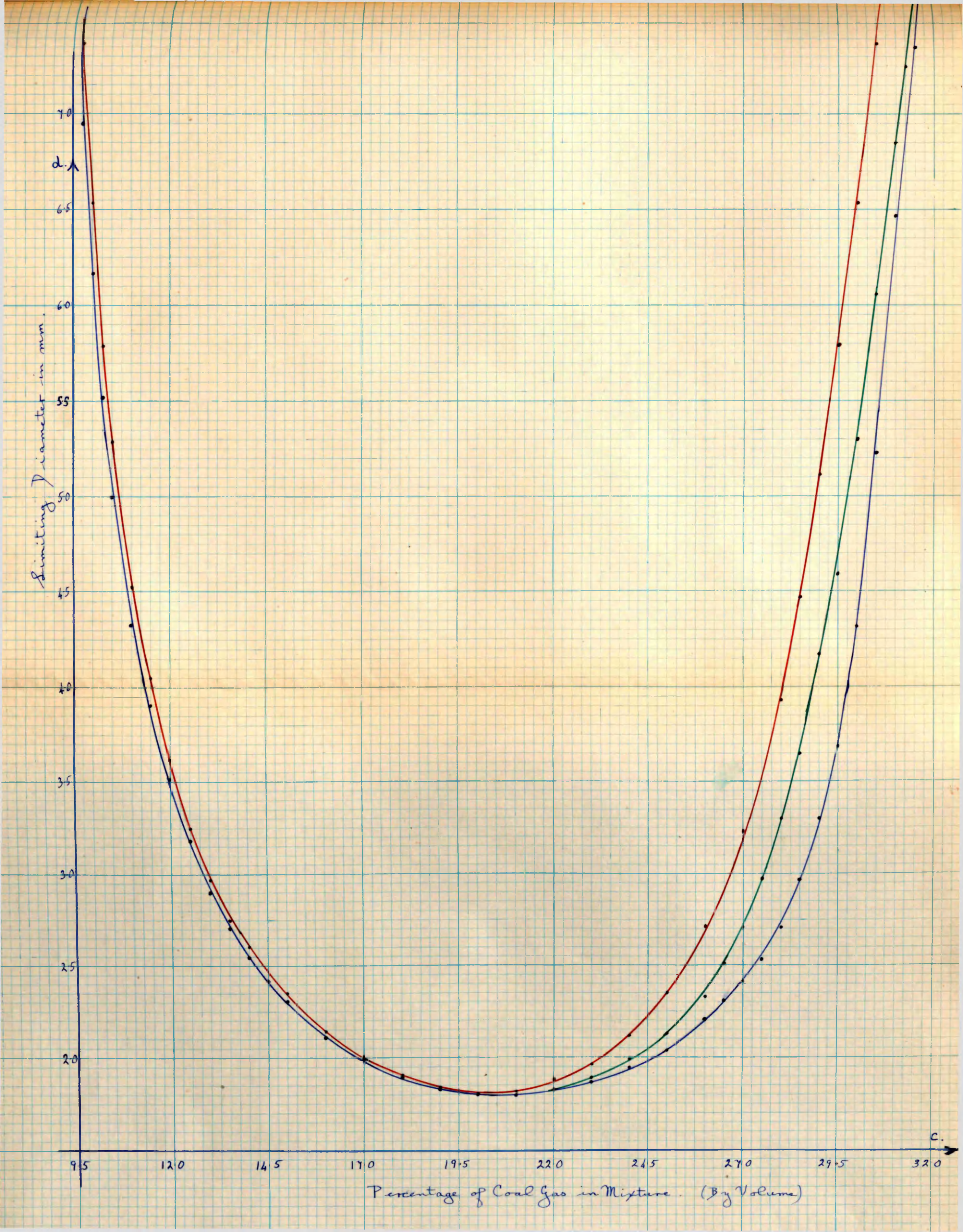
Coal Gas Air Mixtures.

Propagation along copper tubes in Red.

Ignition through copper foil in Blue.

Ignition through copper foil,

Method III, in Green.

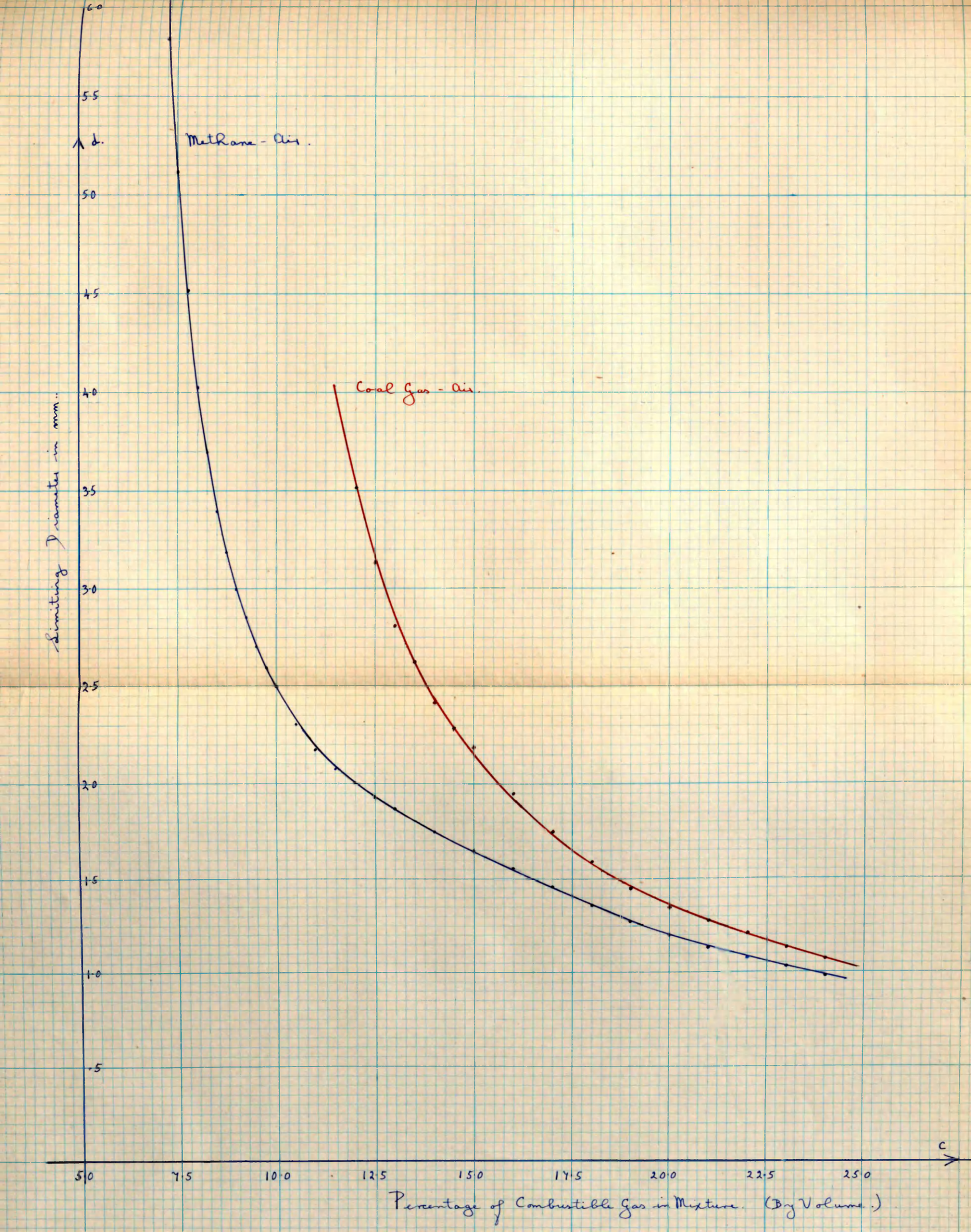

Limiting Diameter in mm.
70
d.
65
60
55
50
45
40
35
30
25
20
C.
9·5
12·0
14·5
17·0
19·5
22·0
24·5
27·0
29·5
32·0
Percentage of Coal Gas in Mixture. (By Volume)

Graph III.

Coal Gas- and Methane-Air

Mixtures.

Method IV.


d.
Methane - Air.
Coal Gas - Air.
Limiting Diameter in mm.
6·0
5·5
5·0
4·5
4·0
3·5
3·0
2·5
2·0
1·5
1·0
·5
C
5·0
7·5
10·0
12·5
15·0
17·5
20·0
22·5
25·0
Percentage of Combustible Gas in Mixture. (By Volume.)

Ignition through Slots in Copper Foil.

Following the above experiments, the effect of changing the shape of the aperture in the copper foil was investigated. The experiments showed definitely that the area of the limiting hole did not remain constant as its shape was changed.

The new apertures were made by drilling two circular holes of equal diameter through sheets of copper foil at a distance L apart, between centres. The part between the centres of breadth b was then cut out with the aid of a sharp knife and a fine file. Thus a slot having semi-circular ends was obtained. See Fig.IV, page 48.

Two such series of slots were made, one in which the average value of $\frac{L + b}{b}$ was 2.18 and another in which the value was 8.99.

With the first series, if b was the limiting breadth for failure of ignition and d the limiting diameter for failure through circular holes for the same concentration, then it was found that

$$\frac{b}{d} = .725$$

over the range from 12 to 26%, within the experimental error. Or, expressed in terms of area, A_s being that of the slot and A_c that of the circle ,

$$\frac{A_s}{A_c} = 1.25,$$

ie. the area of the slot had to be about one and a quarter times that of the circular hole.

It was easy to show by means of the other longer slots that the actual area of the aperture, considered by itself, had really very little to do with determining whether ignition did, or did not, take place. Thus the area of these might be as much as 3.80 times that of the corresponding circular hole without giving ignition.

The average value of the ratio $\frac{b}{d}$ for these long slots over the range from 16 to 24% was .584, or in terms of area,

$$\frac{A_s}{A_c} = 3.80.$$

The two ratios $\frac{b}{d}$ and $\frac{A_s}{A_c}$ are of course not independent for a series of apertures of similar shape. Thus

Thus if

$$\frac{L}{b} = \text{constant for a given series} = \gamma$$

then

$$\frac{A_s}{A_c} = \frac{\pi + 4\gamma}{\pi} \left(\frac{b}{d}\right)^2.$$

The explanation of the increase of limiting area with change of shape of the aperture, is that the flame is extinguished by conduction from the flame surface, the shape of which in three dimensions determines the efficiency of the

cooling effect.

Thus the cooling effect per unit area, per unit time, C_s, at the surface of a sphere, is from equation (7), page 10,

$$C_s = -\overline{k\frac{\partial T}{\partial r}}_{r=r_i} = \frac{\overline{k}(T_i - T_o)}{r_i}, \quad \ldots\ldots\ldots (7).$$

while that at the surface of a cylinder, C_c, is from equation (32) page 22,

$$C_c = -\frac{k\partial T}{\partial R}_{R=R_i} = \frac{k(T_i - T_o)}{R_i(\log R_o - \log R_i)}$$

If the radii of the sphere and cylinder are equal then we have,

$$\frac{C_s}{C_c} = \log\frac{R_o}{R_i}$$

Hence if the radius R_i is small the cooling effect of the sphere is much greater than that of the cylinder . Thus to produce the same effect, the radius of the cylinder must be smaller than that of the sphere.

For infinitely long slots it is obvious that the limiting area would be infinite, while the actual limiting breadth might not be much less than half the diameter of the limiting circular hole.

Methane - Air Mixtures.

Similar experiments were carried out using methane+ as the combustible gas, most of the results being substantially the same as those obtained with the coal gas air mixtures. Apart from the very noticeable diminution in the violence of the methane explosions, the most striking difference was observed when examining the limiting diameters for propagation down tubes and ignition of the mixture in the vertical tube AB

With the coal gas mixtures, see page 43, ignition of the mixture in the tube AB, Fig.III, was produced when the flame travelled down the smallest tube which would give propagation, if the concentration of the mixture was between 14 and 26%, ie. the strongest mixtures. Outside these limits, the diameter necessary to give ignition in AB was greater than that for propagation alone, but was not determined exactly in each case. With the methane mixtures the phenomenon was reversed. ~~With the methane mixtures the phenomenon was reversed.~~ Using vertical copper tubes, the limiting diameters for propagation, and for propagation and ignition of the mixture in AB, were identical for concentrations between 6.5 and 7.25% and also between 11.75 and 12.5%, ie. the weaker mixtures. Between 7.5 and 11.75%, however the diameters for propagation and ignition were considerably greater than those for propagation alone. The behaviour of the flames when the copper tubes were horizontal was similar to the above. These

+ Supplied by Messrs Imperial Chemical Industries. Stevenston.

results are shown in Graph V.

The explanation of the peculiar behaviour of the methane - air mixtures between 7.5 and 11.75%, is that with these mixtures the flame goes into vibration in the lower half of the tube and extinguishes itself when its amplitude upward into the burnt gas above the flame becomes too great. Thus it is not really a case of failure of ignition but one of failure of the flame to reach the mixture in the tube AB. The amplitude of vibration was sometimes quite large and could readily be observed by using the glass tubes. By suitably adjusting the rate of flow, a stationary flame which vibrated continuously at an audible frequency could usually be obtained at a point about 3/4 down the tube.

This was not observed with the coal gas mixtures except for very small concentrations, nor was it obtained with methane mixtures outside the above limits, ie. 7.5 to 11.75%. In these cases the flame travelled steadily down the tube without vibrating.

The phenomenon appears to be very similar to that occurring in a Rijke Sounding Tube[16]. This consists simply of a fairly large vertical tube having a piece of wire gauze stretched across the tube at a distance of about 1/5 of its length from the lower end. When the gauze is heated by a bunsen flame and the flame removed, the tube emits a powerful note as the gauze cools. No sound is produced if the

tube is horizontal. The effect is dependent on the upward convection current of air through the tube and on the fact that the gauze forms a sharp surface of separation between two volumes of air, one hot and the other cold. When the tube is horizontal there is no unidirectional convection current and no sharply marked surface of separation.

With flame propagation along horizontal tubes the same effect is obtained as with vertical ones. The reason for this is that there is ~~that there is~~ still a steady flow of gas along the tube and a sharply marked surface, ie. the flame front, separating the cold unburnt gas from its heated products of combustion.

The phenomenon of the almost spherical flame under the holes in the thin plates was also obtained, though slightly modified, with the methane - air mixtures containing more than 12.25% of methane. This almost hemispherical flame differed from those observed with the coal gas mixtures in that it neither expanded to a diameter greater than that of the hole above, nor vibrated at an audible frequency. It also lasted for a much shorter time under the plate, usually about 2, and never more than 5, seconds.

Flame separation took place with the methane - air mixtures of concentration greater than 12.0%, a bright green hemispherical flame travelling down the tube leaving a pale blue cone burning at the top.

This latter phenomenon is probably responsible for the fact that the limiting diameter for propagation along tubes increases more rapidly for concentrations greater than c_o, than it does for concentrations less than c_o. Thus since combustion in the hemispherical flame is incomplete, the amount of heat liberated therein is less than would be given by the equation,

$$Q = \frac{100 - c}{100 - c_o} Q_o ,$$

where Q_o is the amount of heat liberated by the complete combustion of I cc. of the theoretical mixture of concentration c_o

Results with Methane-Air Mixtures.

Copper Foil.

The graphs of the limiting diameters obtained by Methods I, II, and III, are shown in Graphs IV , and it may be seen that they are very similar to the corresponding ones for coal gas air mixtures. The minimum diameter is 3.46 mm., which is 1.92 times the minimum for coal gas and occurs at 9.88 . Graph III, shows the variation with concentration of the minimum diameter for hole which will just give a self-supporting flame, ie, Method IV, page 41.

Mica Plates.

From 6.5 to 9.25% , the limiting diameters for the mica and copper foil plates were identical. For greater

concentrations the diameters for the mica plates were slightly less than those for the copper foil. See Table II. The curve given by Method III, from 10.5 to 13.0% , was the same, within the experimental error, as the corresponding curve for copper foil.

Tubes.

In agreement with the results for coal gas air mixtures, the limiting diameters for propagation along copper and glass tubes were the same for all concentrations examined, ie. from 6.38 to 12.5% . The minimum diameter for propagation along tubes is 3.80 mm. and occurs at a concentration of 9.63 . With the methane mixtures the difference between the diameters for propagation along tubes and for ignition through circular holes in thin plates was more distinctly marked than with the coal gas mixtures.

A piece of apparatus was assembled which allowed the limiting diameters for horizontal propagation to be determined. With this it was found that the limiting diameters for horizontal and vertically downward propagation were identical for all mixtures examined.

Graph IV.

Methane-Air Mixtures.

Propagation along copper tubes in Red.

Ignition through copper foil in Blue.

Ignition through copper foil,

Method III, in Green.

Limiting Diameter in mm.

90
85
80
75
70
65
60
55
50
45
40
35

d.

6·0 7·0 8·0 9·0 10·0 11·0 12·0 13·0 14·0

c.

Percentage of Methane in Mixture. (By Volume)

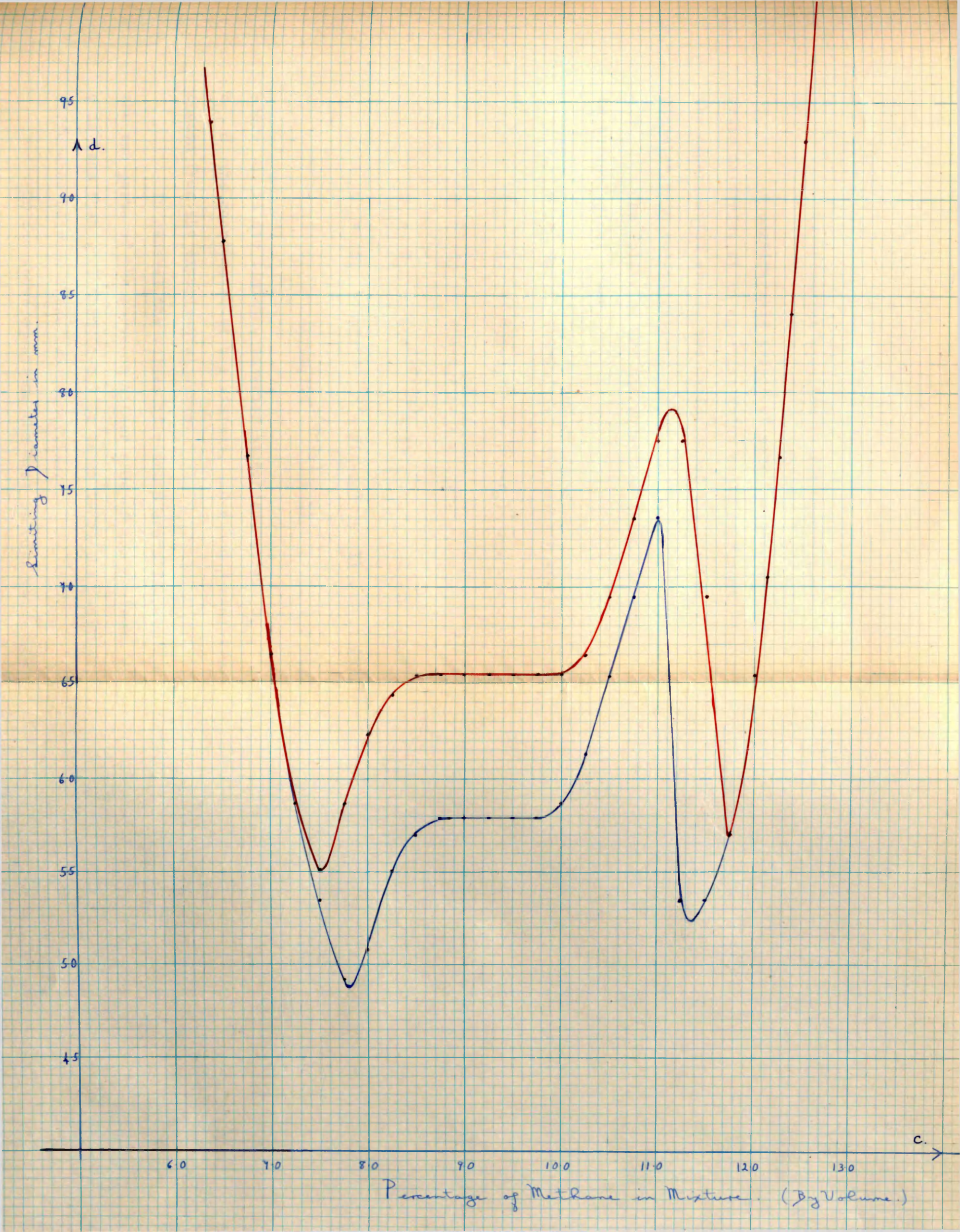
Graph V.

Methane-Air Mixtures.

Ignition after propagation along tubes.

Vertical tubes in Red.

Horizontal tubes in Blue.


95
λ d.
90
85
80
75
70
65
60
55
50
45
Limiting Diameter in mm.
6·0
7·0
8·0
9·0
10·0
11·0
12·0
13·0
C.
Percentage of Methane in Mixture. (By Volume.)

Experimental Equation to fit Observations.

A considerable amount of work has been done in order to arrive at an equation which would represent, within the experimental error, the variation of the limiting diameter with concentration.

The following are the equations tried, arranged in chronological order,

$$d = d_o + \alpha(c-c_o)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (1).$$

$$d = d_o + \alpha(c-c_o)^3 + \beta(c-c_o)^4 \quad \ldots\ldots\ldots (2).$$

$$d = d_o + \alpha(c-c_o)^{\beta} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3).$$

$$d = d_o + \alpha(e^{\beta(c-c_o)} - 1) \quad \ldots\ldots\ldots\ldots (4).$$

$$d = d_o + \alpha(e^{\beta(c-c_o)} - \beta(c-c_o) - 1) \quad \ldots\ldots (5).$$

$$d = d_o + \alpha(c-c_o)(e^{\beta(c-c_o)} - 1) \quad \ldots\ldots\ldots (6).$$

where d is the limiting diameter at concentration c, c_o, d_o the coordinates of the minimum, and α and β constants chosen from the experimental curve.

In general the values of α and β are different for the two parts of the curve on either side of the minimum. If c is less than c_o, then $(c-c_o)$ is taken to be the positive difference between these two quantities.

Of the above equations the best is (6), which can

be fitted to most of the curves within the experimental error. For example, for propagation along tubes with methane air mixtures, the limiting diameter can be represented by

$$d = 3.80 + .2326(9.63 - c)(e^{.6580(9.63 - c)} - 1) \text{ mm.}$$

if c is less than 9.63% and by

$$d = 3.80 + .1553(c - 9.63)(e^{.8974(c - 9.63)} - 1) \text{ mm.}$$

if c is greater than 9.63%.

The agreement between the experimental and calculated values in the case of copper foil is shown in Table II. Further values of the constants for other curves are given in Table III.

Table III.

Methane - Air Mixtures. Equation (6).

Graph.	c_o.	d_o.	Range.	α.	β.
Copper Foil. Method I, II.	9.88	3.46mm.	$6.38 \leq c \leq 9.88$ $9.88 \leq c \leq 13.25$	.2233mm. .05868mm.	.5780. 1.039.
Copper Foil. Method III.	9.88	3.46mm.	$9.99 \leq c \leq 13.25$	.1613mm.	.7109.
Copper Tubes. Methods I, II.	9.63	3.80mm.	$6.38 \leq c \leq 9.63$ $9.63 \leq c \leq 12.50$	.2326mm. .1553mm.	.6580. .8974.

Table II.

Methane - Air Mixtures.

Limiting Diameters for Ignition through Circular Apertures in Copper Foil and Thin Mica Plates by Methods I and II.

Conc. %	Copper Foil.	Calc. Dia.	Mica Plates.	Conc. %	Copper Foil.	Calc. Dia.	Mica. Plates.
5.00		16.82mm.		10.00	3.46mm.	3.46mm.	3.29mm.
5.50		14.25		10.25	3.49	3.47	3.29
6.00		10.75		10.50	3.53	3.49	3.37
6.25		9.24		10.75	3.57	3.54	3.45
6.38	8.65mm.	8.59		11.00	3.64	3.61	3.53
6.50	8.03	8.03		11.25	3.75	3.72	3.63
6.75	7.05	7.03	7.04mm.	11.50	3.88	3.88	3.74
7.00	6.17	6.22	6.15	11.75	4.06	4.12	3.92
7.25	5.52	5.56	5.51	12.00	4.45	4.47	4.24
7.50	5.00	5.03	5.09	12.25	4.92	4.96	4.82
7.75	4.59	4.61	4.62	12.38	5.25	5.28	5.14
8.00	4.25	4.29	4.24	12.50	5.70	5.66	5.51
8.25	4.03	4.03	4.04	12.75	6.66	6.64	6.43
8.50	3.88	3.84	3.88	13.00	8.03	7.98	7.57
8.75	3.75	3.69	3.74	13.13	8.84	8.85	
9.00	3.64	3.59	3.63	13.25	9.88	9.85	
9.25	3.56	3.52	3.52	13.50		12.43	
9.50	3.50	3.48	3.42	14.00		20.80	
9.75	3.47	3.46	3.31				

In some cases equation (4) gives fairly good agreement and although it has the theoretical disadvantage of not having a minimum at c_o, d_o, it has the advantage of simplicity.

The method of obtaining the values of α and β for equations (4) and (6) is interesting, since unless it is used, an equation, which can only be solved by successive approximation, is obtained for β.

α and β are determined from the coordinates of two other points on the curve beside those of the minimum. Let these two points be chosen so that the value of $(c-c_o)$ for one is exactly twice the value for the other. Thus if c', d' are the coordinates of a point about half way along the curve from the minimum, find, from a large scale graph if necessary, the diameter corresponding to the concentration $2c' - c_o$ aand let it be d".

On substituting in equation (6) say, we have,

$$d' = d_o + \alpha(c'-c_o)(e^{\beta(c'-c_o)} - 1)$$

and

$$d'' = d_o + 2\alpha(c'-c_o)(e^{2\beta(c'-c_o)} - 1)$$

Whence on eliminating $e^{\beta(c'-c_o)}$ by squaring and solving for α we have,

$$\alpha = \frac{2(d' - d_o)}{(c' - c_o)\left(\frac{d''-d_o}{d'-d_o} - 4\right)}$$

Using this equation to eliminate α from one of the previous equations we obtain,

$$\beta = \frac{1}{(c'-c_o)} \log_e \left[\frac{(d''-d_o)}{2(c'-c_o)} - 2 \right]$$

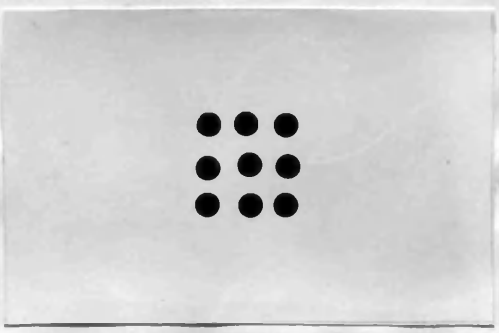
. . .

Nine Hole Gratings.

Some interesting experiments were made with a number of holes (9) drilled fairly close together through sheets of copper foil and mica in order to reproduce approximately the conditions for propagation through a gauze. The object of the experiments was to see to what extent the limiting diameter for ignition was affected when the single flame in the previous experiments was closely surrounded by similar flames.

These gratings, as they will be called, consisted of nine holes of equal diameter drilled through the sheets so as to lie wholly, and as symmetrically as possible, within a square whose side was 1.53 cm. Their disposition is shown in Fig. V , which is obtained by using the 3.25 mm. grating as the negative in the usual photographic printing process.

Fig. V.



For both copper foil and mica sheets five such gratings were made, the diameters of the holes being 3.05, 3.25, 3.44 3.56 and 3.78 mm. and the shortest distances between the edges of adjacent holes in the same row 2.3, 2.0 1.8, 2.0 and 1.8 mm..

As the central flame will be well surrounded by similar flames and possibly the cooling effect from its hemispherical surface considerably reduced, it might be thought that the limiting diameter would have to be appreciably less than that for a single hole. This effect was observed but was comparatively small, a 15% reduction in diameter being sufficient in all cases examined.

Methane-Air Mixtures.

The gratings were secured over the upper end of the vertical explosion tube in the same manner as described on page 34, the central hole in the grating being concentric with the tube. When the rate of flow of the mixture through the grating was sufficient, the flame which formed above it consisted of nine bright bluish-green discs burning directly above the holes, together with a pale blue flame which joined up the bright discs so as to give a continuous flame above the area of the grating. This was a fairly flat flame, the total height being about 5 mm..

When the rate of flow was reduced, if the diameter was less than the limiting diameter, the bright bluish-green discs were replaced by hemispherical flames having long vertical tails which bent in towards the centre and joined together so as to form a tall conical flame about 2.5 cm. high. When the rate of flow was further reduced, this conical flame

went out abruptly without producing ignition of the mixture in the tube AB. Before this happened however, the four flames burning at the corner holes went in and out intermittently, being relit from the central conical flame. Thus these flames were in a constant state of vertical vibration and it is just possible that this was responsible for ignition through smaller holes than normally. See page 45, clause (4).

If the diameter was slightly greater than the limiting value, then ignition was produced before this tall conical flame was formed and seemed to be due to the bright bluish-green discs sinking down simultaneously through the grating.

The results obtained with methane-air mixtures containing between 8.0 and 10.0% methane are given in Table IV. They show that over this range an average decrease in diameter of 6.3% from the limiting diameter for ignition through a single hole in copper foil is necessary to prevent ignition through a grating of the above description. In the case of mica gratings the reduction required is slightly greater, being 7.4%. The difference in limiting diameter for ignition through the copper foil and mica gratings was comparatively small, the diameters for the mica ones being only 2.7% less than those for the copper foil.

Table IV.

Nine Hole Gratings.

Methane Air Mixtures.

c. %	d_c.	d'_c.	$\frac{d_c - d'_c}{d_c}$	d_m	d'_m	$\frac{d_m - d'_m}{d_m}$	$\frac{d'_c - d'_m}{d'_c}$
8.00%	4.25mm.	3.78mm.	11.06%	4.24mm.	3.82mm.	9.90%	
8.25	4.03	3.73	7.44	4.04	3.70	8.42	.85 %
8.50	3.88	3.62	6.71	3.88	3.55	8.51	1.93
8.75	3.75	3.50	6.67	3.75	3.41	9.06	2.57
9.00	3.64	3.41	6.32	3.63	3.35	7.72	1.62
9.25	3.56	3.35	5.90	3.53	3.28	7.09	2.09
9.50	3.50	3.28	6.28	3.42	3.20	6.42	2.50
9.75	3.47	3.28	5.48	3.31	3.11	6.04	5.17
10.00	3.46	3.28	5.48	3.29	3.11	5.47	5.17
			AV.= 6.29%			AV.=7.35%	2.74 %

Where c is the percentage by volume of methane in the mixture,

" d_c " " limiting dia. for a single hole in copper foil,

" d'_c " " " " " " " copper foil grating,

" d_m " " " " " " " single hole in mica,

and " d'_m " " " " " " " mica grating.

Coal Gas Air Mixtures.

The above set of gratings enabled the range of coal-gas air mixtures from 11.0 to 12.5 % to be examined. The results which are given in Table V, were very similar to those obtained with the methane-air mixtures, only the decreases in diameter necessary were greater. This could have been predicted from the Methane results which show that the percentage differences increase as the concentration of the mixture approaches the usual lower limit of inflammability.

The average reduction in diameter found necessary were :-

Single hole in copper foil to copper foil grating . . . 10.4 %

" " " mica " mica " . . . 14.3 %

Copper foil grating to mica grating . . . . . 4.9 %

With the gratings it was possible to maintain a self-supporting flame down to 11.0% , whereas with the single holes this was not possible below 12.5 .

It should be pointed out that the flames in all these experiments, ie. with tubes, single holes in thin plates and nine hole gratings, cannot be left burning indefinitely without ultimately producing propagation or ignition, independently of the rate of flow of the mixture, or of the thermal conductivity of the material of the tube, thin plate or grating. This is due to the heating up of the material by the flame which allows the flame to travel through a smaller diameter than normally. From equation (9) we see that if To increases, then the limiting diameter is reduced. It is obvious that d must tend to zero as the temperature of the unburnt mixture tends to the ignition temperature of the gas, ie. as T_o tends to T_i.

It is only when the under surface of the flame is approximately hemispherical that the temperature of the material remains sensibly at room temperature, no matter how long the flame is allowed to burn or of what material the tube, thin plate or grating is made. In Method I, the rate of flow was adjusted so that when the escaping gas was lit, the flame which formed was of the flat disc type shown in Plate I, page 36 , at (c). The rate of flow was then quickly adjusted so as to give the hemispherical type of flame shown at (d) , Plate I. the disc flame only being allowed to remain for a few seconds.

The time during which a flame of the disc type could be kept burning without affecting the limiting diameter depended on the thermal conductivity of the material and on the

concentration of the mixture. It was less for mica and glass than for copper and decreased as the concentration of the mixture approached the usual upper limit of inflammability. For thin plates it was of the order of 10 seconds for mica and 10 minutes for copper.

These experiments may be interpreted in the following manner. Suppose we have a gauze stretching across a tube which is filled with a stationary explosive mixture and which is greater in diameter than the limiting value for propagation with that mixture. If the mixture is ignited at an open end of the tube, the flame will travel along until it comes to the gauze, where it will either be extinguished in a few seconds, or will propagate through and continue along the tube. Under these circumstances, the effectiveness of the gauze in preventing propagation will be determined primarily by the size of its orifices, the thermal conductivity of its material being comparatively unimportant, The actual size of the orifices will probably have to be less than those specified above, since the flame will have a finite velocity when it reaches the gauze, whereas those already determined refer to zero flame velocity.

If, however, the mixture, instead of being stationary, is flowing along the tube towards the open end with a steady velocity which is greater than a certain minimum and less than the normal flame velocity along the tube, then, when the flame reaches the gauze, it will ~~it will~~ either

propagate through or will continue to burn on the side of the gauze nearest the open end of the tube. I take it that this represents more closely the conditions existing in a safety lamp.

Under these conditions it is not primarily a question of extinguishing the flame immediately, but one of conducting the total heat of the flame away, so as to prevent the gauze being heated up ultimately to the ignition temperature of the gas, or to a temperature at which the flame is able to propagate through its orifices. Hence the thermal conductivity of the material of the gauze will have an important bearing on the effectiveness of the gauze in preventing propagation through time, as well as the size of its orifices.

The minimum rate of flow referred to above is the limiting rate which is just sufficient to ensure that the surfaces of the small flames facing the orifices will be approximately hemispherical. If this rate is not exceeded then the effectiveness of the gauze is still determined primarily by the size of its orifices.

Variation of Velocity of Flame Propagation with Tube Diameter.

In the theory given in the Introduction,(see page 7), it is assumed that, at the limiting diameter for propagation, the small hemispherical flame burning at the top of the tube goes out abruptly when the rate of flow of the mixture up the tube is equal to the limiting value to which the velocity of propagation tends at the limiting diameter.

Let v' be the velocity of the mixture which is just great enough to maintain the hemispherical flame burning at the top of the tube, for diameters less than the limiting diameter and let v" be the velocity of the mixture which is just great enough to prevent the hemispherical flame from travelling down the tube for diameters greater than the limiting diameter. It is thus necessary to prove experimentally that v' and v" tend to the same limit at the limiting diameter for propagation.

The method of measuring v' was as follows:- Having made up a mixture of known concentration in the container, the rate of flow was adjusted so that a hemispherical flame was just able to burn at the top of the tube and the time taken for 500 cc. of the mixture (as measured by displacement with water from the container) to flow through the tube read by a stop-watch. This time was of the order of 300 seconds. The rate of flow was then slightly decreased so that it was

just impossible to maintain a hemispherical flame at the top of the tube and the time taken for 500 cc. to flow again noted. The mean of these two times was used to calculate, knowing the diameter of the tube, the velocity which would just allow a hemispherical flame to burn at the top of the tube. The percentage difference between the two times was usually about 7% . A similar procedure was followed in determining v".

At the same time measurements were made of the greatest rate of flow which would allow any type of flame to burn at the top of the tube, the flame being carried upwards for higher velocities. Usually 1000 cc. of the mixture was used in making these determinations. The type of flame which formed corresponded to either (a) or (b) in Plate I, page 36 .

Results.

The values of v' and v" for 9.5 and 8.5 % methane - air mixtures are shown by the curves AB and BC in Graphs IX and X . It is clear that v' and v" tend to the same value at the limiting diameter, which is represented by BD. The value of this limit is 14.0 cm./ sec. for the 9.5 % mixture and 13.2 cm./ sec. for the 8.5 % mixture.

On plotting the actual rate of flow, ie. $\pi r^2 v"$, against the diameter 2r, it is found that, for the curves BC, the graph is practically a straight line+. Hence for diameters slightly greater than the limitimg diameter, the velocity of

+ See Graph X.

propagation is given by

$$\pi r^2 v'' = -a + br$$

or

$$v'' = \frac{A}{r} - \frac{B}{r^2}$$

From the graphs we find that the curve BC in the case of the 9.5% mixture can be represented by

$$v'' = \frac{14.90}{r} - \frac{2.34}{r^2} \text{ cm./sec.}$$

and in the case of 8.5% by

$$v'' = \frac{13.82}{r} - \frac{2.30}{r^2} \text{ cm./sec.,}$$

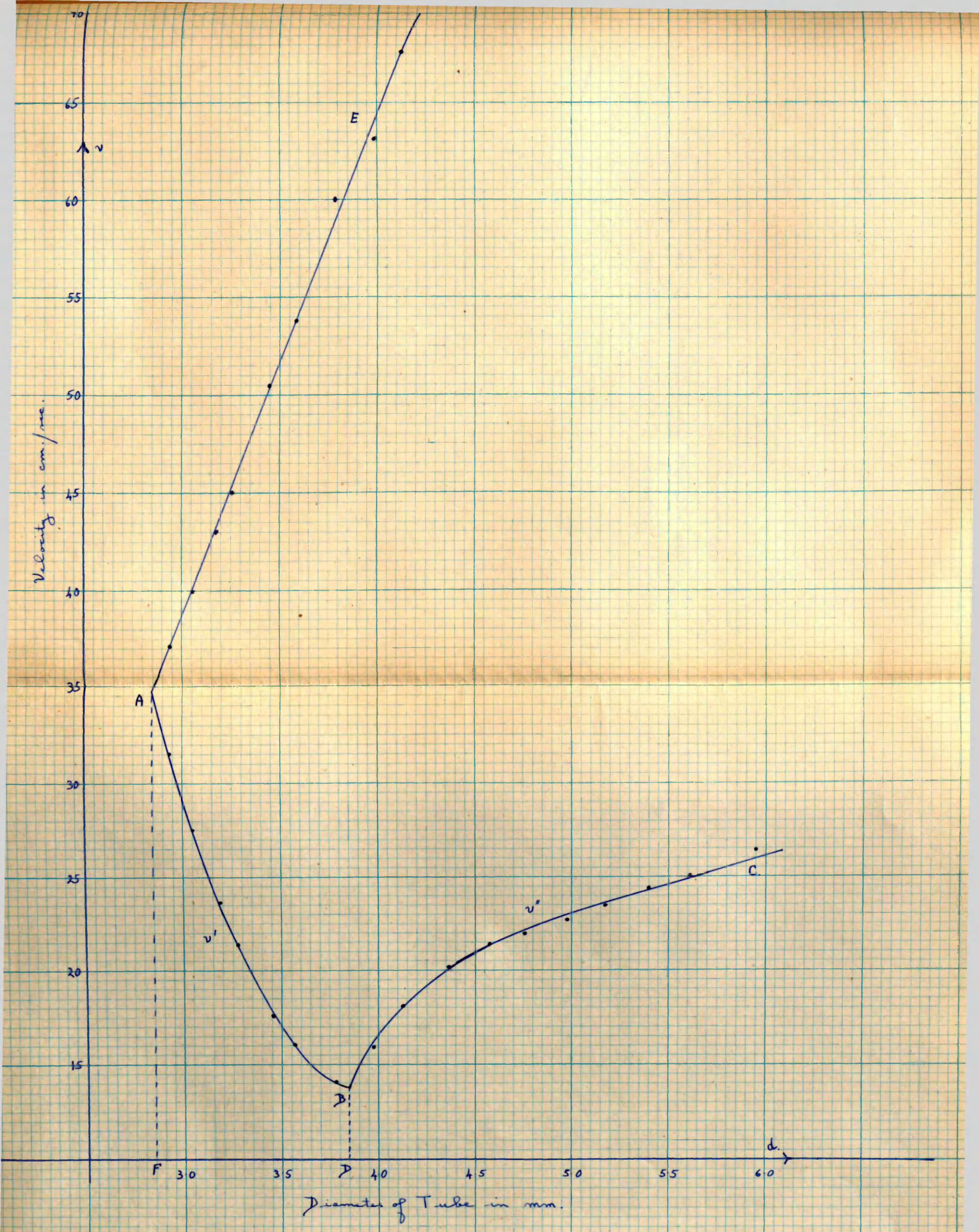
for $r' \leq r \leq \frac{3r'}{2}$, where r' is the limiting radius for propagation.

In both graphs the curves AE show the variation with diameter of the greatest velocity of the mixture which will allow a flame to be maintained at the top of the tube. The diameter corresponding to the point A, at the intersection of the curves AB and AE, is the limiting diameter determined by Method IV, page 41.

By the same method it has been found that the value of v' for a 29.6 hydrogen air mixture is 71.76 cm./sec. for a .89 mm. tube and 66.31 cm./sec. for a .95 mm. tube.

Graph IX.

Values of v' and v" for
a 9.5% methane-air mixtures and
copper tubes 3/8" in external diameter.


70
65
60
55
50
45
40
35
30
25
20
15
v
E
A
B
C
v'
v''
Velocity in cm./sec.
F
30
35
D
40
45
50
55
60
d.
Diameter of Tube in mm.

Graph X.

Values of $\pi r^2 v'$ and $\pi r^2 v''$ for an 8.5% methane-air mixture and copper tubes 3/8" in external diameter.

Rate of Flow in cc./sec.

120
110
100
90
80
70
60
50
40
30
20
10

$\pi r_1^2 v$

E

C

$\pi r_2^2 v$

A

$\pi r_1^2 v$

B

F

3·5 4·0 D 4·5 5·0 5·5 6·0 6·5 7·0

$2r = d$

Diameter of Tube in mm

Hydrogen - Air Mixtures.

The hydrogen[+]- air mixtures have been characterised by the violence of the resulting explosion and the small value of the limiting diameter for propagation over a large part of the explosive range. As before the mixtures were made up over water in a 10.7 litre glass container. The main results were very similar to those described in detail for the coal gas air mixtures. The hydrogen flames were very pale blue in colour and almost non-luminous, so that it was necessary to work in a dark room.

With the hydrogen mixtures it was possible to maintain a self-supporting flame burning at the top of the tubes or above the holes in the thin plates down to 13.5%, so that Method II, page 38 was not employed. The behaviour of the flames in propagating along the tubes was simpler than with the methane-air mixtures, as they did not go into vibration in the lower half of the tube. See page 52. Thus if the diameter of the tubes was great enough to give propagation, the flame, travelling steadily down the tube, produced ignition of the rest of the mixture in the vertical explosion tube AB. This was true for all three sets of tubes and held for all mixtures examined, ie. from 13.5 to 65% of hydrogen. The coal gas air mixtures, (see page 43), behaved in a similar manner over the most explosive part of the range.

+ The hydrogen was supplied by the British Oxygen Company, Manchester, and stated to contain less than 1/2% of impurities

The phenomenon of flame separation was observed with mixtures containing more than 56% of hydrogen, the flame which travelled down the tube being of a deep purple colour, while that which remained at the top was the normal, almost non-luminous hydrogen air flame.

The almost spherical flame burning under the holes in the thin plates was observed when the concentration of the hydrogen was greater than 45% . The time, during which it was possible to keep this flame burning under the plate without producing general ignition, was remarkably long. Thus by allowing a 50.0% hydrogen mixture to escape very slowly into the tube AB, it was possible to keep this almost spherical flame burning for 5 minutes 56 seconds under a 1.05 mm. hole in a mica plate without producing general ignition. As before it was possible, by opening the needle valve slowly, to cause the spherical flame to rise up through the hole and give a disc flame burning as previously above the plate. See page 41.

These spherical flames under the plates did not vibrate at an audible frequency, but with mixtures containing more than 45% of hydrogen, the small flame burning at the top of the tube emitted a high pitched note just before going out, if the diameter of the tube was less than the limiting value for propagation.

Results with Hydrogen Air Mixtures.

Copper Foil.

Graph VI shows the variation of the limiting diameter obtained by Methods I and III for concentrations between 13.5 and 65% of hydrogen. The minimum diameter is .80 mm. and occurs at 35% . This is only .444 that for coal gas air mixtures and .231 that for methane air mixtures.

Mica Plates.

From 13.5 to 28% , the limiting diameters were about 5% less than the corresponding ones for copper foil. For concentrations between 28 and 42% it was not possible to use the mica plates as the force of the explosion was so great that it damaged the plates. Frequently the circular disc of mica inside the clamp ring was blown right out of the plate. This is rather remarkable as the lower end of the explosion tube just dipped under a water surface. For concentrations greater than 42% the ease with which the flames heated the edges of the holes red hot made it difficult to determine the limiting diameter exactly.

Tubes.

As with every other gas examined, the limiting diameters for propagation along copper and glass tubes were identical for all concentrations between 13.5 and 65% . The minimum diameter is .90 mm. and occurs at a concentration of 33 . The curve, shown in Graph VI , differs from those already obtained as it rises more quickly to the left of the

,

minimum than it does to the right.

It is interesting to note that Mallard and Le Chatelier[17] found that the limiting diameter for propagation with a 30.% hydrogen air mixture was .9 mm.. From the graph this limiting diameter is .93 mm.,with an error of ± .023 mm.

The observations of Messrs W.A. Haward and T. T. Otagawa[18] show that the maximum uniform flame speed with hydrogen air mixtures in a 2.5 cm. tube is obtained with a 38.6% mixture. Thus the minimum on the curves again lies between the concentration for theoretically complete combustion and the concentration for maximum uniform flame speed. The concentration for the former is 29.6%, see page 18.

Graph VI.

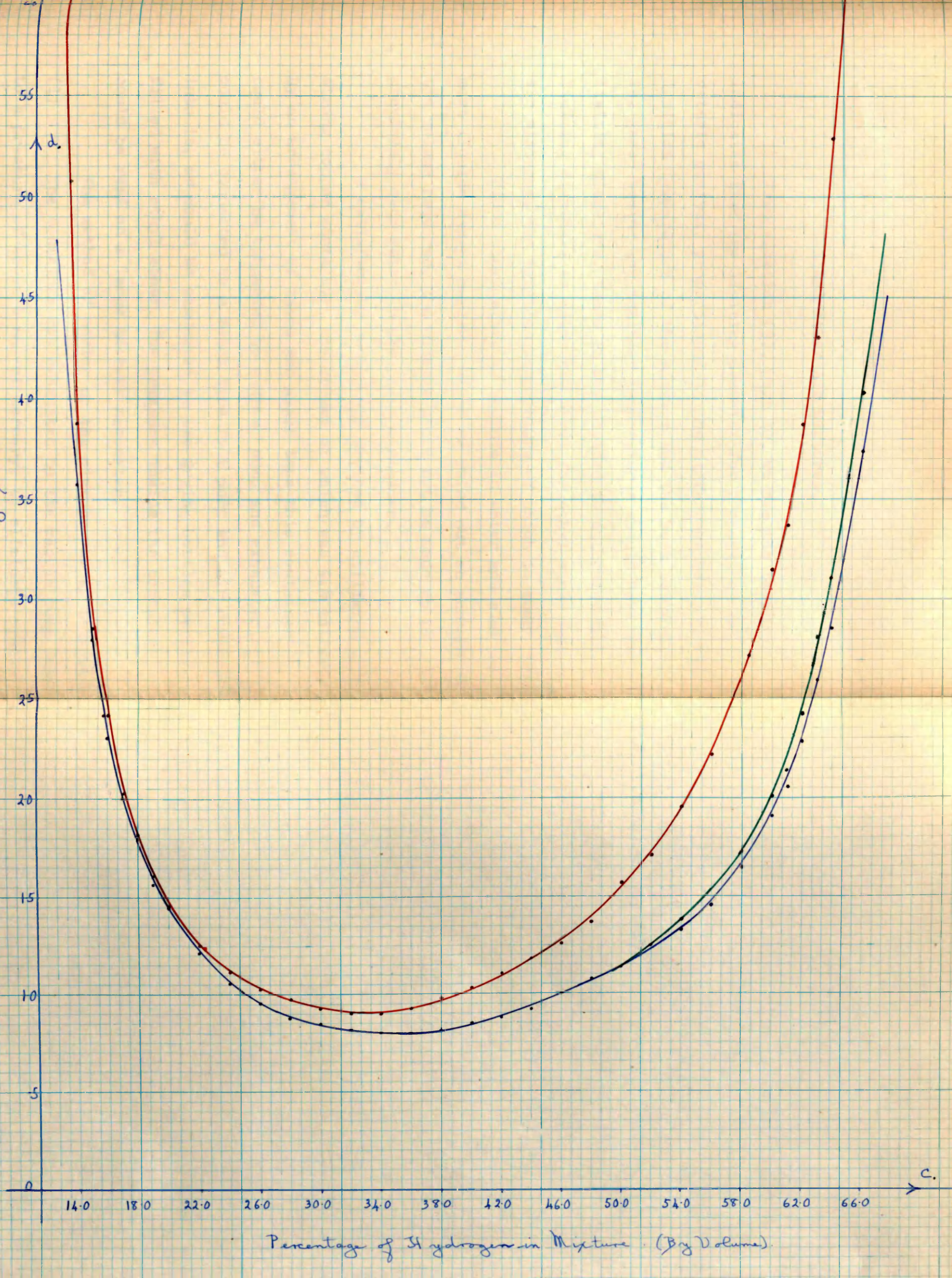
Hydrogen-Air Mixtures.

Propagation down vertical copper tubes in Red.

Ignition through copper foil in Blue.

Ignition through copper foil,

Method III, in Green.


d.
55
50
45
40
35
30
25
20
15
10
5
0
Limiting Pressures in mm.
C.
14·0
18·0
22·0
26·0
30·0
34·0
38·0
42·0
46·0
50·0
54·0
58·0
62·0
66·0
Percentage of Hydrogen in Mixture (By Volume).

Ethyl Ether Air Mixtures.

From equation (9), page 10, we see the theory indicates that the limiting diameter for propagation is, ceteris paribus, proportional to the difference between the ignition temperature of the mixture and the room temperature, ie. gases having low ignition temperatures should have small limiting diameters. Hence it was decided to determine the limiting diameters as described above for ethyl ether vapour air mixtures, the ignition temperature of which is about 190°C[19]

Since ethyl ether is soluble in water and also in most liquids except mercury, which is ruled out on account of the volume required, the mixture could not be made up as previously over water in the glass container.

A satisfactory method was devised by utilising a strong copper container, the volume of which was 4.8 litres. By an arrangement of tubes and glass taps this container could either be connected to a Hyvac pump and exhausted, or could be connected to a motor tyre foot pump and air compressed into it, or could be connected to two drying bottles partly filled with ethyl ether. The pressure inside the container could be read on a large mercury manometer.

The method of making up the mixture was as follows:-

(1) The container was exhausted by the vacuum pump down to a pressure of about 1 mm. of mercury. to eliminate traces of the previous mixture.

(2) Air was admitted to the container through the normal outlet tube till the pressure inside was (p - h) cm. of mercury, p being the barometric pressure and h about 20 cm..

(3) The container was then connected to the ether saturators and air drawn through the ether in the two bottles till the pressure inside was again atmospheric. This air was first dried by bubbling through concentrated sulphuric acid.

(4) The container was connected to the foot pump and air forced into the container till the pressure inside was (p + h') cm., h' being usually 80.0 cm. of mercury.

Let V be the volume of the container and p_s the saturation vapour pressure of the ether at the temperature of that in the second saturator. The temperature of this ether was kept fairly constant by immersing the bottle in a water bath.

Thus the volume of ether vapour at atmospheric pressure drawn into the container by operation (3) is

$$\frac{V p_s h}{p^2}$$

and the volume when compressed to (p + h') is

$$\frac{V p_s h}{p(p + h')} .$$

Thus the percentage of ether vapour in the mixture is

$$c = \frac{100 p_s h}{p(p + h')}$$

In order to determine p_s for the ether used, two barometer tubes were constructed and mounted side by side. A little of the ether was admitted to the top of one of the columns, so that the difference between the level of the mercury in the tubes gave the saturation vapour pressure of the ether at room temperature. The temperature was read on a Cas-ella alcohol thermometer graduated in fifths of a degree Centigrade.

By means of this apparatus it was found that the vapour pressure could be represented by

$$p_s = 11.73 + 1.666\,\theta \text{ cm. of mercury,} \quad . \quad . \quad (2)$$

over the range from 14 to 17°C, θ being the temperature in °C. This equation was used to calculate p_s in the above formula for the concentration of ether in the mixture, θ being taken as the temperature of the water bath surrounding the second ether saturator. During process (3) above, the temperature of this bath never changed by more than .05°C.

From the values of p_s at 0°, 10° and 20°C given in Kaye and Laby's Tables[20], the values of the constants in the Kirchhoff-Rankine-Dupré vapour pressure formula have been calculated, giving

$$\log_{10} p_s = 27.534 - \frac{2345.7}{\psi} - 6.8448 \log_{10} \psi \text{ mm,} \quad . \quad . \quad (3)$$

ψ being the absolute temperature.

This equation gives p_s = 35.81 cm. at 15°C and $\frac{\partial p_s}{\partial \psi}$ = 1.60 cm./°C. at 15°C., while equation (2) above gives p_s = 36.73 cm. and $\frac{\partial p_s}{\partial \theta}$ = 1.666 cm./ °C. at 15 °C. The difference between the two values of p_s amount to 2.54% .

It soon became evident, that the limiting diameters for the ether air mixtures were very sensitive to small changes in the concentration of the ether and on account of this, it was difficult to obtain absolutely consistent results.

Thus on drawing off the mixture from the top of the container, which was only 27.3 cm. high, it was found that the mixture behaved as if the concentration of the ether was steadily increasing as the mixture was used up; ie. for concentrations less than 5.1 % the limiting diameters tended to decrease as the mixture was used, while for greater concentrations they tended to increase. This was interpreted as indicating that the concentration of the ether vapour at the foot of the container was slightly greater than at the top.

To prove this, two outlets were taken from the container, one from the foot and the other from the top, and connected to the needle valve so that, by turning two taps, the mixture could either be drawn off from the foot or the top. In this way it was proved that the ether vapour tended to settle at the bottom of the container.

On making up a mixture of average concentration about 3.70 % and allowing it to stand for 15 hours, it was found that the limiting diameters for the top and foot fractions were

4.05 and 3.52 mm. respectively. From GraphVII, we see that these diameters correspond to concentrations of 3.61 and 3.85%. When used within half an hour of being made up, a mixture of the same average concentration gave limiting diameters of 4.05 and 3.68 mm. for the top and foct fractions. The limiting diameters for the top and foot fractions of an average 6.65 mixture, half an hour after being made up were 4.05 and 4.66 mm., corresponding to concentrations of 6.55 and 6.74 %.

The effect was eliminated by turning the rectangular container on its side so that the vertical height was only 11.3 cm. and by taking an outlet from its centre. The mixtures were allowed to stand for about 15 minutes before being used.

The usual phenomena obtained with the other combustible gases already examined were observed with the ether air mixtures; flame separation taking place with concentrations greater than 6.5 % and the almost spherical flame burning under the plates with concentrations greater than 6.25 %. This spherical flame did not expand to a diameter much greater than that of the hole above it and did not burn for any length of time under the plate, usually about one half and never more than five seconds. This made it difficult to decide whether ignition was taking place immediately (ie. in less than 1/5 sec.) by the hemispherical flame sinking down through the aperture, or by the almost spherical flame expanding and giving very slightly delayed ignition. The diameter which has been determined for ignition through the holes in the thin

plates for concentrations of 6.25% and greater, is the smallest diameter through which ignition can be obtained when the rate of flow is slowly reduced from that giving a hemispherical flame above the plate. It corresponds to the smallest limiting diameter in Table I, page 41.

Except for concentrations between 5.0 and 6.5%, the flame, travelling down the tube just large enough to give propagation, produced ignition of the mixture in the explosion tube AB. This applied to all three sets of tubes. Between these limits, the diameter of tube necessary to give ignition of the mixture in AB was greater than that for propagation alone but was not determined in each case.

It should be explained that with the ether air mixtures, the water surface WW', into which the lower end of the explosion tube AB dipped, was replaced by a mercury surface. See Fig. III. page 33.

Results for Ethyl Ether Air mixtures.

Copper Foil.

The shape of the curve obtained for the limiting diameter by Method I from 3.0 to 6.0% is similar to those previously obtained and is shown in GraphVII. The minimum diameter occurs at 5.10% and is 2.50 mm., ie. intermediate in value between those for coal gas and methane. From 6.0 to 7.0%, the graph shows the limiting diameter corresponding to the smallest one in Table I, page 41. The graph of the limiting diameter given by Method IV is drawn in Graph VIII.

Mica Plates.

The limiting diameters for the mica plates were about 5% less than the corresponding ones for copper foil between 3.0 and 6.0%.

Tubes.

The equality of the limiting diameters for propagation along copper and glass tubes was again verified over the range from 3.0 to 7.0%. The minimum diameter on the curve is 2.69 mm. and occurs at 5.13%.

The theoretical ether air mixture for complete combustion is $(C_2H_5)_2O + 6O_2 + 6.3.76N_2$, or 3.38% of ether. However if we assume that the carbon in the ether molecule is only burnt to carbon monoxide, the theoretical mixture for complete combustion is $(C_2H_5)O + 4(O_2 + 3.76N_2)$ or 4.99% of ether, which is nearer to the concentration at the minimum.

Graph VII.

Ethyl Ether Vapour - Air Mixtures.

Propagation down vertical copper tubes in Red.

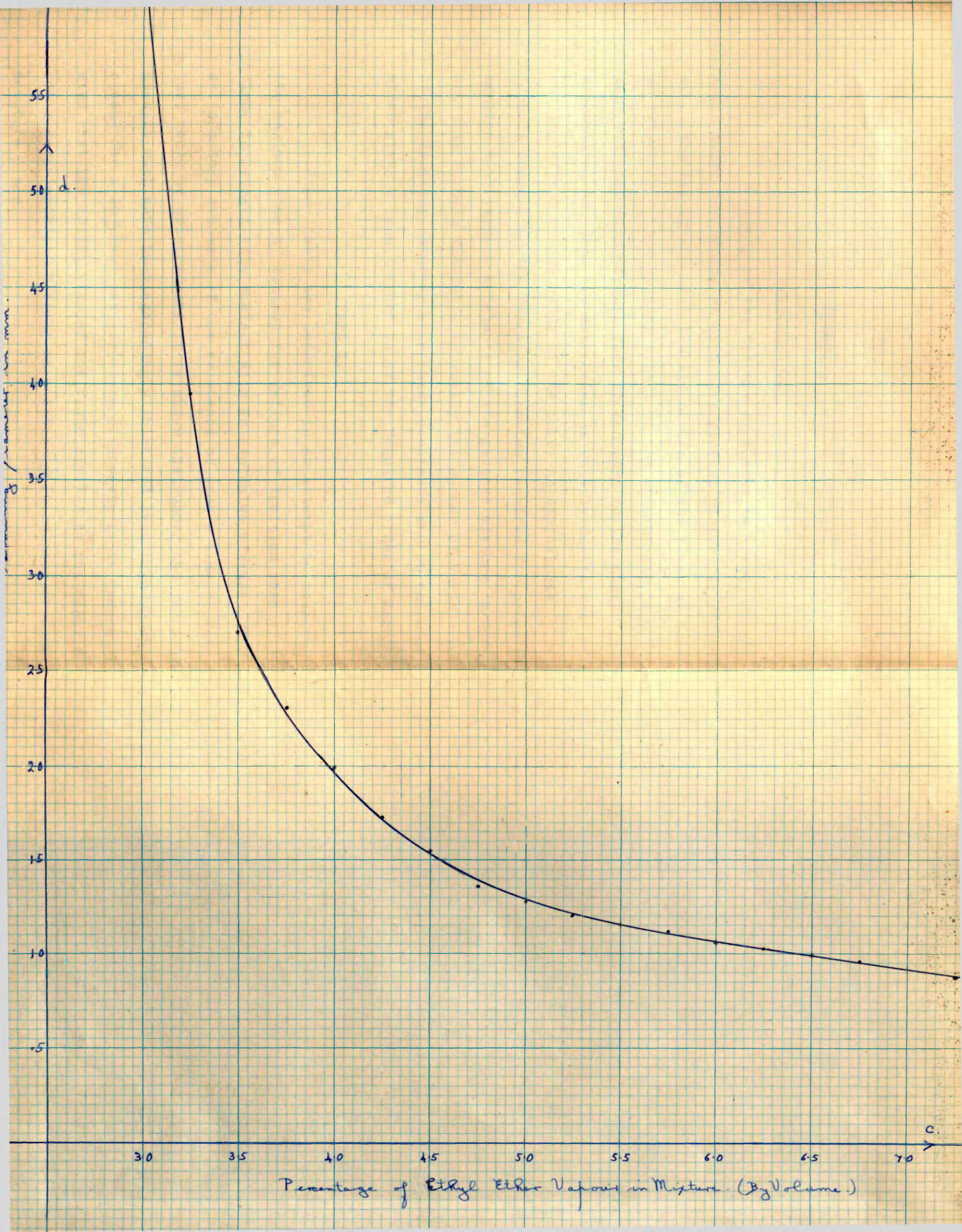
Ignition through copper foil in Blue.


d.
7·5
7·0
6·5
6·0
5·5
5·0
4·5
4·0
3·5
3·0
2·5
c.
3·0
3·5
4·0
4·5
5·0
5·5
6·0
6·5
7·0
Percentage of Ethyl Ether Vapour in Mixture. (By Volume.)

Graph VIII.

Ethyl Ether Vapour - Air Mixtures.

Method IV.


d.
55
50
45
40
35
30
25
20
15
10
5
c.
3·0
3·5
4·0
4·5
5·0
5·5
6·0
6·5
7·0
Percentage of Ethyl Ether Vapour in Mixture. (By Volume.)

Summary.

Introduction.

A theory of the failure of flames to travel along small tubes containing an explosive gaseous mixture is developed on the assumption that the extinction of the flame is caused primarily by the cooling effect of the unburnt gas in contact with the flame front. This is contrary to the usual assumption, ie. that the extinction is chiefly due to the cooling effect of the walls of the tube. An approximate formula connecting the limiting diameter required for propagation with various constants of the gaseous mixture is deduced. This formula indicates correctly the manner of variation of the limiting diameter with these constants and on calculation gives a result which is of the required order of magnitude.

Part I.

Experiments are described in an attempt to measure the maximum time of contact for failure of ignition when a flame is brought into contact with an explosive mixture. No satisfactory evidence of the existence of such a time of contact could be obtained and it is shown that under the conditions used, it must have been exceedingly short and less than .0007 second for a 20 % coal gas air mixture. However it is demonstrated that the actual size of the flame exposed to the mixture has a very important bearing on whether ignition does, or does not, take place.

Part II.

The actual arrangements and methods used for determining the limiting diameters for propagation along tubes and for ignition through circular holes in thin plates are described. It is found that for all explosive mixtures examined the limiting diameters for propagation along copper and glass tubes are identical, (within 2.5%) which is also true over part of the explosive range for ignition through circular holes in copper foil and thin mica plates

Curves showing the variation of the limiting diameters with concentration are given for coal gas air, methane air, hydrogen air and ethyl ether vapour air mixtures. These curves can be represented by an equation of the form

$$d = d_o + \alpha(c-c_o)(e^{\beta(c-c_o)} - 1)$$

where d is the limiting diameter at concentration c , c_o, d_o the coordinates of the minimum and α and constants.

It is shown that the area of the limiting aperture for ignition through thin plates does not remain constant as its shape is changed.

A detailed description and photographs are given of an almost spherical flame which may burn inside the explosive mixture for several seconds without producing general ignition.

Experiments are described in which the limiting diameters for ignition through nine hole gratings in copper foil and thin mica plates are determined for part of the explosive

range of methane air and coal gas air mixtures. These show that the limiting diameters have to be slightly less than those for ignition through single holes, the greatest difference observed being 15 .

Measurements of the velocity of flame propagation in tubes whose diameter is slightly greater than the limiting diameter and of the rate of flow at which the hemispherical flame, burning at the top of tubes whose diameter is less than the limiting diameter, is extinguished, give experimental proof of assumptions made in the theory given in the Introduction.

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The experimental part of the above work was carried out in the Research Laboratories of the Natural Philosophy Department of Glasgow University and it affords me much pleasure to acknowledge my indebtness to Professor E. Taylor Jones for his helpful advice and encouragement.

1932 March 29.

John M. Holm.

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