

CLXXIV.—*The Dilution-limits of Inflammability of Gaseous Mixtures. Part I. The Determination of Dilution-limits. Part II. The Lower Limits for Hydrogen, Methane, and Carbon Monoxide in Air.*

By HUBERT FRANK COWARD and FRANK BRINSLEY.

PART I.—*The Determination of Dilution-limits.*

AN inflammable gaseous mixture may be diluted with excess of one or other of its components or with another gas or gaseous mixture, until the resulting mixture is no longer inflammable. The determination of the dilution-limits of inflammability has attracted considerable attention but the experiments done have led the various observers to give very different figures for one and the same mixture. This is most noticeably the case for mixtures of hydrogen and air, and of hydrogen and oxygen. These results are collected in the following tables, all mixtures of composition between the "lower limit" and the "upper limit" being regarded as inflammable by the individual observers. In those cases where two figures are given in the lower-limit column, the smaller indicates a mixture regarded as non-inflammable, the greater as inflammable. Conversely for the upper limit, the greater figure indicates a non-inflammable mixture, the smaller an inflammable mixture.

TABLE I.
Hydrogen-Air Mixtures.

	Lower limit (per cent. hydrogen).	Upper limit (per cent. hydrogen).	
Wagner (<i>Bayerisches Industrie und Gewerbeblatt</i> , 1876, 8, 186)	7.7—8.3	50—60	
Mallard and Le Chatelier (<i>Annales des Mines</i> , 1883, [viii], 4, 347)	6	80	
Broockmann (<i>J. Gasbeleuchtung</i> , 1889, 32, 189)	7	75	
Roszkowski (<i>Zeitsch. physikal. Chem.</i> , 1891, 7, 485; <i>J. Gasbeleuchtung</i> , 1890, 33, 491, 524, 535, 553)	9.2—9.5	64.7—65.0	
Clowes ("Detection of Inflammable Gas and Vapour," 1896)	5	72	
Le Chatelier and Boudouard (<i>Compt. rend.</i> , 1898, 126, 1510)	10	—	
Bunte (<i>Ber.</i> , 1898, 31, 19)	6.3	80	
Eitner (<i>Habilitations-schrift, München</i> , 1902).	In 1 litre sphere	8.7	75.5
	In Bunte burette	9.4—9.5	66.3—66.5
	In cylinder, downward ignition	8.5	—
	In cylinder, upward ignition	4.5	—
Teclu (<i>J. pr. Chem.</i> , 1907, [ii], 75, 212)	9.73—9.96	62.75—63.58.	

TABLE II.

Hydrogen-Oxygen Mixtures.

	Lower limit (per cent. hydrogen).	Upper limit (per cent. hydrogen).
Humboldt and Gay Lussac (<i>J. Phys.</i> 1805, 60, 129, and <i>Ann. Phys.</i> (Gilbert), 1805, 20, 38)	9.5—10.0	—
Davy (<i>Phil. Trans.</i> , 1817, 45)	6.7— 8.3	95.2—96.3
Turner (<i>Edin. Philos. Jour.</i> , 1824, 11, 311)	4.4— 5.1	95.8—96.7
Regnault and Reiset (<i>Annalen</i> , 1850, 73, 129)... ..	10.0—11.1	91.2—92.5
Bunsen ("Gasometry," 1857, 247)	5.7— 6.7	92.4—93.2
Wagner (<i>loc. cit.</i>)	13 —14	91 —92
Bunsen ("Gasometry," 2nd edit., 1877, 338)	5.8— 6.4	—
Roszkowski (<i>loc. cit.</i>)	9.4— 9.7	90.8—91.0
Eitner (<i>loc. cit.</i>)	9.1— 9.3	—
Fischer and Wolf (<i>Ber.</i> ; 1911, 44, 2956).....	5.45	94.7

This curious want of accord in the results of apparently simple experiments may be due to the fact that none of the observers has attempted to discover why his results differ from earlier values, because each was preoccupied with the problem of comparing the dilution-limits of different mixtures in a chosen apparatus. It seems, too, that no observer has had the whole of the previous results before him, so that he has often been unaware of a large disagreement. Much better understanding of the problem involved might have been reached had the old observations of Humboldt and Gay Lussac not been overlooked. Perhaps, therefore, it is not useless to quote from their paper, as follows:

"Not only are there such proportions of hydrogen and oxygen, or of their mixture with nitrogen, or even with any other gas, that it is impossible to ignite them by means of the electric spark; but there are others with which, the inflammation having been commenced, it stops before the combustion is finished."

Humboldt and Gay Lussac quote the following experimental results of firing hydrogen-oxygen mixtures in a eudiometer:

Hydrogen.	Oxygen.	Contraction on firing.
100 vols.	200 vols.	146 vols.
100 "	300 "	146 "
100 "	600 "	146 "
100 "	900 "	146 "
100 "	950 "	68 "
100 "	1000 "	55 "
100 "	1200 "	24 "
100 "	1400 "	14 "
100 "	1600 "	0 (I)

Thus incomplete combustion was observed with mixtures containing between about 6 and 10 per cent. of hydrogen.

It is not always that observers of the dilution-limit of inflammability of hydrogen have recognised this region of incomplete com-

bustion, but when they have they assume the dilution-limit to be that composition at which the mixture in their vessel is just completely burnt. This procedure is highly arbitrary unless vessels of large dimensions are used, since a flame which would die out before passing through the whole length of a large vessel might nevertheless travel throughout a smaller vessel filled with the same gaseous mixture. It is evident, therefore, that a strict definition of the term inflammability is required.

The Criterion of Inflammability.

Common usage has assigned to the term inflammable a meaning which, although hardly defensible on scientific grounds, is too popular to be alterable. Thus coal-gas is commonly termed inflammable, or an inflammable mixture. In any case of ordinary combustion of coal-gas it is, of course, a gas-air or gas-oxygen mixture which is inflamed. The limits of composition of such mixtures containing air or oxygen are indicated by the term "dilution-limits of inflammability." Where the term inflammable may appear ambiguous, it is desirable to speak of such air, oxygen (or chlorine, etc.) mixtures as inflammable *per se*, or perhaps as self-inflammable, so long as this term avoids completely the idea of spontaneous inflammability. A mixture is inflammable *per se* if it is capable of independent propagation of flame.

It seems most desirable to regard inflammability as a specific property of a mixture independent of the size and shape of the vessel in which it may happen to be contained, and also of any particular igniting arrangement. Two extreme views might be taken: (1) That a mixture is inflammable *per se* only under conditions when it will spontaneously inflame. This would require electrolytic gas to be termed inflammable only at temperatures above 585° , a view which hardly commends itself. (2) That a mixture is inflammable if, by a sufficient elevation of temperature, a flame may be formed in it. The term would then be applied to any mixture which shows a cap of flame above an electric discharge. In fact, air would become an inflammable mixture under this definition.

We propose to define a gaseous mixture as inflammable *per se* at a stated temperature and pressure if, and only if, it will propagate flame indefinitely, the unburnt portion of the mixture being maintained at that temperature and pressure. Inflammability as thus defined is a property of the mixture independent of the shape and size of the vessel containing it, and independent also of the nature of the means used for ignition in the first place. It is a function of the temperature and pressure of the mixture,

but these factors have little influence on the dilution-limits of inflammability within the range of variation of laboratory temperature and atmospheric pressure (compare Roszkowski, *loc. cit.*, and Coward, Cooper and Jacobs, this vol., p. 1069).

In the light of this definition, we propose now to discuss the experiments previously done to determine dilution-limits of inflammability, and to enunciate the principles which governed our own experiments.

In the first place, the igniting source of heat must be sufficiently powerful to ensure inflammation of a not too small bulk of gas. This is easily attained when a small jet of coal-gas already burning in air is brought quickly to the boundary of the mixture to be tested. To this simple mode of testing there have been in the past three objections: (1) The mixture must be in a vessel open to the air for a short time, during which its composition may undergo a significant alteration, especially under the influence of the upward rush of gases from the flame. (2) The continued luminosity of the igniting flame may render invisible the faint flame in some weak mixtures. (3) Even a small flame cannot be applied to a mixture and removed from it with the speed of a spark, so that the continued access of heat to a burning mixture has been unavoidable. Although we have succeeded in eliminating these three difficulties, they have been very real obstacles to the use of an igniting flame by previous workers.

More commonly, an electric spark has been employed. Since this is a less powerful means of ignition (when small) than a flame, it has been usual to employ discharges of gradually increasing intensity, until the observer was convinced that no further increase in the intensity of his discharge would produce a more powerful igniting spark. Unfortunately, the experiments testing this were done with the lower-limit hydrogen-air mixtures, and a spark strong enough to ignite the lower-limit mixture was not strong enough to ignite the upper-limit mixture.

Another point not satisfactorily treated hitherto is that a flame must be observed to travel through a sufficient length of the mixture for the initial excess of heat in the spark to be dissipated so that the mixture is truly propagating flame by means solely of the heat produced by its own combustion. We have therefore used vessels considerably larger than any hitherto used in order to satisfy this requirement; our largest has a capacity of 170 litres, our longest a length of 4.5 metres.

The position of the flame or spark used for ignition of a gaseous mixture is most important to consider. There is no doubt that in weak mixtures the flame travels more slowly than the convection

current of gas rises. Hence such mixtures will burn when ignited from below, but not when the spark or igniting flame is placed at their upper boundary. This difference was recognised by Clowes for coal-gas and for methane mixtures, and later by Eitner for hydrogen mixtures, although he used a flame only for the test, and to this the earlier objections apply (see above). In other memoirs this most important distinction has been disregarded so completely that frequently no mention is made of the position of the spark gap or flame used for ignition. It is possible, however, to group the values for both lower-limit and upper-limit mixtures in tables I and II into two classes, according as the experiments are known to have been done (or have apparently been done) with upward and downward ignition respectively. In the lower-limit mixtures with either air or oxygen, the values in the neighbourhood of 5 per cent. hydrogen were probably all determined by upward ignition, those nearer 10 per cent. by downward ignition. Those of Mallard and Le Chatelier and of Bunte were obtained indirectly by extrapolation of the curves connecting velocity of flame with composition of mixture, to zero velocity. Wagner's very high hydrogen-oxygen lower-limit numbers were determined by using a heated wire for ignition, evidently in this case an unsatisfactory method. Bunsen's results were obtained with a closed eudiometer, apparently with ignition at the top. They are low results, and the explanation seems to lie in the fact that the eudiometer was closed, so that the hot gases had no opportunity of expansion. In the upper-limit hydrogen-oxygen mixtures (table II) a similar grouping is possible, but there are exceptions; for example, Turner's numbers appear to indicate upward ignition for the upper limit and downward ignition for the lower limit. His paper gives no clue as to which was used. In the case of upper-limit hydrogen-air mixtures (table I), such a grouping cannot be made so satisfactorily. The two values of 80 per cent. of hydrogen were obtained by the doubtful method of extrapolation, but the others seem to be dependent upon another factor previously mentioned, namely, the variable igniting power of the different sparks used. Wagner's low value appears to be due to his inefficient hot wire, as previously indicated. Roszkowski's results indicate in each case rather high percentages of the gas present in smaller proportion. His apparatus, illustrated in the paper in the *Journal für Gasbeleuchtung* (*loc. cit.*), contained a 4 mm. spark-gap near the end of a horizontal diameter of a glass sphere. The mixture was evidently regarded as inflammable only when the flame traversed the whole mixture. The short spark-gap makes the upper limit rather low in his experiments.

Finally, since experiments with gases are most conveniently carried out in closed vessels, which do not permit of the natural expansion of a heated gas, then in small vessels, and indeed in all vessels which have been used with the spark, the heat of combustion of the first portions of the mixture has compressed the remaining portions so that the inflammability of a gas under rapidly changing, and indeed very greatly changing, pressure has been tested. Thus, in the most carefully described experiments done so far, namely, those of Burgess and Wheeler on the lower limits for the paraffin hydrocarbons (T., 1911, **99**, 2013), a spark was passed in the centre of a 2-litre globe, and the gas was only regarded as inflammable when a flame rose from the spark, spread outwards, reached the top of the vessel, and then turned downwards and completed the combustion of the mixture. Now, in the first instance, the inflammability of the mixture was tested for ignition upwards, but the flame had not a long enough run to escape from the effect of the initial impetus of the spark. The flame then turned downwards, presumably because the upper portion of the globe contained heated gases, so that convection was precluded; but the unburnt gases had become compressed, so that the limit at atmospheric pressure was no longer under examination. Thus the results of Burgess and Wheeler are not applicable to the general definition of dilution-limits which we have put forward.

We were led to these criticisms as our experiments developed, so that ultimately we tested the inflammability of a mixture by observing whether it would propagate a flame upwards for as great a height as we could conveniently employ in a vessel so broad as to leave no doubt that there was only a relatively insignificant cooling influence by the walls of the vessel. We designate the mixture that will just propagate a flame upwards as inflammable, because these slow-moving flames often travel less rapidly than the convection current of gas which they set up, so that it is impossible for them to pass downwards through an inflammable mixture. At the same time, in order to keep the pressure approximately atmospheric, the bottom of our vessel was only sealed by a few cm. of water, so that immediately the gases began to expand they "blew off" through this valve. The influence of a few cm. of mercury pressure on the dilution-limits of gaseous mixtures is inappreciable at about atmospheric pressure within the limits of experimental error of our observations (compare Coward, Cooper and Jacobs, *loc. cit.*).

PART II.—*The Lower Limits for Hydrogen, Methane, and Carbon Monoxide in Air.*

Description of Apparatus.

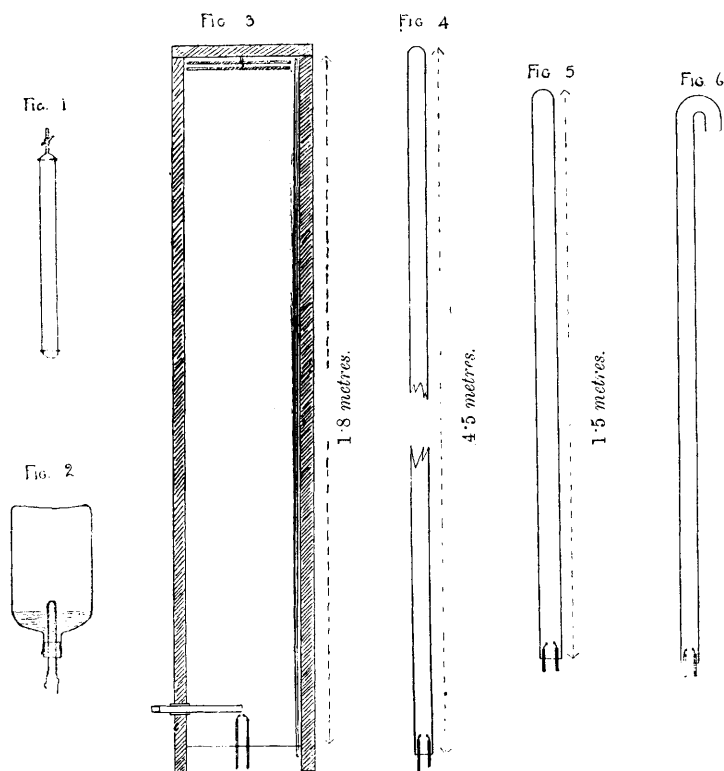
The vessels used to contain the gas mixtures during the test for inflammability are drawn to scale in Figs. 1 to 6.

The earliest of our experiments were carried out in closed glass tubes (Fig. 1), about as long as an ordinary eudiometer tube and twice as wide (50 cm. by 4 cm.). They were fitted with sparking wires at the top and bottom, and in one case in the middle. In experiments with certain weak hydrogen-mixtures, a very pale flame was seen to travel throughout the whole length of the tube, but nevertheless the change in pressure was far too small to correspond with complete combustion of the mixture. This led to the use of an 11-litre bottle (Fig. 2), fitted with a rubber stopper conveying gas and water tubes and insulated leads for the sparking wires. The gases were passed into this vessel by displacement of water from it, the air being added first in nearly sufficient amount, followed by a measured volume of inflammable gas, and finally the total volume was brought to 10 litres by the addition of sufficient air. The water remaining in the vessel, about 1 litre, was used to aid the admixture of the gases by shaking. This procedure necessitated the experiments being confined to moist gases, but with gases of slight solubility enabled mixtures to be made accurately to one-tenth of 1 per cent. For upward ignition, the bottle was supported upside down on a tripod stand and the spark-gap extended about 2 cm. above the surface of the water. For downward ignition, the bottle was placed on its base. In each case the bottle was guarded by the rods of four retort stands heavily weighted, and a network of string was made a short distance above the bottle. This precaution was necessary in order to catch the bottle on its recoil from the forcible expulsion of the stopper in upward ignitions when the whole mixture inflamed. These experiments, carried out on a larger scale than is usual with laboratory experiments, gave us a very different idea of the mechanical effects of the explosion of a weak mixture from that which we had obtained from experiments in closed tubes or globes of 500 c.c. capacity.

In such bottles there was observed with all three gases the formation of beautiful vortex rings of flame, rising through the mixture. The bottles were not long enough to show whether such rings would travel indefinitely, or break up and produce a general inflammation, or become extinguished. Consequently, a vessel was designed, and successfully constructed in the work-

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shops of the School of Technology, of 30 cm. square section and 1.8 metres length, with two opposite sides of wood and two of plate glass (see Fig. 3). The top was of wood, the bottom open, and all joints were carefully packed, so that when the vessel, filled with water like a huge gas-jar, stood in a shallow tank, there was no in-leakage of air. The capacity of this vessel was 170 litres. It was filled with water as it stood in the tank by withdrawing



air through a tube which ran inside to the top. Measured quantities of inflammable gases were admitted through this tube, whilst air was bubbled up through the water. Thorough admixture was brought about by drawing up and down through the gases two square wooden plates, independently supported by cords running through pulleys fixed on the inside of the top of the box, down to the tank, and through the water to the outside, where they were manipulated. It was possible to approach very closely to the composition of any desired mixture by this means, but an

analysis was invariably made of a sample of the mixture taken just prior to the test of its inflammability. The moving plates were drawn close to the top of the vessel during the inflammation test.

For a few experiments, the spark discharge was replaced by a small flame of pure hydrogen. A satisfactory arrangement was devised for introducing such a flame rapidly, and exposing it to the mixture at approximately the place previously occupied by the spark. This arrangement is shown in the figure; a horizontal glass tube (2 cm. diameter) was fixed by an air-tight joint through the wooden side of the box, and its outer end closed by a stopper. This stopper was removed at the moment of the test to allow a small flame burning at the tip of a quartz tube to be thrust along, and so introduced suddenly into the midst of the mixture. This avoids completely the contamination of the mixture with any significant amount of external air. Also, it is easy to push the jet of flame along the tube ahead of the flame of the mixture ignited in the tube.

Even the 1.8 metres length of this vessel was not quite sufficient to assure us that some of the weakest hydrogen flames would travel indefinitely. Before considering the advisability of attempting to construct a box of cross-section similar to the above, and length much greater, some experiments were carried out in a glass tube 4.5 metres long and 4.5 cm. diameter (Fig. 4). These experiments gave satisfactory information to enable us to fix the lower limit for hydrogen.

Figs. 5 and 6 represent tubes used for a few experiments, the latter tube being designed to allow the gases expanded by heat to "blow off" from the upper end of the tube instead of the lower.

Electric ignition was usually employed for the reason that it is possible to initiate a flame by means of a momentary spark without continuing to supply energy to the burning gases from any other source than their own combustion. The induction coil used was modified so that the primary circuit could be broken without re-making.

It should be added that nearly all the experiments described in the following pages were carried out with gases saturated with moisture at the temperature of the laboratory (17° to 18°). Experiments with dry gases on the present scale would be considerably more difficult.

Hydrogen—Air Mixtures. Lower Limit.

The first series of experiments was carried out in the closed cylindrical vessels (Fig. 1) with 5 mm. spark-gaps. The electrodes

in one vessel were bare, in another coated with glass up to their tips; the results observed in the two vessels were, however, identical when other circumstances were maintained the same. A hydrogen-air mixture, roughly dried by sticks of potassium hydroxide, transmitted a flame upwards throughout the mixture when the percentage of hydrogen was 4.15. At 4.0 per cent., exceedingly faint flames were initiated, and travelled about half-way up the tube before extinction. A flame could not be sent down the tube, however, until 8.8 per cent. of hydrogen was present. The effect of a variation in the strength of the spark was merely to vary the distance which a flame would travel in mixtures weaker in hydrogen before extinction. The question of inflaming such mixtures lies rather with the power of the mixture to continue to propagate a flame; the initiation of small flames or caps is easy in many mixtures incapable of giving a self-propagating flame.

In those experiments in which ignition was brought about by a discharge in the lower part of the vessel, a faint flame might be seen to travel throughout the tube, and yet only a small fraction of the hydrogen would be burnt. It seemed advisable, therefore, to attempt experiments in much larger vessels than had hitherto been employed, so the 11-litre bottle of Fig. 2 was fitted up. The results merit detailed description: below they are arranged in order of increasing hydrogen percentage.

A. Ignition from Below (Inverted Bottle).—3.5 per cent. of Hydrogen.—Sparks passed at intervals of a few seconds produced caps of flame, from the tops of which small balls of flame occasionally detached themselves and rose about three-quarters of the way up the vessel, when they became invisible.

3.8 per cent. of Hydrogen.—The first spark gave a plainly visible vortex ring of flame, which travelled to the top of the vessel, and was there extinguished. The next four sparks likewise gave rings, apparently about 3 mm. thick and 2 to 3 cm. diameter. The next ten sparks produced broken rings of flame, and sometimes only small balls of flame, some of them being extinguished before they had reached to the top. The next hundred sparks produced caps of flame, which travelled upwards and occasionally resolved themselves into small balls of flame, which ran to the top of the vessel, and were there deflected towards the side, and soon became invisible.

4.2, 4.6, and 5.5 per cent. of Hydrogen.—Similar phenomena to the above were observed, but the rings were stronger, and showed a tendency to spread outwards. A vertical spark-gap gave results indistinguishable from those of the horizontal spark-gap.

6.0 *per cent. of Hydrogen*.—The first spark formed a ring much thicker than had been observed previously. It expanded to a diameter of perhaps 10 cm. when it was near the top of the vessel. Here it ran outwards, and gave much the appearance of a vortex ring of smoke which is breaking under the influence of violent motion of the air round about, so that it finally showed the form of a flaky, striated cloud. Succeeding sparks still formed rings, of which some broke into pieces before extinction, and others broke into many small balls of flame, moving as though still parts of an invisible ring.

With this 6.0 per cent. mixture the effect of using the trembler on the induction coil was tried. The rapid succession of sparks now gave a thin flame, which shot up to the top of the vessel, and there spread outwards, forming a luminous layer of gas several cm. deep. When a small coal-gas flame was introduced into the lower part of a similar mixture, the flame which shot up the vessel spread so as to appear to fill the upper half of it with flame. This much increased effect is to be attributed to the much greater development of heat in a very small flame of coal-gas than in the series of sparks, and indicates the difficulty of drawing conclusions concerning the question of inflammability of a weak hydrogen-air mixture by bringing a strongly burning flame to it. In the 11-litre bottle it is impossible to judge, even by the use of a single spark, whether a 6 per cent. mixture can propagate a flame indefinitely or not. It is obvious, therefore, that if it is desired to state whether such a mixture is inflammable, all previous observations in small vessels are of no value, and experiments must be done in vessels much larger even than the one we had used.

6.8 *per cent. of Hydrogen*.—The first spark gave a thick, wide ring, which produced much inflammation in the upper part of the vessel, and succeeding sparks gave rings of flame which became extinguished when they had travelled about half-way up the vessel, apparently because most of the hydrogen in the upper half of the vessel had been burnt. This experiment seems to show that the continued luminosity of the ring as it rises is due to the continued combustion of the gases which it traverses. A small coal-gas flame introduced into a mixture of the same composition gave a thin, rapidly rising stream of flame, which spread in the upper half of the vessel so as to consume most of the gas contained there. This flame, like the one produced in the 6.0 per cent. hydrogen mixture, was much paler than the flames resulting from the electric spark or series of sparks, so that the latter seem to owe their luminosity to the yellowness of the spark, presumably

due to the formation of oxides of nitrogen. Experiments were therefore done with varying lengths of spark-gap. The size of the rings increased much with increase in length of spark-gap, and when the spark had changed from the form with a yellow halo to a blue spark, the resulting rings were much paler, but otherwise no different. Finally, experiments carried out with oxygen instead of air gave only faintly luminous rings even with the shorter gaps, but the admission of a few bubbles of air gave an increased luminosity to the rings.

7.8 per cent. of Hydrogen.—The flame produced by the first spark travelled upwards, and rapidly spread outwards, consuming most of the hydrogen contained in the mixture, and forcibly blowing off the rubber tube connected with the exit tube for the water.

9.8 per cent. of Hydrogen.—The rubber stopper of the vessel was blown out forcibly by an apparently complete inflammation of the mixture, and the recoil threw the heavy bottle about 30 cm. into the air.

B. Ignition from Above (Bottle Placed on its Base).—The following results have no bearing on dilution-limits as defined by us, but give an idea of the amount of hydrogen necessary for the propagation of a flame against gravity. The spark-gap was about 2 cm. below the neck of the bottle.

8.5, 8.7, and 9.0 per cent. Hydrogen Mixtures.—The first spark produced a thick vortex ring of flame, which travelled to the neck of the bottle, where it expanded, and went 3 or 4 cm. downwards, and was then extinguished.

9.2 per cent. of Hydrogen.—The vortex ring travelled in different experiments downwards, sometimes only a short way, and sometimes nearly to the bottom of the vessel. In one experiment, a flame seemed to fill the interior of the ring, and only 0.5 per cent. of hydrogen was left unburnt.

9.4 per cent. of Hydrogen.—A wide ring travelled downwards, and resulted in complete inflammation of the mixture. The stopper of the bottle was expelled violently.

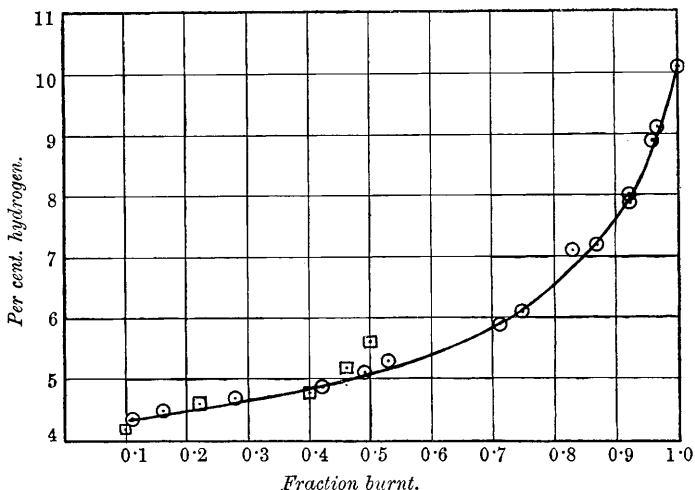
Experiments in the Large Box (Fig. 3).—The box was sealed with a few cm. of water at the bottom. The glass sides were 5 cm. above the bottom of the tank holding it, so that there was room for the gases to blow off, and so adjust the pressure automatically to slightly more than atmospheric. There was, however, in these hydrogen experiments so little pressure developed by inflammation near the dilution-limit, that very little gas was ejected, sometimes none at all.

4.0 per cent. of Hydrogen.—A vortex ring of flame was formed and travelled about 40 cm., then broke and disappeared.

4.2 per cent. of Hydrogen (twice).—A pale ring was formed, broke about 40 cm. above the spark-gap, and an exceedingly faint cloud of flame travelled steadily and slowly to the top of the vessel. To one observer, the cloud appeared to be formed of ten to twenty separate balls of flame, rolling about as they rose.

4.4, 4.6, 4.8, 5.2, and 5.6 per cent. of Hydrogen.—A vortex ring was plainly seen to rise in each experiment about 40 cm., then to break up and travel to the top as a streaky flame extending nearly to the sides of the box. The flames were much more easily followed by the eye as the percentage of hydrogen increased, and in each case it was obvious that a considerable part of the mixture escaped ignition. It was not the cooling influence of the

FIG. 7.



walls of the vessel that retarded inflammation, but apparently the cause lay in the slow propagation of flame from layer to layer, in comparison with the rapid convection effect. This facilitated the upward passage of many streaks of flame, which passed the cooler gases without inflaming them horizontally.

In a much narrower vessel (Fig. 5), the cooling influence of the walls must be proportionately greater than in the box. The amount of hydrogen left unburnt in the two vessels is little different for mixtures of the same initial composition (see table III and Fig. 7), so that the phenomenon of very incomplete combustion in cases where a flame has travelled the whole length of a vessel is to be explained as direct observation of the pale flames indicated.

TABLE III.

Per cent. hydrogen in mixture	4.2	4.35	4.5	4.6	4.7	4.8	4.9	5.1	5.2	5.3
Per cent. hydrogen in } tube		3.85	3.8		3.4		2.85	2.6		2.5
residue } box	3.8			3.6		2.9			2.8	
Fraction of hydrogen } tube		0.11	0.16		0.28		0.42	0.49		0.53
burnt. } box	0.10			0.22		0.40			0.46	
Per cent. hydrogen in mixture	5.6	5.9	6.1	7.1	7.2	7.9	8.0	8.9	9.1	10.1
Per cent. hydrogen in } tube		1.7	1.5	1.2	0.9	0.6	0.6	0.4	0.3	0.0
residue } box	2.8									
Fraction of hydrogen } tube		0.71	0.75	0.83	0.87	0.92	0.92	0.96	0.97	1.00
burnt. } box	0.50									

Experiments in the 4.5 Metres Tube.—The faint flames in the 4.2 per cent. mixture had travelled quite uniformly a distance of about 1.2 metres in the large box. This distance was not quite enough to convince us that the flame would travel indefinitely, especially in view of the fact that such a small proportion of the hydrogen is burnt in this mixture. The construction and use of a glass-sided box much longer than the 1.8 metre one seemed to introduce considerable experimental difficulties, so before attempting this some experiments were carried out in the 4.5 metres glass tube, fixed vertically over water, with sparking wires a little above the surface of the water. The observations were as follows:

4.2 per cent. of Hydrogen.—No inflammation observed.

4.4 and 4.45 per cent. of Hydrogen.—Globular flames travelled through the whole length of the tube. The last 4 metres of their journey was at a uniform rate, and left no doubt in the minds of observers that they would travel indefinitely through such a mixture. The fraction of the hydrogen burnt was 0.11 and 0.045 respectively.

4.7, 4.85, 5.0, and 5.3 per cent. of Hydrogen.—Flames shaped like upright incandescent gas mantles passed slowly to the top. The length of the flame varied from 5 to 10 cm., its diameter being about 2.5 cm.

Since in this narrow vessel a flame travelled uniformly for 4 metres in a 4.4 per cent. mixture, it can hardly be doubted that the flame in the wide box in a 4.2 per cent. mixture would travel indefinitely. Certainly all doubts on this point were removed from the minds of several observers, and in consequence the lower dilution-limit of inflammability of hydrogen in air may now with confidence be stated as 4.1 per cent.

The Vortex Rings of Flame.

The rings of flame observed in weak mixtures of (a) hydrogen, (b) methane, and (c) carbon monoxide, with air, behaved like vortex rings of smoke in the way they travelled and in the way they broke up in an atmosphere in commotion. Rotational motion

could, of course, not be observed, so that the reasons for calling them *vortex* rings should be explained. They are:

(1) The circumstances are sufficient to produce a vortex ring: a sphere of hot gas around the spark, expanding and therefore rising by virtue of convection; the centre rising most rapidly on account of its temperature being highest.

(2) The passage of a similar spark to one producing rings of flame, through a gap in the centre of a cloud of smoke confined in a box with open top, formed a vortex ring, which issued from the smoke cloud and travelled upwards through the air for a few centimètres.

Methane-Air Mixtures. Lower Limit.

Previous determinations of the dilution-limits of methane-air mixtures do not show nearly so much disagreement as the corresponding values for the hydrogen-air mixtures, but there are quite well-marked differences, and, indeed, none of the observations satisfies the criterion of inflammability which we have put forward in Part I of the present communication. The previous determinations are collected in table IV, which for convenience contains the upper-limit numbers, as well as those for the lower limit.

TABLE IV.

	Per cent. methane.	
	Lower limit.	Upper limit.
Davy (<i>Phil. Trans.</i> , 1816, 1)	6.2—6.7	{ 20 —25 14.3—16.7
Mallard (<i>Annales des Mines</i> , 1875, [vii], 7, 355)	7.7	14.5
Wagner (<i>loc. cit.</i>)	5.9—6.25	12.5—14.3
Coquillon (<i>Compt. rend.</i> , 1876, 83, 709)	5.9—6.2	12.5—14.3
Mallard and Le Chatelier (<i>loc. cit.</i>)	5.6	16.7
Wüllner and Lehmann (<i>Ber. der Preuss. Schlagschiffkommission</i> , 1886, B, 3, 193) ...	5.9	12.5—14.3
Broeckmann (<i>loc. cit.</i>)	5.5	13.5
Le Chatelier (<i>Annales des Mines</i> , 1891, [viii], 19, 388)	6.1	—
Roszkowski (<i>Zeitsch. physikal. Chem.</i> , 1891, 7, 485)	{ 5.8—6.1 5.7—6.0	{ 12.4—12.8 13.0—13.2
Clowes (<i>loc. cit.</i>)	{ 5 6	{ 13 11
Bunte (<i>loc. cit.</i>)	5.5	17
Couriot and Meunier (<i>Compt. rend.</i> , 1898, 126, 750)	5.5	12—12.25
Le Chatelier and Boudouard (<i>loc. cit.</i>)	6	—
Eitner (<i>loc. cit.</i>)	{ 6.0—6.2 6.3 5.5	{ 12.7—12.9 — —
Teclu (<i>loc. cit.</i>)	3.20—3.67	—
Perman (<i>Nature</i> , 1911, 87, 416)	2.5	—
Burgess and Wheeler (<i>T.</i> , 1911, 99, 2013)	5.6	14.8*

* Private communication.

Most of the above values may be arranged in two classes, first, when the experimental arrangement involved ignition from above, secondly, when it involved ignition from below. Some of the figures, however, require further comment.

Davy's first upper-limit values are probably the result of incorrect observation, for flame-ignition was employed with a vessel which was too small for proper observation to be made. Mallard's lower-limit number is undoubtedly too high. It was obtained by extrapolation of the curve of flame velocity plotted against composition of the mixture, and the result proves the extrapolation to be unjustified. Mallard and Le Chatelier's figures were, however, obtained in this way, and the lower-limit value is now nearer the truth.

Roszkowski's first values are for dry gases, the second for gases saturated with aqueous vapour at laboratory temperature. Clowes first pointed out the difference between ignition from below and from above, and his figures refer to these conditions respectively. Eitner's lowest lower-limit figure is likewise for ignition from below. His highest figure was obtained in a rather wide cylinder (62 mm.).

The excessively low figure of Perman has been pointed out by Burgess and Wheeler to be the result of faulty observation. The result of Teclu is undoubtedly wrong.

In view of the criticisms in Part I of the present communication, none of the experiments the results of which are quoted above serves to satisfy the criterion of inflammability there put forward. In particular, it may be mentioned that a repetition of the Burgess and Wheeler experiments in a vessel constructed in imitation of theirs, with the addition of a simple mercury pressure gauge, showed the development of from four to five atmospheres' pressure when a 5.7 per cent. mixture was inflamed. Further, when the lower half of their globe was cut out, the electrodes remaining with the upper half, and the upper half prolonged by a cylindrical vessel of the same diameter as the globe, a 5.75 per cent. mixture propagated the flame only part of the way down the cylinder, then drew in to the centre, and was extinguished. Thus the Burgess and Wheeler experiments do not prove that a flame will travel throughout a 5.7 per cent. mixture, although admittedly it burnt the gas in their vessel completely. Their vessel was not sufficiently large to satisfy even their own criterion of inflammability.

Our own experiments were carried out in vessels of increasing capacity, as were used for the hydrogen experiments done simultaneously. The methane was prepared from aluminium carbide and water, with subsequent removal of acetylene, and liquefaction to separate hydrogen. We found no difficulty in

obtaining a pure gas free from any detectable amount of hydrogen or air. The composition of the experimental mixtures was determined by analysis, as a check on the accuracy of the preparation of the mixtures.

Experiments in Closed Tubes (Fig. 1).—A dry mixture containing 5.0 per cent. of methane propagated a flame upwards throughout the vessel, but a 4.9 per cent. mixture failed. For downward propagation, a 5.85 per cent. mixture was just at the limit, for sometimes the flame travelled the whole way and sometimes not. With gases saturated with aqueous vapour at the temperature of the laboratory, the two limits were 5.4 and 5.9 per cent. respectively.

Experiments in 11-litre Bottle (Fig. 2).—Vortex rings of flame were obtained with the first three sparks in a 5.0 per cent. mixture. Weaker mixtures showed "caps" of flame above the spark, in size dependent on the strength of the spark and the amount of methane in the mixture. A 5.2 per cent. methane mixture also gave vortex rings of flame, which, on reaching the top of the vessel, spread and consumed much of the gas there. A 5.7 per cent. mixture gave a solid blue cone of flame, which produced general inflammation when it had travelled about one-third of the way up the vessel. The stopper of the bottle was forcibly expelled, and the recoil sent the heavy bottle about 30 cm. upwards.

In this bottle, a 6.2 per cent. mixture was just at the limit for the propagation of a flame downwards throughout the whole mixture.

Experiments in the Large Box (Fig. 3).—5.1 per cent. of Methane.—A vortex ring of flame was formed, travelled about 30 cm., broke quickly, and formed a tongue of flame, which travelled another 30 cm. before extinction.

5.3 per cent. of Methane.—A stout ring was formed, travelled a few cm., and resolved itself into a steady flame nearly as wide as the box. This flame travelled to the top, swaying in its course, so that first one side, then another, was slightly ahead. Its motion was not unlike that of a thin sheet of paper as it sometimes falls in air. The conditions for its formation cannot be defined at present, for several attempts to repeat the observation were unsuccessful, both with the 5.3 per cent. mixture and with mixtures containing 5.35 and 5.45 per cent. of methane. We are satisfied, however, that the single observation was sound, for not only was the mixture made up to contain 5.3 per cent. methane, but an analysis of a sample of it, taken after admixture and just prior to inflammation, gave quite satisfactory figures for both the contraction on explosion (after addition of a small amount of electro-

lytic gas) and the contraction after absorption by potassium hydroxide of the carbon dioxide formed. The unsuccessful attempts at repetition gave flames the stability of which was evidently quite different—one side of the flame would suddenly shoot upwards, and in the upward rush become extinguished. The flame which travelled to the top was never subjected to such a sudden disturbance, but travelled smoothly with the peculiar swaying motion described.

One attempt to form steadier flames was made by cutting two holes near the lower ends of the wooden sides of the box, just above the level of the water. These holes were 20 cm. long by 5 cm. wide, and were closed by wooden boards with air-tight rubber pads. The boards were removed the moment after the passage of the spark, and the hot gases thus allowed to escape more gently than by bubbling through the water seal. The flames never attained the stable state, however, but were extinguished suddenly.

5.5 per cent. of Methane.—A strong flame was observed, but after filling nearly the whole cross-section of the box it died out about 60 cm. up, one half ending as a large tongue of flame.

5.6 and 5.65 per cent. of Methane.—A steady flame with a convex front passed throughout the mixture in each case.

Experiments in 1.5 metre Tubes (Figs. 5 and 6).—Some confirmation of the possibility of obtaining a self-propagating flame in moist mixtures containing several tenths of a per cent. less than 5.6 of methane was obtained by experiments in 1.5 metre tubes. In the straight tube of Fig. 5, a flame travelled steadily to the top in a 5.5 per cent. mixture, in spite of the comparative narrowness of the vessel. With mixtures containing 5.45, 5.35, and 5.3 per cent., the flame travelled from 30 to 40 cm. up the tube, and was then extinguished, apparently at the moment that the heated gases "blew off" through the water at the bottom. This suggested that the slight shock caused by the sudden release of pressure on blowing off was sufficient to damp out the flame.

The tube of Fig. 6 was water-sealed at both ends, the electrodes being inserted through the lower end. Here again extinction seemed frequently to be synchronous with the bubbling out of the heated gases. A 5.4 per cent. mixture on one occasion propagated flame to the top, but on another the flame was extinguished after a passage of only 45 cm. Samples of the same mixture were used for these two experiments. On another occasion, a 5.3 per cent. mixture propagated flame to within 30 cm. of the top, when the water seal at the top was removed immediately the flame had

started. This flame travelled with a series of gentle vertical vibrations, and was apparently extinguished during one of them.

Our conclusions are therefore that the flames of mixtures containing 5.3 to 5.6 per cent. of methane are very sensitive to extinction by shock, that a 5.6 per cent. mixture will invariably propagate flame when the shocks are no greater than those occasioned by the somewhat violent bubbling of gas through water, but that when the circumstances are such that a tranquil passage is assured, 5.3 per cent. is the lower limit of inflammability of methane in air.

Carbon Monoxide-Air Mixtures. Lower Limit.

A comparatively small number of determinations of the dilution-limits of inflammability of these mixtures has been given. They are collected in table V.

TABLE V.

	Per cent. carbon monoxide	
	Lower limit.	Upper limit.
Wagner (<i>loc. cit.</i>)	14.3—16.7	75—80
Roszkowski (<i>Zeitsch. physikal. Chem.</i> , 1891. 7, 485)	14.1—14.3	74.6—74.8
Clowes (<i>loc. cit.</i>)	13	75
Le Chatelier and Boudouard (<i>Compt. rend.</i> , 1898, 126, 1344)	15.8—16.0	72.5—76.5
Eitner (<i>loc. cit.</i>)	14.4	—
	16.4—16.6	74.8—75.1

The figures of Eitner show that a difference of about 2 per cent. of carbon monoxide exists between the composition of mixtures which will propagate flame upwards and downwards. Le Chatelier and Boudouard have shown in their memoir the great influence which the diameter of the vessel used for the experiment has on the passage of a flame in carbon monoxide mixtures. When the vessel had a diameter less than 14 mm., the dilution-limit was rapidly raised by decrease in diameter; there seemed to be little difference, however, between the dilution-limits in tubes of diameter 13.8 and 40 mm. The observations were apparently made with flames travelling downwards, so that they are not satisfactory in view of the criterion of inflammability which we have adopted.

Experiments in 11-litre Vessel (Fig. 2).—12.0 and 12.2 per cent. of Carbon Monoxide.—Inverted cones of flame, which were extinguished 10 cm. above the spark-gap, were produced by the first few sparks, then tongues of flame reaching sometimes nearly to the top of the vessel. The use of the trembler on the coil resulted in a long, thin blue flame playing on the top of the vessel, without spreading much.

12.4 per cent. of Carbon Monoxide.—The first three sparks each

gave a pair of vortex rings, the smaller (about half the diameter of the larger) being the upper one. In each case these flames were extinguished before they reached the top of the vessel.

12.6 per cent. of Carbon Monoxide.—The first spark produced a large vortex ring, which occasioned general inflammation in the upper half of the vessel.

12.9 per cent. of Carbon Monoxide.—A vortex ring was formed, and resulted in general inflammation. The ring in this mixture, and a solid cone of flame in a 14.0 per cent. mixture, expanded until of the diameter of the vessel, when apparently complete inflammation of the gases above occurred.

When the bottle was inverted so that the spark-gap was at the top, a flame travelled downwards throughout the whole mixture only when the percentage of carbon monoxide reached 15.3.

Experiments in Large Box (Fig. 3).—*12.3 per cent. of Carbon Monoxide.*—A fine vortex ring was formed, and travelled about 20 cm., but was then extinguished.

12.33 per cent. of Carbon Monoxide.—A vortex ring was formed and broke into pieces which travelled about half-way up the box and then became extinguished.

12.5 per cent. of Carbon Monoxide.—A ring of flame followed by and connected with a smaller one, rose, then broke into pieces which rose unsteadily until a portion broke away and travelled to the top. In a second experiment the apertures at the side of the box were opened at the moment of sparking. The flame produced was at first a vortex ring which increased in diameter as it rose until, when about half-way up the box, it almost touched the sides of the vessel. It then broke and filled the upper part of the box with striæ of flame.

12.7 per cent. of Carbon Monoxide.—The result was very like that of the previous experiment, but the whole flame was brighter.

12.9 per cent. of Carbon Monoxide.—A flame as wide as the box itself, with a strongly curved convex front, passed slowly and steadily up throughout the whole mixture.

We therefore put the lower limit of inflammability of carbon monoxide in air as 12.5 per cent. of carbon monoxide.

Photographic Records of the Carbon Monoxide Flames.

The luminosity of the flames in a mixture containing 12.5 per cent. of carbon monoxide with air has proved just sufficient for photographic record, and for the series of pictures (Figs. 8 to 17) of flames we have to thank Mr. J. W. Grundy, of the Manchester School of Technology. Figs. 8 to 16 were obtained by exposures of one-fifteenth of a second to flames produced in the 11-litre

Flames in 12.5 per cent. carbon monoxide mixtures.

FIG. 10.

Flame higher than in Fig. 9.

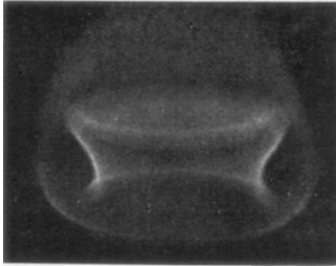


FIG. 9.

Flame higher than in Fig. 8.

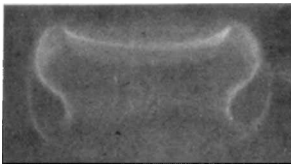


FIG. 8.

Flame a few inches above spark gap.

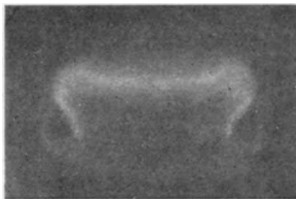


FIG. 11.

Flame near top of bottle.

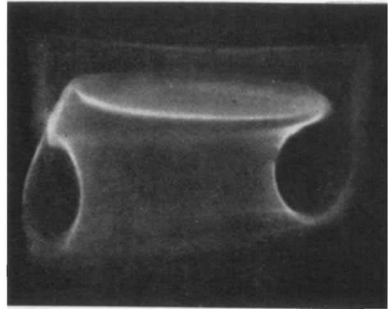


FIG. 12.

Symmetrical flame near top of bottle

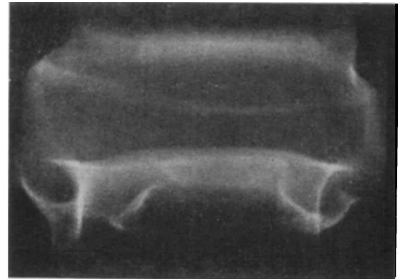
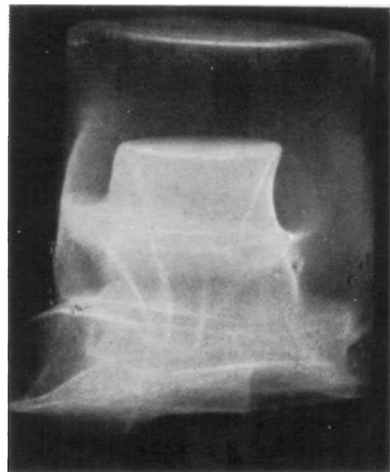


FIG. 13.

Time exposure until flame was suddenly extinguished.



Flames in 12.5 per cent. carbon monoxide mixtures.

FIG. 14.

Exposure cut out when flame reached top of vessel.



FIG. 15.

Exposure cut out when flame reached top of vessel.

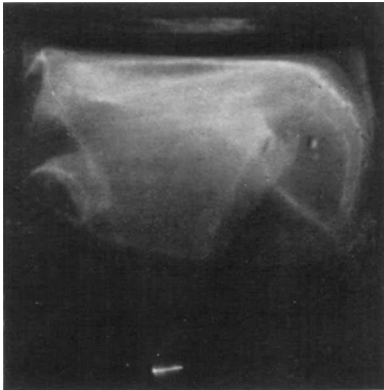


FIG. 16.

Time exposure during whole of combustion.

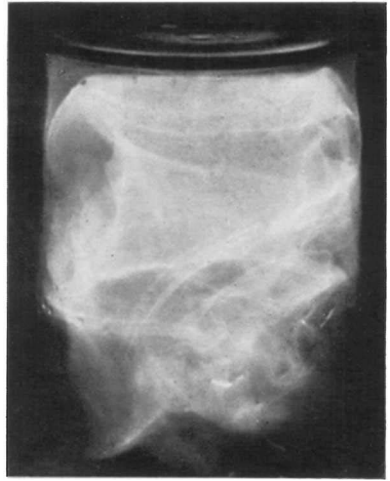
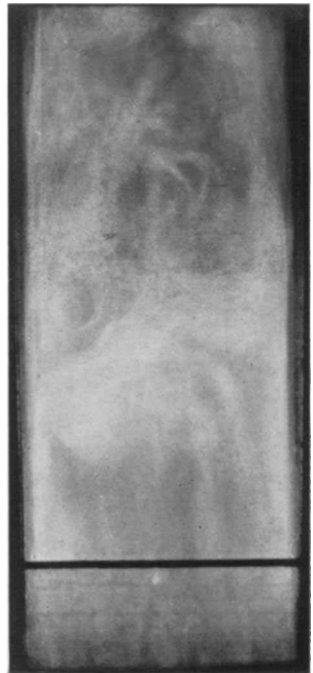


FIG. 17.

Time exposure of flame in lower part of box.



bottle, and show the flame just above the spark (Fig. 8), with a second ring in process of formation; higher (Fig. 9), and still higher (Fig. 10), with the second ring more prominent. The distortion of the flame by contact at one point with the wall of the containing vessel is shown in Fig. 11, and when, in another mixture of the same composition, the flame came into contact with the wall all round, the effect is reproduced in Fig. 12. When the photographic plate was exposed during the whole time of an inflammation until the flame was extinguished by the sudden release of pressure in the vessel, the path of the double ring was recorded (Fig. 13). The lower part of this photograph is complicated by a movement of the bottle when the flame was blown downwards. On other occasions the plate was exposed until the flame had reached the top of the vessel and was just about to travel downwards (Figs. 14 and 15). An exposure during the whole combustion shows the inflammation of the lower layers of gas (Fig. 16). Finally, the photograph of the passage of the flame up the large box, from just above an igniting jet of hydrogen, shows faintly a ring of flame and the subsequent combustion of the mixture. This flame was extinguished before it had reached the top of the box.

The methane and hydrogen flames proved to be too weak to be photographed. To the eye, the methane flames were not unlike the carbon monoxide ones in form. The hydrogen flames were usually single rings, and rarely showed a tendency to the doubling formation; they broke up into separate balls of flame.

A Comparison between the Effects of Spark Ignition and Flame Ignition.

There exists in some quarters a belief that an electric spark is a more effective igniting agent than a flame. It is difficult to understand how this belief has arisen, for the ordinary spark produces much less heat than a small flame of coal-gas or of hydrogen burning for, say, a second. The temperature of the spark, or, better, the concentration of its energy, is obviously high, but, on the other hand, the temperature of an ordinary flame in air is considerably higher than that of the inflamed dilution-limit mixtures. In other words, both means of ignition are well above the ignition-temperatures, but the small flame has a considerably greater bulk than the spark. Regarded as a purely thermal effect, the flame should be at least not weaker than the spark in igniting power. Nevertheless, its electrical nature may have suggested that the spark is stronger, so the matter was put to experimental test by using a modification in the large box (Fig. 3) to permit the introduction of a flame with some rapidity

into approximately the same position as had been occupied by the spark-gap. At the same time, the arrangement prevented the access of any appreciable amount of external air to the mixture in the box. The following observations were made:

Hydrogen Mixtures.—(1) *4.0 per cent. of Hydrogen.*—A very faint flame rose in the mixture, and travelled in one experiment about 60 cm., in another nearly to the top of the box. In both cases a few hundred c.c. of pure hydrogen were run into the very top of the box at the moment the flame was first observed lower down, but this reservoir of hydrogen was not ignited, so that no flame had travelled to the top of the box.

(2) *4.2 per cent. of Hydrogen.*—A visible flame, starting as a ring, which broke into pieces, reached the top of the vessel. It was faint, but quite distinct, so that this observation, as well as the previous one, is quite like those made when electric ignition was employed.

Methane Experiments.—(1) *5.3 per cent. of Methane.*—This mixture gave a vortex ring of flame very like that produced by spark ignition. This developed into general inflammation when about 30 cm. up the box, but immediately afterwards, the commotion produced by the outrush of gases through the water seal caused the flame to break into a number of striations, which were extinguished about 60 cm. up the box.

(2) *5.5 per cent. of Methane.*—A typical ring was observed, rose expanding, and then broke into a steady flame with convex front, which passed to the top of the vessel at a uniform rate. These observations are quite in accord with those seen when electric ignition was employed.

Carbon Monoxide Experiments.—(1) *12.3 per cent. of Carbon Monoxide.*—A ring of flame travelled upwards, developing the double-ring structure, and then breaking into a striated flame one portion of which travelled to within a few cm. of the top of the vessel.

(2) *12.5 per cent. of Carbon Monoxide.*—The flame resembled at first that of the previous mixture, but the resultant flame travelled to the top of the box as a strongly agitated, flickering flame.

We conclude from these experiments that, whether a flame is initiated by a spark or by another flame, its subsequent passage through the upper two-thirds of the vessel used is independent of the nature of the means used for ignition. This is strong support for the belief that in such a vessel a flame can be observed sufficiently far from the source of ignition for it to be independent of the primary ignition.

If a mixture is incapable of propagating a flame indefinitely, the nature and size of the limited flame above the spark or jet of flame depends on the heat of the spark or jet, a strong spark being, roughly, equivalent to a very small jet.

Some Attempts to Trace a Simple Connexion between Dilution-limits and Ignition-temperatures.

In the first edition of his "Gasometry" (1857), Bunsen quoted his determinations of the dilution-limit of inflammability of electrolytic gas mixed with excess of oxygen, of hydrogen, and of carbon dioxide. He proceeded to deduce from these the ignition-temperatures of the three mixtures by assuming that a flame which travelled from layer to layer of the limiting mixture must transmit just sufficient heat to raise each succeeding layer to its ignition-temperature; and, furthermore, that the whole of the heat liberated by the combustion of one layer, after it had been raised to its ignition-temperature, was transmitted to the next layer. This very rapid transmission of heat and equalisation of temperature between a completely burnt layer and the next unburnt layer enabled the ignition-temperature to be determined from the ratio:

$$\frac{\text{Heat produced by the inflammation of one layer}}{\text{Specific heat of the unburnt layer.}}$$

In 1857 Bunsen apparently did not feel much confidence in the results, but in the second edition of his work (1877) the calculated ignition-temperature for the mixture diluted with oxygen was put forward without reservation. Since then, direct observations of ignition-temperatures have been made, and these may be compared with the results of calculations similar to those of Bunsen. This has already been done by Burgess and Wheeler (*loc. cit.*) for the lower limits in air of the three simplest hydrocarbons of the paraffin series; their method was to calculate from the ignition-temperatures given by Dixon and Coward (T., 1909, 95, 514) the dilution-limits, and to compare them with their own observations. Their lower limits are put thus:

	Percentage by volume.	
	Calculated.	Observed.
Methane	1.426	5.60
Ethane	0.754	3.10
Propane	0.495	2.17

They explain the discrepancy as due to two factors: first, that "heat is bound to be communicated from the gases first inflamed, not only to the adjacent layer, but to layers at a further distance"; secondly, the loss of heat by radiation from the flame. No attempt was made to prove these to be adequate reasons, and it

seems to us to be doubtful whether they will prove to be so, for, in the first place, if layers "at a further distance" receive heat prior to contact with the flame, much of this heat will not be dissipated before the flame arrives, so that it is not lost at all; and, in the second place, the radiation losses in much hotter flames have been shown by B. Hopkinson (*Rep. Brit. Assoc.*, 1910, 221) for mixtures of coal-gas and air, and by Bjerrum (*Zeitsch. physikal. Chem.*, 1912, **79**, 513) for mixtures of hydrogen and carbon monoxide with oxygen in their reacting proportions to be far smaller than is necessary to explain the present discrepancies.

Our own calculations on this point are collected in table VI.

TABLE VI.

	Hydrogen.	Methane.	Carbon monoxide.
Ignition-temperature (Dixon and Coward) } Heat of combustion at 18° and constant volume, of one gram-molecule, calculated for steam as a product of combustion. } Heat of combustion as above, but calculated for the ignition-temperature of each gas [A]. } Heat required to raise the dilution-limit mixture (that amount which contains one gram-molecule of inflammable gas) from 18° to the ignition-temperature [B]. } Ratio of "effective heat" of flame [B] to total heat [A]. } Dilution-limit of inflammability calculated from ignition-temperature. } Dilution-limit determined experimentally. }	585° 57640 calories 58230 calories 70430 calories 1.21 5.0% 4.1%	{ 650—750° } { (say 700°) } 191070 188440 69730 0.370 2.0% 5.3%	651° 67670 67100 26590 0.396 5.0% 12.5%

The data used for these calculations must first be specified. The specific heats are perhaps the most important, and the values used are those chosen by Lewis and Randall (*J. Amer. Chem. Soc.*, 1912, **34**, 1128) from a careful consideration of the published values, as follows:

	True specific heat at constant pressure (T represents temperatures absolute).
Hydrogen	$6.50 + 0.0009T$
Nitrogen	$6.50 + 0.0010T$
Oxygen	
Carbon monoxide	
Steam	$8.81 - 0.0019T + 0.00000222T^2$
Carbon dioxide	$7.0 + 0.0071T - 0.00000186T^2$

The specific heats at constant volume were obtained by subtracting the gas constant (1.985 cal.), and by a well-known process the mean specific heats between 18° and the ignition-temperature were obtained. The specific heats at constant volume have been chosen—although there exists no direct experimental evidence to guide the choice—solely for the reason that the specific heats at constant pressure would bring the calculated dilution-limit for hydrogen still further in excess of that observed.

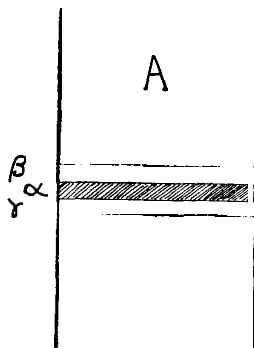
The heats of combustion of the three gases at their ignition-temperatures have been calculated from their heats of combustion at 18° , and the specific heats of the reacting substances and their products of combustion [*A*]. For comparison are put the corresponding amounts of heat required to raise the same amount of mixture to its ignition-temperature [*B*]; and the ratio of the two shows the proportion of the heat of combustion which is used in bringing the unflamed layer of gas to its ignition-temperature

The calculations are expressed somewhat differently by a comparison of the dilution-limits with the calculated percentage of gas required to produce enough heat to propagate combustion, that is, the so-called "calculated dilution-limit" (see the two last rows of the table). The value for methane is considerably lower than the observed dilution-limit, and so, too, is the calculated carbon monoxide dilution-limit.

In the case of hydrogen, the remarkable result is that the calculated dilution-limit is higher than that observed, that is to say, that the amount of heat produced by combustion of the limit mixture is well below the amount calculated as necessary to inflame neighbouring layers.

Whilst we have no further experimental evidence to test any interpretation of these differences, we cannot avoid attempting some speculation in view of our confidence in the dilution-limits which we have determined. Let us first examine more closely the arguments upon which the Bunsen calculations are based. Suppose a flame to travel up the tube *A* (Fig. 18), and let the flame-front at a certain moment be at the point *F*. Suppose α represents the thin burnt layer, β the next layer to be inflamed. The whole of the heat of combustion of layer α must be conducted to layer β prior to the inflammation of the latter if the Bunsen calcu-

FIG. 18.



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lation is sound. This is possible when, and only when, the combustion in α is completed almost instantaneously, and its heat is transmitted forwards only. It is impossible to regard either assumption as quite true, especially the latter, for the whole theory depends on the assumption that the burnt-out layer γ next to α is just at the ignition-temperature of the mixture, and consequently considerably cooler than α itself, and therefore capable of receiving much of the heat of the layer α . In short, if γ is not at the ignition-temperature, the theory is wrong; if γ is at the ignition-temperature, the theory is still wrong.

This consideration renders the interpretation of the results with hydrogen still more difficult. In this case, it is undesirable to put forward some speculations which have suggested themselves until experimental support is forthcoming.

Summary and Conclusions.

A collection has been made of the results of previous determinations of the dilution-limits of inflammability of hydrogen-air and of hydrogen-oxygen mixtures. The complete lack of accord thereby disclosed is shown to be due, in the first place, to want of consideration of the meaning of the terms employed. A dilution-limit of inflammability of a gaseous mixture is, of course, reached when the addition of an indefinitely small amount of the diluent renders the mixture no longer inflammable. The whole definition now turns upon the meaning of the word inflammable, and it is necessary to point out that inflammability must be regarded as a specific property, either present or absent, of any given gaseous mixture under defined conditions of temperature and pressure. We therefore define a mixture as inflammable *per se* at a stated temperature and pressure if, and only if, it will propagate flame indefinitely, the unburnt portion of the mixture being maintained at that temperature and pressure.

On the basis of this definition, a criterion of inflammability was established during the development of the experimental observations. Satisfactory experimental results are to be attained when attention is paid to the following points:

(1) The vessel containing the mixture must be so constructed as to allow free expansion of the heated products of combustion, and thereby to avoid compression of the unburnt gases.

(2) The vessel must be large enough to permit the flame to travel with relatively inappreciable cooling by the walls of the vessel.

(3) The flame must travel through a sufficient distance so as to leave no doubt that, if given the opportunity, it would travel

indefinitely through the same mixture, that is, that its continued propagation had become independent of the initial impetus of the igniting arrangement.

(4) The rate of propagation of flame from layer to layer of a weak mixture is often less than the rate of the convection current which it produces, and so it cannot travel downwards. Such a mixture is nevertheless truly inflammable if it will propagate a flame indefinitely upwards.

It is only by paying strict attention to a definition, and then to a criterion, of inflammability that this subject can be treated scientifically, for disregard of these two points has led to the hopelessly variant results of previous workers. A mixture shall not necessarily be termed inflammable if in a specified vessel it burns completely, or not inflammable if in a specified vessel it fails to burn completely.

The lower limits of inflammability of three gases in air, the mixture being saturated with water vapour at 17° to 18° and the total pressure atmospheric, are:

Hydrogen	4.1 per cent.
Methane	5.3 „
Carbon monoxide	12.5 „

Incidentally, the present communication contains an account of vortex rings of flame observed in each of these mixtures; of mixtures containing hydrogen which propagate flame indefinitely, but leave unburnt a very considerable proportion of the whole mixture; of wide flames, sometimes 30—60 cm. high, which are nevertheless incapable of propagating flame further in the same mixture as that in which they were produced. Finally, the flames formed by primary ignition by a strong spark are ultimately indistinguishable from those produced primarily by a small, strongly burning jet of pure hydrogen.

FACULTY OF TECHNOLOGY,
MANCHESTER UNIVERSITY.
