CXCVII.—*Extinction of Methane Flames by Diluent Gases.*

By Hubert Frank Coward and Francis John Hartwell.

In the course of an investigation on the influence of black-damp (a mixture of nitrogen and carbon dioxide) on the limits of inflammability of firedamp (methane) in air (Safety in Mines Research Board, Paper No. 19; London, H.M. Stationery Office, 1926), some new information has been obtained concerning the factors which determine whether or not a gas mixture is capable of self-propagation of flame. Volume for volume, carbon dioxide exceeds nitrogen in its extinctive action on flame—an effect which is generally attributed to the higher molecular heat capacity of the former. Argon, a gas of lesser heat capacity than either, proves to have less extinctive action. On the other hand, helium is much more extinctive of flame than argon, although the two have almost exactly the same heat capacities.

The limits of inflammability of methane, in various "atmospheres," composed of mixtures of air with one or other of the diluent gases, were determined in a vertical glass tube, 6 feet long and 2 inches in diameter. This tube was filled with an appropriate mixture, the lower end was then opened by sliding away a ground-glass joint and a small spirit-lamp flame was immediately passed across the aperture. The tube was sufficiently long to enable observers to judge whether a flame was self-propagating, for, if the mixture were incapable of continued self-propagation of flame, the "cap" of flame formed above the source of ignition was extinguished within 2 feet of its passage up the tube.*

General Observations on the Flames.

The flame front, as the flame passed up the tube, was in all cases nearly hemispherical in shape, sometimes with a hollow, cylindrical extension of variable length. The blue flame front was followed by a red glow in all upper-limit mixtures, an evidence of some residual chemical reaction. The speed of propagation of flame in all limit mixtures, lower or higher, was remarkably constant at 22 to 23 cm. per second, except that the speed was somewhat higher when helium was the diluent used.

The flames in certain upper-limit mixtures vibrated rapidly when within 1 or 2 feet of the top of the tube. During these vibrations the flame, on occasion, was extinguished; however, when a pad of cotton wool was held loosely over the open end of the tube during the progress of the flame, vibrations were not observed and the normal shape of flame front and speed of propagation were obtained. Furthermore, the flame vibration started at the moment when the contraction due to cooling behind the flame became equal to, or just exceeded, the expansion due to new combustion; *i.e.*, at the moment of change, at the open mouth of the tube, from an outflow of gases to an inflow of air.

These observations afford a clue to an understanding of the causes of vibration in flames travelling along tubes, and will, it is hoped, form the subject of a later communication.

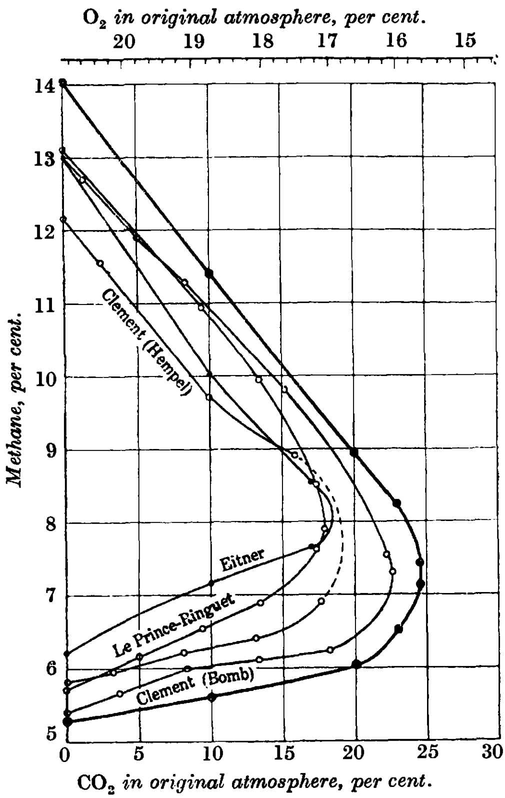
Limits of Inflammability of Methane–Air Mixtures in the Tube Used.—The limits in the circumstances described were 5·24% methane (lower) and 14·02% (higher).† These may be taken as accurate to 0·02%. Most of the results in the following sections were determined within 0·05%.

* In all the experiments recorded here, the gases were roughly dried by passage over calcium chloride, and contained less than 0·1% of moisture. They were at laboratory temperature up to the time of inflammation, and at laboratory pressure during the whole time of passage of the flame; the latter condition was secured by leaving the lower end of the tube open while the flame was passing up the tube. Ordinary variations in laboratory temperature and pressure have no measurable effect on the limits of methane–air mixtures (Mason and Wheeler, J., 1918, **113**, 45).

† When the gases were saturated with water vapour (1·9%) at the temperature of the experiment, the limits proved to be 5·22% methane (lower) and 13·54% (higher). These are the actual proportions of the gas present in the moist mixture; expressed (as usual from gas analyses) as percentages of the water-free mixture, they become 5·33 and 13·80. These last figures may be compared with earlier determinations which are, as a rule, expressed in this manner.

Influence of Carbon Dioxide on the Limits of Inflammability of Methane–Air Mixtures.—The heavy curve in Fig. 1 represents the limits of inflammability of methane in atmospheres composed of pure air admixed with the indicated amounts of carbon dioxide. The limits are narrowed as the amount of diluent gas is increased, until they meet when the atmosphere contains somewhat less than 25% of carbon dioxide. The increase in the lower limit is

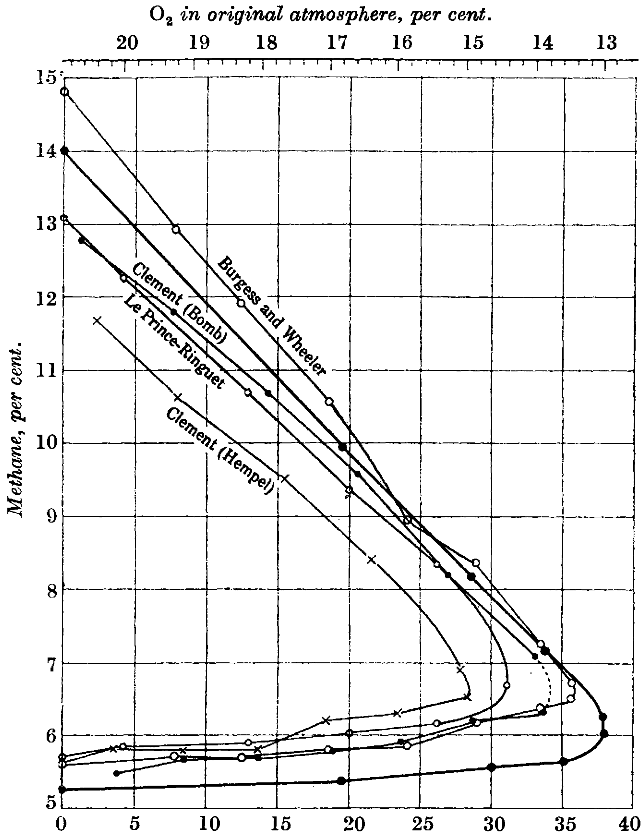
FIG. 1.



apparently due to the greater thermal capacity of the carbon dioxide, whilst the decrease in the higher limit is due to the combined effect of this and of the reduction in oxygen content of the atmosphere.

In the same figure are plotted results obtained by Eitner (*Habilitationsschrift*, München, 1902), Clement (*U.S. Bureau of Mines*, 1913, Technical Paper 43), and Leprince-Ringuet (*Compt. rend.*, 1914, **158**, 1999). They are not strictly comparable, however, for the conditions of experiment were somewhat different in each case. Thus Eitner's and Leprince-Ringuet's refer to experiments on the downward propagation of flame in these mixtures, and Clement's to the propagation from a point near the top of a Hempel burette, or of a steel cylinder of some 3 litres capacity. The wider

FIG. 2.



limits indicated by our experiments, in which upward propagation was observed, were therefore to be expected.

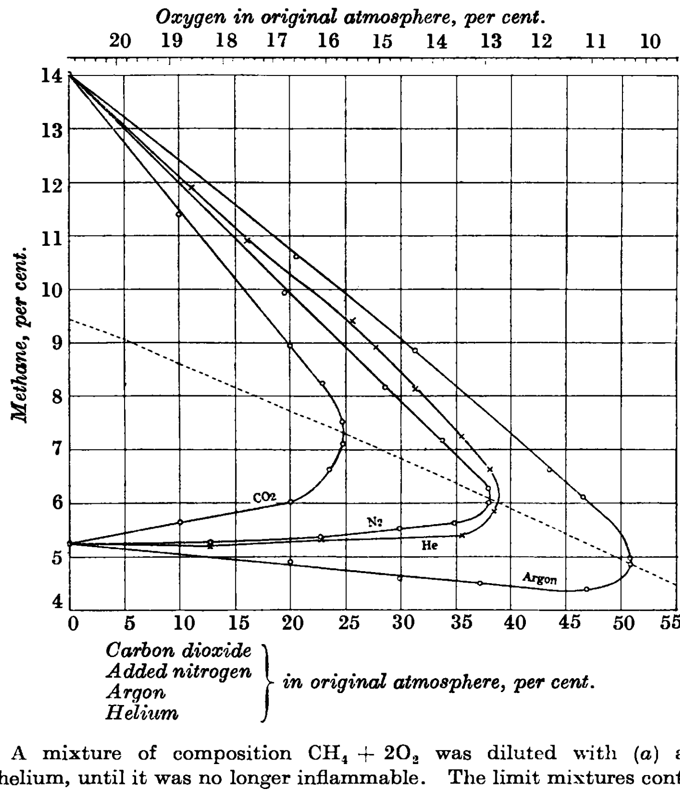
Influence of Nitrogen on the Limits of Inflammability of Methane–Air Mixtures.—The heavy curve of Fig. 2 represents correspondingly the limits of methane in atmospheres composed of pure air admixed with the indicated amounts of nitrogen. The extinctive effect of nitrogen is considerably less than that of carbon dioxide, for the two limits do not coincide until about 38% of added nitrogen is present in the atmosphere, as compared with 25% of carbon dioxide. These figures are almost exactly in the inverse ratio of the mean molecular heats (at constant pressure) of the two gases between room temperature and the flame temperature. Hence the difference in extinctive action is doubtless due to the difference in heat capacities of the two diluents. The lower limit shows a small but definite rise with increase in the proportion of nitrogen. As this diluent has the same heat capacity as air up to, and beyond, the flame temperatures of these experiments, this small rise must be ascribed to the reduction of the oxygen content of the atmosphere. The effect is masked by the operation of other factors when other chemically inert diluents are used.

Fig. 2 shows also the results of Clement (*loc. cit.*), Leprince-Ringuet (*loc. cit.*), and Burgess and Wheeler (J., 1914, **105**, 2596). Here, again, the results are not closely comparable with the present series, for they were obtained under different conditions; but whereas for carbon dioxide–air "atmospheres" all the previous results showed narrower limits than those now presented, one set of the nitrogen results (Burgess and Wheeler's) shows, in general, greater values for the higher limits. Now those experiments were conducted in closed vessels, wherein the pressure rose considerably (several atm.) during the inflammation, and Mason and Wheeler (J., 1918, **113**, 45) have shown that increase of pressure increases markedly the higher limit of methane–air mixtures.

Influence of Argon on the Limits of Inflammability of Methane–Air Mixtures.—If the conclusions drawn from the experiments with atmospheres containing carbon dioxide and added nitrogen are correct, the lower limit of methane will have smaller values in atmospheres made from air and argon than in air itself, for argon has a lower heat capacity than air. Fig. 3 shows that such is the case, and that the minimum value of the lower limit is 4·40% of methane in an atmosphere composed of about 47% of argon and 53% of air, as compared with 5·24% of methane in the case of pure air. It requires nearly 51% of argon in admixture with air to produce an atmosphere which cannot form an explosive mixture with methane.

Influence of Helium on the Limits of Inflammability of Methane–Air Mixtures.—The heat capacity of helium is very nearly equal to that of argon and each, apparently, remains constant up to high temperatures. If, therefore, the extinctive effect of an inert gas is solely due to its thermal capacity and to its effect on the oxygen concentration of the atmosphere, the limits of methane should be identical in atmospheres composed of ordinary air mixed in one case with argon and in another case with an equal volume of helium. Fig. 3 shows the action of helium, which, contrary to expectation, is markedly more extinctive of methane–air flames than is argon.* From a detailed consideration of the physical differences between these two gases, we ascribe the superior extinctive action of helium to its greater thermal conductivity,† which is more than eight times that of argon, at laboratory temperatures. We have no experimental information about the temperature coefficients of the conductivities of such mixtures as we are using,

FIG. 3.



* A mixture of composition $CH_4 + 2O_2$ was diluted with (*a*) argon, (*b*) helium, until it was no longer inflammable. The limit mixtures contained (*a*) 3·95, (*b*) 5·00% methane. For *downward* propagation of flame in a tube of the same size, firing from near the open end, similar results were obtained; in an atmosphere composed of 80% of air and 20% of inert gas, the lower limits were (*a*) 5·50, (*b*) 5·75% methane when the inert gas was (*a*) argon, (*b*) helium.

† The thermometric conductivity, or diffusivity, which is equal to the thermal conductivity divided by the specific heat (C'_p) of unit volume, is the function which would have to be used in a quantitative analysis of the phenomena of flame transmission. In the present argument, the terms may be used interchangeably.

but some indication is given by Stafford's work (*Z. physikal. Chem.*, 1911, **77**, 66) on the temperature coefficients of the conductivities of air and carbon dioxide separately, and Weber's work (*Ann. Physik*, 1917, **54**, 481) on the conductivities of some mixed gases at laboratory temperatures. It seems highly probable that the thermal conductivity of a gas mixed with helium will be greater than that of a corresponding mixture with argon, and that this will be true at the somewhat high temperatures of the flames in limit mixtures. At first sight, it is surprising that the higher thermal conductivity of helium should be responsible for its greater extinctive action; but if the propagation of flame is due to conduction of heat, then at either zero or infinite values of the thermal conductivities flame would not be propagated. Between the two values, zero and infinity, an optimum value for the conductivity must obtain; so it is evident that the higher conductivity of the helium mixtures may well be less favourable to flame propagation in limit mixtures than the lower conductivity of the argon mixtures.

This conclusion is in good accord with, and receives support from, observations made by Coward, Cooper, and Jacobs (J., 1914, **105**, 1069). They found that it was much more difficult to ignite, by the electric discharge, mixtures of various gases when diluted with helium than when argon was used, and they interpreted the results in a similar manner.

General Discussion.

If, therefore, it is probable that the differences between the argon and helium curves are due to the different thermal conductivities of the two gases, it is necessary to consider how far the discovery of the influence of this factor may affect our previous conclusions as to the influence of varying heat capacities.

The thermal conductivities at 0° of the gases under consideration are (Glazebrook, "Dictionary of Applied Physics," 1922, vol. 1, p. 459)

Helium	$32{\cdot}7 \times 10^{-5}$	Nitrogen	$5{\cdot}14 \times 10^{-5}$
Argon	$3{\cdot}85$,,	Air	$5{\cdot}22$,,
Carbon dioxide	$3{\cdot}25$,,		

The difference in thermal conductivity between carbon dioxide and nitrogen (1·9 units) seems far too small to account for the difference in extinctive action between these two gases, for there is about the same difference in extinctive action between helium and argon for a very much greater difference in thermal conductivity (28·9 units). We may therefore adhere to our earlier conclusion that the thermal capacity factor is predominant in determining the relative extinctive effects of two diluent gases, but we may add that, when a gas of very different thermal conductivity is introduced, then this factor will become important.

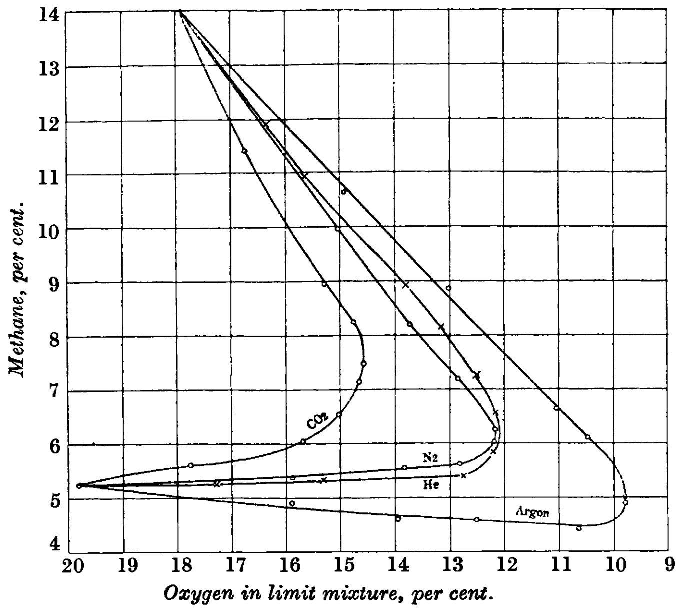
A Connexion between Lags on Ignition and Dilution Limits.—When inflammable mixtures of methane and air are heated to any temperature above their ignition temperature, a distinct interval of time must elapse before inflammation is observed. The relative ease of ignition of methane–air mixtures containing the various diluents used in this research, as indicated by their relative "lags" on ignition, might be regarded as a governing factor in determining the order of the limits. Determinations of such "lags" have recently been made in the Safety in Mines Research Board Laboratories in connexion with another research which will be published shortly. At the temperature of the flames in limit mixtures (calculated to be between 1100° and 1400°) the lags, under the conditions of experiment, were too short to be measured for comparative purposes, but at 950° they were reasonably long, and are shown for 6% methane mixtures in atmospheres containing 30% of diluent. The same table also shows the limiting proportion of the diluent which is completely extinctive at normal temperature and pressure.

Diluent.	Carbon dioxide.	Nitrogen.	Helium.	Argon.
Lag (seconds)	0·275	0·25	0·22	0·19
Limiting proportion (%) ...	25	38	39	51

It is tempting, perhaps, to explain the relative extinctive effects as being the result of the relative lags; but it is more reasonable to regard the lags as determined largely by the same factors as determine the extinctive effects, namely, thermal capacities and thermal conductivities, because the lag is generally explained as being the period in which the gas mixture is heating itself, by partial combustion, to the temperature of rapid reaction. Other circumstances being equal, the lag must therefore be shorter in the presence, not only of inert gases of lower thermal capacity, but also of gases of lower thermal conductivity.

The Most Inflammable Mixture of Methane and Air.—The broken line in Fig. 3 is the locus of mixtures in which the ratio between methane and oxygen is exactly that required for complete combustion, $CH_4 : 2O_2$. This line runs through the "noses" of the limits curves, and therefore, from this point of view, the most inflammable of all mixtures of methane and oxygen is that which burns completely to carbon dioxide and water. This is also the mixture in which the speed of uniform movement of flame is greater than in any other mixture of methane and oxygen (Payman, J., 1920, **117**, 48). On the other hand, the detonation wave is propagated more rapidly in mixtures in which the methane content exceeds that required for complete combustion (Dixon, *Phil. Trans.*, 1893, **184**, 97); in this case, the heat of reaction is evidently subordinated by those physical properties of the explosive mixture which govern the rate of transmission of a disturbance like a sound wave. Moreover, the speed of uniform movement of flame in methane–*air* mixtures reaches its maximum when the proportion of methane is somewhat higher than the theoretical amount for complete combustion (Wheeler, J., 1914, **105**, 2606), whilst mixtures

FIG. 4.



containing an excess of air are more readily ignited by a heated surface or by an electric spark.

Test of the "Limits Generalisation" of Payman.—Le Chatelier (*Ann. Mines*, 1891, **19**, 388) gave a formula which enabled the lower limit in air of a mixture of two inflammable gases to be calculated from the observed limits of the separate gases. This formula was put in more general form by Coward, Carpenter, and Payman (J., 1919, **115**, 27) and was shown to apply to lower and higher limits, in air, of mixtures of hydrogen, methane, and carbon monoxide, and of coal gas. It expressed in mathematical terms the statement that "lower-limit air mixtures, if mixed in any proportions, give rise to mixtures which are also at their lower limits."

Payman (J., 1919, **115**, 1436) gave the statement a still wider form which applies to cases in which the atmosphere is not air : "All mixtures, in any proportions, of limit mixtures remain limit mixtures . . . provided that all of the limit mixtures are of the same kind, that is to say, all lower-limit or all upper-limit mixtures." This statement is tested by the present research for atmospheres which contain large quantities of carbon dioxide, excess nitrogen, argon, and helium. It holds good in each case when mixtures represented by points on the straight part of a curve (Fig. 4) * are considered; it fails when points on the curved parts are considered, and the extent of the failure is represented by the greater or lesser curvatures at the point chosen. The generalisation is therefore fairly accurate for methane in atmospheres composed of air mixed with the inert gases named, except when applied to those mixtures the composition of which approaches the point where the lower and higher limits coincide.

Results.

Limits of inflammability of methane in atmospheres composed of air mixed with various diluent gases, observed in a vertical tube 2 inches in diameter, upward propagation of flame, the lower end of the tube being open; gases at atmospheric temperature and pressure.

Diluent in "atmosphere" %.	Limits of inflammability.		Diluent in "atmosphere" %.	Limits of inflammability.	
	Lower.	Higher.		Lower.	Higher.
Nil.	5·24	14·02	Nitrogen.		
			19·6	5·39	—
Carbon dioxide.			19·8	—	9·97
10·0	5·61	11·40	28·5	—	8·18
20·0	6·07	8·95	30·0	5·55	—
23·0	6·57	8·23	33·8	—	7·18
24·5	7·12	7·47	35·0	5·63	—
Argon.			37·9	6·01	6·26
20·0	4·91	—			
20·6	—	10·62	Helium.		
29·9	4·60	—	12·8	5·27	—
31·3	—	8·85	16·0	—	10·90
37·2	4·48	—	22·8	5·35	—
43·6	—	6·62	25·6	—	9·40
46·6	—	6·11	27·7	—	8·93
46·9	4·40	—	31·3	—	8·14
50·8	4·87	—	35·3	—	7·27
50·9	—	4·99	35·5	5·40	—
			38·2	—	6·56
			38·5	5·83	—

* The replotting of the experimental values on a different basis from that of Fig. 3 is necessary to exhibit the approach to a rectilinear character which tests the validity of the generalisation.

Summary.

1. The limits of inflammability of methane in atmospheres composed of air mixed with (*a*) carbon dioxide, (*b*) nitrogen, (*c*) argon, and (*d*) helium have been determined, and the factors which are mainly responsible for the extinction of flame have been elucidated. They are (1) the reduction of oxygen content by the diluent gas, (2) its thermal capacity, and (3) its thermal conductivity. An exact treatment of the subject would therefore demand a knowledge of the thermal conductivities of certain mixed gases up to high temperatures (say, 1000° to 1500°). Such data are not at present available.

2. The thermal capacity effect of the diluent gas is marked in the case of argon; the lower limit of methane in the conditions described is reduced from 5·24% in air to 4·40% in an atmosphere composed of 47% of argon and 53% of air, and is further reduced to 3·95% in an atmosphere composed of argon with just sufficient oxygen to burn the methane completely.

3. The thermal conductivity effect is marked when a comparison is made between the limits in atmospheres composed of air to which has been added argon, on the one hand, or helium on the other.

4. The limits generalisation " of Payman holds fairly accurately over the whole range of mixtures investigated, except near the point at which the lower and higher limits meet.

5. Of all mixtures of methane and oxygen, that represented by the proportions $CH_4 + 2O_2$ is the last to become non-inflammable as inert gases (nitrogen; or nitrogen with carbon dioxide, argon, or helium) are added in increasing amount.

6. There is a parallel between the " lags " on ignition and the dilution limits of such mixtures as we have used. It is suggested that both are dependent on the same factors, in the case of any one inflammable gas.

This work has been carried out at the suggestion and under the general direction of Professor R. V. Wheeler. We desire to express our appreciation of the able manner in which Miss E. H. M. Georgeson and Mr. G. W. Jones, at Sheffield and Pittsburgh, respectively, have assisted us in this investigation, and to acknowledge the permission granted by the two organisations concerned to publish this work.

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