XXXV.—*Extinction of Methane Flames by Water Vapour.*

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THE limits of inflammability of methane in air are narrowed by the progressive addition of an inert gas to the air. Data for the effect of carbon dioxide, nitrogen, argon, and helium have been published (Coward and Hartwell, J., 1926, 1522). To these is now added a series of results obtained with water vapour, for which no data of any moment have hitherto been recorded.

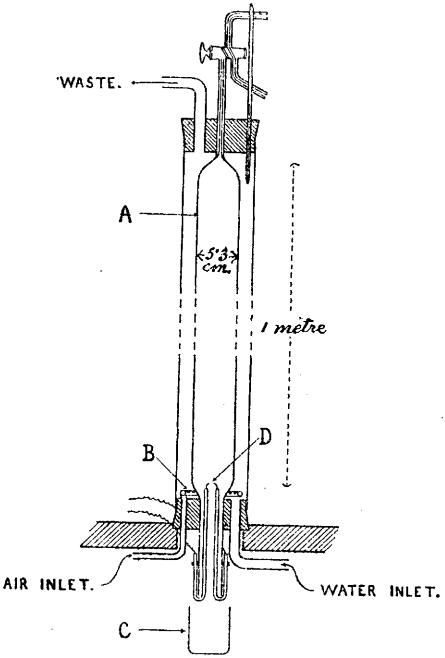
EXPERIMENTAL.

For observations on the limits of inflammability of gas mixtures, it is desirable to use a vessel which is both wide enough to avoid errors due to cooling by its walls and long enough to show whether flame travels independently of the initial impetus of the source of ignition. Constant pressure should be maintained during inflammation, if the observations are to have any precise significance. Experience has shown ("Limits of Inflammability of Gases and Vapors," by H. F. Coward and G. W. Jones, *U.S.A. Bureau of Mines*, Bull. 279, 1928) that a vertical tube 2 inches in diameter, 4—6 feet long, and opened at the end behind the flame at about the moment of ignition, meets these requirements; it gives results nearly the same as those obtained in very much larger apparatus. The source of ignition is preferably near the lower end of the tube, for certain weak mixtures, although capable of indefinite propagation of flame upwards, are unable to burn downwards.

These requirements are met readily when gases alone are under examination, but not so easily when the temperature of the container has to be above the normal to avoid condensation of vapours. Fig. 1 shows the arrangement which has proved satisfactory with mixtures of methane, air, and water vapour up to the temperature (just above 67°) necessary to maintain enough water vapour to extinguish flame in any mixture of methane and air.

The glass tube A was surrounded by a stream of hot water from a gas heater. The water jacket was covered, save for a vertical observation slit, with asbestos cloth, and the water was stirred by air bubbles from the perforated tube B. The difference in temperature between the top and bottom of the water jacket was never more than 0·2°.

FIG. 1.



For an experiment, the tube A was filled with water and water-sealed by the beaker C. The jacket and the beaker were brought to a predetermined temperature which was then maintained constant. The air bubble which had appeared at the top of A was sucked off, and the prepared mixture of methane and air admitted through the tap and finally bubbled through the water in C until about twice the volume of A had passed. A piece of tape, held by thin stainless-steel springs against the inner wall of A, maintained liquid water in contact with the gas throughout the length of the tube.

The inflammability of the mixed methane, air, and water vapour was tested, when it had been heated by the constant-temperature jacket for 10 minutes, by passing a " fat " spark from an induction coil across the 5 mm. gap at D.* At the same moment the beaker C was withdrawn to permit ready escape of the expanded products of combustion. An inflammable mixture propagated a blue flame with

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* Such a spark is strong enough to ensure ignition of any methane–air mixture which is capable of propagating flame—its energy much exceeds the minimum for ignition.

a convex front throughout the whole tube above the spark gap; if the mixture were outside the limits of inflammability, a cap of flame appeared above the spark gap, but did not assume the characteristic shape of the flame in a mixture which is inflammable *per se*, nor did it extend far up the tube. The distinction was clear.

In calculating the composition of the mixture, the ratio of methane to air was obtained by analysis of a sample from the gas holder. The total pressure of the mixture was atmospheric, and the partial pressure of the water vapour was assumed equal to the saturation pressure of water at the temperature of the jacket. The only place where the temperature of the tube A might have been somewhat lower was in and just below the rubber stopper, but, as the mixture at that place would be heavier than the rest, its influence on the composition of the mixture near and above the spark would be inappreciable.

It was possible that radiation from the advancing flame might evaporate some moisture from the tape and from the walls of the tube, just ahead of the flame, and thus produce a mixture of greater water content than we had calculated. To test this point, the tape was removed and a lower-limit mixture was passed through until only a few large drops of water, and (in one experiment) one patch of smaller drops, remained. The mixture was kept until it was saturated, and then ignited; the flame which travelled up the tube showed no change in width or shape as it passed the wet places. In other tests a small length of tape was inserted in the tube. The tape remained wet during the test, but the flame was not affected as it approached or passed the tape. It is concluded that evaporation of water by the flame was without appreciable influence on the limits.

Results.—The limits of inflammability of methane in dry air, in the 3-foot tube of the apparatus described, the water in the vessel C being replaced by mercury, were 5·24 and 14·08%. These agree sufficiently well with the previous observations in a 6-foot tube, *viz.*, 5·24 and 14·02%.

The results which serve to define the limits of mixtures of water vapour, methane, and air are in Table I. As the method of experiment is by trial and error, the range between inflammable and non-inflammable mixtures being narrowed in successive experiments, only the last few results of each series are quoted. When the figures of the first four columns of the tables are plotted on a large-scale diagram, the choice of the figures for the limit mixtures, shown in cols. 5 and 6, becomes clear. The concentration of water vapour is expressed as a percentage on the "original atmosphere" of air *plus* water vapour; whereas that of methane is expressed as a percentage of the whole, *i.e.*, methane *plus* air *plus* water vapour.

TABLE I.

Propagated flame.		Failed to propagate flame.		Limit mixture.		
Water vapour.	CH_4.	Water vapour.	CH_4.	Water vapour.	CH_4.	Temp. (approx.).
21·4	5·97	21·2	5·91*	21·2	5·90	60°
21·3	5·94	21·3	5·90*			
21·2	5·89*	21·3	5·88*			
21·2	5·89*	21·2	5·84			
		21·3	5·81			
26·4	6·43	26·5	6·33	26·4	6·34	64—65
26·4	6·34	26·6	6·32			
29·0	6·87	29·1	6·86	29·1	6·86	67
29·0	6·86	29·1	6·84			
28·9	7·19	29·2	7·17	29·0	7·18	67
23·9	8·42	24·0	8·40	23·9	8·41	62
23·9	8·41	24·1	8·39			
		24·1	8·39			
19·6	9·28	19·6	9·36	19·5	9·37	57·5
19·5	9·34	19·5	9·40			
19·4	9·36	19·6	9·42			

* These five mixtures are scarcely distinguishable one from another, analytically. We estimate the accuracy of the water figure as within 0·2 unit and of the methane figure as within 0·02 unit.

Fig. 2 contains a graph of the limits given in Table I, with lower and higher limits for mixtures saturated with water vapour at laboratory temperature (see Coward and Hartwell, *loc. cit.*, footnote p. 1523). The curves for carbon tetrachloride (Coward and Jones, *Ind. Eng. Chem.*, 1926, **18**, 970) and other diluent gases are included. The broken line is the locus of mixtures in which the molecular ratio $CH_4 : O_2$ is 1 : 2.

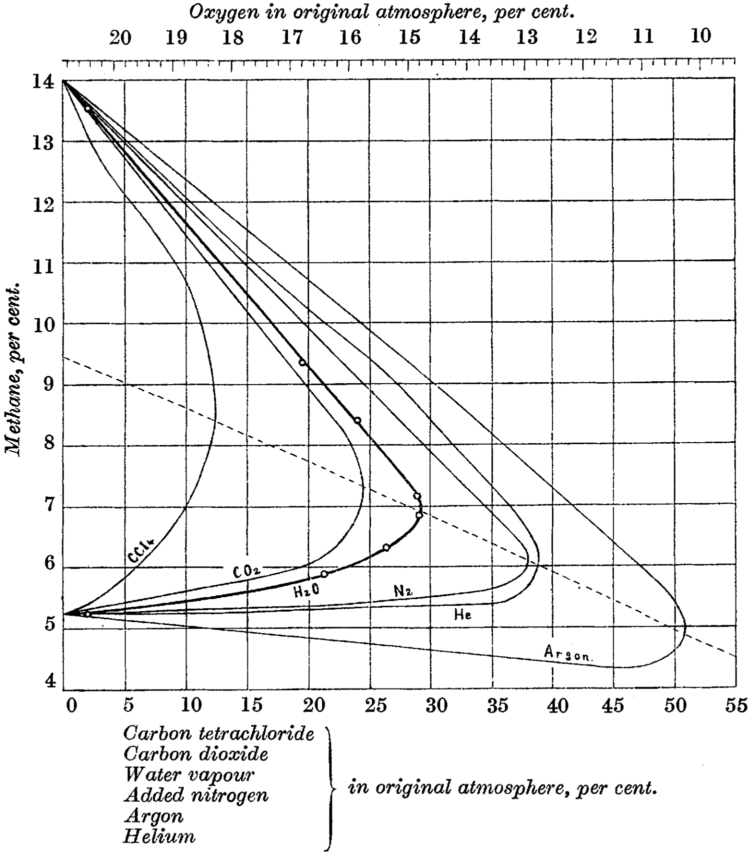
Most of the points on the water-vapour curve were necessarily obtained at temperatures higher than that of the laboratory. The points nearest the " nose " of this curve, for example, were obtained at 67°. For comparison, therefore, the position of the " nose " of the carbon dioxide curve was determined at the same temperature, and found to lie at 27·1% of carbon dioxide, instead of 24·5% at 17°. The " nose " of the nitrogen curve would doubtless be extended similarly by the same increase of temperature. Water vapour therefore lies between carbon dioxide and nitrogen in its extinctive action on methane flames, and is very nearly as effective, volume for volume, as the former.

Discussion.

The extinctive action of five of the six diluent gases runs in the order of their molecular heat capacities, which are (C_p, 0—1200°) :

Carbon tetrachloride, 22 (estimated); carbon dioxide, 10·90; water vapour, 9·20; nitrogen, 7·21; argon, 5·0. Helium is exceptional, for its heat capacity is equal to that of argon, but its extinctive effect on flame is relatively much greater. This is ascribed to its abnormally high thermal conductivity.

FIG. 2.



The extinctive action of water vapour is rather greater than would be inferred from its specific heat. The actual heat capacity of the water vapour present in the limit mixtures is, however, relatively greater than the figure 9·20 would suggest; for, according to Bose (*Z. Elektrochem.*, 1908, **14**, 269), saturated water vapour is about 8·5% associated at 67°. Allowance being made for this and for the heat of dissociation of the complex water molecules ($H_4O_2 = 2H_2O - 9640$ cals.; Bose, *loc. cit.*), the relative heat capacity of water vapour would be nearly 10·0 in the series.

The incidence of the water-gas equilibrium, which is attained in the gases "snatched" from the centre of higher-limit flames of methane, oxygen, and nitrogen (Coward, *Fuel*, 1929, **8**, 470), has but a small effect on the heat of reaction, the heat capacity, and the thermal conductivity of the mixture. The effects of alterations in these three factors, due to the water-gas reaction, may be shown nearly to cancel one another.

The conclusion is, therefore, that, in the relative extinctive effects on methane flames of diluent gases which take no important part in the flame reactions, the chief factor is the heat capacity of the diluent, but that helium stands in an exceptional position by virtue of its high thermal conductivity. Other factors have very little influence. Carbon tetrachloride, although it undergoes extensive reaction in the flame of a methane–air mixture, falls into line with the other diluent gases.

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