250. Flame Speeds during the Inflammation of Moist Carbonic Oxide–Oxygen Mixtures.

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IF we neglect losses of heat to the walls of the tube, the speed of propagation of flame during the "uniform movement," when the flame travels from an open towards a closed end of a tube of given diameter, can be regarded as depending on two factors : (1) The rate of conduction of heat from layer to layer of the mixture, which in turn depends mainly on the difference in temperature between the burning and the unburnt gases; and (2) the rate of reaction of the combining gases : for a given combustible gas, this varies with the composition of the mixture and with the temperature resulting from the reaction. It was demonstrated experimentally (Payman, J., 1920, 117, 48) that the maximum speed of uniform movement of flame in certain series of mixtures of combustible gases with air or oxygen is given by (a) a mixture containing insufficient oxygen for complete combustion when the mixtures are with air, and (b) the mixture containing combustible gas and oxygen in combining proportion when the mixtures are with pure oxygen.

The proof of (b) was given by two series of experiments with (1) methane and (2) hydrogen, but a few experiments were also made (in 1919) with mixtures of moist carbonic oxide and oxygen, with the following results, not hitherto recorded :

CO in mixture, %	54 ·0	67·0	80.0
Speed of uniform movement, cm./sec	94.7	$(200 + 0_2)$ $101 \cdot 2$	92·2

For these experiments a horizontal glass tube of 2.5 cm. internal diameter was used, and the determinations were made at 15° and 755 mm. The mixtures were stored over a dilute solution of potassium hydroxide in water, but no special precautions were taken to ensure their complete saturation with water vapour. The results conform with those obtained with methane and with hydrogen, but they were not published because previous experience had shown that with moist carbonic oxide the speed of flame varies considerably with the concentration of water vapour and is therefore subject to alteration from day to day if the temperature of saturation alters (see Payman, J., 1919, **115**, 1454, and, for later experiments, Payman and Wheeler, J., 1923, **123**, 1251).

Recently, Bone and Fraser (*Proc. Roy. Soc.*, 1931, *A*, **130**, 542) have published results of experiments with moist carbonic oxideoxygen mixtures which are in disagreement with ours, and state that "the mixture giving the maximum initial speed of inflammation would be one containing rather less than 80 per cent. of carbonic oxide." It therefore became necessary to repeat and extend our earlier experiments.

Two points of difference between their results and ours have to be explained. First, there is a difference in the absolute speed of flame for a given mixture; e.g., whereas the speed we had obtained with a mixture containing 80% of carbonic oxide was $92\cdot2$ cm./sec., Bone and Fraser, who used a glass tube of the same internal diameter as ours, record speeds of 195 and 190 cm./sec. This difference might be due to differences in the degree of saturation of the mixtures with water vapour, for, although in Bone and Fraser's experiments the temperature of saturation was lower $(12-13^\circ)$ than in ours (15°) , they had presumably taken special precautions to saturate their mixtures, which were stored over mercury.

The second difference lies in the position of the maximum-speed mixture on the speed-composition curve. Bone and Fraser's recorded results (*loc. cit.*, p. 543 and Fig. 1) present too few determinations to fix the point of maximum speed. The tabulated figures suggest that the highest speed obtained experimentally was with a mixture containing 80% of carbonic oxide; the curve (Fig. 1) suggests 70%. On re-drawing the curve from the tabulated figures (on the assumption that a missing value for the percentage of carbonic oxide is 70), it is apparent that the correctness or otherwise of Bone and Fraser's deduction, previously quoted, depends essentially on the value for the speed of flame obtained with one mixture, that containing 80% of carbonic oxide. The speed of the uniform movement of flame is constant under constant conditions of experiment, but considerable care is necessary in carrying out the experiments, more particularly to avoid disturbance at the mouth of the tube before or on ignition of the mixture (see Mason and Wheeler, J., 1917, **111**, 1054; 1919, **115**, 578).

For the experiments now to be described we used a horizontal glass tube of 2.5 cm. internal diameter and 126 cm. long. Ignition was effected by a coal-gas flame 3 cm. long. To ensure complete saturation of the mixtures with water vapour, they were passed from the storage holder, where they were contained over dilute aqueous potassium hydroxide, into the evacuated explosion tube in a fine stream through a bubbler containing water. To check the completeness of saturation of the mixtures, a test was made in which a measured volume, after leaving the bubbler, was passed through a weighed calcium chloride tube. A similar test with a mixture passed direct from the storage holder showed that the degree of saturation was only 85%.

Although every effort was thus made to maintain the degree of saturation constant, yet it was realised that small changes in the temperature of the laboratory might vitiate the results. Three mixtures were therefore made of sufficient volume to allow of four experiments with each. The mixtures were used in rotation. The speeds of the flames were measured photographically. The results, obtained at $13\cdot1^{\circ}$ and 750 mm., were as follows:

CO in mixture, %	53.5	65.1	78·5
		$(2CO + O_2)$	
Speed of uniform movement, cm./sec	(216	247	221
	210	247	226
) 212	252	226
	209		226

One result with the mixture $2CO + O_2$ was valueless because the record crossed the joined ends of the photographic film.

These records confirm our earlier work, inasmuch as they indicate that the maximum-speed mixture is that corresponding, roughly, with the mixture $2CO + O_2$. The speeds are higher than those obtained for corresponding mixtures in our earlier experiments and in those by Bone and Fraser. In our earlier experiments, the degree of saturation of the mixtures with water vapour was undoubtedly incomplete.

A series of experiments was now made with a range of mixtures around $2CO + O_2$ to determine the maximum-speed mixture more closely. The conditions were the same as in the previous series. The results were as follow:

CO in mixture, % 59.5	64.5	66.1	6 9·0	73.9	79.8
		$(2CO + O_2)$		$(3CO + O_2)$	$(4CO + O_2)$
Speed of uniform (232	239	247	244	230	216
movement, cm./sec. (236	243	252	239	230	213

As a check on these measurements, we asked Dr. O. C. de C. Ellis, of the Safety in Mines Research Laboratories, Sheffield, to make similar determinations. This he did, using a tube of 2.55 cm. internal diameter and 130 cm. long, the mixtures being saturated with water vapour at 18.5° and 755 mm., with the following results :

We can thus state that the maximum speed of uniform movement of flame in moist (*i.e.*, "saturated") carbonic oxide-oxygen mixtures, when ignited at room temperature and barometric pressure at the open end of a horizontal glass tube closed at the other end, is obtained with a mixture corresponding closely to $2CO + O_2$.

Our thanks are due to Mr. H. Titman, B.Sc., for assistance in the experimental work described in this paper.

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[Received, April 6th, 1932.]