# Reports of the Academy of Sciences of the USSR

1957

SovietRxiv

Fig. 1

Figure 1: Fig. 1

## Abstract

## Full Text

*Reports of the Academy of Sciences of the USSR*
1957. Vol. 115, No. 3

## PHYSICAL CHEMISTRY

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# FORMATION OF ACETYLENE DURING INCOMPLETE COMBUSTION OF METHANE IN OXYGEN

*(Presented by Academician N. N. Semenov, 28 February 1957)*

One of the most effective methods at present for obtaining acetylene from natural gas is oxidative pyrolysis, i.e., the process of incomplete combustion of natural gas in oxygen. Several industrial installations are already operating by this method ([1,2]). However, the mechanism of acetylene formation in the flame has been almost completely unstudied. The works of Benedek and Laszlo ([3]) and of Kidd ([4]), in which this question has recently been considered, contain too little experimental data.

In the present work, incomplete combustion of methane in oxygen was studied in the flame of a burner of the Bunsen type; for this purpose, gas samples were taken at various points of the flame. To reduce distortion of the flame during sampling, water-cooled gas-sampling probes with an internal diameter of 0.2–0.3 mm were used.

Temperature was measured with platinum-platinum-rhodium thermocouples with wire diameters of 0.04, 0.15, and 0.5 mm, followed by extrapolation to zero diameter. The sampler and thermocouples were moved in the flame by means of a device with a micrometer screw, with a distance-reading accuracy of 0.01 mm; this made it possible to obtain composition and temperature distribution curves for gases in a zone 2–3 mm thick.

*Fig. 1*

Experiments were carried out with an open and a separated flame at various ratios of methane and oxygen in the initial mixture, as well as experiments with the addition of propane to the methane.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Figure 1 presents the results of analysis of combustion products sampled along the vertical axis of the flame in the region of the tip of the inner cone during combustion of a mixture containing 43.5% $O_2$, 54.8% $CH_4$, and 1.7% $N_2$ in a burner with a separated flame. Separation of the inner and outer cones was achieved by means of a quartz attachment 27 mm in diameter and 70 mm long. The flow rate of the combustible mixture was 2.2 l/min; under these conditions the height of the inner cone was 12 mm.

Examination of the curves shown in Fig. 1 indicates that a large part of the methane and oxygen enters into reaction over a very short section.

flame, from $x = 3.0$ to $x = 3.5$ mm ($x$ is the distance along the flame axis). In this region, essentially all the reaction products are formed: $CO_2$, $C_2H_2$, CO, and $H_2$. In reality, the combustion zone is apparently still narrower, since when the sampling probe is introduced into the flame, some distortion of the combustion front inevitably occurs.

**Fig. 2**

Similar results are also obtained with a different composition of the initial mixture; moreover, as the oxygen content increases, the acetylene concentration decreases. When a methane-propane mixture is burned in oxygen, the concentration of acetylene in the combustion products and the yield of acetylene calculated per carbon of the entering gas increase.

In experiments with an unseparated flame, significant diffusion of outside air is observed; by distorting the results, this leads to an increased content of nitrogen and oxygen-containing components in the gas. Therefore the acetylene concentration in an unseparated flame is lower, and the hydrogen concentration passes through a maximum, whereas in a separated flame a continuous increase in the hydrogen content is observed.

**Fig. 3.** $I$ –experimental curve; $II$ –curve calculated from the equilibrium of the water-gas reaction; $III$ –curve calculated from the heat balance

Figure 2 gives two curves of acetylene content in eleven horizontal sections of the flame for different distances from the burner rim (from $x = 1.90$ to $x = 5.65$ mm). In each section, gas samples were taken at five points. The curves in Fig. 2 show that above the apex of the inner cone, which is located in the section $x = 3.7$ mm, the acetylene concentration on the axis is maximal, while below the apex it is minimal. This is explained by the shape of the inner cone, in which the acetylene-formation reaction in fact proceeds.

The experimental results obtained show that the reaction of incomplete combustion of methane in oxygen, accompanied by considerable formation of acetylene, is completed mainly in a zone several tenths of a millimeter wide.

Beyond this zone, above the apex of the inner cone, the reaction proceeds much more slowly. The acetylene content beyond the oxygen zone increases somewhat until it reaches a maximum located at a distance of 0.3–0.4 mm from the end of the oxygen zone. Then the acetylene content begins to fall.

To study the initial stages of the reaction, experiments were carried out in which the initial gas mixture was rapidly and simultaneously ignited over the entire cross section. For this purpose, a special heater, made of a spiral wound from platinum foil, was placed at the burner outlet and heated by an electric current to a temperature of 1100–1200°. These experiments showed that, at first, only CO, $H_2O$, and $CO_2$ are formed in the oxygen zone, while the formation of acetylene and ethylene from the unburned part of the methane begins later. Thus it may be concluded that acetylene formation occurs mainly at the end of the oxygen zone and is completed in the immediate vicinity of its outlet.

Figure 3 gives the curve of the temperature distribution along the vertical axis of the flame (I) for a mixture containing 57% $CH_4$, 41.3% $O_2$, and 1.6% $N_2$. In the oxygen zone the temperature rises rapidly, and then remains almost constant, at approximately 1850°. Figure 3 also gives two curves obtained by calculation using experimental data on the gas composition. Curve II was obtained by calculation from the equilibrium between the components of the water-gas reaction (the temperature was determined from tables according to the value of the ratio

$$\frac{p_{\mathrm{CO}} \cdot p_{\mathrm{H_2O}}}{p_{\mathrm{CO_2}} \cdot p_{\mathrm{H_2}}},$$

and curve III, from the heat balance without allowance for dissociation.

The considerable discrepancy between curves II and I for values of $x < 3.7$ mm shows that, in the oxygen zone, the components of the water-gas reaction are not in equilibrium. Here there is preferential formation of carbon monoxide and water, the contents of which considerably exceed the equilibrium contents corresponding to the observed temperature. However, immediately beyond this zone, curves II and I merge, which indicates the establishment of equilibrium of the water-gas reaction in the immediate vicinity of the oxygen zone. This result demonstrates the applicability of the method of thermochemical calculation of the acetylene-formation process in incomplete combustion, taking into account the equilibrium of the water-gas reaction (5).

**Fig. 4**

To estimate the relative rate of formation of the various components of the reaction, on the basis of the experimental results obtained, the values of the

Fig. 4

Figure 4: Fig. 4

concentration gradients

$$\frac{dr}{dx}.$$

were calculated. Figure 4 shows the results relating to the change in concentrations along the vertical axis of the flame. These results show that, at the beginning of the oxygen zone, carbon monoxide and water are formed at the highest rate. Acetylene formation reaches an appreciable rate only at the end of the oxygen zone and is accompanied by an increase in the rate of hydrogen formation.

This result contradicts the mechanism proposed by Benedek and Laszlo ([3]), according to which acetylene is formed through the interaction of formaldehyde and methyl alcohol. Apparently, the formation of acetylene, accompanied by the formation of hydrogen, has a purely thermal mechanism and

occurs through the interaction of methane molecules or the corresponding hydrocarbon radicals upon reaching a sufficiently high temperature as a result of the combustion of part of the methane to CO, $H_2O$, and $CO_2$. It should be taken into account, however, that the increase in the rate of hydrogen formation at the end of the oxygen zone is also explained by the water-gas reaction, which here must proceed in the direction

$$CO + H_2O \rightarrow CO_2 + H_2.$$

However, the concentration of $CO_2$ in the combustion products is somewhat lower than the concentration of hydrogen, so this reaction alone cannot lead to the formation of all the hydrogen obtained.

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Received
30 XII 1956

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