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OXIDATION OF METHANE UNDER ADIABATIC COMPRESSION CONDITIONS

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In the studies made by M. V. Polyakov /1/, A. A. Koval'skii /2/, etc., carried out at pressures not exceeding atmospheric pressure, it was established that a number of chain processes go by a heterogeneous-homogeneous mechanism.

In the literature the widespread opinion exists that at high pressures the effect of the walls on the chain reaction is slight. By running the process under adiabatic compression conditions, where the temperature of the gas mixture is sharply different from the temperature of the walls of the apparatus, it becomes possible to establish the effect of the "cold" wall on the progress of the chain reaction.

Taking as the subject of study a methane-oxygen mixture (for which one of us had previously established /3/ that the oxidation reaction takes place even at a pressure of 200 - 300 at [technical atmosphere = 735.5 mm of Hg] and a wall temperature of 400°, and ~~going~~ ^{goes} instantaneously at 500 - 600°), we studied this mixture in the adiabatic compression apparatus designed by Yu. N. Ryabinin /4, 5/. When filling the barrel of the apparatus the barrel and all of feed lines were evacuated well with ^avacuum-pump, and then filled with the methane-oxygen mixture at a pressure exceeding atmospheric.

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This procedure was repeated twice before each experiment, after which we assumed that the apparatus was filled with the studied methane-oxygen mixture (containing 4% oxygen) without any impurities.

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Fig. 1. Temperature of methane as a function of the compression pressure.

1) Pressure

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Then the detonation was made, after which the barrel contents were displaced by a piston into an evacuated vessel, and an analysis was made of the gas mixture and of the products absorbed from it in distilled water.

The pressure in the apparatus was measured with a crusher gauge manometer /4/, while the temperature of the compressed gas mixture was calculated on the premise that under the experimental conditions the methane-oxygen mixture behaves as an ideal gas, the temperature of which is related to the pressure by the isentropy rule.

Knowing the C_p/C_v ratio for methane under conditions corresponding to the ideal gas state /6/, we calculated the temperature of the compressed gas as a function of pressure (Fig. 1).

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The performed experiments (Table 1) disclosed that under adiabatic compression conditions the reaction begins only at temperatures above 1200° K, which was established by the formation of carbon monoxide in the gas phase, and also by the presence of formaldehyde, which was qualitatively determined using Schiff's reagent /7/.

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The obtained experimental data give reason to believe that in the case of the slow oxidation of methane the temperature of the reactor wall plays an important part, since in the absence of a heated wall the reaction begins only at a temperature above 1200° K.

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Table 1

Experimental Results

- 1) Pressure, kg/cm²
 - 2) Temperature, ° K
 - 3) Qualitative determination of CH₂O
 - 4) None
- Slight color
Color
—
Intense color

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Besides this, the performed experiments show that the sole oxide formed under these conditions is carbon monoxide, since the data on the analysis of the mixtures show the complete absence of carbon dioxide.

From the data on the equilibrium constant of the reaction /8/
 $\text{CO} + 1/2 \text{O}_2 = \text{CO}_2$ it can be seen that ~~XXXXXXXX~~ the reaction for the decomposition of carbon dioxide cannot go even at atmospheric pressure and the experimental temperatures. This means that the carbon monoxide detected by us could not have been formed by the decomposition of carbon dioxide.

In none of the experiments was the formation of elemental carbon detected.

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