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Abstract

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FORMATION OF ACETYLENE DURING ADIABATIC COMPRESSION OF METHANE

(Presented by Academician S. I. Volfkovich on 4 V 1961)

The reaction of acetylene formation from methane

$$2CH_4 = C_2H_2 + 3H_2 \tag{1}$$

proceeds in very short time intervals, on the order of 0.001 sec. Acetylene is thermodynamically unstable at temperatures up to 3000° K, and therefore it is necessary to cool the reaction products rapidly. These features of the process make it possible to suppose that, for carrying out the reaction, it is convenient to apply the method of adiabatic compression of gases,* to which the present work is devoted. The experiments were carried out in an apparatus described in detail in the literature ([4,5]). The acetylene content in the gas after the experiment was determined by the colorimetric method ([6]), and in those cases where it exceeded 0.1%, by the argentometric method ([7]).

The equilibrium constant of reaction (1) can be calculated from equation (2)**

$$\lg K = -\frac{18077}{T} + 13.09 \lg T - 0.02347T + 0.6335T^2 - \frac{107520}{T^2} - 23.9. \tag{2}$$

Knowing the equilibrium constant and assuming that at high temperatures (thousands of degrees), even at high pressures, the fugacities of methane, hydrogen, and acetylene differ only slightly from the pressure, we calculated the equilibrium concentrations of acetylene at pressures of 1, 1000, and 10 000 atm.

The calculation showed that at atmospheric pressure and a temperature, for example, of 1500° K, the reaction proceeds almost completely, whereas at a pressure of 10 000 atm at this temperature up to 2% acetylene may be formed. From the equation for the methane adiabat it follows that temperatures of 1500° K can be reached by compressing methane to 1300 atm. However, compressing pure methane even to 10 000 atm, we did not detect acetylene in the gas.

Assuming that a higher temperature is needed for the formation of acetylene at high pressures, we investigated the compression of mixtures of methane with nitrogen, helium, argon, xenon, krypton, and hydrogen, whose heat capacities are lower than the heat capacity of methane and whose compression temperature is higher. Mixtures of methane with nitrogen containing 2, 4, 14, and 38 vol.% methane were investigated; with argon (2, 4, 6, 7, and 14% methane); with helium (3, 6, and 14% methane); xenon with 7% methane; krypton with 3% methane; and hydrogen with 4 and 14% methane. For the investigation we used methane of 99.5% purity, helium and argon of 99.9% purity, and xenon and krypton of 100% purity. Electrolytic hydrogen and nitrogen were purified of oxygen.

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* Recently, works devoted to the study of gas reactions in adiabatic-compression apparatuses have appeared increasingly often in the literature, with compression of the gas mixture being carried out by a piston ([4]) or in a shock wave ([2,3]).

** According to Ya. S. Kazarnovskii.

The results of the investigation are presented in Table 1, which gives graphically smoothed data: the volume percent of acetylene in the gas and the yield of acetylene (η).

To calculate the acetylene yield it was necessary to determine the composition of the mixture after the experiment. In those cases in which we investigated mixtures of methane with nitrogen, the composition of the mixture after compression, as shown by mass-spectrographic analysis, differed little from its initial composition. Thus, in a mixture containing before compression 5.5% methane and 94.5% nitrogen, after compression, in addition to acetylene, the following were found: N_2 94.9%; O_2 0.6%; CO_2 0.036%; CH_4 3.5%; C_2H_4 0.13%, and a small amount of higher hydrocarbons.

When compressing mixtures of methane with argon, hydrogen, helium, xenon, and krypton, i.e., with gases whose molecular weight differs considerably from the molecular weight of nitrogen, it was necessary to take into account the change in the composition of the mixture as a result of the so-called leakage and outflow of gas. When the piston moves along the barrel of the adiabatic apparatus at the beginning of the compression process, when the piston begins to move, the pressure of the driving gas (nitrogen) is greater than the pressure in the barrel, and part of the nitrogen leaks into the gas under investigation through the gap between the piston and the wall. As the piston approaches the closed end of the barrel, the pressure in it rises, while the pressure of the driving gas falls. In this case the compressed gas begins to flow out of the barrel through the gap.

These processes of leakage and outflow in the investigation of mixtures with nitrogen could not noticeably affect the change in the composition of the mixture. In the investigation of mixtures of methane with hydrogen and other gases, however, the addition of nitrogen significantly

Table 1

Acetylene yield during compression of mixtures of methane with nitrogen, argon, helium, and xenon as a function of pressure

Compression pressure, kg/cm²	Mixture CH_4 with 2% CH_4,		Mixture CH_4 with N_2, 4%		Mixture CH_4 with N_2, 14%		Mixture CH_4 with N_2, 38%		Mixture CH_4 with Ar, 2%		Mixture CH_4 with Ar, 4%		Mixture CH_4 with Ar, 6%		Mixture CH_4 with Ar, 7%		Mixture CH_4 with Ar, 14%		Mixture CH_4 with He, 3%		Mixture CH_4 with He, 6%		Mixture CH_4 with He, 14%		$CH_4 + Xe$, 7%,		$CH_4 + Kr$, 3%,	
	a	η	a	η	a	η	a	η	a	η	a	η	a	η	a	η	a	η	a	η	a	η	a	η	a	η	a	η
300	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
500	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1000	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1500	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2000	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2500	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3000	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4000	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5000	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6000	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
7000	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
8000	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
9000	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Note. a is the acetylene content in the gas phase, in volume percent; η is the acetylene yield in percent.

changed the composition of the mixture. To take these changes into account, we determined the molecular weight of mixtures obtained after compression of argon and other gases with nitrogen at different driving-gas pressures, and obtained curves from which the molecular weight of the mixtures under study with methane was determined. Knowing the molecular weight of the mixture before and after compression and assuming that, during the motion of the piston, a mixture of constant composition flows out of the channel, one can calculate the composition of the mixture after compression. The yield η was calculated

Fig. 1. Curves of the dependence of the acetylene yield η on pressure (temperature). 1 –mixture of 2% CH_4, 98% N_2; 2 –mixture of 4% CH_4, 96% N_2; 3 –same, 14% CH_4, 86% N_2; 4 –same, 38% CH_4, 62% N_2

Figure 1: Fig. 1. Curves of the dependence of the acetylene yield η on pressure (temperature). 1 –mixture of 2% CH_4, 98% N_2; 2 –mixture of 4% CH_4, 96% N_2; 3 –same, 14% CH_4, 86% N_2; 4 –same, 38% CH_4, 62% N_2

Fig. 2

Figure 2: Fig. 2

by relating the volume percent of acetylene in the mixture to the equilibrium concentration of acetylene that could form from a mixture whose composition was determined with allowance for flow and leakage.

Fig. 1. Curves of the dependence of the acetylene yield η on pressure (temperature).
1 –mixture of 2% CH_4, 98% N_2; 2 –mixture of 4% CH_4, 96% N_2; 3 –same, 14% CH_4, 86% N_2; 4 –same, 38% CH_4, 62% N_2

The data we obtained showed that the more nitrogen the mixture contains, the greater the yield of acetylene ($\sim$ 9% in a mixture with 98% nitrogen (Fig. 1)). The curves of the dependence of the acetylene yield η on pressure (temperature) have a sharply expressed maximum, which, as the methane content in the mixture decreases, shifts toward lower temperatures (pressures). At high temperatures, soot formation is observed. When mixtures of methane with helium, argon, xenon, and krypton are compressed, acetylene is formed in large amounts. The character of the curves of the dependence of the acetylene yield on pressure upon compression of methane mixtures with argon differs from the analogous curves for nitrogen (Fig. 2).

Unlike nitrogen, for mixtures with argon and helium there is a mixture composition at which the yield is maximal (Fig. 3). From the same figure it is evident that the acetylene yield is greater in mixtures with argon than with helium, xenon, and krypton. This indicates that, although the heat capacity of monatomic gases is the same and, consequently, the compression temperature is the same, apparently the nature of the gas itself also affects the process. The same is indicated by the fact that acetylene is not formed in mixtures with hydrogen.

Consider (8) the process of energy transfer in molecular collisions. At higher gas densities, when collisions of molecules with the wall may be neglected in comparison with collisions in the bulk, changes in the properties of the gas occur as a result of molecular collisions.

Fig. 2

Molecules can enter into a chemical reaction if they are sufficiently rich in energy.

They acquire this energy as a result of favorable collisions with molecules of average energy. These processes of energy exchange were considered using a hard-sphere model. It is known that decomposition of a methane molecule can occur if this molecule possesses sufficient vibrational energy. Consideration (8) of the case of vibrational exchange -

···shows that energy transfer is more effective when the masses of the colliding systems are comparable.

Assessing from this point of view the experiments with monoatomic gases, one can make the following approximate calculation. Taking the mass of methane as unity, we find that the masses of the other gases are: $M_{\mathrm{He}} = 0.25$; $M_{\mathrm{Ar}} = 2.5$; $M_{\mathrm{Kr}} = 5.3$, and $M_{\mathrm{Xe}} = 8.1$. On the basis of this calculation, the best energy transfer should occur between methane and argon. Indeed, the yield of acetylene upon compression of mixtures of methane with argon is the greatest.

Fig. 3

(Graph labels: ordinate—acetylene yield, vol.%; abscissa—methane content in the mixture, vol.%; $p_{comp} = 5000$ *kg/cm*^{2}*. Curves/points labeled krypton, helium, xenon, argon, nitrogen.)*

Fig. 4

(Graph labels: ordinate—acetylene yield, vol.%; abscissa—$M_{gas}/M_{\mathrm{CH}_4}$*.)*

The course of the curve (Fig. 4), where the acetylene yield is plotted against the relative mass of the diluent gas, shows that the maximum yield is obtained at $M \cong 1^{+}$. The absence of acetylene upon compression of methane with hydrogen confirms the conceptions[9] that the first stage of the methane decomposition reaction is the splitting off of hydrogen

$$\mathrm{CH_4} \rightarrow \mathrm{CH_2} + \mathrm{H_2}.$$

Addition of hydrogen to such a system should retard this reaction and prevent the formation of acetylene, despite the compression temperature being almost the same as with nitrogen.

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[*] The point for xenon refers to a mixture with 7% methane. By analogy with other mixtures, it may be assumed that for a mixture with 3% methane in xenon the yield increases to $\sim 20\%$, and the point would lie on the curve.

Note: Figure translations are in progress. See original paper for figures.