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# Pyrolysis of methane in the temperature range 100–1700 K

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ABSTRACT. The results of studies on the pyrolysis of methane in the temperature range 1000–1700 K, which is of greatest practical importance, are surveyed. The influence of heterogeneous factors, pressure, temperature, and the products formed on the process is examined. The composition of the products is analysed and the mechanism of the process is discussed.

The bibliography includes 61 references.

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## I. Introduction

The enhancement of the role of natural gas in the fuel–energy system as well as in many technological processes has aroused a new wave of interest in fundamental problems of the processing of the simplest hydrocarbons, including the main primary processes involved in the conversion of methane—its oxidation and pyrolysis. The complexity of the problem and the enormously wide variety of the real conditions encountered in technological processes have precluded to date a unique theoretical description of these processes. Depending on the specific purpose of the process, the pyrolysis of methane can be carried out over a wide temperature range. This range can be divided arbitrarily into three regions: low temperatures (up to 1000 K), moderate temperatures (1000–1800 K), and high temperatures (above 1800 K). Fairly reliable kinetic data have been obtained for the low temperature range and have already been surveyed.[1,2] Studies in the high-temperature range have developed by virtue of the wide scale adoption of the experimental shock wave method.[3,4] However, the specific features of the method resulted in mainly the initial stages of the pyrolysis being investigated.

The range of moderate temperatures, in which most of the technological processes are carried out, for example, the reduction of sulphur dioxide by methane at 1200–1500 K in the waste gases from non-ferrous metallurgy,[5] has in fact been least investigated at the present time. The pyrolysis of methane in this temperature range is the initial and rate-limiting stage of the entire $SO_2$ process.[6] During the last six years, many studies have been published on the pyrolysis of methane in the range of moderate temperatures, but these were mainly studies with a technological bias. Their fragmentary nature and association with specific conditions precluded a reliable answer to three principal questions: concerning the rate of pyrolysis in this temperature range and its dependence on external parameters, the concentration of the main gaseous pyrolysis products and the kinetic mechanism of the pyrolysis under these conditions. The aim of the present review is to survey the available data on these problems.

The study of the pyrolysis of methane was initiated in 1809 by Dalton, who demonstrated the possibility of decomposing methane into its elements by an electric discharge. On the other hand, the thermal decomposition of methane was first achieved by Davy with the aid of an electrically heated platinum wire. The first study devoted to the thermal decomposition of methane was carried out by Berthelot[7,8] in 1862. He passed methane through a heated porcelain tube and observed the formation, together with carbon, of a mixture of different hydrocarbons, primarily acetylene and olefins, as well as traces as more complex hydrocarbons—benzene and naphthalene. He assumed that the primary stage of the process is the bimolecular reaction

$$2CH_4 \rightarrow C_2H_2 + 3H_2. \quad (1)$$

In 1908 Bone and Coward,[9] who investigated the kinetics of the decomposition of $CH_4$ at temperatures in the range 773–1473 K, put forward the hypothesis of the intermediate formation of the fragment species $CH_3$, $CH_2$, and CH. The experimental demonstration of the formation of hydrocarbon radicals (methylene and methyl) in the pyrolysis of methane was first obtained by Belchetz[10] and Rice and Dooley[11] using Paneth's method (the metallic mirror method). Mayer and Altmayer,[12,13] who investigated the equilibrium

$$CH_3 \rightleftharpoons C + 2H_2, \quad (2)$$

at atmospheric pressure and different temperatures, demonstrated the reversibility of the decomposition of methane into the elements.

The most fundamental study of the kinetics of the pyrolysis of methane up to the 1950s remains that of Kassel,[14] who carried out the pyrolysis under static conditions in a quartz reactor in the temperature range 973–1123 K. He concluded that the reaction is homogeneous and of first order although under certain conditions an induction period of unknown nature is observed. The expression which he obtained for the methane pyrolysis rate constant $k = 7.3 \times 10^{11} \exp(-79385/RT)$ $s^{-1}$ describes the process satisfactorily up to temperatures in the region of 1500 K. Having

surveyed the results of earlier studies[15,16] concerning the influence of hydrogen on the pyrolysis of methane, Kassel established that the rate of pyrolysis decreases markedly in the presence of hydrogen and he derived the empirical relation $W \propto [CH_4]^2/[H_2]^3$. The experiments carried out by Storch,[17] who carried out the pyrolysis of methane on an incandescent carbon filament in a flask whose surface was cooled to a definite low temperature which made it possible to stabilise and isolate the primary reaction product, were very important for the understanding of the mechanism of the decomposition of methane. On cooling with liquid nitrogen (77 K), 95% conversion of methane into ethane was observed, on cooling with liquid oxygen (91 K) cracking resulted in the formation of ethane, ethylene, and acetylene, while on cooling the surface of the flask to 203 and 273 K the cracking products were carbon and hydrogen. On the basis of these data, the following scheme for the consecutive dehydrogenation of methane was put forward:[14]

$$CH_4 \rightarrow CH_2 + H_2, \quad (3)$$

$$CH_4 + CH_2 \rightarrow C_2H_6, \quad (4)$$

$$C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2 \rightarrow C + H_2. \quad (5)$$

Subsequently Storch[18] interpreted data for the rate of the thermal decomposition of methane obtained in earlier investigations,[16,19–21] etc. His conclusions will be partly considered below.

Two important factors in the study of the pyrolysis of ethane were established by Kobozev and co-workers.[22–24] Firstly, a change in the nature of the surface does not affect the rate of decomposition of methane itself but can influence greatly the rate of formation of solid carbon products[22,23] and, secondly, the pyrolysis is accelerated by the addition of ethane.[24] Subsequently the accelerating effect of all $C_2$ hydrocarbons (ethane, ethylene, acetylene) was demonstrated in many investigations. In a series of studies by Germain and Vaniscotte,[25–27] etc. at temperatures near 1273 K and atmospheric pressure, the induction periods in the pyrolysis process were thoroughly investigated and their dependence on the process conditions was established.

Since the end of the 1950s, the shock wave method came to be used widely for the study of the early stages of the pyrolysis of methane,[28,29] but most of the results obtained by this method refer to the high-temperature range. The studies of this period have been briefly surveyed by Khan and Crynes.[1] At the same time, a series of studies devoted to practical problems of the preparation of acetylene by the pyrolysis of methane have been carried out.[30–33]

## II. Heterogeneous factors in the pyrolysis of methane

The results of early studies of the influence of heterogeneous factors on the pyrolysis of methane are fairly contradictory. Whereas Kassel[14] and Holliday and Exell[15] did not detect the influence of a change in the ratio $S/V$ on the pyrolysis of methane in the range of moderate temperatures in quartz reactors and reactors coated with a layer of carbon formed on pyrolysis even when this parameter was varied widely (by a factor of 20 in Kassel's study[14]), Wheeler and Wood[20] claimed that the pyrolysis of methane in a quartz reactor is mainly a surface process (an appreciable catalytic effect in the presence of iron was also noted). The study of Kobozev et al.[22] was devoted to the influence of the nature of the surface (quartz or porcelain) and also of the known catalytic poisons on the pyrolysis of methane at 1433 K. It was established that the rate of formation of products such as ethylene and acetylene is independent of changes in the material of the surface or the presence of catalytic poisons, but these factors do affect greatly the rate of formation of soot on the surface of the reactor. The conclusion that the reaction is homogeneous was confirmed[24] by the identical yields of ethylene and acetylene in carbon and porcelain tubes at 1883 K.

It has been shown[25,34] that at temperatures of about 1273 K an increase in the ratio $S/V$ diminishes the induction period and increases somewhat the maximum rate of reaction. The influence of the state of the surface on the process during the induction period was also noted. However, at higher temperatures (1373 and 1423 K) a change in $S/V$ ceases to influence even the initial stage of the pyrolysis.[35] The claim that the pyrolysis of methane is heterogeneous, made in the study of Shantorovich and Pavlov[36] on the basis of experiments under flow conditions at low pressures, also refers to the initial stage involving the self-acceleration of the reaction. An increase in the rate of reaction as carbon was deposited on the surface of the porcelain reactor was also noted in the above investigation, the activation energy for the pyrolysis on the carbon-coated surface amounting to only 60 kcal mol$^{-1}$ compared with 90 kcal mol$^{-1}$ on the procelain surface.

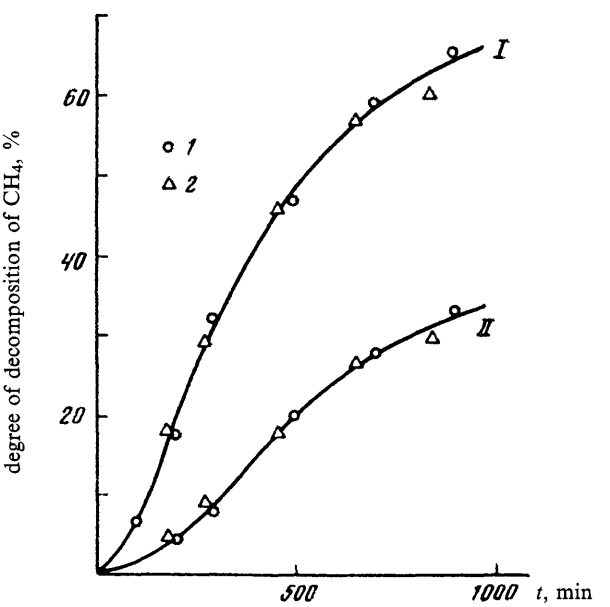



**Figure 1.** Kinetics of the decomposition of methane for $S/V$ = 2 cm$^{-1}$ (*1*) and 4 cm$^{-1}$ (*2*): *I*, initial $CH_4$ concentration $C_0$ = 10% at $T$ = 1423 K; *II*, $C_0$ = 16% at $T$ = 1373 K. $P$ = 740 torr.[35]

A dependence of the pyrolysis of methane on heterogeneous factors was not observed in many studies.[35,37–40] The independence of the degree of conversion of methane and of the quasi-stationary rate of pyrolysis of the surface area of the reactor for times exceeding the induction period has been demonstrated[35,37] for mixtures of methane (10–16%) with nitrogen and helium at temperatures of about 1400 K (Fig. 1). Chen et al.[38] demonstrated

this for lower temperatures (995–1103 K). Arutyunov et al.[39] observed in a static reactor a satisfactory agreement between the kinetics of the decomposition of methane at 1200 K and the kinetics of the production of hydrogen when $S/V$ was altered by a factor of approximately 2.2. They noted that it is virtually impossible to observe differences in the process kinetics and in the composition of the products when the pyrolysis is carried out in a clean quartz reactor, in a reactor where a large number of experiments have already been carried out, or in a reactor flushed repeatedly with oxygen at 1200–1300 K after pyrolysis. The independence of the final composition of the pyrolysis products of the diameter of an alumina flow reactor has been demonstrated.[40]

The formation of soot in the volume of the reactor apparently influences greatly the pyrolysis of methane. Thus it has been shown[35] that the introduction of 1% of naphthalene vapour into the reactor leads to a thirtyfold increase in the rate of decomposition of methane. On the basis of these experiments, the authors concluded that the initial autoacceleration of the pyrolysis on the soot nuclei, formed in the volume of the reactor and on the surface, is heterogeneous.

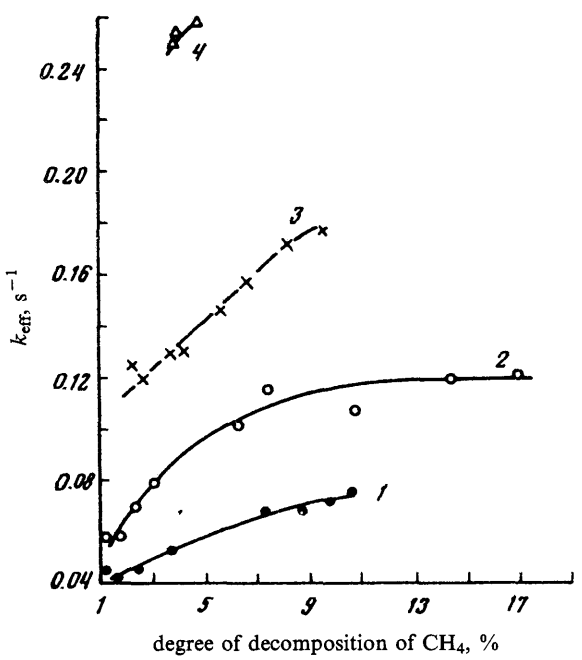



**Figure 2.** Dependence of the effective unimolecular rate constant for the decomposition of methane ($k_{eff}$) on the degree of conversion of the latter at different temperatures (K) (pressure 1 atm): *1*, 1280; *2*, 1306; *3*, 1326; *4*, 1346.

Many workers suggest the existence of a pathway leading to the direct decomposition of methane into carbon and hydrogen, bypassing the formation of intermediate $C_2$ hydrocarbons,[33,41,42] on the surface of the reactor,[42] which might explain the low activation energies for the carbon deposition process on the surfaces of graphite (36.0 kcal $mol^{-1}$ [41]) and alumina (16.2 kcal $mol^{-1}$ [33]) reactors. Similar activation energies (~25 kcal $mol^{-1}$) have been obtained for the methane decomposition and carbon deposit formation reactions in a tubular graphite reactor with a high ratio $S/V$ = 10 $cm^{-1}$ in the temperature range 1573–2473 K, while the temperature dependence of the yield and of the rate constants for the formation of ethylene and acetylene was more marked.[42] This led the authors[42] to the conclusion that a single dehydrogenation mechanism [reaction (5)] is insufficient for the description of the pyrolysis of methane under these conditions.

Only for the very high ratios $S/V > 10^4$ $cm^{-1}$, obtained[43] by introducing finely disperse materials (gas carbon black, $Al_2O_3$ powder) into the reaction zone in quartz and copper flow reactors, does the reaction become fully heterogeneous. According to the authors,[43] this is associated with the fact that the rate of formation of active centres per unit volume is greater by a factor of $10^4$ than per unit surface. Therefore, even for $S/V < 20$ $cm^{-1}$, the induction period reappears.

On the whole, despite the existence of fairly notable contradictions between the results of individual studies, one may conclude that in the range of moderate temperatures and for the usual $S/V$ ratios and reactor materials, heterogeneous factors have an appreciable influence on the pyrolysis of methane only in the initial period of the autoacceleration of the reaction and that with increase in temperture this influence gradually weakens and at $T > 1400$ K is virtually inappreciable. Heterogeneous factors affect much more strongly the deposition of solid carbon on the surface, but examination of these processes is outside the scope of the present review.[44]

## III. Autocatalysis of the initial stage of the pyrolysis of methane

In the vast majority of cases, the pyrolysis of methane is regarded as a first-order reaction and is described by the corresponding kinetic equation. However, the presence of an induction period in this reaction was already established in the early studies. Kassel[14] noted that the presence of the induction period is most striking at low pressures and in reactors which have not yet been coated by a layer of carbon; in the case of large $S/V$ ratios, there are no induction periods. An increase in the rate of pyrolysis of methane with increase in the degree of pyrolysis, i.e. the occurrence of autocatalysis, has been demonstrated[34] for low degrees of conversion (Fig. 2). The phenomenon of autocatalysis and its dependence on the process parameters have been investigated by Germain and Vaniscotte[25–27] at temperatures near 1273 K. According to their results, changes in the $S/V$ ratio for the reactor have a fairly appreciable albeit not very strong influence on the induction period and the rate of reaction in the initial period (Figs. 3 an 4). Evidently an increase in $S/V$ approximatley by a factor of 10 leads to only a twofold decrease in the induction period and increase in the maximum rate of reaction. Small amounts of added ethane (0.5–3%) have approximately the same effect.[27] The influence of added ethane on the initial period of the pyrolysis has been investigated[45] over a wider temperature range: from 1323 to 1823 K. At 1323 K, the presence of even 0.21% of ethane alters qualitatively the nature of the methane decomposition curve, leading to the disappearance of the reaction autoacceleration section (Fig. 5). Similar changes have been obtained also for the kinetics of the evolution of hydrogen in this process. With increase in temperature,

the autoacceleration becomes less marked and at $T > 1500$ K neither autoacceleration (Fig. 6) nor the influence of added ethane (0.69%) on the kinetics of the pyrolysis are observed.[45] Apart from an increase in temperature, an appreciable increase in the $S/V$ ratio (S/V > 20 $cm^{-1}$) leads to the disappearance of the autoacceleration period.[43]

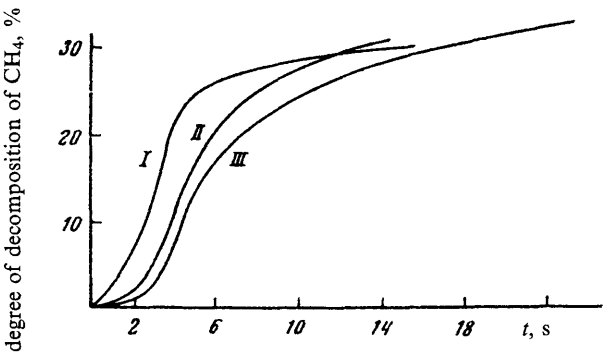



**Figure 3.** Kinetics of the decomposition of methane for different $S/V$ ratios ($cm^{-1}$): *I*, 25.3; *II*, 5.0; *III*, 2.8. Temperature 1273 K; pressure 1 atm; methane concentration 95%.[25]

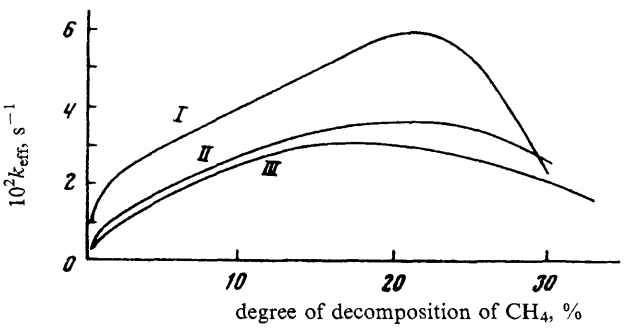



**Figure 4.** Dependence of the effective unimolecular rate constant $k_{eff}$ for the decomposition of methane on the degree of conversion of the latter for different $S/V$ ratios ($cm^{-1}$): *I*, 25.3; *II*, 5.0; *III*, 2.8.[25]

In a review[2] devoted to the pyrolysis of methane at temperatures of about 1000 K, it was shown on the basis of a series of experimental studies that the autocatalysis in this reaction cannot be accounted for by the formation of a layer of carbon on the surface of the reactor. Thus the formation of carbon on the surface of the reactor was followed from the absorption of light in a static system at about 1000 K.[46] The sensitivity of the method made it possible to detect less than a monolayer of the carbon formed. It was noted that carbon begins to be formed appreciably after the start of the autoacceleration of the reaction (Fig. 7). Furthermore, the use of a reactor in which the initial stage of the pyrolysis had already been carried out up to the onset of autocatalysis and then all the volatile products were removed did not affect appreciably the formation of products, i.e. the autoacceleration effect cannot be attributed to the presence of small amounts of undetected carbon on the surface. Probing of the volume of the reactor with the beam from a helium–neon laser also demonstrated the absence in this stage of even small carbon particles in the reactor volume which could be responsible for the autocatalysis, since their presence should have given rise to the corresponding scattering of the laser beam.[2] Thus it was necessary to seek an explanation of the phenomenon of autocatalysis in the gas-phase processes, which was in fact done for the above conditions ($T$ = 1038 K, $P$ = 433 torr) by Roscoe and Thompson[47] and Dean.[48] Mathematical modelling of the process showed[47] that the main causes of the autoacceleration are the secondary initiation of the pyrolysis by hydrocarbon products more complex than ethane and the subsequent chain processes involving methyl radicals. With increase in temperature, the role of higher hydrocarbons in the pyrolysis of methane diminishes, which reduces the autocatalytic effect up to its complete disappearance at $T > 1500$ K.

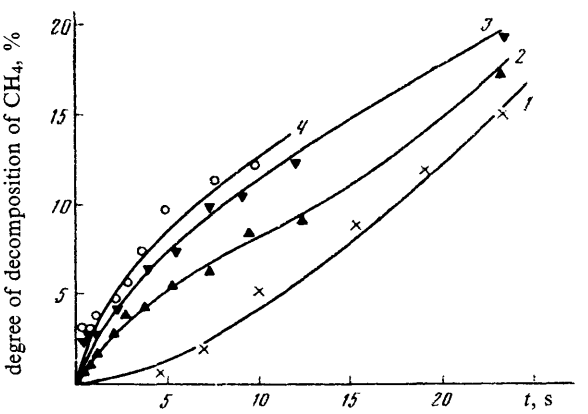



**Figure 5.** Dependence of the kinetics of the decomposition of methane on the initial $C_2H_6$ concentration $C_0$ ($T$ = 1323 K, $P$ = 760 torr); $C_0$ (%): *1*, 0; *2*, 0.21; *3*, 1.02; *4*, 1.45.[45]

## IV. The influence of hydrocarbons on the pyrolysis of methane

The acceleration of the pyrolysis of methane in the presence of added ethane was already observed by Kobozev and Shneerson.[24] Gordon[34] showed for pyrolysis under flow conditions at temperatures near 1273 K that the addition of 0.72% of acetylene increases the rate of pyrolysis by a factor of 2–2.5 and that acetylene itself is initially vigorously consumed in the reaction. At the addition of 1% of ethylene to methane being pyrolysed has a similar effect but in this case the concentration of ethylene itself does not fall below 0.85% and the catalytic effect was attributed solely to the acetylene formed in the reaction and detected in the products in approximately the same amount as for the addition of acetylene itself.

A detailed study of the influence of small amounts of added ethane on the initial stage of the pyrolysis of methane was carried out by Germain and Vaniscotte[27] under flow conditions at $T$ = 1273 to

1373 K. A decrease in the induction period and an increase in the maximum rate of pyrolysis after the addition of 0.5–3% of ethane were demonstrated, but with increase in the ethane concentration the relative efficiency of the additive fell. With increase in temperature in the above range, the influence of ethane also diminishes. The accelerating effect of ethane on the pyrolysis of methane under flow conditions was also observed in the temperature range $T$ = 1100–1200 K.[37] The influence of ethane on the initial period of the process, manifested by the disappearance of the induction period and of the reaction acceleration region,[45] was examined in a previous section. It is of interest that, regardless of the initial concentration of the added ethane, a concentration characteristic of the pyrolysis of pure methane is established after a certain time (Fig. 8), i.e. the accelerating effect of hydrocarbon additives is manifested in the initial period of the reaction.

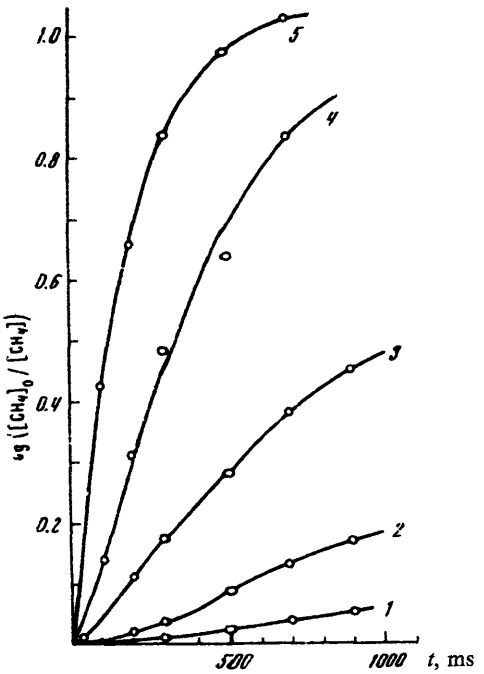



**Figure 6.** The influence of temperature on the kinetics of the decomposition of methane in the initial period; pressure 740 torr; methane concentration 10%;[35] $T$ (K): *1*, 1323; *2*, 1373; *3*, 1423; *4*, 1473; *5*, 1523.

Using a radiochemical method,[49–51] the influence of the addition of 0.5–3% of acetylene, ethylene, and ethane on the pyrolysis of methane at $T$ = 1293 and 1343 K was studied systematically. A clear accelerating effect of the $C_2$ hydrocarbons was observed in all cases, but, as in the study of Germain and Vaniscotte,[27] the effectiveness of the additives fell appreciably as their concentration approached 3%. Apparently further increase in the concentration of the additive has only a weak effect on the pyrolysis.

Added hydrocarbons exert the greatest influence on the yield of hydrogen for short reaction times. For example, in the pyrolysis of methane at 1293 K for 1.96 s, the presence of 1.5% of ethane increases the yield of hydrogen by a factor of approximately 10.[51] The yield of $C_2$ hydrocarbons can also increase severalfold under these conditions. With increase in the reaction time (8–8.5 s) and especially at a higher temperature (1343 K), the addition of hydrocarbons has almost no effect on the yield of hydrogen and $C_2$ hydrocarbons. In all three cases, the use of initiating additives with the $^{14}C$ radioactive isotope results in almost the entire radioactivity being concentrated in methane even after the shortest period of observation. This agrees well with the concept of the leading role of the $CH_3$ radicals in the pyrolysis, whose ready formation on decomposition of $C_2$ hydrocarbons is apparently responsible for the initiating effect in the initial period of the pyrolysis of methane.

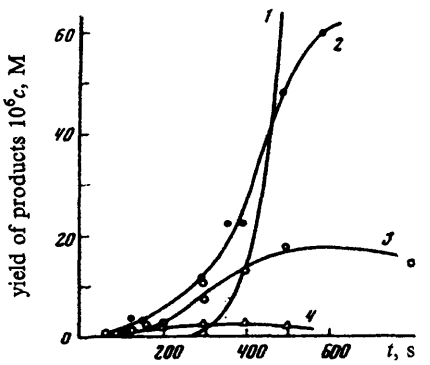



**Figure 7.** The yield of certain methane pyrolysis products at $T$ = 1118 K and $P$ = 307 torr;[2] products: *1*, carbon; *2*, $C_2H_6$; *3*, $C_2H_4$; *4*, $C_4H_6$.

## V. The influence of hydrogen on the pyrolysis of methane

The inhibiting effect of hydrogen on the pyrolysis of methane was already established by Holliday and Exell[15] and Wheeler and Wood,[20] who explained it by the formation of a layer of adsorbed hydrogen on the reactor surface. According to the authors, this layer does not allow the heterogeneous pyrolysis of methane to go to completion, which results in the establishment of a false equilibrium in the system which is far from thermodynamic equilibrium.[20] On the basis of the scheme involving the consecutive dehydrogenation of methane [Eqns. (3)–(5)], Kassell explained the inhibiting effect of hydrogen by the occurrence of the corresponding reverse hydrogenation reaction, which enabled him to obtain, in terms of the approximation of quasi-stationary concentrations, a relation for the rate of pyrolysis, namely $W \propto [CH_4]^2/[H_2]^3$, describing satisfactorily the experimental results which he obtained in a static reactor at $T$ = 1033 K. The only study where the accelerating effect of hydrogen was reported was that of Gordon,[34] who described the pyrolysis of methane at $T$ = 1280 K and $P$ = 1 atm in a porcelain

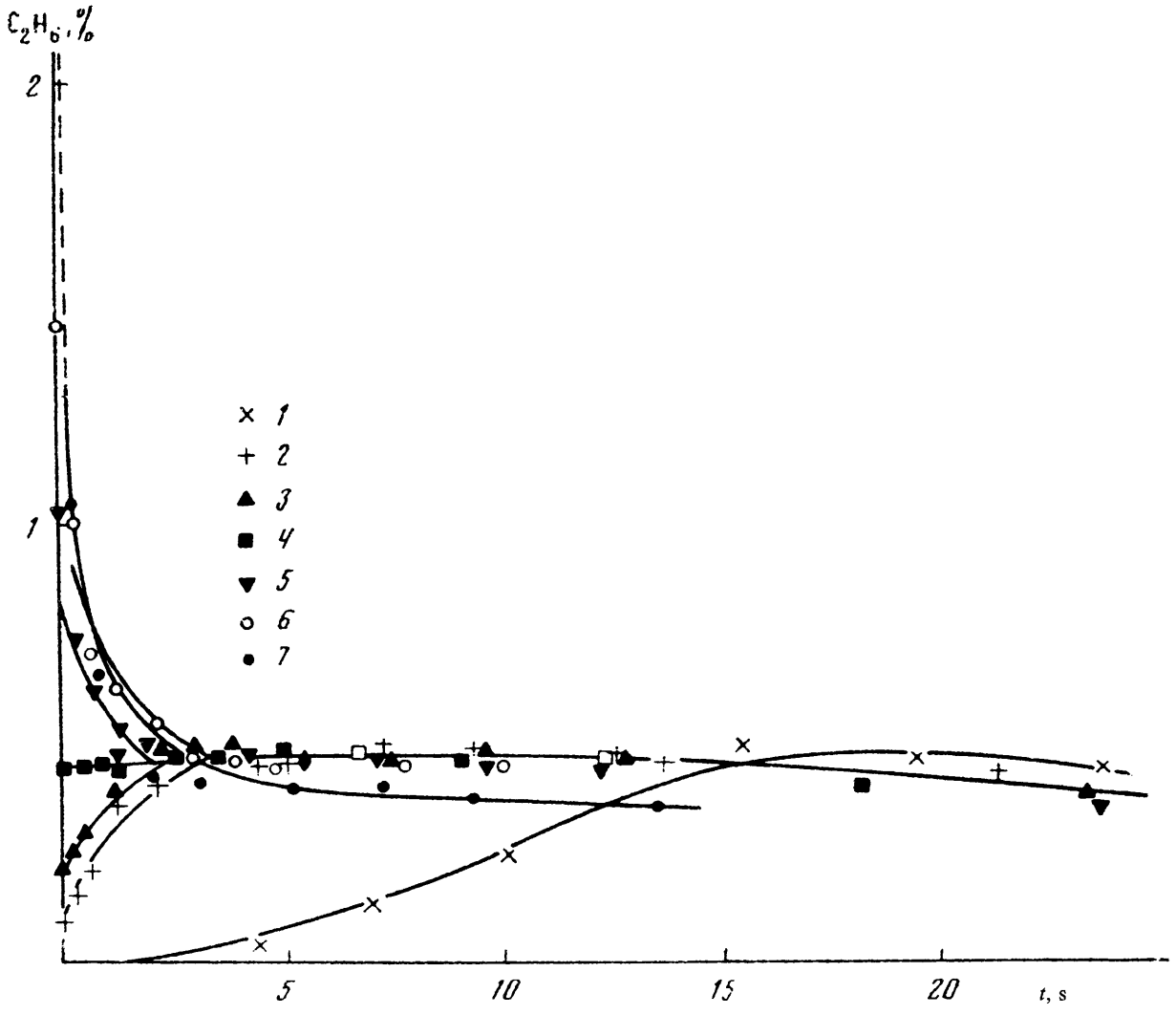



**Figure 8.** Kinetics of the formation and decomposition of $C_2H_6$ in the pyrolysis of methane at different initial $C_2H_6$ concentrations ($T$ = 1323 K, $P$ = 760 torr);[45] $C_2H_6$ concentration (%): *1*, 0; *2*, 0.09; *3*, 0.21; *4*, 0.45; *5*, 1.02; *6*, 1.45; *7*, 4.56.

flow reactor. It was noted that the addition of 2% of $H_2$ accelerates the rate of the initial stage of the decomposition of methane by 20–30% (degree of decomposition of methane 1.64–3.09%). There has been yet another study[52] in which an inhibiting effect of hydrogen was not observed when the decomposition of methane was investigated by the shock wave method in the higher temperature range 1656–1695 K. This may be explained by the fact that the effect of hydrogen is associated with later stages of the reaction, which do not manage to be manifested for the short times characteristic of the processes in shock waves.

The identity of the inhibiting effects of the hydrogen formed during the reaction and specially added to the initial mixture has been demonstrated[53] at $T$ = 1123 K, $P$ = 150 torr, and for degrees of decomposition of methane not exceeding 1% (Fig. 9).

The influence of the addition of 50% of hydrogen on the pyrolysis of methane at 1273–1373 K has been investigated.[26] In contrast to nitrogen, the addition of which has only a slight effect on the pyrolysis, dilution of the mixture with hydrogen in proportions of 1 : 1 led to an appreciable increase in the induction period and to an approximately fivefold decrease in the maximum rate of the process (Fig. 10). However, such appreciable dilution with hydrogen and nitrogen had no effect on the process activation energy (87 kcal $mol^{-1}$).[26] These results have been confirmed[37] in a flow reactor at 1458 K for mixtures containing 15% of $CH_4$ in nitrogen and $H_2/CH_4$ ratios ranging from 0.1 to 2. It has been shown[39] in a static reactor at 1200 K and a pressure of 400–450 torr that dilution of methane with hydrogen in proportions of 1 : 3 diminishes the maximum concentration of ethylene in the course of the reaction by a factor of 10–15 and entails a decrease in the overall rate of pyrolysis by a factor of 2–3. The formation of ethane and acetylene under these conditions could not be detected at all (volume concentration < 0.01%).

In a number of studies devoted to practical aspects of the pyrolysis of methane, the influence of dilution of the reaction

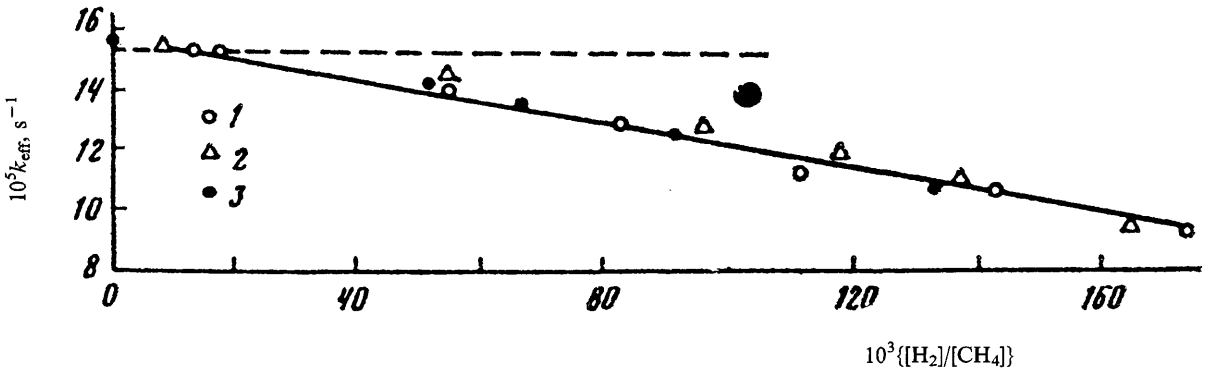



**Figure 9.** Dependence of the effective unimolecular rate constant $k_{eff}$ for the decomposition of methane at 1123 K on the degree of accumulation of $H_2$ in the reacting gas:[53] *1*, $P$ = 150–162 torr, $H_2$ added to the initial mixture; *2*, $P$ = 101.0 torr; *3*, $P$ = 158.3 torr, $H_2$ accumulating in the reacting gas.

mixture with hydrogen on the yield of acetylene in this reaction was investigated. Kunugi et al.[30] carried out the process in a quartz flow reactor, filled with lumps of quartz, in the temperature range 1373–1673 K. The dependence of the yield of acetylene on the dilution of methane with hydrogen is illustrated in Fig. 11. Evidently, the yield of acetylene increases with increase in the hydrogen/methane ratio and reaches a maximum when the ratio is approximately 2.5 at 1473 K and approximately 3.5 at 1573 and 1673 K. With increase in the hydrogen/methane ratio, the time required for the attainment of the maximum yield of acetylene also rises. The increase in the yield of acetylene on dilution with hydrogen, which clearly diminishes the rate of pyrolysis, is associated with the fact that it suppresses to an even greater extent the rate of formation of hydrocarbon products from acetylene. It may be that the latter process is heterogeneous and takes place when hydrogen interacts with the soot deposits in the system.[33]

Yampol'skii et al.,[42] who investigated the pyrolysis of methane in a graphite flow reactor for high dilutions with hydrogen ($H_2/CH_4$ up to 21) and at high temperatures (2003–2173 K) also concluded that hydrogen inhibits certain heterogeneous processes associated with the pyrolysis of methane. Under these conditions, dilution with hydrogen reduced the formation of carbon deposits in the reactor and diminished the concentration of unsaturated $C_3-C_4$ hydrocarbons in the reaction products, increasing simultaneously the yield of acetylene. However, the decrease in the yield of carbon deposits on dilution of methane with hydrogen was attributed[42] primarily to the selective inhibition of the direct heterogeneous decomposition of methane into carbon and hydrogen.

A marked influence of hydrogen on the heterogeneous decomposition of methane at 1088–1373 K has been observed[43] in a reactor with a high $S/V$ ratio (up to $10^5$ $cm^{-1}$). However, the effect diminishes with increase in temperature. Thus at 1073 K the addition of 10% $H_2$ reduces the rate of formation of pyrocarbon by a factor of 140, while at 1573 K the decrease is only by a factor of 5. According to the hypothesis put forward by Makarov and Pechik,[43] the much stronger inhibiting effect of hydrogen under the conditions of pure heterogeneous pyrolysis is associated with the fact that under these conditions the inhibition is by atomic hydrogen, while in homogeneous pyrolysis the inhibitor is molecular hydrogen.

## VI. Dependence of the process on the concentration of methane and on pressure

Data concerning the influence of the concentration of methane on its pyrolysis have been obtained in a number of studies. An appreciable influence of 50% dilution of methane by nitrogen or water vapour on the rate of pyrolysis was not observed in a study[34] at $P$ = 1 atm and 1280 K. A similar dilution of methane with nitrogen in proportions of 1:1 and 1:2 at 1273–1373 K led to a slight increase in the degree of decomposition of methane (Fig. 10).[26] The reverse effect was observed in a study[27] where an increase in the methane concentration in nitrogen in a flow reactor from 15 to 25% ($T$ = 1373 K, $P$ = 1 atm) resulted in a slight (~10%) increase in the degree of its decomposition for a fixed observation time. On the other hand, in another study,[35] when the concentration of methane in helium was increased from 1 to 10%, the degree of its decomposition in a porcelain flow reactor at $T$ = 1473 K and $P$ = 740 torr remained virtually constant. Only for short reaction times was an increase in the degree of decomposition with increase in the methane concentration observed, but it was so slight that the authors themselves expressed doubts about the reliability of the effect. The contradictory nature of the data presented above combined with the smallness of the effect in those cases where it was observed apparently mean the dilution with inert gases in the above temperature range at atmospheric pressure hardly affects the pyrolysis of methane.

The dependence of the rate of pyrolysis of methane on pressure is related primarily to the pressure dependence of the reaction rate constant:[38,54]

$$CH_4 \rightarrow CH_3 + H. \qquad (6)$$

It has been established[55] that this transitional range of pressures in the above temperature range extends almost up to 500 atm. Fig. 12 illustrates the increase in the unimolecular rate constant for the pyrolysis of methane with pressure, observed[39] in the range 115 to 700 torr at $T$ = 1100 and 1200 K. Although in certain early studies, for example, those of Kassel[14] (pressure range 13.0–296.4 torr, temperature 1008 K) and Shantorovich and Pavlov[53] (low degrees of conversion not exceeding 2–2.5%, methane pressure range 28.7 to

232.0 torr, temperature 1123 K), no pressure dependence of the rate of pyrolysis of methane was observed, nevertheless, such a dependence undoubtedly exists.

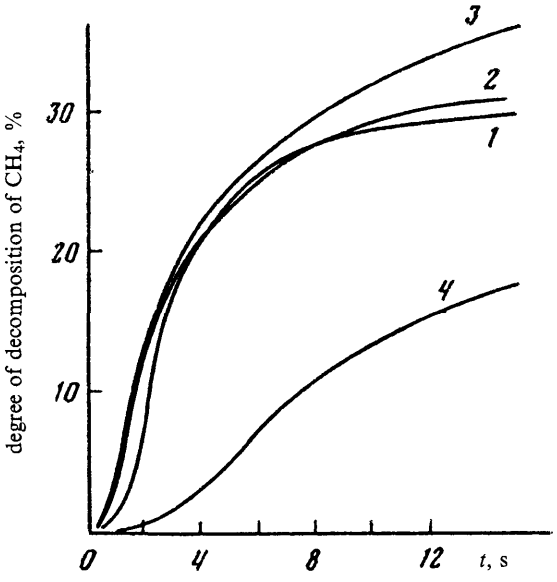



**Figure 10.** Kinetics of the decomposition of methane on dilution of the mixture with $N_2$ and $H_2$ ($T$ = 1273 K, $P$ = 1 atm):[26] *1*, 100% $CH_4$; *2*, $CH_4/N_2$ = 50/50; *3*, $CH_4/N_2$ = 33/66; *4*, $CH_4/H_2$ = 50/50.

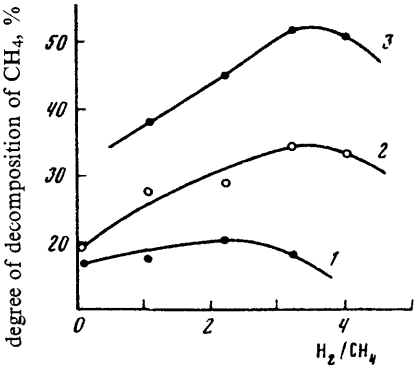



**Figure 11.** Dependence of the degree of conversion of methane into $C_2H_6$ on the $H_2/CH_4$ ratio at different temperatures ($T$, K):[30] *1*, 1473; *2*, 1573; *3*, 1673.

## VII. Composition of the methane pyrolysis products

Thermodynamic calculations of the equilibrium composition of the gaseous pyrolysis products (of the gaseous C/H system), taking into account the existence of more than 70 seperate components, have been carried out[56] for C/H ratios from 1/10 to 3, at temperatures of 500–5000 K, and at pressures of 0.1, 1.0, and 10 atm. Calculations taking into account the formation of solid carbon were performed separately. In all cases the main gaseous product in the relevant temperature range is $H_2$ (up to 70%) (Fig. 13). In this temperature range the stable hydrocarbons with a small number of atoms reached their maximum concentrations, after which their concentrations decreased monotonically with increase in temperature. At $T$ > 1400 K the dominant hydrocarbon is acetylene (Fig. 13), whose concentration reaches 25% of the total volume of the gas phase. The concentrations of the remaining stable hydrocarbons are appreciably lower and even for ethylene the maximum concentration does not reach 1%. In this temperature range, there is an appreciable amount of methane at thermodynamic equilibrium in the gas phase. The equilibrium concentrations of atoms and radicals are extremely low at such temperatures. When the ratios C/H and the pressure do not vary appreciably in this system, the situation does not change significantly.

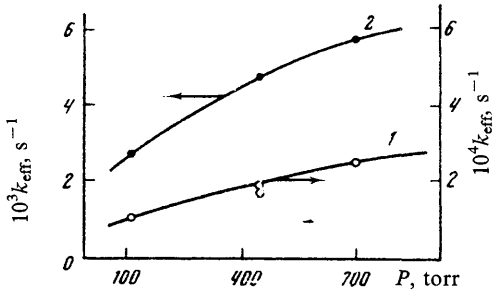



**Figure 12.** Dependence of the effective unimolecular rate constant $k_{eff}$ for the decomposition of methane on pressure at different temperatures ($T$, K): *1*, 1100; *2*, 1200.[39]

The picture changes sharply when account is taken of the formation of the solid carbon phase. In this case, in the temperature range from 1000 to 3000 K the gas phase consists almost exclusively of hydrogen (~100%). The equilibrium concentration of methane falls sharply (<1% at $T$ > 1200 K) and the concentrations of all the remaining hydrocarbons decrease. Since it is difficult to claim that the solid phase was taken adequately into account in the above calculations (one of two ratios, C/H = $10^3$/1 or 10/1, was adopted for the composition of the solid phase), the practical value of the results of these calculations is primarily an indication of the qualitative trends associated with the presence of the solid phase. However, the real formation of the solid phase precludes a direct comparison with experiment of the results of thermodynamic calculations on a single-phase system, although it may be that such single-phase description reflects to some extent the ratio of the gaseous products of the initial stage of pyrolysis. Thus the uncertainty of the results of the thermodynamic calculations, associated with the inadequate allowance for the formation of the solid phase during pyrolysis, necessitates the analysis of the available experimental yields of the final methane pyrolysis products.

The kinetics of the formation and the final composition of the gaseous methane pyrolysis products in the range of moderate temperatures have been investigated in many studies. Germain and

Vaniscotte[25] studied the formation of $C_2$ hydrocarbons at 1273 K at atmospheric pressure in quartz reactors with $S/V$ ranging from 2.8 to 25.3. Under these conditions, the concentration of methane at the end of the experiment was about 50% of the volume of the gas phase, the concentration of ethylene was less than 1%, and the concentrations of ethane and acetylene were approximately an order of magnitude smaller (slow conversion of methane and of the remaining products continued also for the maximum observation time, which was 20 s in the given study). The concentrations of all the $C_2$ hydrocarbons passed through a maximum, the time of attainment of which diminished with increase in $S/V$, but neither the size of the maxima ($\sim$1.5% of the volume of the gas phase for ethylene) nor the degree of decomposition of methane depended significantly on this ratio. Similar results were obtained by Schneider[45] (temperature range 1323–1823 K). An increase in the maximum concentrations of ethylene and acetylene is observed with increase in temperature—$[C_2H_2]_{max}$ is approximately 10% at 1833 K and approximately 1% at 1323 K. Small amounts of added ethane (up to 4.5%) have a similar effect as an increase in $S/V$, diminishing the time of attainment of the maximum concentration of $C_2$ hydrocarbons but not affecting its value.[45]

The kinetics of the reaction of methane and the formation of the principal gaseous products in the temperature range 1100–1400 K in a static reactor at a pressure of 440 torr have been investigated.[39] The kinetic curves for $T$ = 1200 K are presented in Fig. 14*a*. At this temperature the pyrolysis virtually terminates after 5 min and the final degree of conversion of methane is about 50%. Direct measurement of the final pressure and the decrease in the relative concentration of the nitrogen added to the mixture as a permanent reference standard ($\sim$10%) indicate a pressure rise by about 22% (Fig. 14*b*). Such a change in pressure combined with the insignificant content of $C_2$ hydrocarbons in the pyrolysis products lead to the formula CH for the solid product remaining on the walls of the reactor and partly deposited on the cold connecting tubes during its evacuation. The principal gaseous hydrocarbon pyrolysis product in this temperature range is ethylene, but, whereas at 1100 K its concentration exceeds by a factor of approximately 10 the concentrations of the hydrocarbons next in importance (acetylene and ethane), at 1300 K the concentrations of ethylene and acetylene are almost comparable. Nevertheless, even at 1300 K the maximum concentrations of these products remain at the level of 1% of the total volume of the mixture. Although the maximum concentration of ethane increases somewhat with increase in temperature to 1300 K compared with the value at $T$ = 1100 K, it is still amost an order of magnitude lower than the maximum concentration of ethylene.

At 1300 K the maximum concentrations of ethylene and acetylene are attained almost simultaneously but later than the attainment of the maximum concentration of ethane, which is consistent with Gordon's data.[34] At 1200 K, the maximum concentrations of all three $C_2$ hydrocarbons are attained almost simultaneously (Fig. 14*a*). Apparently the dehydrogenation scheme involving the successive transformation of methane during pyrolysis,[14] which describes satisfactorily the kinetics in the region of low temperatures ($T$ < 1000 K), [2] becomes less suitable with increase in tempereature. An increase in temperature entails a sharp shortening of the time of attainment of the maximum concentrations of ethylene and acetylene—from 60 s at 1200 K to 5 s at 1300 K. At 1100 K the ethane and ethylene concentration profiles have very broad maxima, which are virtually converted into quasi-stationary concentrations, attained after 7–15 min and maintained for periods exceeding 30 min. Only the concentration of acetylene passes through a maximum at $t$ = min and then falls sharply, so that at $t$ > 15 min acetylene cannot be detected at all.[39] The time of attainment of the maximum in the ethane concentration coincides with the time of attainment of the maximum rate of decomposition of methane (induction period) (Fig. 14). This is clearly seen also on comparing the corresponding kinetic curves obtained under flow conditions at a higher temperature (1373 K).[35]

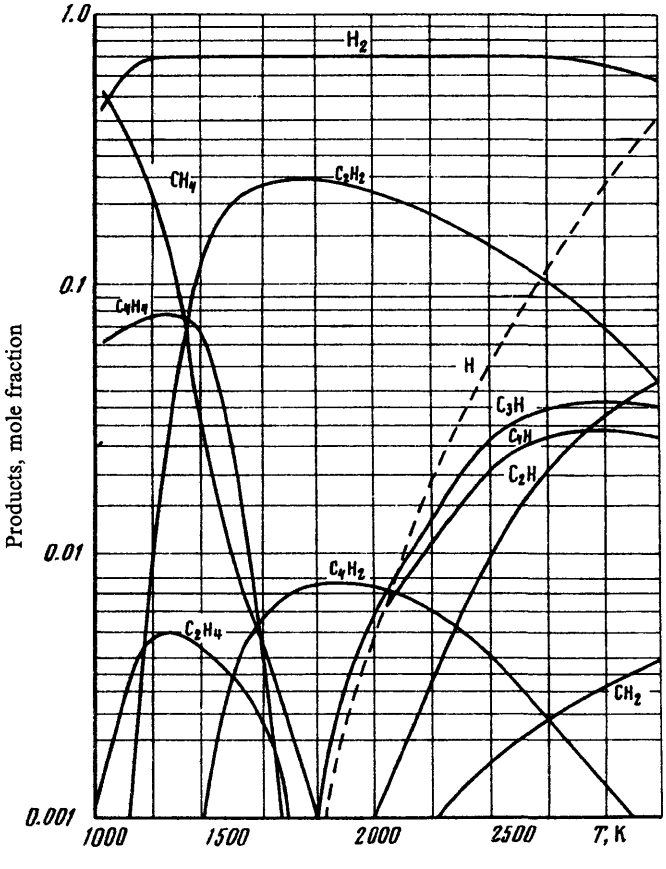



**Figure 13.** Results of the thermodynamic calculation for the C/H equilibrium system at temperatures in the range 1000–3000 K without taking into account the formation of a solid phase; $P$ = 0.1 atm; C/H = 1/4 (methane).[33,56]

The temperature variation of the yield of the main final gaseous methane pyrolysis products is illustrated in Fig. 15. The results obtained can be compared with those of thermodynamic calculations[56] (Fig. 13) although the system is apparently still fairly far from thermodynamic equilibrium. Whereas the final concentrations of methane and hydrogen are virtually identical with the values calculated without taking into account the solid phase, the final amounts of $C_2$ hydrocarbons are several times lower than the calculated values. The results of the calculations of the equilibrium composition taking into account the solid phase[56] show that, in the experimental temperature range used by Arutyunov et al.[39]

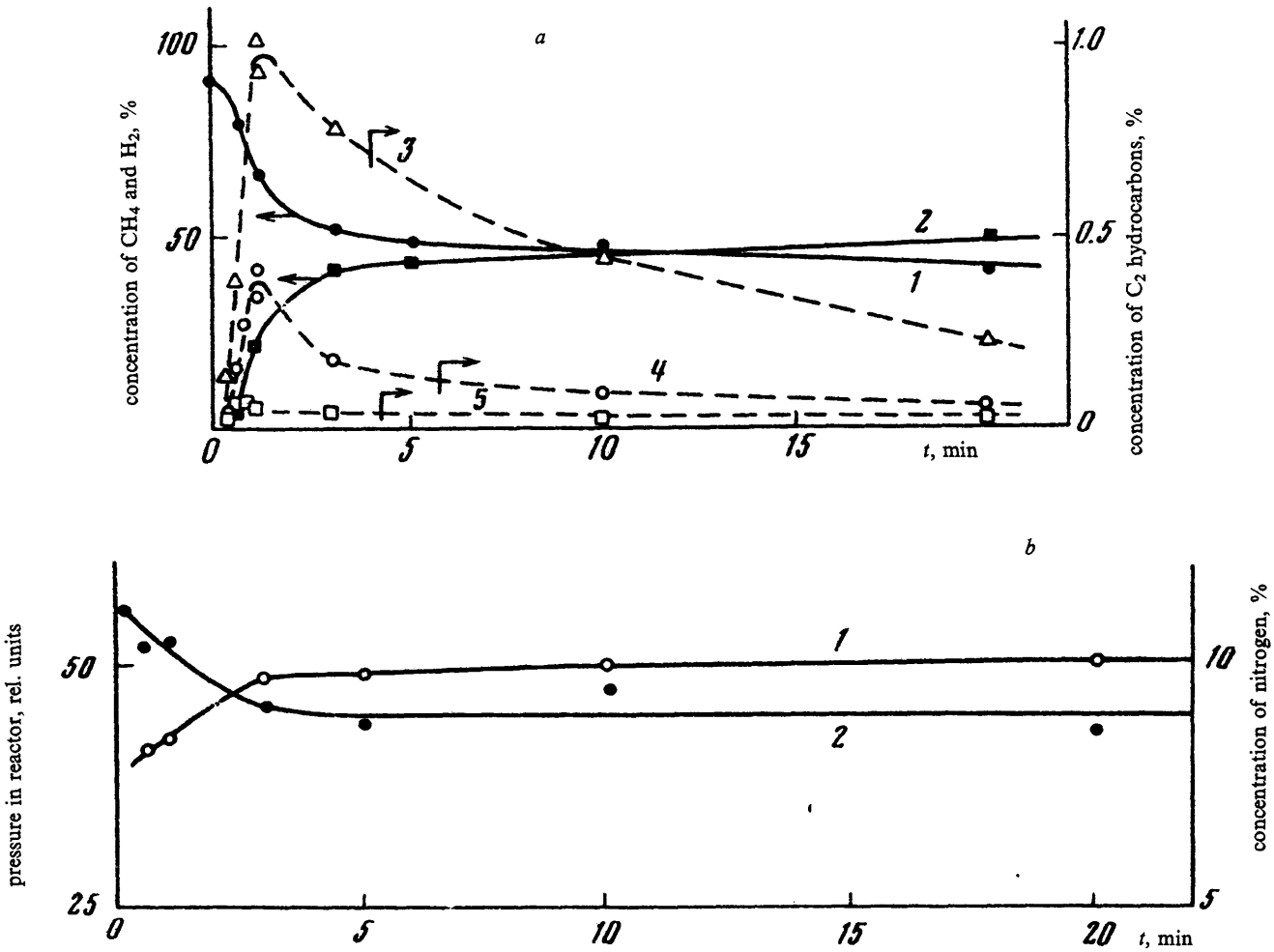



**Figure 14.** Kinetics of the variation of the concentrations of the principal gaseous products (*a*) and variation of the pressure and concentration of nitrogen in the pyrolysis of methane (*b*); initial mixture: $CH_4$ (90%) + $N_2$ (10%); $T$ = 1200 K, $P$ = 438 torr;[39] *a*: *1*, $CH_4$; *2*, $H_2$; *3*, $C_2H_4$; *4*, $C_2H_2$; *5*, $C_2H_6$; *b*: *1*, variation of pressure; *2*, variation of $N_2$ concentration.

(1100–1400 K), almost the only gaseous product should be hydrogen, since even the calculated residual concentration of methane is less than 1%, and those of the remaining hydrocarbons are lower by several orders of magnitude. The cause of such appreciable discrepancy may be either inadequate allowance for the composition of the solid phase in the calculation or appreciably longer times of attainment of equilibrium in the heterophase system.

The temperature variation of the yields of methane, ethylene, and acetylene obtained in a flow reactor at a pressure of 5–10 atm and over a very wide temperature range (1573–2473 K) has been published.[42] The detection of small amounts of $C_3$–$C_4$ products (propene, allene, methylacetylene, buta-1,4-diene, and vinylacetylene) is indicated in the above communication. These substances are the products of the thermal transformation of ethylene and acetylene at high temperatures. At lower temperatures, a wide range of high-molecular-weight products can also be detected.

Chen and Back[46] followed the kinetics of the formation of pyrolysis products ranging from ethylene to fluoranthene at 1118 K and 307 torr. The maximum concentration of fluoranthene reached $\sim 1.5 \times 10^{-6}$ M, which is only an order of magnitude lower than the maximum concentration of actylene under these conditions. The formation of the solid product followed directly the formation of the most complex of the aromatic compounds detected—fluoranthene. Since in the overall amount of aromatic compounds formed on pyrolysis of methane on silica gel those with an even number of carbon atoms constitute 97%,[57] it was concluded that they are formed from $C_2$ hdyrocarbons. Apparently the mechanism of the formation of polyatomic hydrocarbons involves both radical and molecular processes, their relative roles in the formation of any product depending on the process temperature and pressure. Products with a low molecular weight are formed mainly in radical reactions. The rate of formation of large polyatomic molecules can be determined by addition reactions of the Diels–Alder type.[2] We shall not dwell on a detailed consideration of the mechanisms and

kinetics of the formation of macromolecular pyrolysis products and solid carbon, because these questions are outside the scope of the present review.

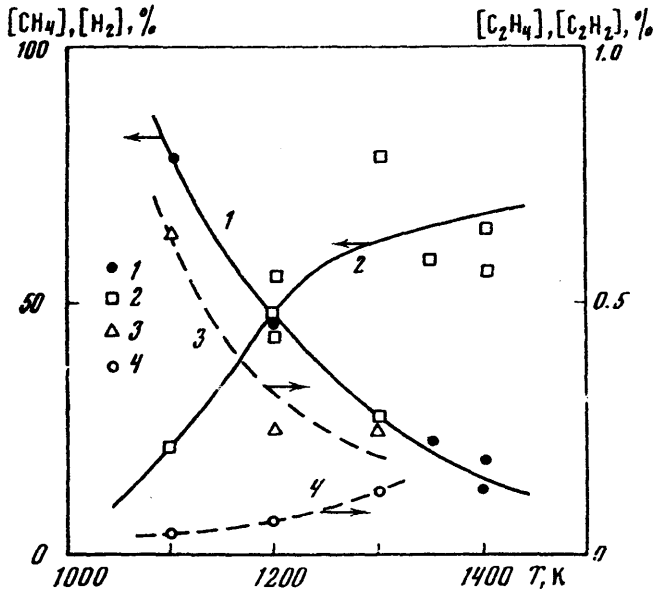



**Figure 15.** Temperature variation of the yields of the principal gaseous methane pyrolysis products:[39] *1*, $CH_4$; *2*, $H_2$; *3*, $C_2H_4$; *4*, $C_2H_2$.

Since the concentrations of $C_2$ hydrocarbons pass through a maximum in the course of the pyrolysis of methane (Fig. 14*a*), there is in principle a possibility of obtaining them in amounts greatly exceeding the values corresponding to thermodynamic equilibrium. Fig. 16 presents the maximum degrees of conversion of methane into ethylene and acetylene $C_{max}/\Delta[CH_4]_{t_{max}}$ obtained by Arutyunov et al.[39] The results of experiments at higher temperatures are also presented.[30] At 2100 K the maximum concentrations of ethylene and acetylene reach respectively ~35 and ~65%,[58] i.e. in the region of 2000 K the maximum concentrations $C_{max}$ reach their highest values.

## VIII. Temperature dependence of the pyrolysis of methane

The temperature dependence of the effective unimolecular rate constant for the pyrolysis of methane has been determined in numerous studies, the activation energies obtained varying from 63 to 104 kcal $mol^{-1}$. Many studies undertaken to determine the rate constants and activation energies for the initial stage of the pyrolysis [reaction (6)] in the range of temperatures from 1700 to almost 3000 K were carried out by the shock wave method.[59] The rate constant for reaction (6) was determined by Chen et al.[38] for the region of 1000 K. All these results refer to a transitional range of pressures, which makes it possible to determine also the pressure dependence of the rate constant for reaction (6). The recommended values of this constant for the temperature range from 300 to 2500 K have been published,[59] the recommended activation energy amounting to 104.4 kcal $mol^{-1}$. In the region of moderate temperatures 1100–1700 K, the experimental activation energies for the pyrolysis of methane differ from the activation energy for reaction (6) and are close to 80–85 kcal $mol^{-1}$. Certain activation energies obtained for this process in the range of moderate temperatures are given blow (in kcal $mol^{-1}$): 79.4,[14] 85,[53] 87,[26] 87.3 [45] and 83.2.[42] Fig. 17 illustrates the temperature variation of the effective unimolecular rate constant for the decomposition of methane obtained by Arutyunov et al.[39] Evidently, although the rate of pyrolysis depends on the pressure, the activation energy remains constant at 82 ± 3 kcal $mol^{-1}$. The expression obtained[39] for the effective unimolecular rate constant for the pyrolysis of methane, i.e.

$$k_{eff} = (3.0 \pm 1.0) \cdot 10^{12} \exp[-(82\,000 \pm 3000)/RT],\ s^{-1}$$

described satisfactorily the majority of the experimental results for the temprature range 1100–1700 K.

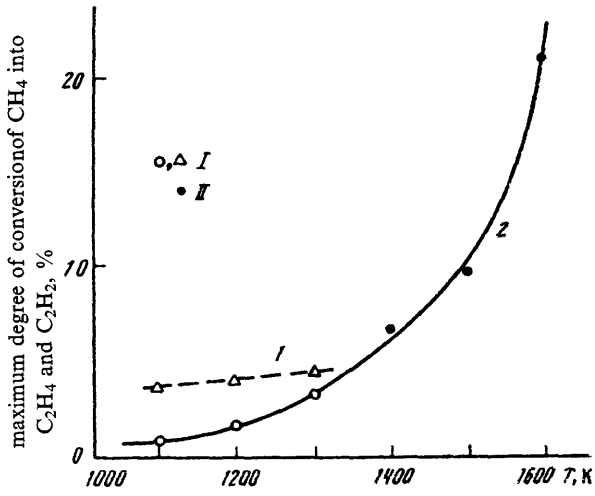



**Figure 16.** Maximum degrees of conversion of methane $C_{max}/\Delta[CH_4]_{t_{max}}$ into $C_2H_4$ (curve *1*) and $C_2H_2$ (curve *2*) at $P$ = 440 torr: *I*, according to the data of Arutyunov et al;[39] *II*, according to the data of Kunugi et al.[30]

Fig. 18 presents the literature data for the rate of pyrolysis of methane under various conditions in the temperature range 1100 to 1700 K. Mathematical treatment of these results by the method of least squares yields a pyrolysis activation energy of 82 kcal $mol^{-1}$, which agrees with the value obtained by Arutyunov et al.[39] It is readily seen that, with the exception of several clearly deviating results, the entire set of experimental data is described satisfactorily by the expression quoted above, which may be recommended for these conditions.

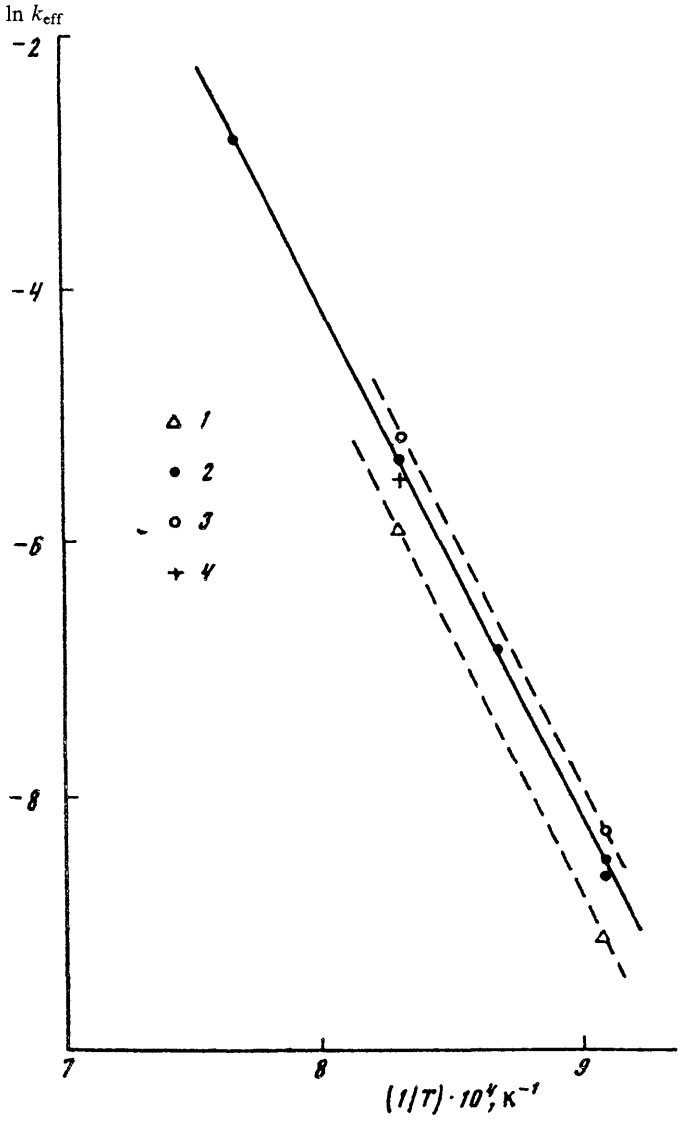



**Figure 17.** Temperature variation of the effective unimolecular rate constant for the decomposition of methane in reactors 46 mm (*1*–*3*) and 21 mm (*4*) in diameter at different pressures (*P*, torr):[39] *1*, 115; *2*, 440; *3*, 700; *4*, 435.

## IX. The mechanism of the pyrolysis of methane

There is at present no generally accepted mechanism of the pyrolysis of methane up to the carbon formation stage. The problem of devising such a mechanism is extremely complex, since it is necessary to take into account a large number of parallel processes occurring simultaneously in this complex system, their relative roles varying markedly as the external conditions are altered. At moderate temperatures, the initial stages of the pyrolysis of methane are apparently fairly well described by a simple scheme taking into account the parallel occurrence of chain dehydrogenation and methylation reactions, which explains and describes the formation of both simple hydrocarbons ($C_2$) and the highest unsaturated hydrocarbons with increasing molecular weight and descreasing hydrogen content up to the formation of carbon.[2] The key hypotheses on which the above scheme is based are (1) the dominant role of methyl radicals, chain reactions with the latter constituting the main pathway leading to the removal of all the hydrocarbon products, (2) the insignificant role of the thermal dissociation of secondary hydrocarbon products and the mainly thermal decomposition of higher hydrocarbon radicals, and (3) the involvement in the reaction with methane molecules of almost all the hydrogen atoms formed. These hypotheses are entirely realistic for temperatures in the region of 1000 K and a little above.

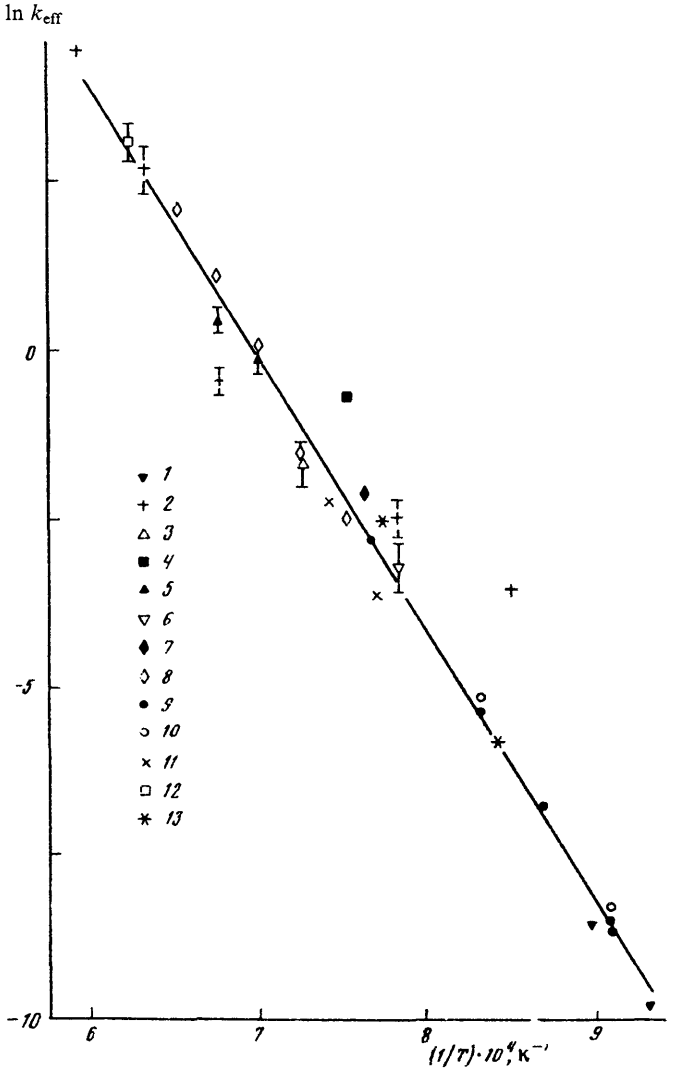



**Figure 18.** Temperature variation of the effective unimolecular rate constant for the decomposition of methane in the temperature range 1100–1700 K plotted on the basis of the set of literature data: *1*, Ref. 14; *2*, Ref.16; *3*, Ref. 19; *4*, Ref. 20; *5*, Ref. 21; *6*, Ref.25; *7*, Ref.34; *8*, Ref. 35; *9*, Ref. 39 (*P* = 440 torr); *10*, Ref. 39 (*P* = 700 torr); *11*, Ref. 43; *12*, Ref. 60; *13*, Ref. 61.

The mathematical modelling of the pyrolytic process carried out[47] on the basis of this scheme for $T = 1038$ K and $P = 433$ torr made it possible to explain the phenomenon of autocatalysis in the formation of ethane, which was observed experimentally by Chen et al.[38] Calculations confirmed the hypothesis[2] that the most important causes of autocatalysis are secondary initiation and subsequent methylation propagated by the addition of methyl radicals to olefins. The same model makes it possible to describe satisfactorily the experimental profiles for the formation of ethane, ethylene, acetylene, and propene in the pressure range $5 < P < 50$ atm and the temperature range $1073 < T < 1148$ K in the initial stage of the reaction (up to the onset of autocatalysis).[55] According to the results of Barnes and Pratt,[55] the main cause of autocatalysis under the given conditions is secondary initiation, mainly via the reaction

$$C_3H_6 \rightarrow C_2H_3 + CH_3.$$

However, the model proposed[47] has been criticised[48] because of the lack of consistency in many instances between the constants adopted for the forward and reverse reactions. After the adjustment for such consistency in the case of reverse reactions, the results changed significantly and the phenomenon of autocatalysis vanished from the model. A new mechanism has been proposed[48] for the pyrolysis, according to which the acceleration of the reaction is achieved as a result of the dissociation of cyclopentadiene formed in large amounts even for the very lowest degrees of conversion of methane (~0.1%). However, even if this mechanism is the real cause of the autocatalysis at 1000 K, it is difficult to say to what extent it is valid at higher temperatures, especially those exceeding 1500 K.

There exist several models† for the description of the high-temperature pyrolysis under shock wave conditions. However, the question of the modelling of the pyrolysis in the range of moderate temperatures remains essentially open.

* * *

The data considered in the present review refer to the study of the pyrolysis of methane in the range of moderate temperatures which is of greatest practical importance. Attention was concentrated on the process kinetics, the composition of the products, their influence on the course of the process, and the role of external factors (pressure and temperature) on the reactor surface. The limited size of this review precluded the consideration of many aspects of the pyrolysis of methane which are of practical importance, in particular, the questions of promotion, for example, by halogen compounds. All the technological aspects of the process remain outside the scope of the review. Apparently it would be desirable to devote a separate review to these questions. As regards further investigations, in our view attention should be concentrated on the construction of a quantitative kinetic model of the pyrolysis of methane in the region of moderate temperatures taking into account all the reliably established facts, including the occurrence of autocatalysis, the acceleration by hydrocarbon additives, and the influence of hydrogen on the yield of hydrocarbons, the rate of the process, and the composition of at least the principal pyrolysis products. The existence of such a model would make it possible to predict reliably the course of high-temperature processes involving methane, which is extremely important bearing in mind the rapid expansion of the range and scale of the industrial applications of natural gas.

† See, for example, one of the latest studies.[3]

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