

It should be noted that in most cases which we came across, we are dealing with a simultaneous effect of high pressure on the equilibrium position and the velocity of chemical reactions. If, for example, during the atmospheric oxidation of propane the pressure is raised from 5 to 65 atm., the composition of the resulting mixture of alcohols is considerably changed; the percentage of methyl and ethyl alcohols falls from 95.4 to 59.9%, while the percentage of n-propyl and isopropyl alcohols rises from 4.6 to 40.1%, which is nearly a ten-fold increase.¹⁶⁾ Such an effect of an increase in pressure may be explained by kinetic factors (higher reaction velocity, caused by the diminution of volume) together with thermodynamic factors (a shift of the equilibria of parallel reactions towards those products which are formed with a diminution of volume). Another example is furnished by the thermal decomposition of methyl alcohol at 350°C.¹⁷⁾ Increasing the pressure from 600 to 6000 atm. led to the following changes in the composition of the gaseous reaction products:

Composition of gas (%)	(CH ₃) ₂ O	CH ₄	H ₂	CO	CO ₂
at 600 atm.	8.05	39.8	31.2	10.95	7.3
at 6000 atm.	46.3	27.0	13.7	2.9	7.8

The marked increase in the percentage of dimethyl ether in the reaction products as the pressure is increased is similarly caused by the effect of pressure on the equilibrium and the velocity of the various reactions which take place during the thermal decomposition of methanol.

In the preceding section we have examined briefly the basic mechanisms of the effect of high pressure (up to a few thousand atmospheres) on the velocity and the course of chemical reactions. Higher pressures (of the order of tens of thousands of atmospheres) may lead to far-reaching qualitative changes in the reactivity of substances and therefore these pressures cannot generally be used to investigate the mechanism of chemical reactions.

From the data given here, it may be gathered that in a number of cases even the sign of the pressure effect (+ or -) allows us to determine the character of the rate-determining step in a complex process. Analysis of quantitative changes (reaction velocity or yield of products) caused by an increase in pressure makes it possible to choose between various schemes describing the mechanism of the reaction in question. Finally, qualitative data on the change in reaction products as a result of increased pressure also provide a very useful basis for choosing the most likely reaction mechanism.

We now pass on to an account of some results of the investigation of the mechanism of chemical reactions using high pressures.

Investigation of the Mechanism of Reactions in the Gaseous Phase

A) Thermal Cracking of Paraffinic Hydrocarbons

Previous investigations have established that at low pressures (of the order of a few atmospheres) the velocity of thermal cracking increases with an increase in the pressure in most cases which have been investigated (decomposition of ethane at 750 and 800°C.¹⁸⁾, decomposition of propane at 600°C.¹⁹⁾, decomposition of n-butane at 575°C.²⁰⁾ and 600°C.¹⁹⁾, decomposition of n-pentane at 580°C.²¹⁾); only in one investigation²²⁾ was high pressure observed to retard the cracking of ethane at 635°C.

In some recent work²³⁾, the effect of high pressure on the velocity of the thermal cracking of n-hexane and n-heptane was investigated. Some results of this investigation are shown in Table 1.