Table 1

The thermal cracking of n-hexane and n-heptane (duration of experiment 3 hours).

Temperature (°C)	Mean pressure of hydrocarbon (atm.)	Yield of liquid products	Unreacted hydrocarbon
		(% of initial hydrocarbon)	
		n-hexane	
430	300	40.0	11.3
430	560	54.3	20.0
430	910	71.8	32.4
430	1680	80.0	39.4
420	160	78.5	52.9
420	860	89.7	68.5
		n-heptane	
420	620	68.3	19.7
420	940	78.9	28.6
420	1150	88.5	39.8
420	1860	94.2	56.6
420	3100	96.7	59.3

From the data of Table 1 it may be seen that high pressure retards the thermal cracking of paraffinic hydrocarbons. This inhibition cannot be attributed to a change in the chemical equilibrium. This is especially borne out by comparison of the results of thermal and catalytic cracking carried out in the course of the same work (see below)*; such a comparison shows that during catalytic cracking the decomposition of hydrocarbons and the production of gaseous and volatile liquid products proceed considerably faster than in thermal cracking under the same conditions of temperature and pressure. A similar retardation of the cracking of paraffins was also found in an investigation of the decomposition of propane at 600°C and 98 and 197 atm., and also of n-butane at 550°C and 104 and 172 atm.[24]

It may be noted that as the pressure increases the yield of volatile products from the cracking decreases, and the proportion of higher-boiling hydrocarbons increases (in comparison with the original)[23].

From such investigations we gather that at low pressures (a few atmospheres) cracking is normally speeded up as the pressure is increased, and at high pressures (hundreds or thousands of atmospheres) it is retarded.

In one paper [25] a chain-reaction scheme for the decomposition of paraffins has been put forward. It was assumed that the original hydrocarbon molecule R_oH first of all split to give smaller radicals which, reacting further with R_oH form the radical R_o:

$$R_oH \xrightarrow{k_1} R' + R'' \xrightarrow{+2R_oH} 2R_o + R'H + R''H \,. \qquad (1)$$

The radical R_o may decompose to give a smaller radical R_1 and an olefine:

$$R_o \xrightarrow{k_2} R_1 + \text{olefine} \qquad (2)$$

It is also possible that R_o reacts with olefine molecules to produce longer radicals. Such reactions apparently play an important rôle in the cracking of paraffins mixed with olefines, but they cannot serve as the principal chain-breaking step in the absence of any addition, especially at high pressures (see [26]); therefore they are not further considered.

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* Translator's note: while it may be true that the above-mentioned retardation is not caused by a change in equilibrium, this is not borne out by the facts adduced here.