345. *The Ignition of Gases. Part IX. Ignition by a Heated Surface. Mixtures of Methane and Air at Reduced Pressures.*

By C. A. NAYLOR and R. V. WHEELER.

THE ignition of mixtures of methane with oxygen and nitrogen, argon, or helium, at atmospheric pressure, was discussed in a previous paper (J., 1931, 2456), and the conclusion was reached, from the experiments recorded, that at temperatures leading to ignition the oxidation of methane is a thermal reaction catalysed by the products of an initial slow and flameless combustion. This conclusion is now supported by observations on the ignition of methane–air mixtures at reduced pressures; it is not necessarily in conflict with the views of those who, experimenting with methane–oxygen mixtures at lower temperatures, have explained the results as being due to a chain mechanism. In the present work, the reactions are not isothermal, for a notable self-heating towards the end of the period of " lag " is proved by a much greater rise in pressure than that due to the change in the number of molecules present.

Neumann and Serbinov (*J. Physical Chem., U.S.S.R.*, 1933, **4**, 41) found three limits of pressure for the ignition of methane–oxygen mixtures containing from 2·9 to 35·5% of methane. With more methane, the limits rapidly became less distinct until with the mixture $CH_4 + 1{\cdot}7O_2$ (37% of methane) they merged into one. The lags on ignition, at a constant temperature, decreased as the proportion of oxygen in the mixture was increased up to 90—95%, but on further addition of oxygen the lag began to increase.

Similar results have been obtained by us with methane–air mixtures at the high-pressure limits (the " upper " and the " third " as described by Neumann and Serbinov), but we could not readily determine the low-pressure limit because of difficulty in observing an ignition at low pressures in the apparatus used. Fig. 1 shows that there is a tendency for the ignition temperature to increase as the methane content of the mixture is increased. Fig. 2 shows that the variation of the ignition temperature with pressure is not uniform; with mixtures containing more than 10·7% of methane the ignition temperatures decrease progressively as the pressure is increased, but with mixtures containing less than this amount of methane two pressure limits for ignition are found. The mixture at which the pressure limits merge contains $CH_4 + 1{\cdot}74O_2 + 6{\cdot}58N_2$ and its CH_4/O_2 ratio is the same as that at which Neumann and Serbinov (*loc. cit.*) found the limits to merge when no nitrogen was present.

Fig. 1.

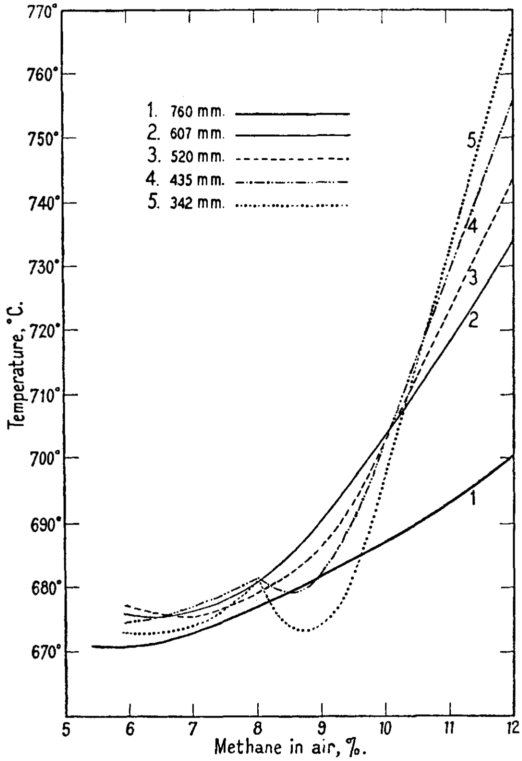
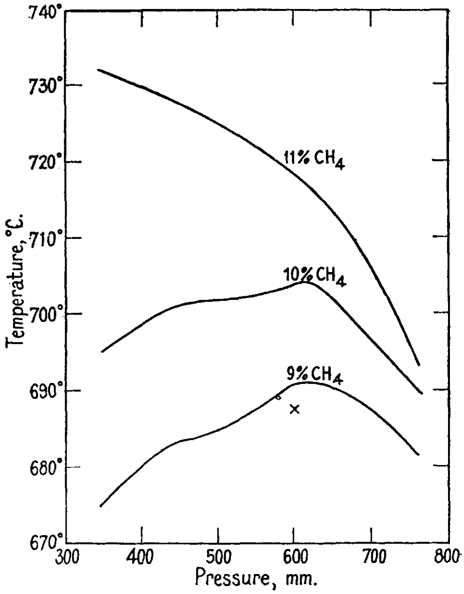


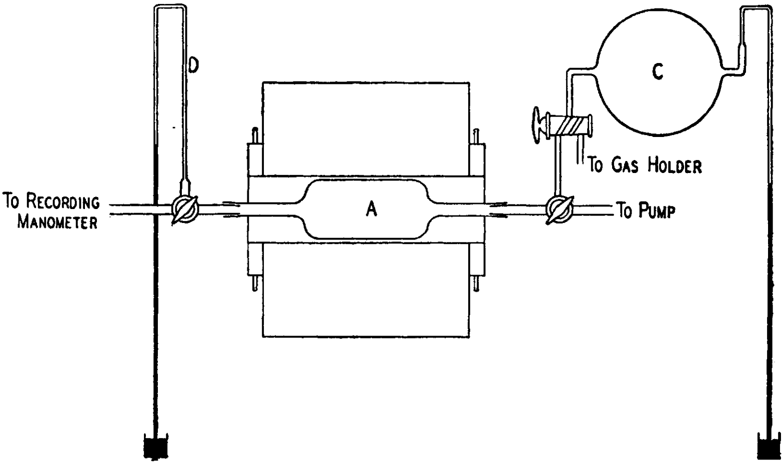
Fig. 2.



Semenov (*Z. physikal. Chem.*, 1929, *B*, **2**, 161) adduced a relationship, $\log P = A/T + B$, between ignition temperature and pressure, applicable to both chain and thermal reactions and to the upper and lower pressure limits of ignition; and he and others have found that this formula holds for a number of reactions. Graphs of our results with mixtures containing more than 10·7% of methane show that the relationship does not apply to methane–air mixtures, and a graph of Neumann and Serbinov's figures for the mixture $CH_4 + O_2$ is not nearly a straight line. Coward (J., 1934, 1405), also, has demonstrated that for the "rapid" ignition points of hydrogen or carbon monoxide in air or in oxygen, as measured by the "concentric tube" method of experiment, the relationship between the logarithm of the pressure and the inverse absolute temperature, although rectilinear over a certain pressure range, changes when a particular pressure is exceeded.

In view of a further study of the oxidation of methane which we are now making, we do not wish to attempt a complete explanation of the results here recorded, but suggest a tentative one based on change in the type of reaction, from surface to gas phase, and on the rate at which different mixtures become non-inflammable as a result of pre-flame combustion. From experiments with methane–air mixtures containing an inhibitor which poisoned the surface of the reaction vessel (J., 1931, 2467), we may conclude that most of the initial chemical change at normal pressure, in the absence of the inhibitor, takes place at the surface, so that at reduced pressures, when the reaction tends to leave the surface, either a longer time or a higher temperature is required to bring about ignition. Mixtures with air near that containing methane and oxygen in combining proportion inflame at lower temperatures when the pressure is reduced because the reaction, although initially extremely slow, accelerates in a mixture that still contains a high proportion of reactive constituents. Outside this narrow range of mixtures, higher temperatures are required to cause ignition as the pressure is reduced, because the mixtures tend to become non-inflammable, as a result of pre-flame combustion, before the reaction accelerates sufficiently to produce flame.

FIG. 3.



EXPERIMENTAL.

The apparatus described in Part VII of this research (J., 1931, 2459) was modified so that the gas mixture could be introduced into the quartz vessel (50 c.c. capacity) at any desired pressure. One end of the reaction vessel, A (Fig. 3), was connected through a three-way tap to a "Hyvac" rotary oil pump and to a glass globe, C, to which a mercury manometer was attached; the other end was connected to a T-tap which communicated with either a mercury manometer, D, or a recording manometer.

When an experiment was carried out, the temperature of the furnace was adjusted with the reaction vessel filled with nitrogen. The gas mixture was then introduced into the glass globe, C, at the necessary pressure, and the manometer, D, was set to the pressure which would be attained by the mixture when it entered the reaction vessel. After evacuation of the nitrogen from the reaction vessel the mixture was allowed to enter rapidly. The progress of the reaction (and ignition if it occurred) was observed on the manometer D.

Ignition Temperatures.—The ignition temperatures recorded in Table I and plotted in Fig. 1 were obtained, as just described, for chosen pressures. Fig. 2 was drawn from readings on Fig. 1, but many points on the curves of Fig. 2 were checked by a different method of experiment: after the gas mixture had been admitted to the furnace at a temperature and pressure such as that represented, *e.g.*, by point X in Fig. 2 for a 9·0% mixture, the pressure was altered whilst the temperature remained constant. Ignition occurred when the limiting pressure was reached, provided that the experiment was carried out within the period of lag. The curves in Figs. 1 and 2 were established by repeated confirmation.

TABLE I.

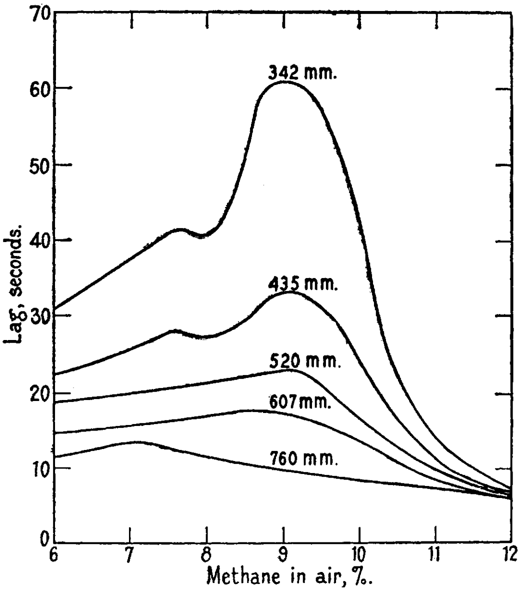
Relative ignition temperatures of methane–air mixtures.

	Pressure, mm.					
CH_4, %.	760.	607.	520.	435.	342.	263.
12·50	707°	—	—	—	—	—
12·35	—	739°	750°	764°	776°	—
11·35	695	—	—	—	—	—
10·65	—	713	718	721	722	—
10·10	687	—	—	—	—	—
10·00	—	704	702	701	695	—
9·15	682	692	689	685	676	669°
9·10	683	—	—	—	—	—
8·70	—	682	681	679	673	—

	Pressure, mm.				
CH_4, %.	760.	607.	520.	435.	342.
8·00	—	681°	680°	681°	681°
7·95	677°	—	—	—	—
7·40	—	678	679	678	676
7·10	672	—	—	—	—
7·00	—	676	675	677	673
6·50	—	675	676	676	674
6·20	671	—	—	—	—
5·85	—	676	677	674	673
5·35	671	—	—	—	—

The time for the reactions to be completed may be seen from Fig. 4, which shows the lags at the ignition temperatures for the range of methane–air mixtures used. The longest lag recorded during this research was 133 secs. at the ignition temperature of a 9·15% methane–air mixture at a pressure of 263 mm.

FIG. 4.



The Lag on Ignition.—At any one temperature above the ignition temperature, the lag on ignition becomes shorter as the percentage of methane in the mixture is decreased. Since the lag measures the time required for the reaction to attain a certain velocity, it is evident that the rate is governed mainly by the concentration of oxygen in the mixture. The lag increases as the pressure is lowered, but at each pressure the form of the curve relating lag with temperature is the same.

Neumann and Egorov (*J. Physical Chem., U.S.S.R.*, 1932, **3**, 61) have shown that the relationship between temperature, pressure, and lag in their experiments may be expressed by the formula $P^n 10^{-A/T} . \tau = K$ (where P = pressure; τ = lag; A is an energy term and, together with n, is constant and characteristic of the combustion process). According to Neumann and Serbinov (*loc. cit.*) this relationship holds for mixtures of methane and oxygen containing between 3 and 50% of methane, but we find that it is not true for mixtures of methane and air. This may be seen from the following values of A/n and n, obtained from our results:

CH_4, %.	A/n (τ = 10 secs.).	Average value of n at the lower pressures.
10·00	7·000	1·8
9·20	7·000	1·8
8·00	6·500	1·65
7·00	6·500	1·4
5·85	7·000	1·3

Graphs of log P against $1/T$ (for various constant values of τ) show that the magnitude of A/n for a given mixture changes with the value of τ, whilst graphs of log P against log τ (for various constant values of T), which give different values for n at different temperatures, are composed of two intersecting straight lines. The point of intersection on the curves occurs at pressures between 500 and 600 mm. At this point there is probably a change in the mechanism of the reaction. We have already shown (*loc. cit.*) that the magnitude of E, obtained by use of the Arrhenius equation, changes with the composition of the mixture and with the temperature.

The values of the lags for a number of mixtures, at different pressures and at temperatures up to 50° above their ignition temperatures, are recorded in Table II.

TABLE II.

The Lags on Ignition of Methane–Air Mixtures at Temperatures Higher than their Ignition Temperatures.

		Lag, seconds, at:						
CH_4, %.	Pressure, mm.	680°.	690°.	700°.	710°.	720°.	730°.	740°.
5·85	760	8·0	5·6	4·6	3·7	3·0	2·5	2·0
	607	12·2	8·4	6·3	5·0	3·9	3·4	2·8
	520	15·5	11·0	8·5	6·5	5·2	4·3	3·5
	435	19·0	14·3	10·7	8·4	6·8	5·4	4·2
	342	24·5	19·5	15·1	11·6	9·0	7·0	5·5
7·00	760	8·3	6·0	4·8	4·2	3·6	3·1	—
	607	13·0	9·2	7·0	5·1	4·2	3·6	—
	520	17·0	12·0	8·7	6·8	5·4	4·5	—
	435	22·3	16·0	11·9	8·8	6·9	5·6	—
	342	30·1	21·8	16·0	12·3	9·7	7·6	—
8·00	760	—	6·7	5·1	4·3	3·6	3·1	2·6
	607	—	12·1	8·3	6·7	4·5	3·6	3·0
	520	—	15·7	11·4	8·6	6·2	5·0	4·0
	435	—	19·8	14·6	11·3	8·7	6·7	5·1
	342	—	29·8	22·9	17·3	13·0	10·0	7·3
9·20	760	—	7·0	5·3	4·3	3·6	3·1	2·5
	607	—	—	11·5	7·0	5·0	3·9	3·1
	520	—	21·2	15·5	10·3	7·7	5·8	4·0
	435	—	26·9	19·9	14·6	11·0	8·3	5·7
	342	—	33·0	25·0	19·0	14·7	11·5	8·8
10·00	760	—	—	5·6	4·5	4·0	3·6	3·2
	607	—	—	—	8·5	5·7	5·1	4·5
	520	—	—	—	12·5	8·0	6·7	5·7
	435	—	—	—	17·5	11·8	9·0	6·7
	342	—	—	35·6	26·6	19·9	14·4	10·2

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