The Ignition of Methane-Oxygen Mixture by Shock Wave

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The ignition of detonable gaseous mixtures by shock wave has been investigated by several authors. In many of those investigations the shock tube was used for the measurement of the ignition temperature of gaseous mixtures. Most of the authors[1-3] claimed the ignition temperature generated by shock waves is essentially lower than that obtained by any other means. Recently, however, Steinberg et al.[4] reported that they could not find any appreciable difference in temperatures between the various methods. Shepherd[2] has made similar investigations on the methane-oxygen mixture under ordinary pressure, for the purpose of measuring the ignition temperature. The present investigations dealing with a variety of pressures and gaseous compositions determined the minimum ignition pressure under these various experimental conditions.

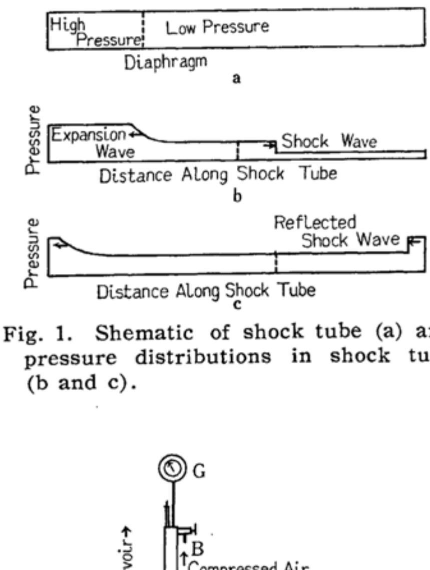


Fig. 1. Shematic of shock tube (a) and pressure distributions in shock tube (b and c).

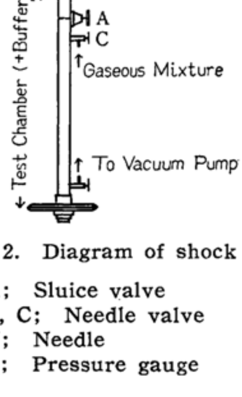


Fig. 2. Diagram of shock tube.

A; Sluice valve
B, C; Needle valve
N; Needle
G; Pressure gauge

Experimental

The brief scheme of the measuring system is given in Fig. 1. As shown in Fig. 2, the shock tube made of mild steel of 2.5 cm. internal diameter and 214.7 cm. length is divided into two sections, the reservoir chamber of 51.3 cm. length and the ignition test chamber of 163.4 cm. length, respectively. Furthermore, the test chamber can be divided into two; the first portion or buffer chamber, which is adjacent to the reservoir, has a length of 57.2 cm. and can be separated with a

1) J. A. Fay, "Fourth Symposium on Combustion", p. 501, Baltimore, The Williams and Wilkins Co. (1953).
2) W. C. F. Shepherd, "Third Symposium on Combustion" p. 302, ibid. (1949).
3) D. J. Berets, E. F. Greene and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **72**, 1080 (1950).
4) M. Steinberg and W. E. Kaskan, "Fifth Symposium on Combustion", p. 664 (1955).

sluice valve A from the second or remaining part of the test chamber on necessary occasions. The second portion then serves as the actual test chamber. The reservoir and the test chamber are separated by suitable sheets of cellophane films of 0.040 and 0.027 mm. thickness. The number of sheets of cellophane films is so chosen that it barely withstands the pressure difference between the two chambers without rupturing before the start of the experiment.

To carry on the measurement, compressed air is first sent into the reservoir chamber and this air pressure acts as firing pressure for the gaseous mixture. The test chamber is filled with a detonable gaseous mixture of desired composition of methane and oxygen. After valve B is closed, the diaphragm is punctured by the needle N through a side tube attached obliquely to the shock tube.

When the buffer chamber is used, it is filled with air of the same pressure as that of the detonable gaseous mixture in the test chamber after the two chambers are separated by closing the sluice valve A. The reservoir chamber is filled with compressed air in the same way as described above. After the sluice valve A is opened, the diaphragm is broken with the help of a hand-operated needle N.

As shown in Fig. 1, the air in the reservoir spurts out and generates a shock wave. The gaseous mixture will be ignited by the direct shock wave or by the wave reflected from the bottom of the tube and superposed on the direct shock wave. At the ignition, the sound of detonation is clearly audible. On opening the tube after the experiment, the cellophane diaphragm is found to be discolored, and white smoke drifts out from the interior of the shock tube. As the bottom of the tube, the plane end plate is mainly used but, on necessary occasions, the conical bottom of the vertical angle 90° as shown in Fig. 3 is used, so as to cause the reflected shock wave to converge at a certain distance from the bottom on the center axis of the tube and thus produce a high temperature and high pressure region locally.

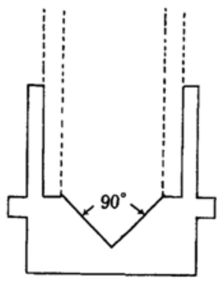


Fig. 3. Conical end of shock tube.

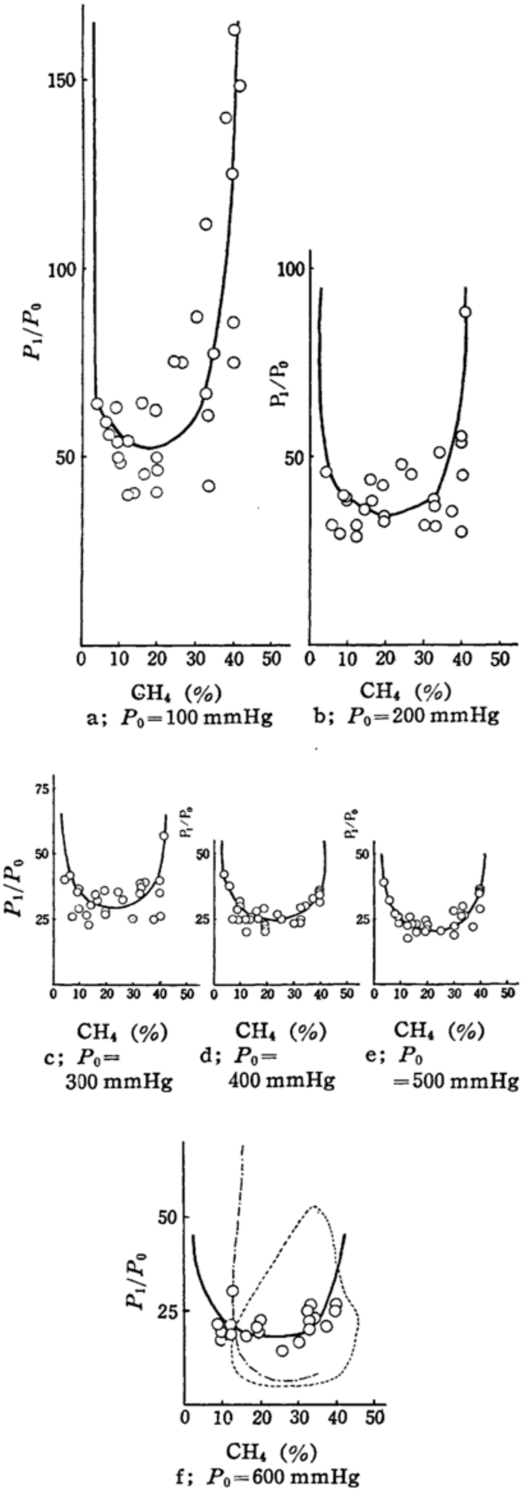
As to the experimental materials, commercial oxygen and methane in cylinders were used. For the experiment, both gases, through a sodium hydroxide tube to eliminate the carbon dioxide, are mixed to the desired composition and the mixture was kept in a tank over 24 hours. The methane in the cylinder consists usually of 87.8% methane, 9.7% nitogen, 0.3% carbon dioxide and 0.2% oxygen.

The buffer chamber serves to eliminate the effect of puncturing the diaphragm. As both sluice valve A and the needle N are operated by hand, the opening of the valve and puncture of the diaphragm can not possively be carried out at the same moment. Especially the fact that the opening of the valve has taken time, seems to cause the diffusion of the gases of the buffer and test chambers. Also the experimental result with the buffer chamber often shows poor reproducibility. At the puncture of the separating films the fragments of these will be scattered all about in the ignition mixture and these may cause some error in the experiment. To avoid the effect, some authors used a trap device such as metal coil or gauze to catch the fragments. In the experiment of Shepherd[2)], he found some effect of fragments of copper film on the pressure value under which ignition occurs but in case of using cellophane films he could not find any of these effect. Accordingly, we eliminated the trap, as we used cellophane films only.

Results and Discussion

We have carried out a series of experiments of ignition by shock waves with various pressures in the reservoir against a certain gaseous mixture with definite composition and definite pressure. With a pressure in the reservoir lower than a certain limiting value, the ignition does not take place. The lowest pressure value necessary for the ignition is called minimum ignition pressure P_1 for the gaseous mixture of definite composition and definite pressure P_0. In Fig. 4, the ratio P_1/P_0 is plotted against various compositions of methane and oxygen. The values of P_1/P_0 correspond to the temperature of ignition for the mixtures of pressure P_0.

Owing to the mechanical strength of the shock tube used, the maximum pressure of the reservoir was limited to 30 kg./cm^2. Up to this value it was not possible to find any pressure values above which ignition does not occur. Such upper limiting pressure values for the ignition of gaseous mixtures of various compositions were reported by Shepherd[2)]. In his case a higher pressure in the reservoir could be attained than is possible for us. As will be seen from Fig. 4, the minimum values of P_1/P_0 tends to decrease with the increase of P_0, and at the same time the minimum point drifts to the methane rich side. The limit concentration for the explosion of this gaseous mixture lies between 3 to 42% methane,



------ Shepherd's data with trap at 760 mmHg

-·-·- Shepherds's data without trap at 760 mmHg

Fig. 4. Variation of P_1/P_0 with concentration of CH_4.

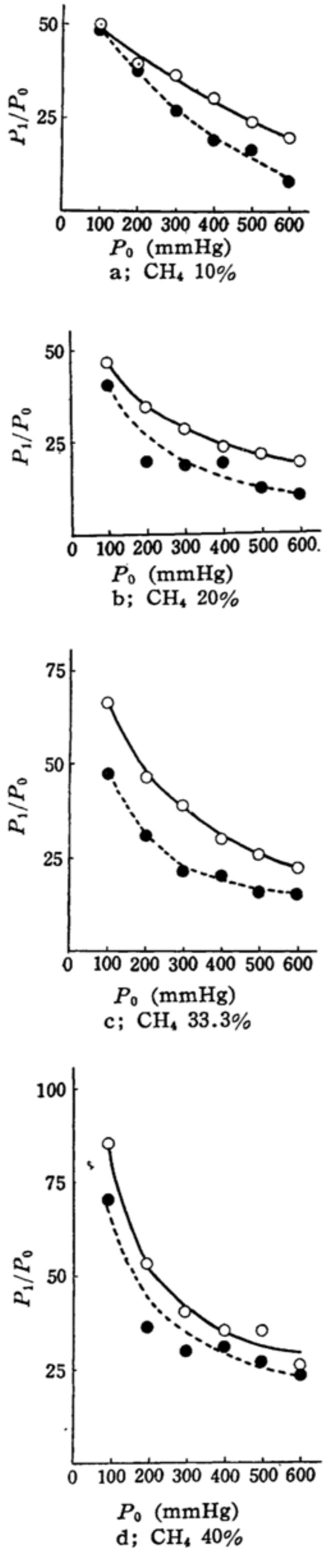


Fig. 5. Variation of P_1/P_0 with pressure of gaseous mixture.

○; with plane end

●; with conical end

and is entirely independent of the gaseous pressure. The minimum ignition point observed is at the gaseous mixture of about 20—25% methane.

As seen from Fig. 5, P_1/P_0 values decrease in accordance with the increasing value of P_0, which means that the higher the pressure of gaseous mixture, the easier to detonate the gas under the same conditions. The curves in thick lines in Fig. 5 denote the values using the plane bottom, and the dotted lines the conical bottom of the shock tube, respectively. The values obtained using the buffer chamber were found not to be sufficiently reproducible, probably for the reasons described above. We have selected some reliable values of both cases, with and without buffer which are tabulated in Table I. Though it seems that the ignition with buffer is easier than without buffer, the differences are by no means remarkable.

TABLE I

COMPARISON OF P_1/P_0 BETWEEN WITH AND WITHOUT BUFFER

P_0 (mmHg)	P_1/P_0 with buffer	P_1/P_0 without buffer
200	46.1	52.4
300	32.8	34.4
400	25.8	27.6

The ignition limits in Fig. 4f manifest some difference from those obtained by Shepherd. The discrepancies may be attributed to the fact that, in our experiment, a shock tube with closed end was used and in his case open tube was employed. Accordingly, in his experiment the gaseous mixture in the ignition chamber may have been diluted by the air diffused through open end. In spite of these differences, the concordance of the results from both investigations manifest themselves to be satisfactory.

In our experimental conditions the ignition temperatures could not be determined directly. But they may be estimated indirectly and theoretically with help of the equation[5)]

$$[yP_0/P_1]^{(\gamma_1-1)/2\gamma_1} = 1-C_0(\gamma_1-1)(y-1)/C_1[2\gamma_0\{(\gamma_0-1)+(\gamma_0+1)y\}]^{1/2} \quad (1)$$

where P is the pressure of the shock wave; C_1 and C_0 are each the sound velocity in the reservoir and the test chamber respectively; γ_1 and γ_0 are the ratio of specific heat at constant volume and at constant pressure of both gases in two chambers cited above; and $y=P/P_0$. The gases are all assumed to be perfect gases. In taking $\gamma_0=\gamma_1=1.4$, $C_1=C_0$ and $T_1=T_0$ where T_0 is the temperature of the gas in reservoir and T_1 that of the test chamber, we have

$$P_1/P_0=y[1-\{(y-1)/(7+42y)^{1/2}\}]^{-7} \quad (2)$$

The values of y or the values of P can be determined by substituting the experimental values in the equation (2). Furthermore the temperature T of the direct shock wave and T_r of the reflected one can be expressed as follows[5)];

$$T/T_0=(P/P_0)(1+\mu^2 P/P_0)/(P/P_0+\mu^2) \quad (3)$$

$$T_r/T_0=\{(2\mu^2+1)P/P_0-\mu^2\}\{2\mu^2P/P_0-(\mu^2-1)\}/\{(P/P_0+\mu^2)(\mu^2+1)\} \quad (4)$$

where $\mu^2=(\gamma_0-1)/(\gamma_0+1)$.

Using the expressions (2), (3) and (4) the values of T and T_r can be estimated approximately. In spite of those simplifications used above, the values obtained may serve as an orientation of the ignition temperature. In Fig. 6 we have shown the temperature values of T and T_r with plane end shock tube together with the

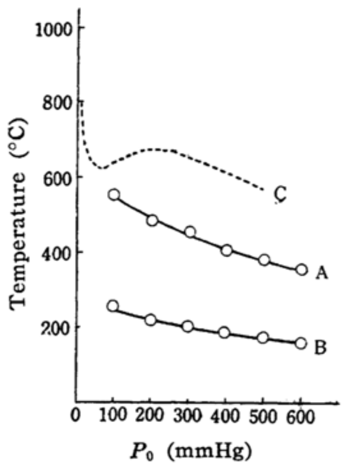


Fig. 6. Variation of ignition temperature with pressure of gaseous mixture $CH_4 + 2O_2$.
A; Reflected shock ignition
B; Direct shock ignition
C; Thermal ignition

5) W. Bleakney, *Rev. Mod. Phys.*, **21**, 584 (1949); I. I. Glass, W. Martin and G. N. Patterson, *UTIA Report* No. 2 (1953); R. N. Hollyer, Jr., "Engineering Research Institute Report", Univ. of Michigan, July (1953).

6) N. Semenoff, "Chemical Kinetics and Chain Reaction", p. 308, Oxford at the Clarendon Press. (1955).

results of thermal ignition[6]. In the respective cases, the higher the pressure of the detonable gaseous mixture, the easier the ignition. The peninsula-shaped region which is seen in thermal ignition is lacking in both direct and reflected shock wave detonation. Ignition in the shock tube with conical bottom is more easily produced by the reflected shock wave, than it is with the plane bottom. In general the temperatures of shock wave ignition are essentially lower than those of thermal ignition.

All these estimations however are indirect. They should be determined in a more direct way, and we are now preparing to take up such further investigations.

Summary

Using the shock tube, the authors measured the minimum ignition pressure P_1 of the reservoir for the methane-oxygen mixture of various pressure P_0 and various compositions, and obtained the following results.

1) The higher the value of P_0, the easier the ignition.

2) The concentration range of methane in the gaseous mixture for shock ignition is 3—42%, and the minimum value of P_1/P_0 or the ignition temperature, was found at a gaseous mixture of about 20—25% methane.

3) The ignition easier is by the use of the shock tube with conical end rather than with the plane end.

4) Shock ignition temperatures estimated indirectly were found to be remarkably lower than the thermal ignition temperature.

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