27. *An Examination of the Mechanism by which "Cool" Flames give Rise to "Normal" Flames. Part III. The Physical Characteristics of the Two-stage Process of Ignition of Ether–Oxygen Mixtures.*

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In a recent communication (J., 1939, 337) evidence was adduced that the two-stage process of ignition depending on prior " cool " flame formation is the same whether the " cool " flames are induced (a) *spontaneously* at high temperatures and suitably low pressures or (b) *artificially* by means of a heated wire at room temperature and at high enough pressures. In both circumstances ignition is the outcome of the initiation of a second flame in the " cool " flame products.

The phenomena associated with the development of the second flame, now termed the " blue " flame, are much more marked in ether–oxygen than in ether–air mixtures; moreover, the " blue " flame is distinguishable from the " cool " flame by a marked increase in the volume of its products.

In mixtures of adequate oxygen content the " blue " flame may in narrow tubes overtake and extinguish the " cool " flame, leading to a normal flame; this normal flame is not self-propagating and dies out. In wider tubes the normal flame may degenerate into a " cool " flame, the two-stage process then being repeated again and again, resulting in oscillatory propagation.

Under conditions where the products of the " blue " flame are released and constant pressure maintained, it is shown that the " blue " flame is not self-propagating; it is always preceded by a " cool " flame, the distance between the two being a function of pressure and mixture composition. The " blue " flame is now recognised as having characteristics differing from both " cool " and normal flames.

In Parts I and II (J., 1939, 337, 341) it was shown with ether–air mixtures how the two-stage spontaneous ignition of higher hydrocarbons and their derivatives can be reproduced in *cold* media by using artificial ignition, provided adequate working pressures be employed. In such circumstances, on the attainment of a critical experimental pressure depending on the composition of the mixture, a flame, hitherto thought to be a normal flame, is initiated in the " cool " flame products some way behind it, the subsequent events depending on the available oxygen in the medium. Also, " cool " flame ranges of inflammability were located in *cold* media with the higher paraffin hydrocarbons in admixture with air at experimental pressures of a few atmospheres, these pressures being found to be in the same order as the minimum pressures requisite to induce " cool " flames in *spontaneous* ignition experiments; and at 100° they were as follows: ether, below atmospheric pressure; hexane, above 5 atm.; butane, above 9 atm.; propane, above 12 atm.

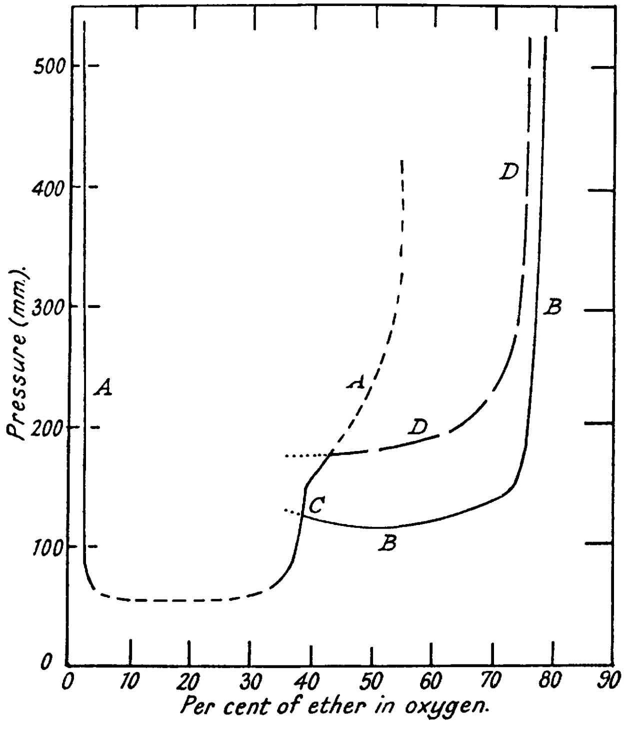
The discovery that the two-stage process of ignition can be observed in cold media at sufficiently high pressures has opened up a new line of attack for investigating its mechanism and Parts III and IV embody the results of our further investigations upon the phenomenon with ether–oxygen mixtures.

Results.

The Influence of Pressure on the Inflammable Ranges of Ether–Oxygen Mixtures.—The influence of pressure on the inflammable ranges for both normal and " cool " flames in ether–oxygen mixtures was determined in the same manner as that employed with the ether–air mixtures (J., 1939, 333, 339), and the results for horizontal propagation of flame in a closed tube 4·5 cm. in diameter and at room temperature and pressures up to 500 mm. are illustrated in Fig. 1. The normal flame range is shown by curve *A*, and the " cool " flame range by curve *B*, these two independent ranges overlapping at *C*. The ranges are much the same in character as those found with the ether–air mixtures. Thus the " cool " flame range is seen again to centre upon the 1 : 1 mixture of ether and oxygen; moreover, the minimum pressure necessary for " cool " flame initiation with this mixture (115 mm.) was rather lower than the partial pressure of combustible and oxygen similarly requisite in an ether–air mixture (J., 1939, 338). This suggests that diluent nitrogen plays little part in the " cool " flame process, but may by virtue of its heat capacity lower the temperature of the system. There was, however, a marked difference between the shapes of the flame envelopes in the two series of experiments, so that further investigation of these issues is necessary.

FIG. 1.

Influence of pressure on the inflammable ranges of ether in oxygen mixtures.

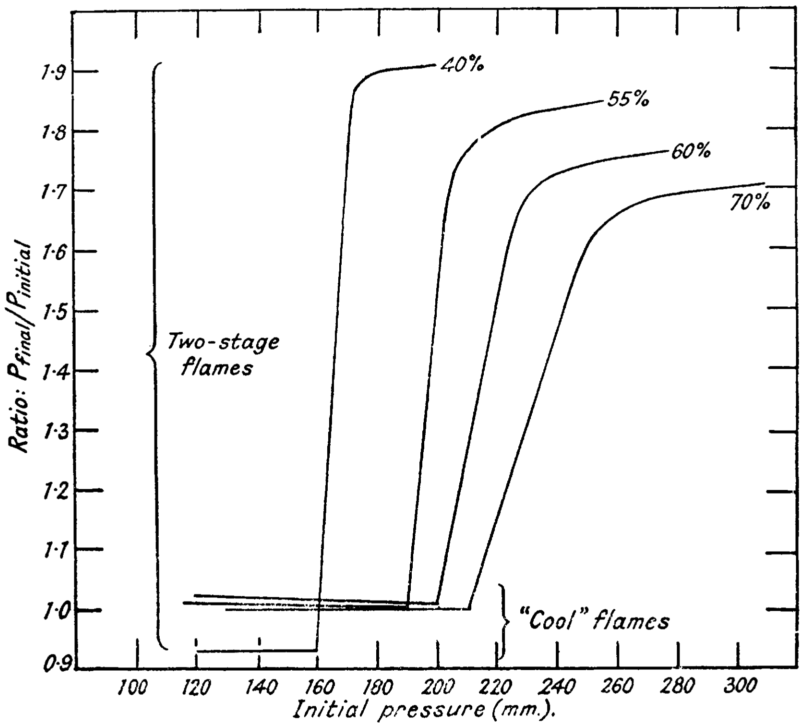


It may be recalled that with the ether–air mixtures at pressures above that at which the normal and the " cool " flame range overlapped, difficulty was experienced in locating with precision the upper limit for two-stage ignitions, for (*a*) in the spontaneous-ignition experiments the pressure development was so low that there was no sharp demarcation between that of the two-stage ignition and that of the " cool " flames alone, and (*b*) in the experiments in glass tubes with artificial ignition it was difficult to decide the precise limit at which a superposed flame was initiated behind the " cool " flame owing in the circumstances to its poor luminosity and comparatively low velocity. Accordingly, the boundaries concerned were indicated by broken lines (Part I, Fig. 2).

In the present series of experiments with ether–oxygen mixtures it became simpler to define the conditions at these limits owing (*a*) to the increased brightness of the second flames initiated in the " cool " flame products and (*b*) to a discovery due to an earlier observation of Dr. H. S. Hsieh that such initiation led always to a marked increase in the volume of the gaseous explosion products which did not occur when a " cool " flame alone had traversed the mixture. A criterion for the occurrence of the two-stage process was thus available, and as will be seen, this was very critical to variation in the initial experimental pressure.

FIG. 2.

Influence of initial pressure on the ratio final : initial pressure after passage of flame.



In Fig. 2 the influence of initial pressure on the ratio of the final to the initial pressure following the passage of flame is illustrated graphically for four representative ether–oxygen mixtures containing severally 40, 55, 60, and 70% of ether. It will be seen that, whereas the passage of a " cool " flame was responsible for hardly any permanent change in the pressure of the medium, the initiation at a critical pressure of the second flame, which we have termed the " blue " flame, was responsible for a marked increase of pressure; and with mixtures of high oxygen content the pressure became almost doubled. For instance, with the 55% ether–oxygen mixture a " cool " flame alone was propagated at initial pressures between 115 and 190 mm., the ratio final/initial pressure being almost constant at about 1·0; at slightly higher initial pressures, however, the " blue " flame was initiated behind the " cool " flame after a time interval which decreased sharply with successive small increases in initial pressure, and the final pressure after the passing of flame rapidly increased. At about 220 mm. initial pressure the transition phenomenon became too rapid to be followed by the eye; it gave rise to more violent flame propagation, the pressure ratio being about 1·8. With increase in the oxygen content of the mixtures, the incidence of the " blue " flame occurred at somewhat lower initial pressures, and the two-stage inflammation became very violent if the pressure was raised much above that indicated by curve *D* (Fig. 1). With increase in the ether content of the mixtures above 55%, the effect of small increases in the initial pressure was less abrupt and the explosions less violent; the incidence of the second " blue " flame, however, was always marked quite sharply by a large increase in the final/initial pressure ratio.

It may be pointed out that, provided care is taken that the ignition wire is not overheated, " cool " flames can be initiated in mixtures lying within the normal flame range and indicated by the dotted extensions of the curves *B* and *D*. The initiation of " cool " flames in this area, however, is more difficult with ether than with other materials, *e.g.*, acetaldehyde; moreover, if pressures above *D* be allowed to develop, detonation may ensue.

In Fig. 1 the marked widening (broken line) of the upper (normal) ignition limit *A* indicates the boundary at which it is impossible to discriminate between the " blue " flame and the normal flame; at the boundary there is an apparent increase in both the speed of the flame and the completeness of combustion; so far, however, we have not attempted to measure flame speeds in this region owing to the violence of the explosions. Within the limit *A* also, marked deposition of carbon was observed, this being almost absent outside it.

Curve *D* defines the pressure limits for the initiation of the second " blue " flame in the cool flame products; depending upon the oxygen content of the mixture and the experimental pressure it may either catch up, coalesce with and visibly enhance the velocity of the " cool " flame, or alternatively travel independently behind it. With the mixtures of oxygen content greatly in defect the initiation of the " blue " flame could only be detected visually after considerable experience; measurement of the final pressures of the media, however, never failed as a criterion in this respect.

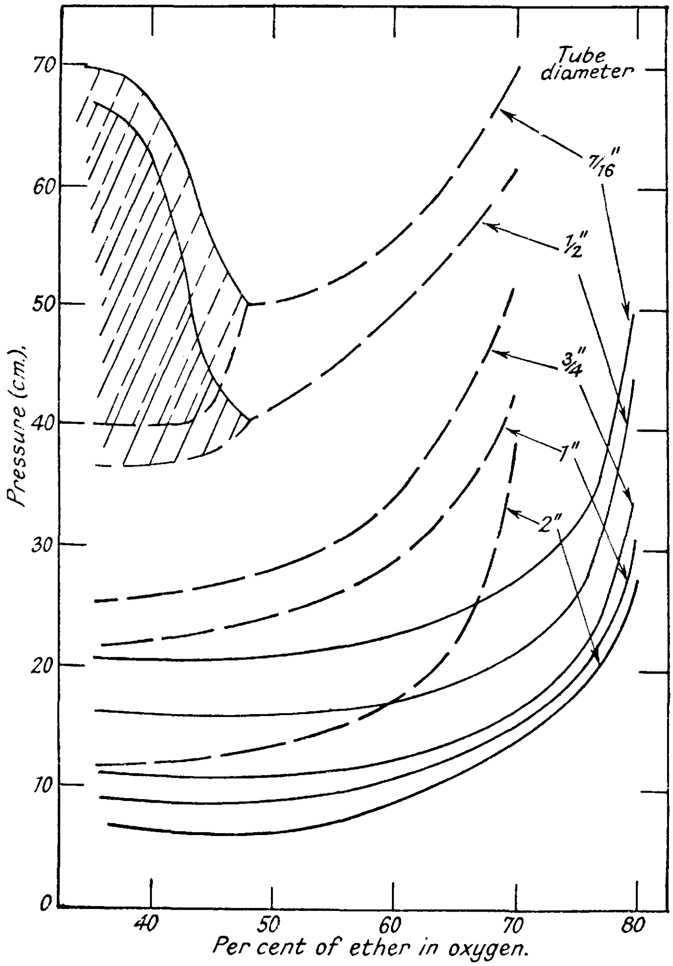
Perhaps the most interesting aspect of this part of the investigation was the difference in character of the " cool " and the succeeding " blue " flames as revealed by the difference in the volume of the gaseous products in each instance. In experiments described later, and designed with the ultimate view of examining separately the chemical processes responsible for each type of flame, it was found that under conditions of *constant* pressure the two flames retain their separate existence over much wider ranges of initial pressure; and, although at adequate pressures the two flames do actually coalesce and form a composite structure which travels with enhanced velocity, yet the incursion of the normal flame range into the " cool " flame range in closed-tube experiments is mainly the outcome of the conditions of pressure and temperature superimposed in the confined space by the volume of products rapidly liberated by the initiation of the second " blue " flame.

The Influence of Tube Diameter on the Pressure Limits of the " Cool " and " Blue " Flames through Ether–Oxygen Mixtures in Closed Tubes.—Having observed that the character of the two-stage ignition process in cold media depends on the initiation of two characteristically different types of flame, we designed an apparatus in which these flames could be maintained under the conditions of requisite pressure indefinitely, so that the products of combustion could be collected and analysed. For this purpose the simplest means of stabilising the flame appeared to be to employ a conically shaped tube in which any small variation in the rate of supply of the mixture under examination would be compensated by the change of flame speed with tube diameter. In order to obtain the necessary information on which to base the design of such an apparatus, however, it became necessary to determine (*a*) the pressure limits for both " cool " and the succeeding " blue " flames in tubes of varying diameter, and (*b*) the approximate velocities of these flames under such conditions. In the first part of this investigation experiments were carried out in closed tubes; later, it became evident that the information so obtained was inadequate, and a second series of experiments was undertaken to meet the need for information relative to conditions of constant pressure, with results which have been very informative.

In Fig. 3 two series of curves relating to experiments at 30° with ether–oxygen mixtures have been drawn showing (*a*) the variation with mixture composition of the limiting pressure for " cool " flames in tubes of five representative diameters, *viz.*, 2, 1, $\frac{3}{4}$, $\frac{1}{2}$, and $\frac{7}{16}$ in., and (*b*) the corresponding limiting pressures for the development of the " blue " flames in the " cool " flame products. In these tubes no flame could be propagated below atmospheric pressure in mixtures containing more than 80% of ether. Those containing 70—80% of it were capable of propagating " cool " flames only, but if the oxygen concentration was further increased " blue " flames occurred at adequate initial pressures. When the ether concentration fell below 46% the tails of the " blue " flames became yellow until, with mixtures containing 35—40% of ether the " blue " flame was almost entirely luminous,

FIG. 3.

The limiting pressures for the initiation of " cool " and " blue " flames in tubes of varying diameter.



and travelling with high velocity it caught up the " cool " flame, the subsequent explosion being violent.

The Oscillating Flame.—In this investigation a new and interesting phenomenon was observed, particularly with mixtures rich in oxygen and in the narrower tubes. A " cool " flame was initiated by the hot wire, and according to the usual behaviour a " blue " flame appeared behind it and, travelling with high velocity, overtook it, producing a normal flame. Under the conditions of experiment, however, the resulting normal flame was outside the inflammability limit and unstable, hence it reverted to a " cool " flame after a short time; this was propagated for some distance down the tube, after which the procedure was repeated. This cycle of events recurred a number of times with gradually decreasing amplitude, until the oscillations were finally damped out, leaving a coalesced flame with a yellowish tail. This oscillating mode of propagation was most marked in narrow tubes; but it might occur in any of them, and in daylight, when the " cool " flame is invisible, it appears as a discontinuous luminous flame propagation.*

An interesting result of this oscillating type of propagation was observed in the narrow tubes with mixtures containing less than 45% of ether. On ignition of the mixture, the first cycle took place in the usual way; but the succeeding flame was so violent that it flashed along the tube for about 15 cm., extinguished the cool flame, but itself failed to survive, being outside the normal inflammability limit. Repeated attempts to make a flame propagate all the way down the tube under the conditions referred to, and represented by the shaded areas in Fig. 3, were without success; on elevation of the pressure to the limits indicated by the upper boundaries of such areas, the flames would propagate successfully, the oscillations referred to being less marked.

The Pressure Limits of the " Cool " and " Blue " Flames through Ether–Oxygen Mixtures at Constant Pressure.—The oscillating phenomena just described, and other observations on the reversibility of the transitions from " cool " to normal flames, led to an examination of the part played by pressure in regard to the development of the " blue " flame in the " cool " flame products. In a preliminary experiment with a 50% ether–oxygen mixture in a 1″ tube, a " blue " flame was allowed to overtake and coalesce with the " cool " flame and travel down the tube, while at the same time the products of combustion were evacuated from the firing end. As the pressure was reduced, the " blue " flame was seen to grow smaller and less intense, while a " cool " flame was seen to detach itself from the " blue " flame and travel on ahead. The lower the pressure, the further behind did the " blue " flame recede, until at a pressure as nearly as could be judged equal to that previously found as the limit for the transition phenomenon, it went out altogether.

This process was obviously the reverse of the " cool " to " blue " flame transition, and it appeared therefore that the maintenance of the coalesced flame, or indeed of the " blue " flame at all, was solely dependent on the maintenance of an adequate pressure in the system. It also suggested that the coalesced flame could have no separate existence without a " cool " flame; moreover, the high speed with which the blue " flame caught the cool flame at the transition limit was apparently due to the fact that the " blue " flame liberated products which built up the pressure, the distance between the " cool " flame front and the " blue " flame being very sensitive to pressure under these conditions. In other words, the time lag before the " spontaneous ignition " in the " cool " flame products as represented by the formation of a " blue flame " was considerably decreased by a small increase in pressure. As a natural outcome of this it was also observed that if a " cool " flame was propagated at a *constant* pressure just above the transition limit, the two flames travelled down the tube together keeping a constant distance apart.

In order to investigate this matter further, as well as to obtain data relative to the conditions required to maintain a stationary flame in a cone apparatus, a tube was set up to enable the flame speeds to be measured at constant pressure. An explosion tube 2·5 cm. in diameter and 145 cm. long was used, the 120 cm. furthest from the igniting wire being enclosed in a water jacket at 30°. Flame speeds were measured in the water-jacketed portion of the tube only by means of a stop-watch; and the firing end of the tube was connected through a copper-gauze flame trap, to an expansion volume of 6 l. capacity, this expansion volume proving sufficient for the purpose.

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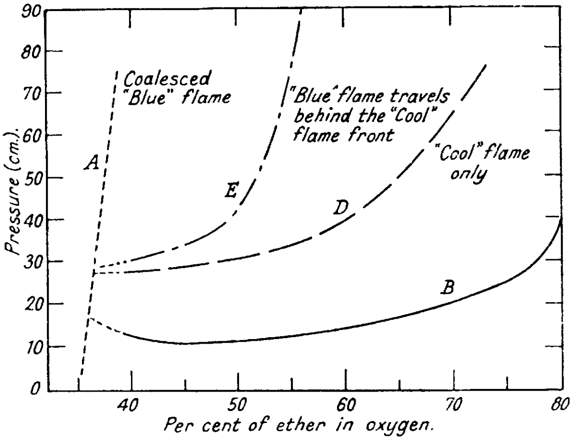
* Cf. Jost's interpretation (*Z. physikal. Chem.*, 1939, **42**, *B*, 136) of the intermittent phenomenon in detonation (spin) revealed by high-speed flame photography. According to Jost, in a detonating gas mixture the velocity of the principal shock wave is so great that the zone of active flame reaction cannot keep pace with it and the flame falls behind; the high pressure and temperature attained in the wave, however, prepare the mixture for spontaneous ignition which actually occurs behind the wave after a definite interval, thus providing the additional energy requisite for its maintenance. This process is repeated continuously, and the " retonation " waves from the successive ignitions account for the striæ observed behind the flame front in most high-speed photographic records of " spinning " detonation. It seems to us that a close analogy exists between Jost's interpretation of the behaviour of the detonation wave and our own observations, the mixture being sensitised for ignition by a shock wave in the one case and by a " cool " flame in the other.

The pressure–composition ranges of the various phenomena are shown in Fig. 4, and Fig. 5 illustrates the manner in which the velocity of the flame varied with pressure in the case of four typical mixtures, containing severally 38·2, 50, 59, and 73% of ether.

FIG. 4.

Influence of pressure on the " cool " flame inflammability range in experiments at constant pressure.



With the 73% mixture only cool flames could be propagated, their velocity increasing rapidly from about 12·5 cm./sec. at the low pressure limit * (20 cm.) to 16 cm./sec. at 30 cm. pressure; and thereafter increase in pressure up to 1 atm. was without appreciable influence.

With the 59% mixture the cool-flame velocities increased in much the same manner with increase in initial pressure; at about 32 cm. pressure, however, a blue flame was formed in the tail of the cool flame. Its occurrence, and consequent liberation of gaseous products, caused an apparent increase in the velocity of the cool flame, but this was probably partly due to some mass motion of the mixture as well as radiation from the front of the " blue " flame which helps to propagate the " cool " flame, thus increasing its speed. Over the pressure range studied, however, the " cool " and the " blue " flame fronts in this mixture were always separated by a measurable distance.

In the 50% mixture, only " cool " flames could be propagated at pressures up to 30 cm., their velocities varying in the usual way; also, as far as could be judged, the " cool " flame velocities at any one pressure are greatest with this mixture. At about 30 cm. pressure, the " blue flame " first made its appearance in the tail of the cool flame; but grew larger, and travelled closer to the cool flame front as the pressure was raised above this, until at 41 cm. pressure the two flames coalesced. In other words, the " cool " flame was no longer visible in front of the " blue " flame; there was reason, however, for the belief that the " cool " flame still existed as a separate combustion stage, although the flame as a whole had the outward appearance of a single stage flame. Curve E, Fig. 4, indicates the pressures at which this apparent coalescence occurs. There is possibly an analogy between this coalescence and the single stage ignitions observed at adequate pressures by Kane (*Proc. Roy. Soc.*, 1938, *A*, **167**, 62) and by Neumann (*Compt. rend. Acad. Sci. U.S.S.R.*, 1938, **18**, 333).

In the case of the 38·2% mixture, cool flames were propagated at pressures between 15 and 27 cm. Over a narrow range above this pressure a " blue " flame travelled in the tail of the cool flame. Coalescence in the case of this mixture resulted in violent oscillations such as have already been described, so the flame speeds indicated in Fig. 5 should be regarded as overall speeds in this particular mixture, and without any special significance. At a pressure of 60 cm. this oscillating type of propagation was replaced by a normal flame having a velocity of more than 200 cm./sec.

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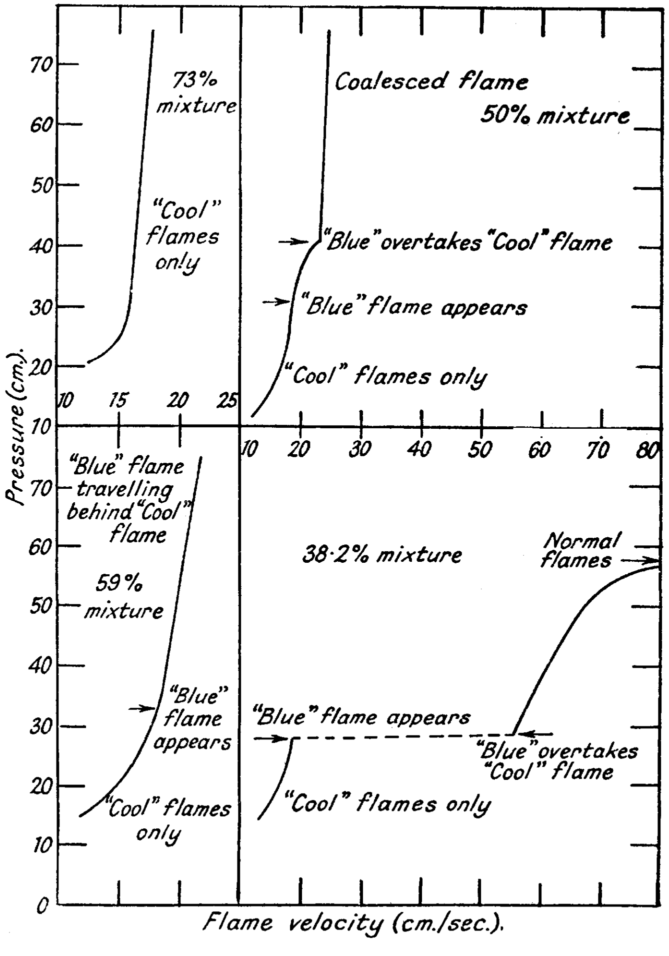
* It is probable that the increased velocity of the cool flame which occurs in all mixtures as the pressure is raised above the lower pressure limit, is for the most part due to the fact that at the limit the flame front does not fill the cross-section of the tube.

There is no doubt an abrupt change in the mechanism of flame propagation as the limit *A* (Fig. 4) is crossed, for at this point there is an abrupt increase in the temperature of the flame front.

From the foregoing, therefore, it appears that the velocity of the " blue " flame is not much greater than that of the " cool " flame; this is contrary to the impression created by earlier observations on experiments in closed tubes, where the expansion of the products of the " blue " flame pushed the flame forward, giving it an apparently abnormal velocity.

FIG. 5.

Influence of pressure on flame velocity at constant pressure through mixtures containing 38·2, 50, 59, *and* 73% *ether in oxygen.*



The experiments with ether–oxygen mixtures thus recorded, and particularly those under conditions of constant pressure, have made much clearer the physical characteristics of the mechanism of the two-stage ignition process and have paved the way for investigations into the chemical processes operative in the various types of flame concerned.

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