418. *Carbon Formation in Flames.*

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The fundamental chemical processes leading to carbon formation in hydrocarbon flames are not understood. In simple diffusion flames of acetylene in air or oxygen examined at low pressure, carbon formation depended markedly on pressure, in agreement with observations of other authors. For hydrocarbon gases during pyrolysis and in the pre-heating zone of a flame, continuous absorption in the ultra-violet region spread as the temperature was raised. This effect is probably related to carbon formation. None of the results can be fully accounted for by existing theories, however, and two alternative explanations are tentatively suggested.

The formation of carbon particles in hydrocarbon flames is well known and of considerable industrial importance. Although the technique of controlling carbon formation has been successfully developed in some cases, the fundamental chemical processes involved are not understood.

Data in the literature are meagre. Davy first attributed the luminosity of hydrocarbon flames to the presence of incandescent carbon particles; early studies by Marchand, Berthelot, Lewes, Bone, and others on how these carbon particles occur in the flame are summarised by Bone and Townend (" Flame and Combustion in Gases," Longmans, Green & Co., 1927, p. 406). More recently Rummel and Veh (*Arch. Eisenhüttenwesen*, 1941, **14**, 489) considered the conditions required for carbon formation and suggested that the soot particles are precipitated as residual carbon skeletons of big aromatic or polycyclic molecules. These molecules are formed in the gas phase, and largely dehydrogenated, during pyrolysis of the hydrocarbon in the flame. The greater tendency of aromatic fuels to deposit soot, and the similarity of the graphitic structure of this soot to the structure of the higher homologues of benzene, appear to support this hypothesis. On the other hand, a spectroscopic study of ethylene flames led Smith (*Proc. Roy. Soc.*, 1940, *A*, **174**, 110) to suggest that carbon deposition is due to the polymerisation of C_2 molecules; he recalled the work of Klemenc, Wechsberg, and Wagner (*Z. physikal. Chem.*, 1934, **170**, 97) on the thermal decomposition of C_3O_2 in which C_2 was formed and recognised by its absorption spectrum but rapidly polymerised to normal solid carbon.

The tendency of organic substances to smoke on burning freely in air has been examined by Clarke, Hunter, and Garner (*J. Inst. Petroleum*, 1946, **32**, 627). They show that with hydrocarbons it is not merely a question of the C/H ratio : other factors concerning the structure of the molecule are involved. Thus the tendency of normal paraffins to smoke is relatively slight and increases with increasing chain length, but it is greater with branched-chain paraffins than with their normal isomers. Unsaturated compounds give appreciably more smoke than do the paraffins, but there is a different variation with structure. Increase in chain length of the olefin results in decreased smoke formation, as does an increase in the number of carbon atoms in the diolefin, benzene, and naphthalene series. For compounds containing oxygen, the content of this element is also of significance. In general, increased oxygen content results in a decreased tendency to smoke, provided that the hydrocarbon portion of the molecule does not exert an over-riding effect. Methyl alcohol for example does not form any carbon.

The voluminous literature on the pyrolysis of hydrocarbons shows that carbon and hydrogen are the ultimate products of a purely thermal process. In diffusion flames the rôle of pyrolysis is undoubtedly significant, and in pre-mixed gas flames the presence of oxygen during the pre-heating stage profoundly alters the conditions in which carbon is formed. Gaydon and Whittingham (*Proc. Roy. Soc.*, 1947, *A*, **189**, 313) described the influence of oxides of sulphur on the luminosity of pre-mixed gas flames; the effect, which is apparently catalytic, was not observed by us in diffusion flames. These and other facts bearing on the problem seem to us too limited experimentally for solution of this complex problem.

The first step in the present investigation was consideration of experimental methods. Diffusion flames have been burned at low pressure, and a number of new features relating to carbon formation have been observed, including a pressure limit below which no carbon was obtained. This may be related to Smith's observations (*loc. cit.*) that sooting was more pronounced in an ethylene–air flame at pressures greater than one atmosphere. The size and uniformity of the particles which we collected from the luminous zone of a diffusion flame have been examined under an electron-microscope, and absorption spectroscopy has been applied to hydrocarbons during pyrolysis and in the pre-heating zone of a flame. Many of the results obtained from these experiments cannot be adequately explained by existing theories and an alternative is suggested which is admittedly speculative.

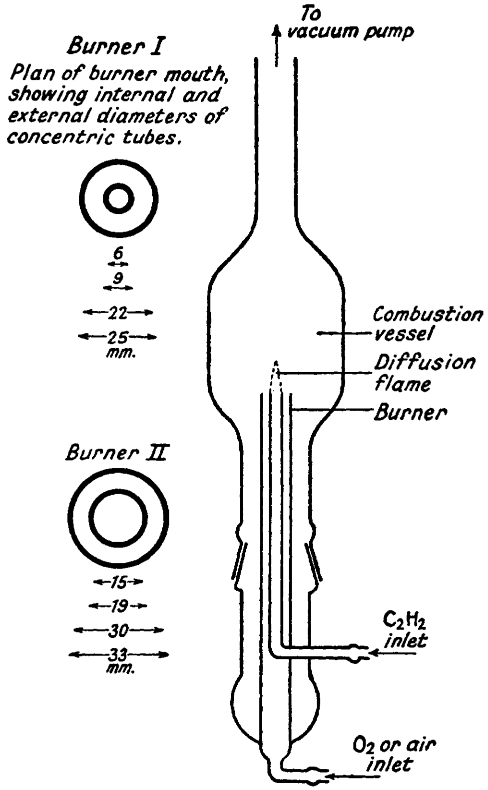
The investigation has been restricted to diffusion flames in their simplest form. The majority of technical applications of combustion employ diffusion flames although the conditions in the flames are complicated by turbulence.

EXPERIMENTAL.

Examination of Diffusion Flames at Reduced Pressures.—Careful observations were made of the changes occurring in the reaction and the luminous zone of a non-aerated gas flame on a circular burner when the external pressure was reduced. For work at low pressure the following technique was adopted: A large glass vessel (Fig. 1) was connected to a powerful vacuum pump. Two concentric glass tubes entering at the bottom through a ground-glass joint and passing vertically into the vessel, formed the burner, and the dimensions were such that the ratio, area of annulus : area of inner tube, was very nearly equal to the ratio, volume of air/sec. : volume of fuel/sec. The linear velcities of the air and the fuel gas were thus approximately equal. In contrast to conditions in an open gas jet burning in an unlimited amount of still air it was possible to change the mixture strength by changing the dimension

FIG. 1.

Apparatus for the study of diffusion flames at low pressures.

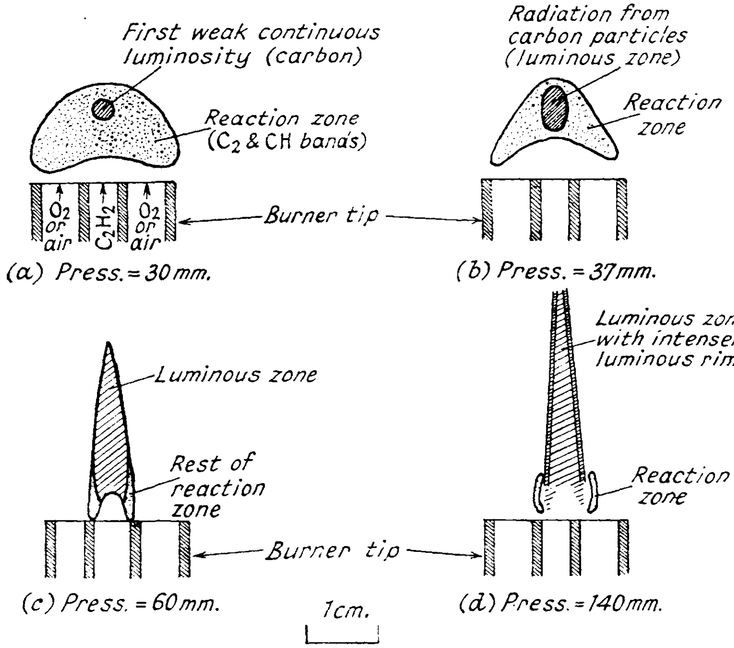


of the burner and still to keep the linear velocities of air and gas equal, thus avoiding frictional problems. With this arrangement the flame burned very steadily and was surrounded by its own exhaust gases. The Reynolds numbers were very low and there was no turbulence.

In experiments with acetylene and air in burner I (see Fig. 1) the volumetric flows at N.T.P. were 1 and 11·9 c.c./sec. respectively. The corresponding mass flows were kept constant and independent of the pressure in the combustion vessel, so that as the pressure was reduced the velocity of the emergent gases increased. After ignition the reaction between the two concentric streaming gases depended on interdiffusion. Since the diffusion coefficient was inversely proportional to the pressure, the rate of mixing increased as the pressure was reduced. In this way the height of the diffusion flame (dependent on both the gas velocity and the diffusion rate) should theoretically remain constant, if diffusion is the rate-determining process of the combustion (Wolfhard and Parker, *Proc. Physical Soc.*, 1949, **62**, 722, and unpublished work). The diffusion flame at reduced pressure behaved as predicted, as long as no carbon formation occurred, but, as described below, carbon formation depended markedly on the pressure. The reaction mechanisms for the oxidation of acetylene molecules and for the burning of carbon particles are different, which in turn influences the height of the flame.

FIG. 2.

Special features of an acetylene–air diffusion flame at low pressures.



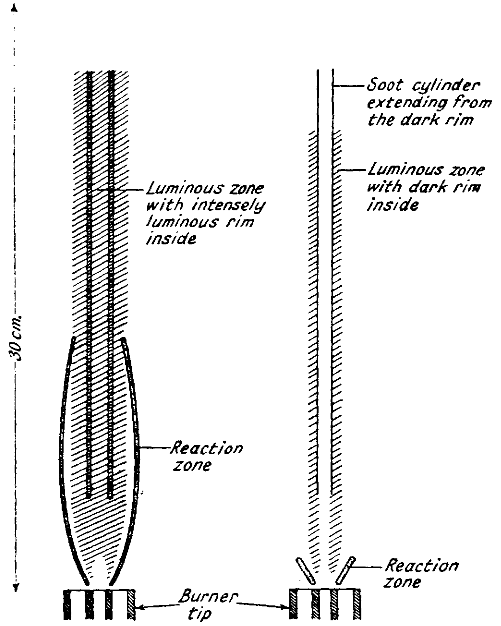
The lowest pressure at which burning could be maintained with this mass flow in burner I was 29 mm. Hg. At lower pressures the flame suddenly lifted off the burner. The features of the flame at various pressures are shown in Fig. 2*a*—*d*. At the limiting pressure, the reaction zone was cone-shaped, and radiation consisted only of the C_2 and CH bands in the visible region together with a weak continuum from electron recombination. The C_2 bands were slightly stronger in the upper part of the cone, and the reverse held for the CH bands. Fig. 1*a* depicts the flame at 30 mm. pressure: the appearance was much the same except for a small red patch due to carbon particles nearly in the centre of the cone. At 37 mm. (Fig. 2*b*) the cone remained of about the same size and shape, but the red patch was larger, reaching the upper boundary of the flame. At 60 mm. (Fig. 2*c*) the blue cone became smaller but remained essentially the same in length, while the red centre (caused by radiation from carbon particles) was level with the base of the blue cone at the bottom and extended above the blue cone at the top. The growth of the carbon region beyond the blue cone was rather sudden and effected in some cases by a pressure change of only a few mm., and the overall height of the flame was doubled or even trebled. At 140 mm. (Fig. 2*d*) the blue cone was small and unimportant but the carbon region was considerably changed. Instead of being very uniform in intensity, as at 60 mm. pressure, it had a fine structure and a more intense rim. The region was no longer closed but was open at the top, and at 180 mm. this opening increased so much that soot could be seen escaping at the top. At 270 mm. the rim of the luminous cone had become very sharp indeed and the flame looked like a hollow luminous cylinder when viewed from above or below. At 340 mm. a new feature was observed: the sharp rim of the luminous carbon region was surrounded by a thin pale luminous skin which extended to the base of the flame.

An increase in mass flow to 16 c.c. of acetylene and 190 c.c. of air per second made the flame much taller. Fig. 3*a* illustrates the flame at a pressure of 130 mm. (cf. Fig. 2*b*). The blue cone was about sixteen times as high as before and the carbon region was 30 cm. high. The sharp brightly luminous rim which gave the flame a hollow appearance already had a rather thick pale luminous skin around it, while inside the radiant cylinder the luminosity was weak and may have been an optical effect caused by overlapping luminous layers. At 220 mm. the luminous rim, hitherto very bright, became black. The pale luminous skin was then the only source of radiation and it was lined inside by the thin deep black layer in place of the former sharp brightly luminous rim. On top of the flame, where the luminosity faded away, the black thin layer continued into a hollow cylinder of soot. Again the blue cone had become small and unimportant. Fig. 3*b* shows these features for a pressure of 600 mm.

In experiments in which oxygen was used instead of air it was possible to burn the flame at much lower pressures with the pump capacity and burners available. It was clear too that as long as no carbon appeared the flame height was essentially independent of the pressure and proportional to the mass flow in accordance with diffusion considerations (Burke and Schumann, *Ind. Eng. Chem.*, 1928, **20**, 998).

FIG. 3.

More features of the acetylene–air diffusion flame at low pressure (increased mass flow).



(a) Press. = 130mm. (b) Press. = 600mm.

The oxygen flames, too, were much hotter and the burner rim became red hot, which led to cracking of the fuel on the rim of the inner tube. A carbon deposit grew in branching form and this growth was sometimes very rapid and built up 1—2 mm. in 10 seconds. Finally a network of branches formed a cone which restricted the acetylene flow. Examined under the microscope this carbon was obviously different from soot: it had a smooth shiny surface similar to that of methane carbon found on the walls of the reaction vessel after the pyrolysis of methane and generally agreed with the description of vitreous carbon given by Ephraim (" Textbook of Inorganic Chemistry," 4th Edn., 1943, p. 137). This suggests a difference in the mode of formation and it seems that soot particles may be formed in the gas phase, whereas vitreous carbon and methane carbon are the products of surface reactions.

Low-pressure Termination of Carbon Formation.—Observations were made on the limiting pressure of carbon formation for an acetylene–oxygen diffusion flame in burner II. The dimensions of this burner were such that the mass flow of acetylene and oxygen were in stoicheiometric proportions, and the linear velocities of the two gases were equal, as with burner I. In Fig. 4 the results are shown by plotting (on a log–log scale) the total pressure in the combustion vessel and the mean velocity of the gas before it reached the flame. For a given mass flow a straight line inclined at 45° was obtained. The 0·5 c.c./sec. acetylene line terminates at 43 mm. pressure; at this pressure the flame reached its minimum point for self-propagation. The heat loss by conductivity and diffusion reached a value such that the flame was unable to persist. For the 1·0 c.c./sec. acetylene mass flow line the minimum point moves towards lower pressures; for the 4·0 c.c./sec. line the minimum point was beyond the pump capacity.

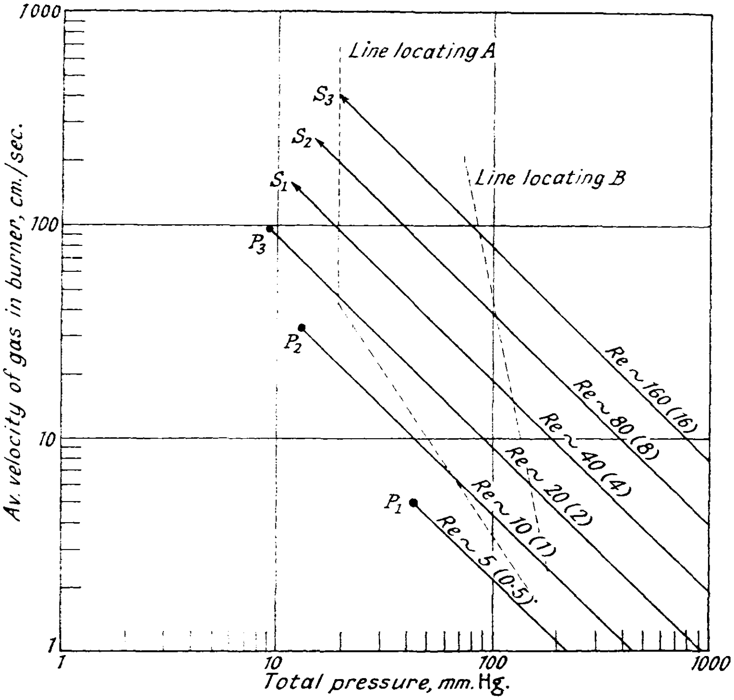
In these results there seemed to be one general fact, that from the minimum point and over a certain pressure range there was no luminosity due to carbon particles. When, however, the minimum point was low enough—this required a mass flow of about 2 c.c./sec. or more of acetylene—carbon formation set in at about 19 mm. pressure and above. This value (*A* in Fig. 4) seemed to be a constant for stoicheiometric acetylene–oxygen mixtures and was independent of the mass flow over the range tested (2—16 c.c./sec. of acetylene; reduced to N.T.P.). It is of course possible that this pressure limit depends to some extent on the overall burner size. Moreover difficulty was sometimes experienced in observing the low pressure limit of carbon formation, because even at pressures lower than 19 mm. the flame was very bright through the presence of CH and C_2 bands and some electron recombination continuum. The first weak luminosity caused by carbon formation could usually be located more readily by using a pocket spectrograph. The fact that carbon formation ceased at the same pressure over a wide range of mass flows seems to indicate a real low-pressure limit for this burner size.

Another characteristic of the flame, marked *B* in Fig. 4, is the point at which the luminous cone was hollow and accompanied by the onset of very marked soot formation. The line locating *B* is inclined to the line locating *A* (the first appearance of luminosity) and forms a triangle within which the luminosity is due to incandescent carbon particles. All of these are ultimately burned. Free soot formation occurs to the right of this triangle.

If oxygen was used with acetylene in burner I, the oxygen supply was virtually unlimited and the pressure limit of carbon formation was about 50 mm. The flame was very bright indeed and carbon growth very rapid. The luminous cone was mostly hollow but no free soot was observed. The carbon apparently burned away in the excess of oxygen.

FIG. 4.

Stability region for a stoicheiometric C_2H_2–O_2 *diffusion flame* (*Burner II*).

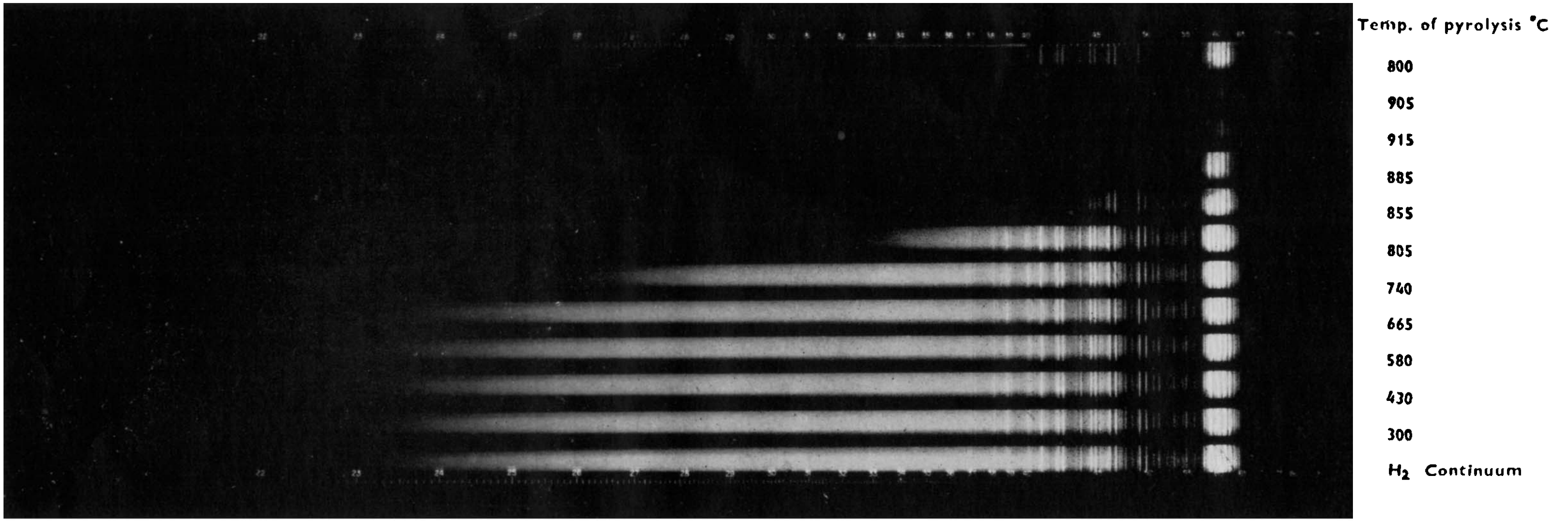


P_1, P_2, and P_3 indicate the "minimum points" for propagation of the flame. S_1, S_2, and S_3 indicate the lowest pressures the pump could achieve. Numbers shown in parentheses are the mass flows of the C_2H_2 in c.c./sec. at N.T.P. Re indicates the Reynolds number of the fresh gas.

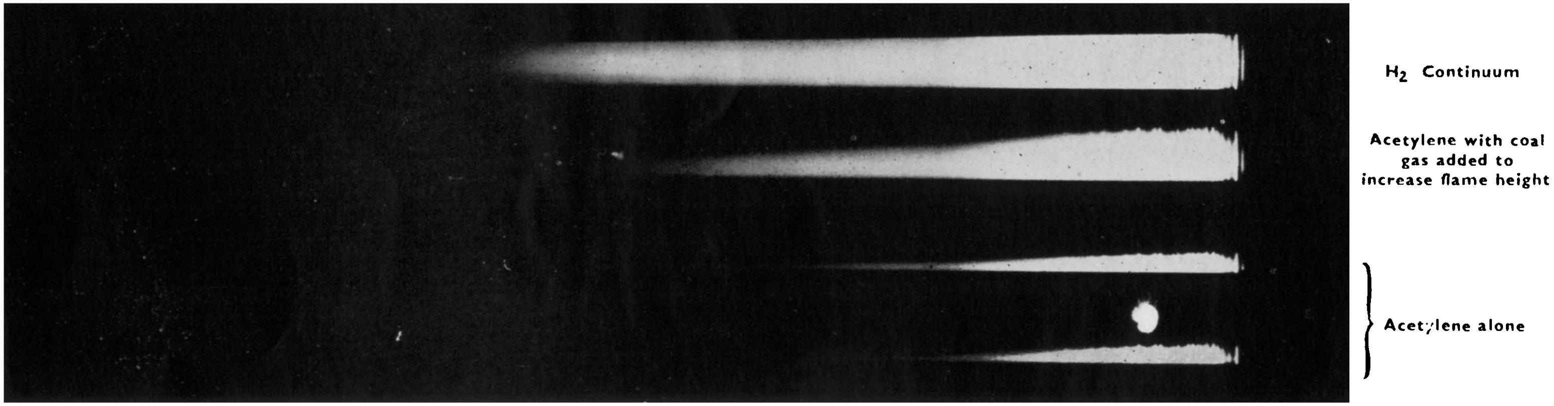
In diffusion flames with oxygen the bright rim in the luminous zone never underwent the inversion to opaque soot which was so characteristic in the air diffusion flame, though in other respects the flames were similar. The oxygen flames were of course much brighter.

The air diffusion flame of acetylene had a low-pressure limit of carbon formation at about 30 mm. and again a luminosity triangle similar to that described for the oxygen flame could be contructed by plotting the results in the manner of Fig. 4.

Size of Carbon Particles in a Diffusion Flame.—To get some information on the size of carbon particles in a diffusion flame a standard Hefner candle was used containing amyl acetate. The carbon particles were collected on a copper grid or a wire passed rapidly through the flame and subsequently photographed under an electron microscope. The Hefner candle could be made smoky or non-smoky by adjusting the height of the wick. In a non-smoky flame all carbon particles (which built into filaments or chains on the sampling grid) were nearly equal in size, approx. 100 A. In a smoky flame, however, some large particles of approx. 500 A. were also found. The latter result must be treated with some reserve because it is difficult to obtain a representative sample from the grid, and the ratio of small to big particles varied considerably in different parts of the grid. Two other facts were apparent: (1) the particles collected near the top of the flame were similar in size to those collected near the base,



(a). ABSORPTION SPECTRA OF ETHANE AT ELEVATED TEMPERATURES



(b). ABSORPTION SPECTRA OF GAS EMANATING FROM A FISH-TAIL BURNER

FIG. 7. ABSORPTION SPECTRA OF HYDROCARBONS.

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and the size was not noticeably affected when the candle was burning very brightly in pure oxygen; and (2) when the particles collected on a grid were heated in a hydrogen flame some increase in size seemed to take place. The latter fact however is again subject to the limitations of the method.

The most reliable and significant fact of this analysis is therefore the uniformity of size of the particles throughout the luminous zone. In a non-sooty flame the particles do not grow and must have reached their final size before entering the luminous zone.

Absorption Spectroscopy.—The application of visible and ultra-violet absorption spectroscopy to pyrolysis has not been attempted hitherto, as far as the authors are aware. This is understandable since all the lower hydrocarbons (except the aromatics) are transparent even in the ultra-violet region, and little useful information would be expected from the method. Spectro-analysis is of course used in photolysis, *e.g.*, for acetylene (Dunicz, *J. Amer. Chem. Soc.*, 1941, **63**, 2461), but the conditions are very different from those of pure pyrolysis. Carbon formation in flames which results in the production of incandescent soot particles with an extensive continuum limits this method for the present purpose to an examination of the regions below the luminous zones. Measurements of absorption in a benzene diffusion flame on a Hefner candle indicated that the benzene bands disappear a short distance above the wick and before the vapour reaches the luminous zone of the flame. No other bands appeared in their place.

The absorption spectra of straight-chain and aromatic hydrocarbons were then examined, both during pyrolysis and in diffusion flames of more suitable dimensions. Several new facts were observed which may be relevant to the process of carbon formation.

For the pyrolysis experiments the arrangement was as follows: A quartz tube, 40 cm. long and 2 cm. in diameter, was closed at each end by plane quartz windows. The tube was inserted in a furnace, 33 cm. long, which could be heated to 1000°. Hydrocarbon gases could be admitted to the tube through inlets at both ends and leave the tube again from an outlet at the centre. This arrangement had two special features, first, the inlets being at the ends prevented condensation of pyrolysis products on the plane quartz windows, and, secondly, the outlet pipe was brought out of the furnace again and the products passing through it were burnt as a diffusion flame at the end. Ultra-violet light from a hydrogen discharge tube of the low-tension type was passed in a parallel beam through the quartz tube and then focussed on the slit of a medium quartz spectrograph (Hilger E3). The absorption spectra were obtained for each of a number of different hydrocarbons flowing continuously at a fixed rate (approx. 5 c.c./sec.) through the tube at various temperatures. The results were as follows.

Ethane. From room temperature to 580° there was no absorption in the available wave-length range, *viz.*, 2150—6000 A.; the tube was clear and there was no change in the outlet tube or the flame burning on the end of it. At 665° a continuous absorption began from the short wave-length end of the spectrum and the hydrogen continuum was absorbed up to 2450 A.; no change occurred in the outlet pipe or the end flame. At 805° the absorption had increased to 2800 A. and a mist was noticed in the cool part of the outlet tube; the luminosity of the flame on the outlet pipe had also noticeably increased. At 855° absorption was complete up to 3700 A.; condensation in the outlet tube was very marked and the flame was so luminous that it began to become sooty. At 885° absorption had reached 4200 A. and the hydrogen continuum seen through the tube appeared clear but slightly yellowish owing to the onset of absorption in the visible region. At 915° the absorption reached 5500 A. and the continuum was completely absorbed in the ultra-violet blue and the green region.

On lowering the temperature of the furnace the absorption decreased again in the reverse order, which indicated that the effect was real and not due to some extraneous cause such as condensation on the windows.

This continuous absorption which increases with temperature is a major feature of thermal reaction of hydrocarbons and seems to have been overlooked hitherto. It was found for all the hydrocarbons investigated (*viz.*, methane, ethane, butane, ethylene, acetylene, and benzene) and also for ethanol, but not for methanol.

The spectra obtained for ethane are shown in Fig. 7*a*.

Methane. A continuous absorption began at a higher temperature (870°) than with ethane (665°) but increased more rapidly with temperature. At 980° it had already reached 3300 A., while at 1000° absorption was complete in the ultra-violet. The effect of pyrolysis on the diffusion flame at the outlet was very interesting. The luminosity of the flame did not change much with the furnace temperature and the mist formed by condensation of the products of pyrolysis entered the flame. Some of the mist became radiant before it reached the true luminous zone of the flame and appeared as intensely luminous streaks which passed right through the luminous zone and escaped as soot from the top of it. It is certain that the contact times in the flame are insufficient to give soot particles of this size and they must be produced during an extensive thermal reaction in the furnace.

Ethylene. The continous absorption of ethylene began at about 400° and was spread over the ultra-violet region up to 4600 A. at 750°. The process extended over a wider range than with methane.

Acetylene. This began to absorb at still lower temperatures than ethylene. The effect of pyrolysis can only be distinguished above 2300 A. since acetylene absorbs in the region 2000—2400 A. at ordinary temperature. Moreover, at elevated temperatures higher vibrational levels are activated (an effect which does not appear to have been recorded hitherto) and even at 100° some increasing absorption begins in the far ultra-violet for that reason. At 330°, however, there was an absorption which could be attributed to pyrolysis and the whole of the ultra-violet region was affected within the temperature range 330—500°.

Benzene. This has a strong absorption band at about 2600 A., which may be useful for observation of the effects of pyrolysis or of combustion. The experimental arrangement was not suitable for following the disappearance of this band (cf. experiments with the Hefner candle) because relatively cool benzene vapour was always present at the two ends of the tube. It was, however, possible to see whether other aromatic compounds were formed through decomposition or polymerisation of the benzene during pyrolysis, since all more complex aromatic compounds have bands at longer wave-lengths than benzene. (The last statement must be slightly qualified because present knowledge is very limited on the absorption spectra of these compounds in the gas phase but it is true of spectra obtained from solutions.) No unidentified bands were observed between 2700 and 4000 A. in any of the spectra and it is concluded that the benzene molecules decompose before polymerisation to polycyclic compounds.

The experiments with benzene were carried out in two ways. At first a stream of nitrogen, saturated with benzene vapour at room temperature, was passed through the quartz tube in the furnace. The concentration of benzene was relatively low and the absorption was not too strong, so that the short-wave side of the 2600 A. band could be examined. It must be remembered of course that the thermal reaction is also retarded at a low concentration of benzene. Interpretation of the spectra is complicated by the strong temperature influence on the natural absorption spectrum of benzene. Higher vibrational levels appear to be activated and the bands spread to longer wave-lengths, though not beyond about 2750 A. Near 2300 A. a small continuous absorption originating in benzene exists, which becomes stronger even at 250°, and it is possible that more than one effect is really observed. At 750° a continuous absorption set in beyond 2700 A. and this was definitely due to thermal reaction. Other experiments were made with pure benzene vapour and precautions were taken to prevent condensation of the vapour in the supply tubes and at the cool ends of the pyrolysis tube. Continuous absorption beyond 2800 A. began to increase with certainty at about 500° or even below, and spread slowly to 3350 A. at 800°.

FIG. 5.

Upper wave-length limits of strong absorption at higher temperatures.

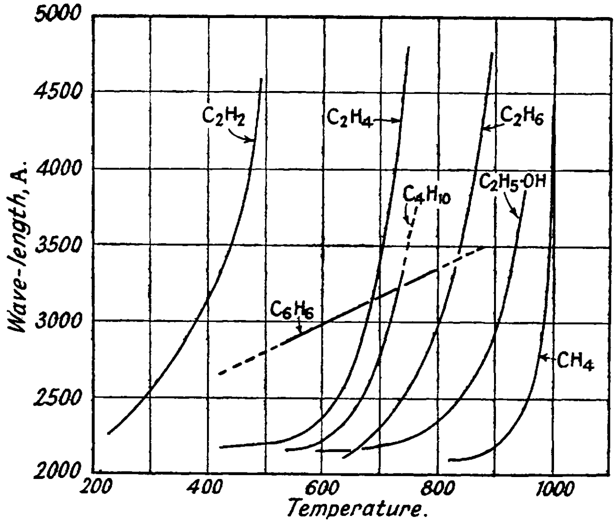
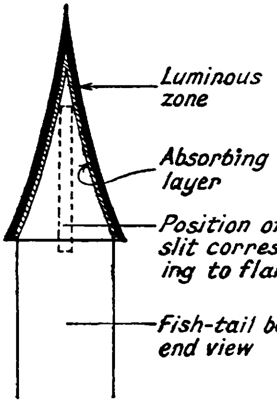


FIG. 6.

Arrangement of fish-tail burner for absorption experiments.



Methyl alcohol. This compound was included because it is well known that its flame contains no luminous carbon or soot. The pyrolysis has also been thoroughly investigated (Fletcher, *Proc. Roy. Soc.*, 1934, *A*, **147**, 119), and formaldehyde has been identified as an intermediate product. In these experiments, using very pure methanol to start with, no continuous absorption was observed at any temperature up to 1000° and the outlet flame did not acquire luminosity. Above 600° formaldehyde bands appeared and remained up to 900°, whereafter they began to disappear again. The maximum strength of these bands was observed at about 700—800°. This result is very important for the present investigation and also suggests a good method for studying the decomposition reaction in detail.

Ethyl alcohol. The luminosity of an ethyl alcohol diffusion flame is comparable with that of methane and ethane. The vapour was passed into the pyrolysis tube with the usual precautions against condensation. A continuous absorption began at about 600° and had eliminated nearly all the ultra-violet light by about 960°. Formaldehyde bands appeared initially at 550° and afterwards in strength comparable with those observed in the methanol experiments. This might be explained by assuming that the C–C bond is broken first

$$H_3C{-}CH_2{\cdot}OH \longrightarrow CH_4 + CH_2O$$

and that the formaldehyde then decomposes further while the methane is pyrolysed. Continuous absorption, however, began at a somewhat lower temperature than in the experiments with methane and was more in accord with that of ethane. Formation of ethane through a bimolecular reaction such as $2H_3C{\cdot}CH_2{\cdot}OH \longrightarrow C_2H_6 + 2CH_2O + H_2$ may explain the similarity.

In Fig. 5 the wave-length at which strong absorption began for each hydrocarbon has been plotted against the temperature of pyrolysis. The curves are of course relative and depend, *inter alia*, on the intensity of the light source. The latter was kept constant and the same lamp was used for all experiments. The curves indicate the thermal stability of the various substances, but the reason for the different shapes is unknown and benzene is clearly very different from the others.

Another important observation in these experiments was the absence of characteristic aromatic absorption bands during the pyrolysis of ethylene or acetylene. Since some aromatic compounds are readily formed and can be isolated in the products after pyrolysis it seems clear that their formation from olefins or acetylenes is not a straightforward process.

Absorption Spectra of Diffusion Flames.—Since there may be some theoretical objection to considering the pre-flame reactions in diffusion flames as purely thermal processes, the results of the pyrolysis experiments were compared with similar spectroscopic measurements in a diffusion flame. In order to do this a large fish-tail burner, 10 cm. long and 1·3 cm. wide, was placed with its length along the axis of an optical system. Light from a hydrogen discharge lamp passed over the top of the burner and lengthwise through the tunnel formed by the inclined sides of a flame on this burner and was brought to a focus on the slit of the spectrograph by means of a quartz–fluorite achromatic lens. An end view of the burner and flame is shown in Fig. 6 and the portion focussed in the slit is indicated by the dotted rectangle. A uniform flame was obtained by filling the burner with glass beads which smoothed the gas flow and flickering was avoided by placing the burner in a channel between two bricks.

With this arrangement absorption measurements included the long gas tunnel under the luminous mantle of the flame together with the two luminous layers at each end. The absorption due to the end layers could be estimated by turning the burner through 90° and measuring the absorption of two similar luminous layers and a relatively short gas space. With an acetylene or a benzene diffusion flame (in which the burner was kept at a temperature above the b. p. of benzene) it was observed with the naked eye that, just before reaching the luminous zone, the gases absorbed all visible light from the hydrogen lamp and a dark layer was visible under the luminous zone.

Fig. 7*b* shows a spectrum of the H_2 continuum partly absorbed in the acetylene flame. As indicated in Fig. 6 the lower part of the spectrum coincides with the base of the flame. There is very little absorption at this point but on proceeding up the flame, *i.e.*, also up the spectrogram, the absorption increases from the short-wave into the ultra-violet and finally reaches the visible region. The overall effect is a wedge-shaped spectrogram caused by increasing absorption by the gas from the top of the burner to the reaction zone. Other gases behaved similarly, especially ethylene. Methane and ethane gave rather tall flames which were difficult to keep steady with the apparatus used, but sufficient evidence was obtained from them to confirm the result. Since the temperature of the gases increases from the burner to the reaction zone the effect observed is probably directly comparable with the absorption effect on pyrolysis, and substantially the same processes occur.

DISCUSSION.

The principal results of our experiments can be summarised as follows:

(*a*) A diffusion flame can probably exist at any pressure provided that conditions of burner size and mass flow are suitably adjusted, but carbon formation in the flame depends markedly on pressure.

(*b*) Carbon deposits on the mouth of the burner, which formed very rapidly under certain conditions, were of a hard vitreous type, different from soot particles collected from the luminous zone of the flame.

(*c*) Carbon particles in the luminous zone of a non-smoky flame are uniform in size and do not grow in the luminous zone.

(*d*) The absorption spectra of hydrocarbons undergoing pyrolysis show an increasing continuous absorption spreading from the far ultra-violet and towards the visible region as the temperature of pyrolysis is raised. The relative temperatures at which this occurs for different hydrocarbons are in agreement with their known thermal stabilities. Similar effects were observed with ethyl alcohol but methyl alcohol behaved differently.

(*e*) Measurements in the pre-heating zone of a diffusion flame revealed similar absorption effects which increased from the burner mouth to the top of the zone.

(*f*) Measurements of absorption in a benzene diffusion flame on a Hefner candle indicated that the benzene bands disappeared a short distance above the wick and before the vapour reached the luminous zone of the flame. No other bands appeared in their place.

The similarity between the observed changes in absorption spectra of hydrocarbons in the pre-heating zone of a flame and those during pyrolysis supports the view that pyrolysis is an essential factor in combustion processes of diffusion flames.

There is a marked difference in the conditions under which carbon formation occurs in pre-mixed flames (*e.g.*, a Bunsen flame) and in diffusion flames. Although the latter are more important for the purpose of this investigation, pre-mixed flames have been more fully studied in the past (Klaukens and Wolfhard, *Proc. Roy. Soc.*, 1948, *A*, **193**, 512; Gaydon and Wolfhard, *ibid.*, 1948, *A*, **194**, 169). The truly pre-mixed flame which will be considered is the inner cone of the Bunsen flame. The velocity of the pre-mixed fresh gas is much greater than that of the gas in the diffusion flame. The hydrocarbon fuel molecules are subject to a high temperature for a shorter time and the degree of decomposition before oxidation may be less. The fuel molecules are also in intimate contact with oxygen, whereas in diffusion flames, or at least in the core of a diffusion flame where carbon formation is strongest, the fuel molecules are first heated and later diffuse into a region of oxygen. The presence of a reaction zone around the diffusion flame acts as a barrier to the oxygen (Wolfhard and Parker, *Proc. Physical Soc.*, *loc. cit.*, and unpublished work). The presence of oxygen may have in some cases a profound effect on carbon formation and retard it.

The flame front in the region of the inner cone of a pre-mixed flame can be dvided into two parts : (1) a pre-heating zone where no appreciable exothermic reaction occurs, and (2) a reaction zone characterised by light emission due mainly to C_2, CH, and OH bands. The reaction which is exothermic begins at about 800° for acetylene–oxygen and acetylene–air flames (Klaukens and Wolfhard, *loc. cit.*). Most hydrocarbons, however, undergo pyrolysis at a lower temperature and the fuel molecules probably undergo a certain amount of change before the exothermic reaction with oxygen begins, and the first steps in carbon formation may also occur before this. It should be stressed that the contact time for the thermal reaction is much shorter than in the corresponding diffusion flame.

Mention has been made of the presence of C_2 molecules in the inner cone, but the way in which they are formed is not understood. Since they generally occur very early in the zone they may be formed by pyrolysis, being actually produced before the main reaction with the oxygen molecules occurs. In fuel-rich flames the C_2 radiation is greater and, since carbon formation also increases, it has been suggested that condensation of the C_2 molecules is responsible (Smith, *loc. cit.*). At first sight this theory is attractive since the condensation process is strongly exothermic and will certainly occur if sufficient C_2 molecules are present. The number of C_2 molecules is probably very small, however, as indicated by the very low absorption coefficient in a pre-mixed acetylene–oxygen flame ($0 \pm 2\%$ abs.; Wolfhard, *Z. Physik*, 1939, **112**, 107) despite the normal transition probability measured by Brewer *et al.* (*J. Chem. Physics*, 1948, **16**, 797). Moreover, the fact that the C_2 disappears from the reaction zone earlier than CH and other intermediate molecules identified spectroscopically (Gaydon and Wolfhard, Faraday Soc. Discussion, 1947, **2**, 161) suggests that the C_2 molecule is very reactive and has little chance to survive and condense. Experimental results with a flat diffusion flame which has an absorbing layer of 5 cm. at atmospheric pressure (Wolfhard and Parker, *Proc. Physical Soc.*, *loc. cit.*) support this argument. It was impossible to detect any C_2 absorption in flames of methane or coal gas with air or oxygen, only some weak C_2 band in emission located on the oxygen side of the luminous carbon region. The location of these bands strongly suggests that carbon formation does not depend on the existence of C_2 molecules. In view of these objections it seems unprofitable to attempt to interpret our results by this theory.

It has been suggested that the formation of benzene rings and polycyclic structures precedes the formation of carbon. Rummel and Veh (*loc. cit.*) postulate that the hydrocarbon undergoes pyrolysis in the flame with the formation of large polycyclic intermediate molecules which suffer dehydrogenation and finally condense as solid carbon residues. The graphitic structure of carbon particles resembles the molecular structure of the benzene ring, or more exactly that of its polycyclic homologues. Thus, if one benzene ring becomes attached to the next or if side chains on a benzene nucleus link up to give naphthenic and aromatic structures, and this process is repeated, one plane of the graphite structure is formed. By adding one plane to another and eliminating the hydrogen atoms between them, a particle of the kind found in a flame might be formed. This attractive theory is apparently supported by observations such as the greater tendency for aromatic fuels to smoke, and by the results of pyrolysis in which benzene and its homologues are formed by heat treatment of olefins and nearly every kind of hydrocarbon.

The absorption spectra which were obtained from the lower part of the benzene flame in experiments with a Hefner candle do not appear to support this theory. The flame was approximately double the height of the slit on the spectrograph and from the benzene absorption bands which disappear in the vertical direction it is concluded that the benzene is consumed in the lowest part of the flame. More important, however, is that no other absorption appears. Naphthalene, anthracene, etc., have molar absorption coefficients (measured in solutions) as great as that of benzene, and these absorption bands lie in the most convenient part of the spectrum. Hence it must be concluded that naphthalene, anthracene, etc., are absent. Their absence at this point is believed to be evidence against Rummel and Veh's hypothesis. The benzene flame from a Hefner candle is hollow and carbon formation occurs only in the cylindrical layer. There is an appreciable gap between the early disappearance of the benzene and the appearance of the carbon particles, yet none of these aromatic intermediate products which should absorb so strongly is found in this gap.

It is true, of course, that the Hefner candle burning benzene is much more sooty than it is with amyl acetate or a paraffin, and the tendency for aromatic fuels to give coking troubles in combustion chambers is well known, but this is not necessarily evidence for the aromatic-ring-building theory of carbon formation. The tendency to smoke as measured in the soot lamp is actually smaller for the homologues of benzene than for benzene itself.

In pyrolysis of hydrocarbons, carbon and hydrogen are always the end products if the temperature and contact time are sufficiently great but there is no real evidence on the individual step leading to the deposition of carbon. Typical results with the simpler hydrocarbons are those of Tropsch and Egloff (Ellis, " The Chemistry of Petroleum Derivatives," Vol. II, 1937) for the pyrolysis of propane, ethane, and *n*-butane at 1100—1400° and 50 mm. pressure, in which the products are either hydrocarbons of fairly low molecular weight, such as ethylene, acetylene, and propylene, or carbon but nothing between. It is, however, certain that carbon particles of 100-A. diameter cannot be formed from these hydrocarbons in a single step and it is pertinent to ask whether there is any evidence of an intermediate product.

Before pursuing the question of an intermediate we shall discuss the nature of the carbon particles which form the end products. Hofmann and Dietrich (*Z. Elektrochem.*, 1936, **42**, 504) compared the breadth of the *X*-ray lines of various soot and carbon particles with the natural width of the lines on the *X*-ray diagram of Ceylon graphite. In this way it was possible to calculate the dimensions of the crystallites in the material. The height of the crystallites in soot from acetylene was 13 A. and the length was 21 A. Hence the carbon particles which were examined in this investigation and which had an irregular shape with an overall diameter of about 100—500 A. are probably not single crystals but are aggregates of many smaller crystals.

Hofmann and Dietrich also showed that the lattice constants are different : in Ceylon graphite $a = 4{\cdot}25$ and $c = 6{\cdot}69$ A., whereas in acetylenic soot the values are 4·21 and 7·1 A., respectively. The lattice is therefore deformed in soot, perhaps by residual hydrogen (usually about 1% by wt.) which is somehow attached and presumably located between the planes of the graphite. These planes still seem to be parallel in soot particles, as in graphite, but situated one on top of the other at random. Hofmann and Dietrich assume that the graphitising of any solid organic material such as a sugar at 1000° proceeds as follows : Nuclei of graphite are formed and the graphite crystallites grow from these nuclei by absorbing the surrounding material. The size of the final crystallite is given by the number of original nuclei. Below 1400° there is no further increase in size, but above that temperature aggregation occurs and the crystallites grow at the expense of each other. The last process is probably very slow and may not ordinarily occur to carbon particles in flames.

We believe that we may have observed a graphitising process of this kind in a liquid droplet during the pyrolysis of methane at high temperature. Liquid droplets in the mist which formed in the exit tube passed through the flame at the outlet and in doing so changed rapidly into a luminous streak and a soot particle. Complete vaporisation of the droplets probably did not occur.

The carbon particles which we collected from a non-smoky diffusion flame were approximately 100 A. in diameter and very uniform in size over the whole of the luminous zone. Although the particles are probably aggregates of small crystals, it seems fairly certain that they do not grow in the luminous zone in spite of the collisions which they undergo through Brownian motion. If these graphite particles do not grow after entering the luminous zone and their formation is through a graphitising process similar to that suggested by Hofmann and Dietrich, then the material from which they form must be of similar size, *viz.*, 100 A. Thus two possibilities arise : either (*a*) the material is all in the gas phase and the pregraphite particles are truly large molecules, or (*b*) the material is in the form of fine droplets which subsequently graphitise. Condensation of higher hydrocarbons of extremely low volatility may occur locally, even at elevated temperatures, if their saturation vapour pressure is reached.

An alternative explanation might be that some nuclei of carbon are formed spontaneously and that these grow by a surface reaction with the gaseous fuel molecules which come into contact with them. This is analogous with the way in which carbon is deposited on hot surfaces in contact with hydrocarbon gases, the carbon initially formed seeming to catalyse the reaction which leads to further deposition. Carbon formed in this way has a different structure, however, and is of a vitreous type with an *X*-ray pattern more closely resembling that of diamond. The structure of soot particles is definitely graphitic and this important difference seems to rule out this alternative mode of formation.

We may now consider whether the absorption experiments have any bearing on carbon formation. We believe that they have, partly because a rapid spread of the absorption accompanied the onset of stronger luminosity in the diffusion flame at the outlet, and partly on account of the different behaviour of methyl alcohol. On pyrolysis methyl alcohol decomposed and formaldehyde was among the products, but the diffusion flame at the outlet remained non-luminous even at high temperature. No continuous absorption was observed comparable with that of the hydrocarbons. All lower hydrocarbons are transparent in the visible and ultra-violet regions and do not begin to absorb strongly above 2000 A. Recent data collected by Sponer and Teller (*Rev. Modern Physics*, 1941, **13**, 75) show that information about the gaseous state of higher hydrocarbons is very limited. Unsaturated 2 : 3-dimethylbut-2-ene shows the greatest shift in the ultra-violet region and absorption begins at 2300 A. With triple-bonded compounds the effect is more marked : acetylene has a banded spectrum reaching 2400 A. but a long optical path is necessary to observe it. The absorption of vinylacetylene (but-1-en-3-yne) reaches up to 2553 A. and is also banded. Aromatic compounds absorb strongly in the ultra-violet region but have characteristic bands. Similarly, poly-unsaturated compounds such as conjugated polyenes and the cyanine dyes have banded spectra. The bands progress from the ultra-violet towards the visible region as the number of double bonds increases, but even a mixture of such compounds would not show an absorption which could be mistaken for a continuum. In short it is impossible to relate the experimental results to existing data. It might be argued that the effect is caused by carbon particles or liquid droplets which absorb preferentially in the ultra-violet region. This, however, is very unlikely because the observed cut off is complete. Moreover, the absorption begins to spread at relatively low temperatures, at which the amount of carbon formed is negligible. We suggest that the absorption is due either to higher hydrocarbons in the gas phase which increase in molecular size as the temperature is raised, or to unstable intermediate compounds which have not been isolated. Small quantities of light oils are known to be produced during pyrolysis, this being direct evidence of the formation of higher hydrocarbons, but the possibility of an unstable intermediate cannot be eliminated. Unsaturated compounds, such as olefins and acetylene, which are present during the pyrolysis of any hydrocarbon may form temporary molecular associations under transient conditions. Moreover, an unstable intermediate might have continuous absorption because of the loose character of the bonds.

Tentatively we suggest that carbon formation in the flame occurs by one of the following two processes : (1) Higher hydrocarbons are formed by pyrolysis. The molecular weight and concentration of these increase until the saturation vapour pressure is exceeded, whereupon condensation occurs and fine droplets are formed. These droplets contain nuclei of graphite, and graphite crystallites grow in the manner described by Hofmann and Dietrich (*loc. cit.*) until each droplet is converted into carbon and hydrogen is largely eliminated. Since the droplets are moving in an increasing temperature gradient the process of graphitising must be more rapid than that of re-evaporation of the droplet.

(2) During pyrolysis of the hydrocarbon large unstable molecules are formed which tend to decompose again into their original material. If conditions are favourable, however, very large molecules may be formed which graphitise on entering a region of sufficiently high temperature. The graphitisation process is again similar to that proposed by Hofmann and Dietrich and depends on the spontaneous formation of carbon nuclei within the molecule. Each nucleus grows into a graphite crystallite until it meets the next crystallite growing from an adjacent nucleus inside the same molecule. The hydrogen atoms are freed and escape from the graphite structure.

Either process provides an explanation of the limited experimental evidence.

So far it has not been possible to offer any explanation of the results which were obtained with diffusion flames at low pressure, but these results will now be considered on the basis of the above theory. Data on pre-mixed flames indicate that each fuel molecule undergoes the same probable number of collisions to complete its reaction, whatever the total pressure. Similar data on diffusion flames are lacking, but it was found that at low pressures larger burners were again necessary and the flame was thereby enlarged. If the same processes are assumed to apply as in the pre-mixed flame, the decrease in the number of bimolecular collisions per second at the lower pressure is counterbalanced by the increased time available in the enlarged zone of the flame. Hence a low pressure limit seems unlikely for the diffusion flame as well as for the pre-mixed flame. Nothing in the experimental results contradicts this, as far as observations on the pale blue reaction zone is concerned, but there definitely is a marked decrease in carbon formation as indicated by the extinction of the luminous zone at low pressure. Now, if we assume that condensation of higher hydrocarbons precedes carbon formation, a low-pressure limit is readily explained since the partial pressure of these substances will eventually fall below the saturation vapour pressure. If, however, we admit the existence of unstable intermediates which are supposed to be responsible for carbon formation, there must be a pressure limit at which the life time of the unstable molecule approaches the interval between collisions and the molecule has a greater chance of decomposing than of being built up by a subsequent collision. As the pressure is reduced, therefore, the formation of large unstable molecules and consequently of carbon would be retarded and eventually stopped.

Another observation, from the investigation of diffusion flames at reduced pressure, also seems capable of explanation in this way. The height of the diffusion flame should be independent of the pressure (for constant mass flow), but it was observed that the acetylene–air diffusion flame changed rather suddenly with pressure and the luminous zone opened out abruptly into an enlarged hollow cylinder (see Fig. 2*d*). Combustion below the strongly luminous rim takes place through interdiffusion of the acetylene molecules and the outside air or oxygen. This diffusion process is not seriously affected by the presence of bigger particles. Carbon dioxide, carbon monoxide, water, and other reaction products, which in a normal flame diffuse towards the centre, will be present in this enlarged flame. The acetylene molecules also diffuse freely and must have diffused away completely at a distance above the burner mouth equal to the height of a normal flame. If large fuel molecules have commenced to form low down they may be restricted from diffusing outside on account of the smaller diffusion coefficient relative to their size. Above the normal flame height, therefore, the central core of hot gases contains only carbon dioxide, carbon monoxide, water, and enlarged fuel molecules. The latter eventually lead to carbon formation.

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