

XVI.—*Note on the Structure of Luminous Flames.*

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THE following are extracts from Davy's book "On the Safety Lamp for Coal Miners, with some Researches on Flame" (1818), a reprint of his papers in the Philosophical Transactions and elsewhere.

(1.) "Flame must be considered as the combustion of an *explosive mixture* of inflammable gas or vapour and air, for it cannot be regarded as a mere combustion at the surface of contact of the inflammable matter, and the fact is proved by holding a taper or a piece of burning phosphorus within a large flame made by the combustion of alcohol, the flame of the candle or of the phosphorus will appear in the centre of the other flame, proving that there is oxygen even in its interior part.

(2.) "The form of flame is conical, because the greatest heat is in the centre of the explosive mixture. In looking steadfastly at flame, the part where combustible matter is volatilised is seen, and it appears dark, contrasted with the part in which it begins to burn, that is where it is so mixed with air as to become explosive. The heat diminishes towards the top of the flame, because in this part the quantity of oxygen is least.

(3.) "The luminosity of flames is due to 'the decomposition of part of the gas towards the interior of the flame where the air is in smallest quantity and the deposition of *solid charcoal*, which, first by its *ignition* and then by its *combustion*, increases in a high degree the intensity of the light.'

(4.) "At the bottom part of the flame where the gas burned blue in its immediate contact with the atmosphere, charcoal ceased to be deposited in visible quantities."

The above extracts contain the essence of all that Davy contributed to the subject of luminous flames so far as their structure is concerned.

The description of an ordinary luminous flame as consisting of the four parts now generally recognised, appears to have been first given by Berzelius. In the English edition (1822) of his work on "The Use of the Blowpipe" (p. 22), the following description occurs:—If we attentively consider the flame of a candle, we may remark several unequal divisions of it, of which four may be distinguished. We see at its base a small part of a dark-blue colour, which becomes thinner as it gets farther from the wick, and disappears entirely where the external surface of the flame ascends perpendicularly. In the middle

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of the flame is a dark place seen through its brilliant covering. This space encloses the gases which issue from the wick, which, not being yet in contact with the air, cannot undergo combustion. Round this space is the brilliant part of the flame, properly so called, and, lastly, beyond this we may perceive, by attentive inspection, the outer covering of all, slightly luminous, and whose greatest thickness corresponds with the summit of the brilliant flame. It is in this outer part that the combustion of gases is completed and the heat the most intense.

In a striking paper by D. Waldie (*Phil. Mag.*, 1838, **13**, 88), a description very like the above is to be found, but the author recognises a fifth area, namely, an area of unburned carbon. This seems to have been nothing more than the lurid and smoky tip of flame, which, in the days of tallow candles and straight wicks, was, perhaps, worthy of distinction.

In 1847, Volger published (*Pogg. Ann.*, 1847, 72—82) a highly speculative account of a candle flame, in which he distinguishes no less than six parts. It is, perhaps, unnecessary to discuss these views; they were never generally accepted, and rest upon assumptions which in many cases are obviously untenable.

I am not aware that anyone, since the last-named date, has deliberately put forward new views on the actual *structure* of flame, and it may be taken as a matter of general belief that there really are four regions in what is ordinarily called a luminous flame. For convenience we will name them according to their appearance, the dark region, the yellow region, the blue region, the faintly luminous region. These are shown in Fig 1.

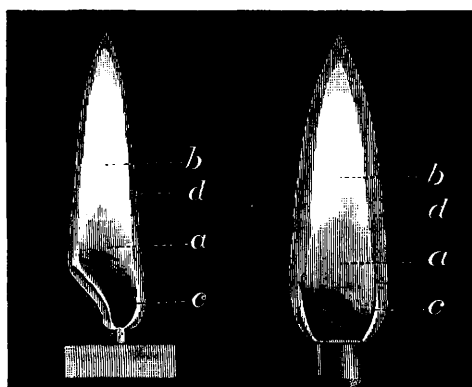


FIG. 1.—Sketches to scale of candle flame and small gas flame: *a*, dark region; *b*, yellow region; *c*, blue region; *d*, faintly-luminous region.

Whilst there has been general agreement as to the number of distinct parts in a luminous flame, there has been from time to time considerable difference of opinion as to the causes, whether chemical or otherwise, which give rise to or define them, and I will now give a brief summary of the views which have been held regarding each of the four parts of the flame.

The Dark Region or Zone of Unburned Gases.

All observers agree in regarding this as due to combustible gas in which no combustion is taking place. The fact that no combustion takes place in this part of a flame, or, in other words, that flames are hollow, was noticed by Francis Bacon.*

Hilgard, in 1854 (*Liebig's Annalen*, **92**, 129), showed that in a candle flame this region also contained nitrogen and products of combustion. He found in the lower parts 66 per cent. of nitrogen, 10 per cent. of carbon dioxide, 5 per cent. of carbon monoxide, 6 per cent. of water, and no free oxygen. The rest was combustible gas.

Landolt (*Pogg. Ann.*, **99**, 389) obtained similar results with a coal-gas flame, but found also a very small quantity of free oxygen in the lowest parts.

The Yellow Region.

Davy's explanation of the luminosity of ordinary flames has already been quoted (the exact wording should be carefully noticed), and this explanation, together with the general doctrine that the luminosity of flames is due to incandescent, solid particles, was not questioned until 1868, when Frankland showed (*Proc. Roy. Soc.*, **16**, 419) that flames containing only gaseous matter, for example, that of hydrogen in oxygen, could be made luminous by compression. Frankland also concluded that the luminosity of ordinary flames was due not to solid particles of carbon but to the incandescent vapour of dense hydrocarbons. This latter view was combated by several chemists, amongst whom Heumann is chiefly to be mentioned. In 1876, Heumann brought forward (*Liebig's Annalen*, **181**, 129 **182**, 1; or *Phil. Mag.*

* "Take an arrow and hold it in flame for the space of ten pulses, and when it cometh forth you shall find those parts of the arrow which were on the outsides of the flame more burned blacked and turned almost into a coale; whereas that in the midst of the flame will be as if the fire had scarce touched it. This is an instance of great consequence for the discovery of the nature of flame, and sheweth manifestly that flame burneth more violently towards the sides than in the midst; and which is more, that heat or fire is not violent or furious but where it is checked and pent."—*Sylva Sylvarum or a Naturall History in Ten Centuries*. By Francis Bacon. 6th Ed. (1615), p. 9.

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[5], 3 (1877), 1, 89, 366) a number of experiments and arguments in confirmation of Davy's view that the separation of solid carbon is the cause of the luminosity of ordinary flames. I am not aware that Heumann's conclusions on this point have ever been contested; they have, indeed, been confirmed by independent methods of experiment (see Soret, *Phil. Mag.*, 1875, 50; Burch, *Nature*, 31, 272; Stokes, *ibid.*, 45, 133).

The cause of the separation of carbon is another question. According to Davy it is due to the *decomposition* of the hydrocarbons within the flame, and though he adds the words "where the air is in smallest quantity," it is not explicitly stated that the decomposition is due to anything but the heat alone. No mention of any other cause is made by Berzelius, Waldie, Hilgard, Landolt, or any other author that I have been able to consult, so far as original memoirs are concerned. But prior to 1860 a view had become current that the separation of carbon in a luminous flame was due to the preferential burning of the hydrogen. There not being enough oxygen in the luminous region of a flame for the complete combustion of the hydrocarbons, it was inferred that the hydrogen, being the more inflammable element, burned first and so liberated the carbon. I have so far been unable to trace this doctrine to its source. It may have been an inference from Davy's words, but can scarcely be justified by them. He says nothing whatever as to what happens to the hydrogen when carbon is separated in a flame. Not only was this view generally maintained at the time alluded to, it survives at the present day and, as I can vouch from personal enquiries, it is still widely taught.

The doctrine in question was challenged in 1861 by Kersten (*J. pr. Chem.* 84, 290), who pointed out that there was no *a priori* reason for believing hydrogen to be more combustible than carbon. He points out that whilst previous admixture with chlorine increases the luminosity of a methane flame by virtue of the superior affinity of chlorine for hydrogen, previous admixture with oxygen has the reverse effect. Again, a mixture of 1 volume of methane and 2 of carbon monoxide burns with a non-luminous flame, although it contains only enough oxygen for complete combustion of the hydrogen:— $\text{CH}_4 + 2\text{CO} = 2\text{H}_2\text{O} + 3\text{C}$; or again, the amount of oxygen necessary to produce a non-luminous coal-gas flame in a Bunsen burner is only one-third of the quantity necessary for complete combustion. Kersten remarks, as it appears to me, very justly, that the experiments of Hilgard and Landolt, in which gases were aspirated from luminous flames and then analysed, do not give any definite information as to the main chemical changes occurring in luminous flames. By the methods used by these investigators it is impossible to explore the luminous part of the flame, owing to the stopping up

of the aspirating tube by carbon; nor can any precise information be gained as to the changes taking place in the external layer of the flame, owing to its movement and the infiltration of gases from within and without this layer. Kersten was accordingly led to make experiments on the explosion of hydrocarbons with quantities of oxygen insufficient for complete combustion, and (as mentioned in the preceding paper) he obtained results directly opposed to the view that the hydrogen burns preferentially to the carbon. He concluded, therefore, that the separation of carbon in a flame was due simply to the decomposition of the hydrocarbons by heat.

I have not met with any explicit contradiction of Kersten's views, but they seem to have been neglected to a remarkable extent by subsequent writers.

The *glow* of the carbon in the yellow region is due to the heat of its own combustion, and is increased probably by the concomitant combustion of hydrogen. The view occasionally met with, that the carbon is glowing only by the heat of the burning hydrogen, is manifestly erroneous. The carbon is in the solid state, and must either undergo the usual glowing combustion, or else escape from the flame unburned. As it does not do the latter to any appreciable extent, it must burn, and the cessation of its combustion as a solid marks the limit of the yellow or luminous region of the flame.

The Blue Region.

The blue region has been unanimously regarded as a part of the flame where the hydrocarbons are mixed with sufficient air to cause immediate combustion without the separation of carbon.

The Faintly Luminous Region or Mantle.

This part of the flame was not referred to by Davy as distinct from the blue region. Berzelius describes it, and states that "it is in this outer part that the combustion of the gases is completed and the heat the most intense." Waldie states that it consists of "the proper combustible mixture," and is the hottest part of the flame, and that to its heat is to be attributed the separation of the carbon within the flame.

No intelligible distinction appears to have been made between this region and the blue one until 1861, when Kersten published the paper already referred to, and even his description is not easy to grasp. He appears to have regarded the faintly luminous region as the place in which hydrogen and carbon monoxide coming from the yellow region undergo combustion, ignoring the fact that it surrounds not only the yellow region, but the blue one as well.

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I have only met with one other attempt to explain this part of a luminous flame as distinct from the blue portion, and have not been able to trace it beyond the text-books. It ascribes this faintly luminous region to products of combustion (carbon dioxide and water) mixed with air and raised to feeble incandescence, that is, it is not a region of chemical action at all. If for no other reason, this explanation could scarcely be maintained in face of the observations made by Siemens (*Ann. Phys. Chem.*, **18**, 311), that such products of combustion have not perceptible luminosity at 1500° .

Having thus summarised the views hitherto held regarding the parts of a luminous flame, I will now submit the matter to a brief discussion from a different point of view.

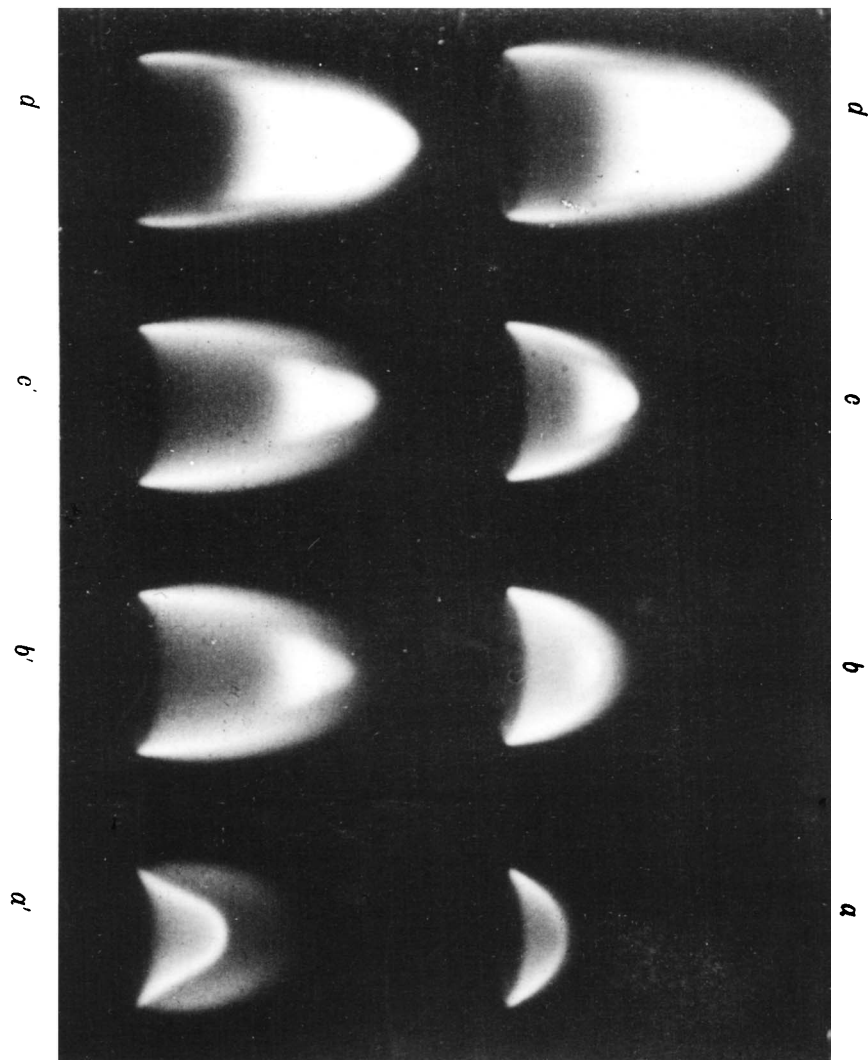
The best way to study flame structure seems to me to consist in tracing the development of the flame. By using a very small quantity of combustible, that is to say, in the case of gases, by almost turning off the tap, and, in the case of solids and liquids, by having a very close cropped wick, we obtain a tiny flame which is ordinarily called non-luminous. It has the appearance represented in Plate II, *a*, and consists of a hollow, bright-blue cone, surrounded by a lilac-coloured border. If more gas be turned on, or if the wick becomes longer, a luminous spot is developed in the flame, as shown in Plate II, *b*. This spot is at first a small fraction of the whole flame, but as the supply of combustible is increased it rapidly extends, as shown in Plate II, *c* and *d*, the original inner cone becomes a "vestige," and forms, in fact, the blue region. Still the original formation is evident, the luminous spot being indented at points corresponding to it.

The question now arises, is the non-luminous flame *a* a single or a double cone, and, in any case, what chemical changes are taking place in it?

I think an answer to this question may be obtained by carefully watching the change undergone by a luminous flame when air is gradually added to the gas prior to combustion. For this purpose a small flame from a Bunsen burner, with the air-holes at first closed, may be employed. If attention be fixed on the blue and on the faintly luminous regions of the flame, and the air-holes be now slowly opened, the flame loses luminosity, and the two regions grow more distinct, and ultimately become, without any perceptible break of continuity in the process, the inner and outer cones of the ordinary Bunsen flame.

These changes are shown in Plate II, taken from photographs; *a*, *b*, *c*, and *d* show the gradual development of a luminous flame as the gas is turned on. The blue region of the flame appears white, but it is easily distinguishable from the yellow region which also appears white. The lilac or faintly luminous region is barely visible

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in the pictures, as it has very low photographic power. c' , b' , a' represent the flame d with gradually increasing quantities of air admitted through the air valves, the gas supply being kept constant. The structure of c and c' , b and b' , a and a' obviously corresponds. In a' the outer cone has just impressed an image on the photographic plate.*

If the conclusion be admitted that the blue and the faintly luminous regions of an ordinary flame correspond to the inner and outer cones of a Bunsen flame, then, in accordance with the results detailed in the preceding paper, we must consider the blue region to mark *incomplete* combustion (CO , H_2 , CO_2 , and H_2O being the chief substances there originating), and the faintly luminous part to mark *completed* combustion (the CO and H_2 above named being burnt to CO_2 and H_2O).

In other words, I conclude that there is no essential difference in kind between an ordinary luminous flame and a so-called "non-luminous" flame. The latter may be regarded as a gas-air flame with the blue and the non-luminous regions at a maximum, and the yellow, luminous region at a minimum, whilst the luminous flame is to be regarded as a gas-air flame with the blue and the non-luminous parts at a minimum and the yellow luminous region at a maximum.

As it has been repeatedly shown that the dark, central part of a luminous flame is a region of no combustion, there only remains now one question for solution—how is the carbon separated in the yellow, luminous region? It would seem scarcely necessary after a perusal of Kersten's paper (*loc. cit.*) to argue this point at any length. The doctrine that the hydrogen of a hydrocarbon burns before the carbon when the supply of oxygen is limited is not borne out by any experiments of which I am aware, with the possible exception of those of Berthelot and Vieille (*Compt. rend.*, **98**, 705—711; this Journal, Abstr., 1884, 804). From the fact that the velocity of explosion of hydrocarbons rich in hydrogen approximates to that of hydrogen itself, they conclude that the hydrogen burns before the carbon. The experiments of Dalton, Kersten, E. von Meyer, and those recorded in the preceding paper, all point to exactly the opposite conclusion, namely, that the carbon burns preferentially to the hydrogen. If this conclusion is accepted, we can only explain the separation of carbon in a luminous flame as due to a *decomposition by heat*, whereby a given hydrocarbon is split up into carbon and hydrogen or carbon and some more richly hydrogenised hydrocarbons. Hydrocarbons are well known to undergo such decompositions when passed through hot tubes.

* I am largely indebted to the skill and patience of Mr. Herbert Ingle for these photographs, as well as for those used in the preceding paper.

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A very simple experiment, which seems sufficient to prove the truth of this view, is made by introducing a circular loop of thin wire into any small gas flame in which the luminous part is only slightly developed. The immediate result is that the luminous part disappears and the flame presents the simple structure of a non-luminous flame, at the same time becoming slightly larger. This change is represented in Fig. 2.

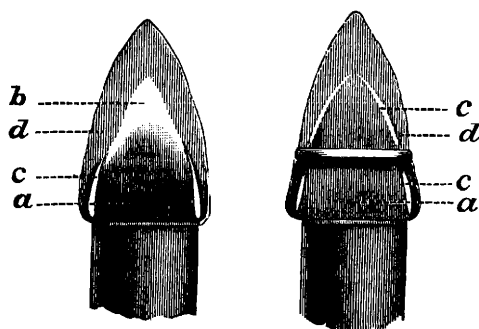


FIG. 2.—*a*, the dark region; *b*, the yellow region; *c*, the blue region; *d*, the faintly luminous region.

Now if the flame is luminous because, the hydrocarbons in the middle being short of oxygen, the hydrogen burns first, the intrusion of the wire will block out and still further limit the supply of oxygen, and so either increase the area of luminosity or cause the escape of unburned carbon.

If, on the other hand, the luminosity is due to the heat of the external perfectly burned layers decomposing the hydrocarbons, then the intrusion of the wire by tapping the heat should diminish the luminosity, and the hydrocarbons which previously gave light should pass on until they obtain enough oxygen to burn as those hydrocarbons on the exterior of the flame. The flame, therefore, would become larger and non-luminous. This is exactly what happens in the experiment.

The above experiment only holds good if the wire conducts heat away at a certain rate. If the flame be relatively large, the introduction of the wire may produce an opposite effect, for, whilst checking the separation of carbon (to an appreciable extent), it will also cool down the carbon which is separated, and so cause some of it to escape unburned as smoke.

A problem remaining to be studied concerns the exact course of the decomposition of the hydrocarbon in the flame, and the only method available seems to be the one alluded to in the preceding paper.

By taking an ethylene-air flame, and separating the cones before the luminosity has entirely disappeared, an examination of the interconal gases under these conditions will disclose what is being produced along with the separated carbon, and in this way I hope to trace the course of the decomposition. As the matter rests at present, the development of a luminous hydrocarbon flame may be described as follows:—

The hydrocarbon issues from the burner or wick, let us suppose, as a cylindrical column. This column is not sharply marked off from the air, but is so penetrated by the latter that we must suppose a gradual transition from the pure hydrocarbon in the centre of the column to the pure air on the outside. Let us take a thin, transverse slice of the flame, near the lower part of the wick or close to the burner. At what lateral distance from the centre will combustion begin? Clearly where enough oxygen has penetrated the column to give such partial combustion as takes place in the inner cone of a Bunsen burner. This, then, defines the *blue region*. Outside this, the combustion of the carbon monoxide, hydrogen, and any hydrocarbons which pass from the blue region takes place, and constitutes the *faintly luminous region*. These two layers form a sheath of active combustion, surrounding and intensely heating the hydrocarbons in the central parts of the column. These heated hydrocarbons rise, and are heated to a higher temperature as they ascend. They are accordingly decomposed with the separation of carbon in the higher parts of the flame, giving us the *yellow region*, but there remains a central core in which neither is there any oxygen for combustion nor a sufficiently high temperature for decomposition. This constitutes the *dark region* of unburned gases. A flame is, however, not cylindrical, but has a conical or (in the case of a candle) an inverted peg-top shape. Again, the blue region only surrounds the lower part of the flame, whilst the faintly luminous part surrounds the whole. The above explanation is, therefore, not quite complete. Let us suppose that the changes have gone on in the small section of the flame exactly as described, and consider how the processes will differ in parts above this section. The central core of unburned gases will pass upwards, and we may treat it as a new cylindrical column which will undergo changes just as the original one, leaving, however, a smaller core of unburned gases, or, in other words, each succeeding section of the flame will be of smaller diameter. This gives us the conical structure of the flame. Again, the higher we go in the flame, the greater proportionally is the amount of separated carbon, for we have not only the heat of laterally outlying combustion to effect decomposition, but also that of the *lower parts* of the flame. The

lower part of a luminous flame is accordingly cooler, and contains less separated carbon than the upper. Now, where the hydrocarbons are cool until admixed with sufficient air for combustion (that is, in the lower parts of the flame), we have every facility for the occurrence of the chemical changes to which the existence of the blue region has been ascribed, and the blue region is here most evident; whereas in the upper parts of the flame, where the quantity of hydrocarbon decomposed (with separation of carbon) by heat is relatively much greater, there is not enough left to form outside the yellow part the mixture to which the blue region of flame is due. The blue region, therefore, rapidly thins off as we ascend the flame. But whether the first combustion taking place within the flame is that of the undecomposed hydrocarbon with limited oxygen, or of the decomposed hydrocarbon with limited oxygen, we may be sure that the products will contain carbon monoxide, and probably hydrogen, and we shall therefore have *all round the flame* a faintly luminous region of completed combustion. In this way, then, we may reasonably account for the existence, position, and relative sizes of the four regions of an ordinary luminous flame.
