XXV.—*The Luminosity of Coal-Gas Flames.*

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IN the autumn of 1890, I gave a course of Cantor lectures on gaseous illuminants, and in connection with these made a considerable number of experiments on the causes of luminosity in flames. Since then I have, from time to time, worked at the subject, and in view of the interest created by Professor Smithells' paper, read before this Society in December, I venture to bring my results before you.

I do not propose to enter into the vexed question of how far carbon particles are essential for luminosity, or under what conditions flames containing dense vapours may become luminous, but will restrict myself to the causes of luminosity in the flame of ordinary coal gas

and similar mixtures of gaseous hydrocarbons with combustible diluents.

The researches of Heumann, Soret, Burch, and the recent observations by Professor Stokes, place beyond question the presence of solid particles in a luminous gas, oil, or candle flame, and the only point on which any doubt still lingers is the kind of decomposition which leads to the liberation of the solid carbon particles.

Many attempts have been made to trace the chemical changes taking place within a flame, by withdrawing the flame gases during combustion, and determining their composition, and analyses made by Landolt (*Ann. Phys. Chem.*, 1856, **99**, 389—417) give a great deal of information about the actions taking place.

I have also made analyses of flame gases in order to trace the variations in quantity of the hydrogen, hydrocarbons, and carbon monoxide present in the centre of the flame at various heights, with the following results:—

	Hydrogen.	Hydrocarbons.		Carbon monoxide.
		Unsaturated.	Saturated.	
Gas in tube	57·08	4·38	33·99	2·63
$\frac{1}{2}$ inch above burner..	52·90	4·00	32·00	3·00
$1\frac{1}{2}$ inch above burner.	12·30	1·53	10·20	3·26
Tip of inner cone....	2·35	1·98	7·80	6·52
Centre of outer cone .	0·13	0·45	0·50	1·51
Escaping unburnt from tip of flame..	nil	nil	0·39	1·18

These figures, as well as those obtained by Landolt, point to the fact that the hydrogen in the gas burns first, and that the saturated hydrocarbons also undergo a rapid diminution in quantity, whilst the unsaturated hydrocarbons only diminish very slowly until the top of the inner non-luminous zone has been reached, after which they quickly disappear in the luminous portion of the flame.

Carbon monoxide, however, increases largely in quantity up to the top of the inner cone, and then rapidly burns away in the luminous zone. This increase of the carbon monoxide during the first part of the combustion has been shown to take place in the Bunsen flame by Dr. Blochmann (*Annalen*, **168**, 295), and has also been observed by Professor Smithells under the conditions existing in his beautiful experiment of burning a flame in two parts.

The fact that the unsaturated hydrocarbons only slowly decrease in the inner zone, and then rapidly disappear in the luminous part of the flame, has naturally suggested the idea that it is to these compounds that the flame owes its luminosity; but, as far as I know, no one has attempted to ascertain whether the unsaturated hydrocarbons

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present at the top of the inner non-luminous zone are of the same character as those found in the coal-gas.

The undoubted presence of acetylene in the products escaping from a cooled flame, and the fact that the incomplete combustion of hydrocarbon gases always gives rise to the formation of this compound, suggested the idea that it might play an important part in the changes taking place in the interior of a flame, and experiments were made to ascertain if any appreciable quantity was formed by the destruction of hydrocarbons in the flame gases.

The coal gas used was that supplied by the South Metropolitan Gas Company, and analyses give as its composition :—

Hydrogen	57·08
*Unsaturated hydrocarbons	4·38
Saturated hydrocarbons	33·99
Carbon monoxide	2·63
Carbon dioxide	0·79
Nitrogen	0·96
Oxygen.....	0·15
Bisulphide of carbon	0·02
	<hr/>
	100·00

* Containing acetylene, 0·035.

And this gas, when burnt in a standard London Argand at the rate of 5 cubic feet per hour, is of an illuminating value which averages 16·3 candle power.

The gas was burned at the end of an open tube and the flame gases were aspirated from the centre of the flame by means of a small platinum tube, 2 mm. in diameter, and were led into a glass bulb-tube, in which the sample for analysis of the total hydrocarbons was collected, and then through two Volhard's absorbing bottles, containing 20 c.c. of concentrated ammoniacal silver nitrate solution. This absorbs the acetylene with formation and precipitation of silver acetylide and silver, owing to the reducing action of the carbon monoxide, two absorbing vessels being quite sufficient to prevent any traces of the gas escaping absorption. The contents of the two bottles were filtered, the precipitate of silver acetylide carefully washed with water, and then treated on the filter very cautiously with dilute hydrochloric acid, until all action ceases. Acetylene is given off, and the precipitate then consists of a mixture of silver chloride and metallic silver. This, after washing, is digested with dilute ammonia, and the ammoniacal solution, after filtration, is then treated with nitric acid to precipitate the chloride, which is weighed in the usual

manner, 1 gram of silver chloride corresponding to 0.09 gram or 87.03 c.c. of acetylene (Winkler).

Acetylene formed during the Incomplete Combustion taking place in the Interior of a Luminous Flame.

	Total unsaturated hydrocarbons.	Acetylene.
Gas in burner	4.38 per cent.	0.035 per cent.
$\frac{1}{2}$ an inch above rim of burner	4.00 "	0.340 "
$1\frac{1}{2}$ inches above rim of burner	1.53 "	0.560 "
Tip of inner cone	1.98 "	1.410 "
Centre of luminous zone.....	0.45 "	0.045 "
Tip of luminous zone.....	nil	nil

Showing that in the interior of the luminous flame the hydrocarbons at once begin to undergo decomposition, giving rise to acetylene, which, by the time the top of the inner non-luminous zone is reached, constitute over 70 per cent. of the unsaturated hydrocarbons present. A small proportion of the other hydrocarbons, however, remains undecomposed, and penetrates into the luminous zone, where it and the acetylene are both decomposed by the higher temperature attained, a carbon is liberated, and this, being for a moment heated to incandescence, gives luminosity to the flame.

An ordinary flat flame was now experimented with, the gases being withdrawn and analysed in the same way as before.

Acetylene formed in the Inner Zone of a Flat Flame from a No. 7 Bray Burner.

Portion of flame.	Total unsaturated hydrocarbon.	Acetylene.	Other unsaturated hydrocarbons.
	Per cent.	Per cent.	Per cent.
$\frac{1}{2}$ an inch from top of burner...	3.565	0.115	3.450
$1\frac{1}{4}$ inches from burner	2.063	1.303	0.760
$1\frac{3}{4}$ " "	1.393	1.133	0.260
$2\frac{1}{4}$ " "	trace	trace	—

Showing that by the time the top of the non-luminous portion of the flame was reached over 81 per cent. of the hydrocarbons present had been converted into acetylene.

The next step was to determine the thermal conditions existing in the flat flame in order to see if they would give any definite information as to the actions taking place.

The beautiful platinum and platinum-rhodium thermo-couple devised by Le Chatelier, and introduced to us by Professor Roberts-Austen, gives a means of measuring the temperatures of flames with ease and comparative accuracy.

I made a small thermo-couple of platinum and 10 per cent. rhodium platinum wire, using it as thin as possible to reduce errors from loss of heat by conduction, and keeping the wires of considerable length to prevent any rise of temperature introducing conflicting currents at the connections with the galvanometer wires; a reflecting galvanometer of low resistance was employed, and sufficient resistance introduced into the circuit to keep the spot of light upon the scale at the highest temperature attained in the flame, and the scale was then graduated for temperature by taking water at 0° and 100° , and checking the higher temperatures by the fusing points of the chlorides of the alkalis and alkaline earths, as determined by Carnelley (*J. Chem. Soc.*, 1876, i, 489).

On mapping out the temperatures existing in a flat flame from a Bray burner consuming 7 cubic feet of gas per hour, it was found that in the inner non-luminous portion the temperature steadily increased from 500° , half an inch from the burner, to 1267° at the commencement of luminosity at the apex, whilst the centre had a temperature of 1014° , rising to 1216° at the luminous edges. In the centre of the luminous portion of the flame the temperature was 1166° , whilst the highest temperature was reached at the top of the flame, which gave 1368° .

These results, I think, help to explain the action taking place in the flame. In the inner non-luminous zone, the hydrocarbons heated up by the combustion of the hydrogen and some of the methane, undergo certain changes, which result in their conversion into acetylene, and this, being an endothermic compound, readily decomposable by heat or detonation into carbon and hydrogen, breaks up when a sufficient temperature is attained; owing, however, to the diluting action of the nitrogen and other flame gases, this does not take place until the top of the non-luminous zone is reached, where, at a temperature of a little over 1000° , the decomposition occurs with an increase of temperature, and the liberated carbon, being heated to incandescence, gives the luminosity to the flame.

Other luminous hydrocarbon flames were then tried, and the percentage of acetylene formed in the inner zone determined.

	Oil gas of 30 candle power.	Paraffin lamp.	Candle.
Acetylene	3.09 per cent.	2.222 per cent.	2.163 per cent.

I have made attempts to trace the actions which give rise to the

acetylene, and to see if the carbon monoxide, which increases so rapidly in quantity in the inner flame, is due to the same actions, or is formed in some other way.

If it be heat alone which converts the hydrocarbons present into acetylene, then this result should be obtained by passing them alone, or diluted with hydrogen, through a very narrow tube, heated to the same temperature as that existing near the top of the dark zone of a luminous flame, that is, to a little way over 1000° .

The difficulty at once arises of obtaining a tube sufficiently narrow in bore to ensure the gas being heated to nearly the same temperature as the walls of the tube without using platinum, as all attempts to obtain a nickel or iron tube of the desired dimensions failed, and the use of platinum is open to the objection of the actions induced by its surface at the temperature employed.

In order to see if surface action would in any way affect the amount of acetylene formed, a very fine platinum tube and a pipe-stem glazed with borax were heated in the same furnace to the same temperature, and an equal amount of ethylene was passed slowly through both, and the acetylene formed estimated.

Acetylene formed with platinum tube = 0.494 per cent.

Acetylene formed with glazed pipe-stem = 0.432 per cent.

On now heating the pipe-stem to a higher temperature, the acetylene formed from the same amount of gas was 0.808, so that the smaller amount obtained in the previous experiment with the pipe-stem was evidently due to the thick, clay walls.

From this it appeared as if the platinum exercised no influence on the production of acetylene in the experiment, but as I also wanted to determine the action of small quantities of air upon the hydrocarbons, under the influence of the temperature existing in the inner zone of a flame, I made a second experiment, in which methane, free from unsaturated hydrocarbons, was passed with 10 per cent. of air through a pipe-stem, and through the platinum tube, both being heated to the same temperature, which was a little under 1000° :—

Gases after Heating.

	Pipe-stem.	Platinum tube.
Unsaturated hydrocarbons	1.92	1.52
Carbon monoxide	2.30	2.10
Carbon dioxide	1.01	0.51
Oxygen	0.54	0.51
Acetylene	trace	trace

With the pipe-stem it was almost impossible to get an even tem-

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perature much above that used in this experiment, but on passing the same mixture of methane and 10 per cent. of air through the platinum tube heated to about 1100—1200°, acetylene appeared in quantity :—

Unsaturated hydrocarbons.....	3·10
Acetylene.....	2·07

These experiments pointed to the platinum tube having so little action on the gases as to render its use admissible in the following experiments, and the difficulties arising from the pipe-stems not being straight, from the thick walls rendering it nearly impossible to attain even heating, and from constant fracture, were so great that I decided to use a platinum tube 2 mm. in diameter and a foot long for the following experiments :—

Methane was prepared by the action of the copper-zinc couple upon a mixture of methyl iodide and methyl alcohol, with the usual precautions, and was then passed through the tube, 6 inches of which were heated to 1000° in the flat flame of a broad Bunsen.

The methane employed contained 99 per cent. of saturated hydrocarbons, and was analysed for other constituents before and after heating :—

	Before heating.	After heating.
Unsaturated hydrocarbons.....	0·5	3·2
Acetylene.....	0·000	1·798
Carbon dioxide.....	0·00	0·00
Carbon monoxide.....	0·0	0·0

The effect of heating the methane with other gases present in the inner zone of the flame was then tried.

	Methane heated with			
	3 p. c. oxygen.	15 p. c. air.	50 p. c. carbon monoxide.	60 p. c. hydrogen.
Unsaturated hydrocarbons ...	2·0	2·0	1·0	1·47
Acetylene	1·426	0·656	0·887	0·473
Carbon monoxide	1·1	1·0	—	0·490

These experiments seem to point to acetylene being formed by the action of heat alone upon the methane, whilst as soon as oxygen is present carbon monoxide is also produced.

The experiment with oxygen and air also shows the retarding effect of dilution upon the formation of the acetylene.

The presence of carbon monoxide in the methane diluted with hydrogen was probably caused by the latter gas containing nearly

2 per cent. of oxygen, whilst I think the experiment with carbon monoxide shows that interactions between it and methane cannot give rise to acetylene, as the amount formed is just one-half that produced on heating methane alone, the reduction in quantity being due to dilution.

The action taking place is most probably a splitting up of the methane into acetylene and hydrogen—

and some of the acetylene is then polymerised into benzene, as noticed by Berthelot (*Compt. rend.*, **54**, 515).

The methane takes a far higher temperature for the formation of acetylene than any of the other hydrocarbons experimented with.

Ethane was prepared from ethyl iodide by the action of the copper-zinc couple, and contained 93 per cent. of saturated and no unsaturated hydrocarbons or acetylene; it, however, contained a trace of air, which would render estimation of carbon monoxide, after heating, useless.

Heated alone.

Unsaturated hydrocarbons	19.47
Containing acetylene	8.224

Ethane Diluted with 80 per cent. Hydrogen.

	Gas used.	Heated with		
		15 p. c. air.	20 p. c. air.	25 p. c. air.
Unsaturated hydrocarbons	0.00	7.69	5.58	5.05
Acetylene	0.00	3.89	3.20	3.11
Carbon dioxide.	0.00	0.00	1.01	1.51
Carbon monoxide.	0.00	1.54	2.53	3.03

Showing that the carbon monoxide is being formed in increasing quantities with the increase in the percentage of air, and that the amount of unsaturated hydrocarbons, other than the acetylene, are reduced in quantity more quickly than the acetylene itself; this, however, being probably due to their splitting up with formation of acetylene, and both slowly being oxidised.

These experiments show that when between 15 and 20 per cent. of air is present, carbon dioxide, as well as monoxide, begins to form.

Ethylene.—The gas was prepared by the action of sulphuric acid upon alcohol, and contained 93 per cent. unsaturated hydrocarbons, and neither carbon monoxide nor acetylene.

	Gas heated	
	Alone.	With 3 per cent oxygen.
Acetylene	8.894	7.165
Carbon monoxide.	0.000	5.74

Ethylene diluted with Hydrogen.

	Gas used.	Heated with	
		20 p. c. air.	25 p. c. air.
Unsaturated hydrocarbons ...	14.50	6.81	3.66
Acetylene.....	0.00	2.03	1.59
Carbon monoxide	0.00	5.30	3.73

These experiments, I think, show that dilution has a distinct effect in preventing the "over-cracking" of the hydrocarbons, as the proportion of acetylene to unsaturated hydrocarbons is far higher in the gas diluted with hydrogen than in the rich gas.

In another experiment, hydrogen was charged with 1.02 per cent. of benzene vapour, and heated with varying proportions of air, with the following results:—

	8 p. c. air.	13 p. c. air.	18 p. c. air.
Acetylene formed	0.026	0.032	0.218

It has been suggested that if acetylene is formed simply by the action of heat, it ought to be present in quantity in coal and oil gas, which it undoubtedly is not. This, I think, is purely a question of temperature; the fire-clay gas retort is never above an orange-red, which means 800° to 900°, and the gas inside the retort probably never approaches that temperature. Again, in oil-gas making, 800° would be the outside temperature employed, whilst to convert any large proportion of diluted hydrocarbons into acetylene requires at least 1000°. Indeed, if diluted hydrocarbons are passed through a half-inch tube heated to 1000°, the yield is very small, as only the thin layer in contact with the walls of the tube is raised to the required temperature, and it was for this reason that it was necessary to use so fine a tube in the preceding experiments.

In order to see how temperature affected the amount of acetylene formed during the manufacture of gas, I made separate batches of oil gas from Russian petroleum in a Patterson retort.

Acetylene formed in the Manufacture of Oil Gas.

Oil used—Russian "distillate oil," sp. gr. 0.0864.

Temp. of retort	500°	700°	800°	900°
Yield of gas per gallon, cub. ft.	12	60	72	84
Illuminating power ..	54.8	50.7	57.1	42
Unsaturated hydrocarbons.	39.13	36.56	36.55	22.40
Acetylene	0.052	0.084	0.38	0.46

Showing that the quantity of acetylene steadily increases with rise of temperature.

The analyses of flame gases made by Landolt (*Ann. Phys. Chem.*, 1856, **99**, 389—417), Blochmann (*Annalen*, **168**, 295), and myself all point to the hydrogen present in the gas burning first, and there is no doubt but that the water vapour so formed and superheated in its passage up the flame interacts with the hydrocarbons, giving hydrogen and carbon monoxide, whilst in the luminous zone the action of water vapour and carbon dioxide upon the incandescent carbon particles again gives rise to the same products, so that their production in reality never ceases until the outer non-luminous zone of the flame is reached.

In this zone it has always been supposed that the presence of a free supply of oxygen caused complete combustion, and that with a properly constructed burner only carbon dioxide and water vapour escaped into the air.

Delicate analyses made and described by me in the *Journal of the Society of Chemical Industry* (1891, **10**, 413) show that this is not the case. Heumann noticed that if a luminous flame was made to spread itself out over a cold surface, luminosity was destroyed, but could be restored by heating the substance over which the flame was playing, and this reduction of luminosity is produced by withdrawal of heat from the flame, the temperature falling below the point necessary for the decomposition, or in some cases even the production of acetylene, and in the outer zone of the flame the inrush of cold air sucked into the flame so cools it as to render it non-luminous, and finally extinguishes it, and if the air and products of combustion be collected close to the flame but not in absolute contact with it, anywhere between 2 inches and $4\frac{1}{2}$ inches above the burner, it will be found to contain small traces of carbon monoxide, acetylene, methane, and even hydrogen. At the extreme tip, however, combustion is more perfect, and only carbon monoxide and minute traces of methane are to be found escaping.

It is usual to describe the structure of flame as built up of four zones, but if any such division into parts be necessary, I think it would be better to found them upon the main reactions taking place, due to the heat generated, and to describe them as three:—

1. The inner zone, in which the temperature rises from a comparatively low point at the mouth of the burner to between 1000° and 1100° at the apex of the zone, and in this portion of the flame the constituents of the gas undergo various decompositions and interactions, which culminate in the conversion of part of the hydrocarbons into acetylene; carbon monoxide and hydrogen being also produced, and passing into the next sphere of action, together with some methane and the products of combustion.

2. The luminous zone, in which the temperature ranges from 1100°

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to a little over 1300° ; here the acetylene formed in the inner zone becomes decomposed by heat with liberation of carbon, which at the moment of separation is heated to incandescence by its own combustion and by the combustion of carbon monoxide and hydrogen, and gives luminosity to the flame.

3. The extreme outer zone, in which the cooling and diluting influence of the entering air renders a thin layer non-luminous, and finally extinguishes it.

With an ordinary coal-gas flame, this results in the escape of traces of hydrogen, methane, acetylene, and carbon monoxide, whilst with a very rich gas unconsumed carbon also escapes.

This description of a luminous flame is of necessity far from complete, as it leaves out of consideration the numerous subsidiary interactions which are taking place, but I think it gives the general outline of the main reactions.

When Knapp and others first showed that a luminous gas flame could have its luminosity destroyed by mixing the gas before burning with inert diluents, such as nitrogen, carbon dioxide, and steam, it was recognised that the nitrogen in the air was an important factor in rendering such flames as those of the Bunsen burner non-luminous, and most valuable contributions were made to our knowledge of the subject by Landolt, Blochmann, Heumann (*Annalen*, 181 and 182), and others, but, as far as I know, no quantitative attempt has been made to arrive at an idea of the relative importance of the various factors which influence the combustion of coal gas and the light-giving value of the flame.

In these experiments, I used a Bunsen, fitted with two supply pipes leading into the chamber at the foot of the upright tube, each pipe being connected with a small meter, which was from time to time checked with a standard meter, so that the flow of gas and air could be accurately regulated and measured. Working with this arrangement, the amount of air necessary to render the flame non-luminous was first determined:—

6.0 volumes of gas required 13.5 volumes of air.

13.5 volumes of air contain roughly 2.7 volumes of oxygen and 10.8 volumes of nitrogen, and on now passing coal gas and nitrogen through the burner, at the rate of 6 volumes of coal gas to 10.8 of nitrogen, a flame was obtained which had only a faintly luminous tip, whilst on passing coal gas as before, at the rate of 6 volumes to 2.7 volumes of oxygen, a luminous flame is produced, which flashes back unless the tube is covered with fine wire gauze.

This experiment was then repeated on the photometer.

Bunsen burning gas alone (5 cub. ft. per hour), 5·6 c. p.
 „ „ 5 cub. ft. gas and 2·2 cub. ft. oxygen, 3·1 c. p.
 „ „ „ „ 9 of nitrogen, not readable.

It appears from this experiment that the amount of oxygen in the volume of air necessary to destroy luminosity does less than one-half the work, and I then tried the effect of varying the amount of oxygen added, with the following results:—

5 cub. ft. gas alone	= 5·6 c. p.	
5 „ gas to 1·1 cub. ft. oxygen	= 5·4 „	
5 „ „ 1·5 „ „	= 8·0 „	
5 „ „ 2·2 „ „	= 3·1 „	Gauze used.
5 „ „ 2·5 „ „	= 0·0 „	„ „

It has been already shown that the amount of nitrogen present in the volume of air required to render the flame non-luminous just falls short of the quantity necessary to bring about the same effect by dilution only, and in order to determine the volume required to entirely destroy luminosity, coal gas was burnt at the rate of 6·2 cubic feet per hour, and was supplied with pure nitrogen, which had to pass at the rate of 14·2 cubic feet per hour before all luminosity disappeared, or practically the same amount of nitrogen is required as of air:—

1 vol. of gas required 2·30 vols. of nitrogen.
 1 „ „ requires 2·27 vols. of air.

This result at first sight looks as if the oxygen in the air really only acted in the same way as the nitrogen, that is as a diluent; but if this were so, then mixtures of oxygen and nitrogen, richer in oxygen than air, should only affect the luminosity to about the same extent as air, which is not the case, as is shown by the following results:—

Volumes of Varying Mixtures of Nitrogen and Oxygen required to render 1 vol. of Coal Gas Non-luminous in Bunsen Burner.

Gas.	Volume of mixture required.	Composition of mixture.			Volume of oxygen present in amount required.
		Nitrogen.		Oxygen.	
1 vol. requires 2·30 of		1	to	nil	nil
1 „ „ 2·30 „		5	„	1	0·38
1 „ „ 2·27 „		4	„	1	0·45
1 „ „ 2·02 „		3	„	1	0·50
1 „ „ 1·49 „		2	„	1	0·50
1 „ „ 1·00 „		1	„	1	0·50
1 „ „ 0·50 „		nil	„	1	0·50
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This set of experiments shows very beautifully that until the percentage of oxygen reaches the amount present in the atmosphere, the diluting influence of the nitrogen is so strong that it prevents the oxygen having any practical effect in the destruction of the luminosity, but that as soon as the quantity of oxygen present has risen above 25 per cent., then its activity has so far overcome the diluting influence of the nitrogen that the latter has ceased to exercise any retarding influence upon it.

In almost every laboratory it may be noticed that whereas most of the Bunsens are burning with their normal blue, noiseless combustion, some one or two are roaring and burning with a sharply defined green centre, and experiment shows that this is brought about by the gas delivery jet having become partly stopped up, and a far larger supply of air than is necessary to cause non-luminosity being sucked in:—

Ratio of Gas to Air in Blue and Green Non-luminous Combustion.

Blue, 1 vol. of gas to 2·27 of air.

Green, 1 vol. of gas to 3·37 of air.

The green centre shows, therefore, that a large excess of air is passing in, and such a flame is on the point of flashing back in the burner and lighting at the bottom.

In this case, the kind of action taking place in the flame has undergone considerable alteration, the flame being fiercer and smaller than in the normal combustion, the change being due to the fact that the proportion of oxygen to coal gas in the mixture is such that the chemical activity of the oxygen is able to overcome the diluting and cooling action of the nitrogen, so that the latter has practically ceased to act.

The next step was to determine the proportions by volume of various gases required to render the Bunsen flame non-luminous, the number being limited by having to use a wet meter for their measurement.

Volumes of Gases required to render 1 vol. of Coal Gas Non-luminous.

1 vol. of gas requires 0·5 vol. of oxygen.

1	“	“	“	1·26	“	carbon dioxide.
1	“	“	“	2·27	“	air.
1	“	“	“	2·30	“	nitrogen.
1	“	“	“	5·11	“	carbon monoxide.
1	“	“	“	12·4	“	hydrogen.

Showing that a diluent which burns and adds to the general temperature of the flame must be added in far greater quantity than an inert and non-combustible diluent such as nitrogen, a result fully borne out by experience.

Some observers have attributed the varying effect of diluents to the effect of density (D. Waldie, *Phil. Mag.*, 1838), but the destruction of luminosity in a flame can be brought about by cooling as well as by dilution, as is well shown by the experiment described by Heumann (*loc. cit.*).

It is evident that, this being the case, if one diluent has the power of abstracting more heat from the flame than another, it will be more active in reducing the luminosity, and a smaller quantity will be required to render the flame non-luminous. And on comparing the specific heats of equal volumes of the diluents used in the last experiment, the reason for the small quantity of carbon dioxide required is at once seen.

Specific Heats of Equal Volume.

Oxygen	0·2405
Carbon dioxide	0·3307
Nitrogen.....	0·2370
Air	0·2374
Carbon monoxide	0·2370
Hydrogen	0·2359

If this be the true explanation, then it should be easy to trace the action by the decrease in temperature of the flame when carbon dioxide is used to render it non-luminous.

In order to take the temperatures of the inner cone of the flame by means of the thermo-couple before described, it is manifest that the wires, even when protected by glass, must not be passed through the outer zone, as with mixtures of coal gas and air the heated platinum would set up rapid combination on its surface. To overcome this difficulty, the wires, insulated with glass, were passed up the interior of the burner-tube, and the gas supply was kept constant at 6 cubic feet per hour, whilst the diluents were supplied under pressure at the same rates as before determined, and the results in table, p. 336, were obtained.

These results fully bear out the inferences derived from the behaviour of the flames in the former experiments. In the flames rendered non-luminous by diluents, the inner cone for the first $1\frac{1}{2}$ inches is decidedly cooler than in the luminous flame, owing to the cooling action of the nitrogen or carbon dioxide; in the upper

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Temperature of Flame from Bunsen Burner, with Consumption of 6 cub. ft. of Coal Gas per hour.

Point in flame.	Flame rendered non-luminous by			Luminous flame from Bunsen.
	Air.	Nitrogen.	Carbon dioxide.	
$\frac{1}{2}$ inch above burner	54°	30°	35°	135°
$1\frac{1}{2}$ inch above burner . . .	175	111	70	421
Tip of inner cone	1090	444	393	913
Centre of outer cone	1533	999	770	1328
Tip of outer cone	1175	1151	951	728
Side of outer cone, level with tip of inner cone .	1333	1236	970	1236

portion of the inner cone of the flame rendered non-luminous by air, however, the oxygen of the air is acting, and the temperature is therefore higher than in the luminous flame; whilst, in both, the hottest portion of the flame is almost half way between the tip of the inner and outer cones.

In flames rendered non-luminous by inert diluents, this is not the case, as the full amount of air necessary for combustion only being obtained at the side and tip of the outer cone, these are the hottest points.

The low temperature registered at the tip of a luminous flame is probably due to the impossibility of keeping that portion of the flame steady when the gas is burning from a Bunsen with the air supply closed.

Experiments with a Bunsen burning a mixture of air and coal gas in such proportions as to give the green inner cone showed that although the excess of air caused a low temperature at the bottom of the inner cone, the increase in rapidity of oxidation due to excess of oxygen caused a rapid rise of temperature, and that a hotter and smaller flame was the result:—

	Blue inner cone.	Greenish inner cone.
Tip of inner cone	1090°	1575°
Centre of outer cone	1533	1630
Tip of outer cone	1175	1545
Side of outer cone, level with the tip of inner cone	1333	1511

These experiments, as well as the researches of Heumann, show that oxidation, dilution, and cooling all help to bring about the destruction of luminosity in a Bunsen flame.

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At this point it seemed important to determine how dilution acted towards gases richer than ordinary coal gas; in order to do this, I decomposed Russian distillate oil in a "Patterson" retort, and made two batches of oil gas, one of 24-candle power, the other of 43-candle power.

These gases were then analysed with the following results:—

Oil Gas.

	24 c. p.	43 c. p.
Carbon dioxide.....	0.95	1.52
Oxygen	0.74	0.00
Unsaturated hydrocarbons.	18.06	33.16
Saturated hydrocarbons ..	43.62	45.15
Carbon monoxide	0.95	0.52
Hydrogen.....	34.58	19.65
Nitrogen.....	1.12	0.00
	100.00	100.00

The gases were then tested in the Bunsen burner, at a carefully regulated rate of flow, with air, carbon dioxide, and nitrogen, and gave the following figures:—

Amount of Diluent required by 1 vol. of Gas to render a Bunsen Flame Non-luminous.

Gas.	Candle power.	Air.	Nitrogen.	Carbon dioxide.
Coal gas	16.3	2.27	2.30	1.26
Oil gas	24.0	5.38	4.20	2.29
Oil gas	43.0	7.86	4.71	3.12

These figures reveal the interesting fact that with a rich gas far less nitrogen than air is required to bring about loss of luminosity, on account of the high temperature produced by the combustion of the heavy hydrocarbons with the oxygen in the air. The effect of the inert diluents was also noticeable, as at the point of non-luminosity the flame separated itself $\frac{3}{4}$ inch from the mouth of the burner, and became very elongated.

The question now arises as to how dilution, apart from its cooling action, reduces the luminosity.

On passing 1.5 cubic feet of coal gas slowly through a platinum tube, 0.15 metre long and 12 mm. in diameter, packed with platinum

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foil and heated to redness by a Bunsen burner, it deposited 0·2200 gram of carbon. The same volume of gas was then diluted with 3·3 cubic feet of nitrogen, and the experiment repeated under exactly similar conditions, when only 0·0013 gram of carbon was deposited, dilution reducing the amount of decomposition to this enormous extent. A second experiment was then made in which, by means of a blow-pipe flame, a higher temperature was obtained, and 1·5 feet of gas, as before, was passed through the tube, when it deposited 0·2780 gram of carbon.

	Gas before heating.	After heating.
Carbon dioxide	0·2	0·8
Oxygen	0·3	0·2
Unsaturated hydrocarbons	4·2	3·0
Carbon monoxide	2·6	2·8

whilst, under the same conditions, a mixture of 1·5 cubic feet of coal gas and 3·45 cubic feet of nitrogen deposited 0·0640 gram of carbon, showing that the effect of dilution is decreased by increase of temperature.

These experiments, I think, show that when coal gas is diluted to the degree necessary to give a non-luminous flame in the Bunsen burner, the liberation of free carbon is reduced by the retarding action of the inert gas, but as the temperature rises this action gets less and less.

The action of diluents in increasing the temperature necessary to bring about deposition of carbon was, I believe, first noticed by Wartha, and is probably due to two distinct causes. As has already been shown, the formation of acetylene from the hydrocarbons in the gas is retarded by dilution, whilst if any be formed the temperature necessary to decompose it into carbon and hydrogen is greatly increased.

These two retarding influences give time for the oxygen present in the air introduced with the gas, and in the air sucked into the flame, to burn up the hydrocarbons without previous decomposition, and so prevent luminosity, and it is probable that the prevention of the formation of acetylene is the chief factor, as only the merest trace can be detected in a non-luminous Bunsen flame. Collecting the results, we can now explain the various actions which lead to loss of luminosity as follows:—

1. The chemical activity of the oxygen introduced in the air, which causes loss of luminosity by burning up the molecules of hydrocarbons before, in their diluted condition, they can form acetylene.

2. The diluting influence of the nitrogen which increases the temperature necessary for the formation of acetylene from the hydro-

carbons, whilst if any be formed a higher temperature is necessary for its decomposition. In this way diluents alone will render a flame non-luminous, and in the normal Bunsen flame nitrogen acts in this way until the hydrocarbons have been destroyed by oxidation.

3. The cooling influence of the air introduced, which is able to add to the general result, although the cooling is less than the increase in temperature brought about by more rapid oxidation.

4. In a normal Bunsen flame, the nitrogen and the oxygen are of about equal importance in bringing about non-luminosity, but if the quantity of air be increased the oxidation becomes the principal factor, and the nitrogen practically ceases to exert any influence.

I should have liked to have worked out the secondary reactions taking place in a luminous flame, and so have completed this paper; but, as Professor Smithells proposes to undertake this, I leave the question in his hands, and trust that he may be successful in clearing up the many points which remain to be solved.

In conclusion, I wish to express my thanks to my assistants, Messrs. F. B. Grundy and H. S. Marsh, for the help they have given me in the work entailed in this paper.