PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Radiation in Explosions of Coal-Gas and Air

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X. *Radiation in Explosions of Coal-Gas and Air.*

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IN the first part of this paper results of experiments are given on the radiation emitted during the explosion and subsequent cooling of mixtures of various strengths and densities of Cambridge coal-gas and air. Bolometric measurements were made of that part of the radiation from the hot gaseous mixtures which was transmitted through clear plates of fluorite, quartz, plate glass, and water (contained between two plates of glass). The fluorite (6 mm. thick) transmits very approximately 95 per cent. of the total radiation emitted by the gas; the quartz (also 6 mm. thick) transmits about 70 per cent. of the radiation from water vapour and cuts off a very large proportion of that from CO_2; the water cell transmits practically only luminous radiation. It has been therefore possible to estimate fairly accurately the total radiation emitted by the gas, and, roughly, the proportions emitted by water vapour and by CO_2, and also the amount of energy in the luminous radiation. The radiation emitted in the explosion of a 25-per-cent. mixture of hydrogen and air has also been measured.

The second part of the paper consists of an investigation into the diathermancy and emissive power of the hot gaseous mixture after explosion. The conclusions drawn from these experiments offer an explanation of many of the peculiar results given in the first part.

Prof. HOPKINSON has already shown that the heat lost by radiation in explosions of coal-gas and air is a considerable fraction of the total heat of combustion of the gas. Recently he has made a very complete investigation of this radiation loss in 15-per-cent. mixtures.* He exploded mixtures of the same strength in a vessel of about $\frac{3}{4}$ cub. ft. capacity whose walls were silver-plated, first, when the walls were highly polished, and then when these same walls were coated with a thin layer of dull black paint. In the first case the maximum pressure developed was about 3 per cent. greater and the subsequent rate of cooling much slower than in the second

* 'Roy. Soc. Proc.,' A, vol. 84, p. 155.

case. By measuring the radiation emitted by the hot gaseous mixture (by means of a bolometer protected by a plate of fluorite) he shows that these results are in a large measure, if not entirely, due to this radiation being reflected back by the polished walls and reabsorbed by the gas, this reabsorption of the radiation being ultimately realised, at any rate in part, as pressure or translational energy.

No other work has been done on radiation in gaseous explosions. Some interesting measurements, however, have been made on the radiation emitted by flames and by heated gas. Those made by Prof. CALLENDAR on flames and by Prof. PASCHEN on heated CO_2 are particularly interesting and will be referred to later on in this paper.

Description of Apparatus.

The explosion vessel used in these experiments consists of a cast-iron cylinder, 30 cm. in diameter and 30 cm. long, on to which are bolted two end plates. It is shown in section in fig. 1*a* together with the bolometer holder H.

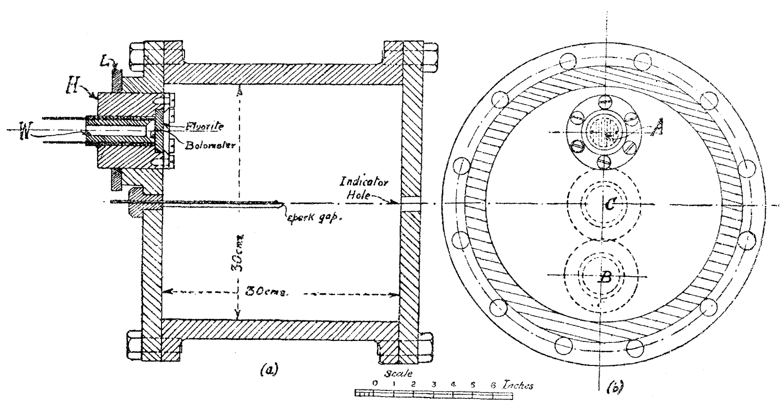

Fig. 1.

The bolometer was cut into the form of a grid from a circular disc of platinum about $\frac{1}{8}$ mm. thick, weighing 0·25 gr. per sq. cm., and had, therefore, a thermal capacity equivalent to 0·008 gr. of water per sq. cm. (the specific heat assumed to be 0·032). Its resistance measured about 0·115 ohms at 15° C. The temperature coefficient was measured and found to be 0·0036. The bolometer was mounted on a hollow cylinder of wood (W in fig. 1) and was pushed into the gunmetal holder H, which carried at its inner end the plate of diathermanous substance. The holder H was screwed into a boss on the end cover of the vessel and was tightened up with the lock nut L.

In the experiments described in the first part of this paper the bolometer was placed close up to the diathermanous plate, so that all the radiation from the hot gaseous mixture, which was transmitted through the diathermanous substance, fell on its blackened surface. In order to measure the amounts of radiation absorbed by the bolometer it was necessary only to measure its rise of temperature. This was

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done by recording the rise of its electrical resistance, which is proportional to its rise of temperature, as it warmed up. The arrangements used to record its rise of resistance were in principle exactly the same as those used by HOPKINSON for determining the rise of resistance of the copper strip in his Recording Calorimeter.* The method consists in passing through the bolometer a constant continuous current sufficient to produce a convenient difference of potential at its terminals, balancing this difference by means of a source of constant E.M.F., and recording by means of a mirror galvanometer the rise of potential which occurs when the bolometer gets warmed up. The deflection of the galvanometer is proportional to this rise of potential difference, which, since the current through the bolometer is constant, is proportional to the increase of its resistance and, therefore, to its rise of temperature.

The connections are shown diagrammatically in fig. 2. The current C_1 passing through the bolometer B is taken from a battery of storage cells giving about 100 volts. In this circuit are included a bank of lamps, L, and ammeter, A_1. With this arrangement the small variation in the resistance of the bolometer as it gets warm has no appreciable effect on C_1 since the resistance of the lamps L is very large compared with that of the bolometer. The current C_1, which is measured by the ammeter A_1, is adjusted to a convenient value before the experiment. The terminals of the bolometer are connected also to the galvanometer G through a resistance, R, in which a constant current, C_2, is maintained by means of two storage cells, the direction and magnitude of C_2 being such that the potential difference at the terminals of the bolometer before the experiment is balanced, or approximately balanced.

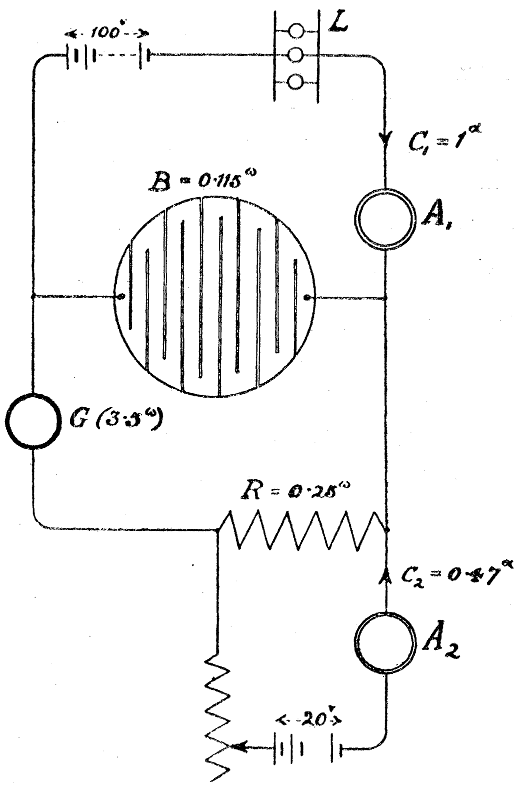

Fig. 2.

NOTE.—C_1 was kept constant during each experiment, but was, in general, different in different experiments.

The relation between the rise of potential difference at the terminals of the bolometer and the galvanometer deflection was found by passing small currents through the bolometer, when it was at a known temperature, and noting the galvanometer deflections, C_2 having been reduced to zero during the calibration.

The recording galvanometer used in these experiments had a resistance of about 3·5 ohms. It was of the suspended coil type, with a fairly stiff phosphor-bronze

* 'Roy. Soc. Proc.,' A, vol. 79, p. 140.

suspension, having a period of about $\frac{1}{25}$ second. The field was produced by means of an electromagnet, magnetised nearly to saturation value.

For recording the pressures a Hopkinson Optical Indicator was used.

The mirrors on both the indicator and the galvanometer were concave, and by means of them two spots of light were reflected on to a photographic film, revolving at a known speed, care being taken that the two spots of light were on a line at right angles to the direction of rotation of the film. By this means both the rise of temperature of the bolometer and the pressure of the gas were recorded at the same time.

The inflammable mixture was introduced into the vessel in the following way:—The vessel was first exhausted by means of an air pump, and the quantity of coal-gas required to give the mixture a certain strength was admitted; air was then allowed to rush in bringing the pressure up to atmospheric. The gas when let in to the explosion vessel at low pressure quickly diffused throughout the whole space, and the air afterwards rushing in at high velocity thoroughly stirred up the mixture. To make certain that the mixture was homogeneous, it was allowed to stand for about half-an-hour before firing. This is a method of mixing recommended by Mr. DUGALD CLERK.*

In all the following experiments the mixture was fired by means of an electric spark at the centre of the vessel.

Fig. 3 is a print from an actual record taken during the explosions of a 9·8-per-cent. mixture of coal-gas and air when the bolometer was protected by the plate of fluorite. Curve P gives the rise of pressure (measured downwards from the atmosphere line P_0)

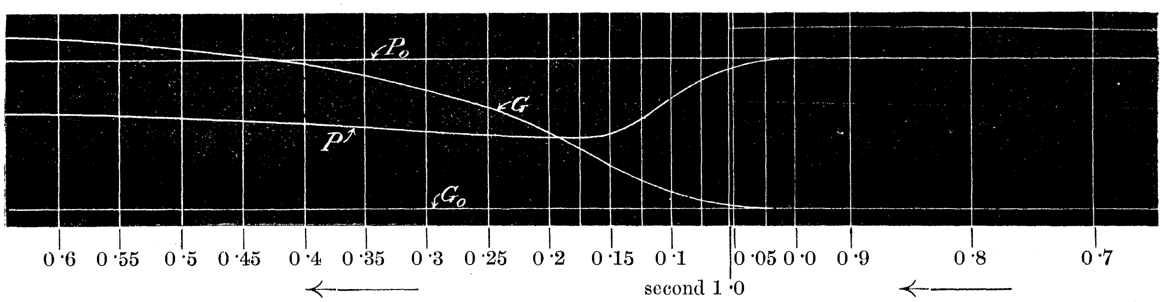

Fig. 3.

and curve G the galvanometer deflection (measured upwards from the zero line G_0). On the pressure curve P, 1 mm. deflection corresponds to a rise of pressure of 4 lbs. per sq. in., equivalent to a rise of temperature of 80° C.† On the curve G, showing the galvanometer deflection, 1 mm. corresponds to a rise of temperature of the bolometer of 1·36° C., or, since the thermal capacity of the bolometer was equivalent

* 'The Gas, Petrol, and Oil Engine,' vol. I., p. 156.

† Temperature before firing 14° C., barometer 760 mm. of mercury, contraction of volume on combustion 2·5 per cent.

to 0·008 gr. of water per sq. cm., to an absorption of heat of 0·0109 calories per sq. cm.

In order to apply a correction for the loss of heat by the bolometer as it warms up the record was continued for some time after the radiation from the gas was inappreciable.* From the rate at which the galvanometer deflection decreased the rate of loss of heat by the bolometer was determined. In this way it was found that in this particular record the loss amounted to 6·1 per cent. of the heat in the bolometer at 0·5 second after ignition, and 13·5 per cent. at 1 second after ignition.

Results of Experiments.—Part I.

The following radiation measurements were made in explosions of mixtures of Cambridge coal-gas and air of various strengths and densities. Measurements of the radiation received by the walls per sq. cm. of surface were made at three different places on one of the end covers, A, B, and C, as shown in fig. 1*b*. The amounts measured in the three places were distinctly different and showed peculiarities which will be discussed later. In all the experiments about to be described in this section the interior surface of the explosion vessel was painted over with a thin layer of dull black paint, so that practically all the radiation emitted by the gas was absorbed by the walls.†

Two or three records were generally taken under the same conditions; those taken on the same day gave precisely the same results.

Mixtures of Various Strengths at Atmospheric Density.

The results shown in figs. 4–11 refer to experiments made with the fluorite window. An allowance of 5 per cent. has been made for the absorption of the fluorite,‡ but no allowance has been made for reflection from the blackened surface of the bolometer. The curves in these figures, therefore, show the radiation *absorbed* by the blackened walls.

Fig. 4 shows the amount of radiation received by the walls, in calories per sq. cm.

* This part of the record has been painted out in the print shown in fig. 3. All measurements refer to the original film. The reproduction is approximately five-eighths of the original.

† The absorbing power of a surface painted with this black paint was compared with that of one which had been blackened with camphor smoke and was found to be the same. Féry's experiments show that a smoke-black surface would reflect about 5 per cent. of the radiation emitted by the hot gaseous mixture which is of wave-length between 2μ and 5μ.

‡ A clear plate of fluorite, from 5 mm. to 10 mm. thick, transmits very approximately 95 per cent. of incident radiation up to 8μ. This figure was checked in the following way:—The radiation was measured when the window consisted of a quartz plate only, and also when the plate of fluorite was placed in front of the quartz in explosions of identical mixtures. In the latter case the radiation measured was almost exactly 95 per cent. of that in the former case. There is very little energy in the emitted radiation of wave-length greater than 8μ.

of surface, in the three positions A, B, and C, as ordinates with times from ignition as abscissæ in explosions of approximately 9·8-per-cent. mixtures. These curves were taken from those on the films traced by the recording galvanometer after allowing for a small loss of heat from the bolometer. This loss was determined for each film in the manner shown previously. The curves marked B, b were taken from the record, a print of which is shown in fig. 3.

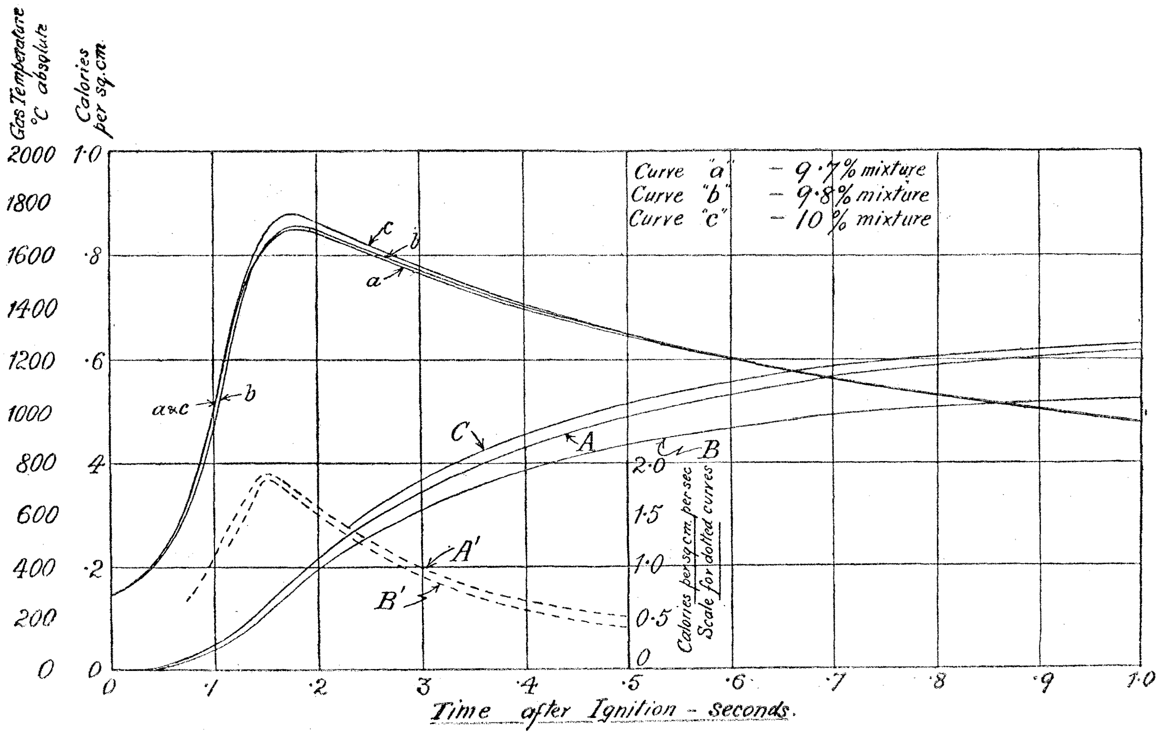

Fig. 4.

Gas-temperature curves are also shown in the same figure, corresponding to the radiation curves. These curves were deduced from the pressure curves on the films by means of the equation $pv = R\theta$, after allowing for a 2·4-per-cent. contraction of volume (which occurs in the combination of a 9·8-per-cent. mixture of Cambridge coal-gas and air). They give the mean absolute temperatures of the gaseous mixture, assuming it to be a perfect gas, or, at any rate, having the difference of its specific heats at constant pressure and constant volume independent of the density and temperature.

Fig. 5 shows the rates at which the walls are receiving heat by radiation in calories per sq. cm. per second at the three places A, B, and C, plotted against the mean absolute temperatures of the gas. These curves have been obtained from the radiation curves in fig. 4 by differentiation. It will be noted that the top parts of the end cover receive more heat by radiation than the bottom parts, or, in other words, the hot gas at the top of the vessel radiates more strongly than the colder gas at the bottom.

The dotted curves A′ and B′ in fig. 4 are the differentials of the radiation curves A and B in the same figure. These curves show very plainly that the gas at the top of the cylinder radiates much more strongly than that at the bottom during explosion (except for a moment just before the attainment of maximum pressure) as well as

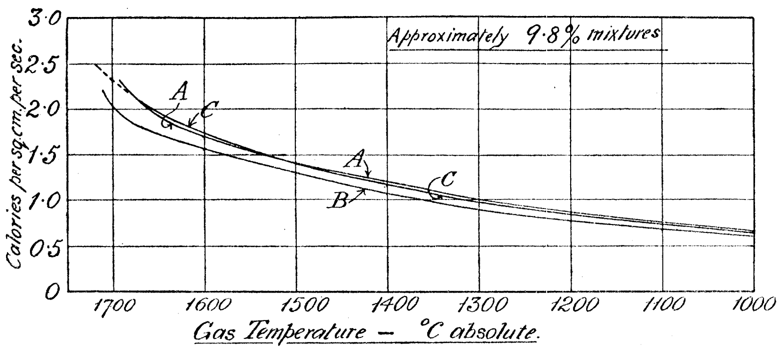

Fig. 5.

during cooling. The most interesting point, however, shown by these curves is that the rate at which the gas emits radiation is less at the moment at which the mean temperature of the gas is a maximum (which is the same as the moment of maximum pressure) than it is some little time before. An examination of the curves shows that the rate of emission of radiation is a maximum about $\frac{1}{40}$ of a second before the attainment of maximum temperature, the "time of explosion" being 0·18 second. At this point the temperature of the gas is about 1600° C. (abs.), and pressure about 65 lbs. per sq. in., the maximum temperature and pressure subsequently attained being 1700° C. (abs.), and 70 lbs. per sq. in., respectively. Prof. HOPKINSON,* experimenting with a very much larger explosion vessel (of 6·2 cub. ft. capacity), found that in a 10-per-cent. mixture of coal-gas and air the flame completely fills the vessel about $\frac{1}{30}$ second before maximum pressure is attained, the "time of explosion" being 0·25 second. The pressure at this point was about 70 lbs. per sq. in. and the maximum pressure reached $\frac{1}{30}$ of a second afterwards 82 lbs. Thus it appears that the maximum rate at which the gas emits radiation occurs very approximately at the moment when the flame completely fills the vessel.†

Experiments were next made with 15-per-cent. mixtures. The results are shown in fig. 6, the radiation curves again showing the amount of radiation received in calories per sq. cm. of surface at various times after ignition in the same three positions, A, B, and C. The corresponding gas-temperature curves are also shown in the same figure; these were deduced from the pressure records after allowing for a

* 'Roy. Soc. Proc.,' A, vol. 77, p. 389.

† I have several records which show that the gas radiates most strongly some time before the attainment of maximum pressure in explosions of from 10-per-cent. to 12-per-cent. mixtures. The period of the galvanometer is not sufficiently low to determine definitely whether the same thing happens in stronger mixtures.

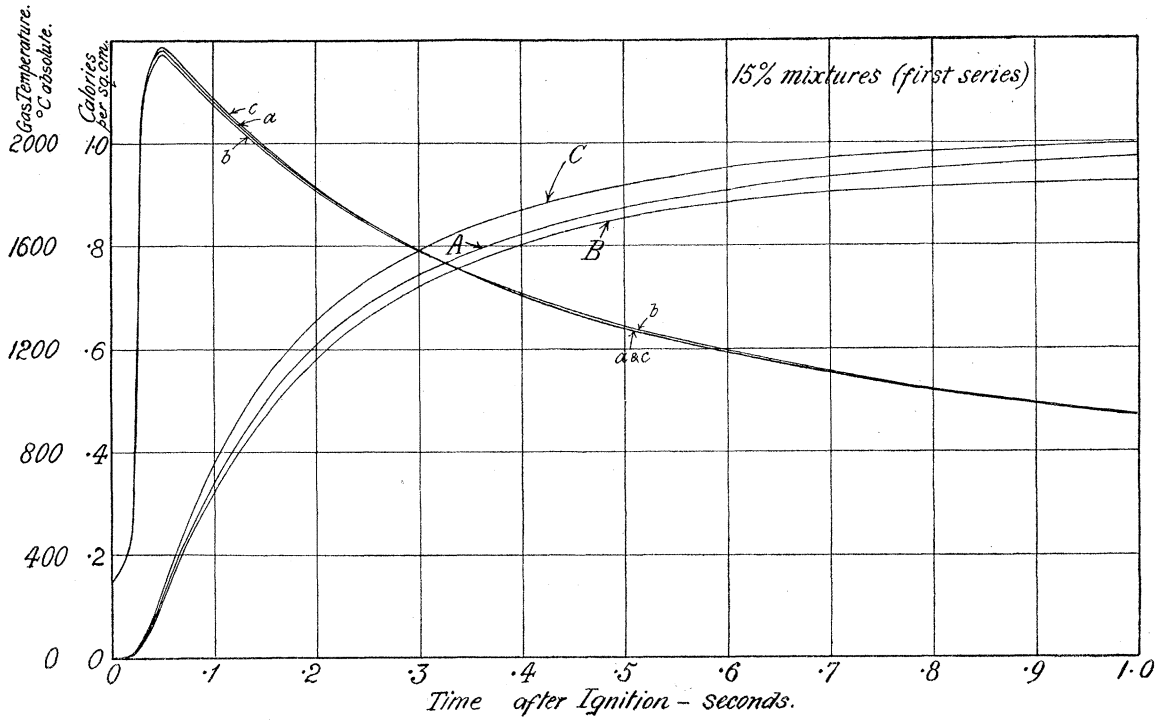

Fig. 6.

3·6-per-cent. contraction of volume which occurs in the combination of a 15-per-cent. mixture.

Fig. 7 shows these radiation curves differentiated, the rates of radiation in calories per sq. cm. per second being plotted against the mean absolute temperatures of the gas as was done for the 9·8-per-cent. mixtures in fig. 5.

At the moment of maximum pressure the rate of receiving heat by radiation at the

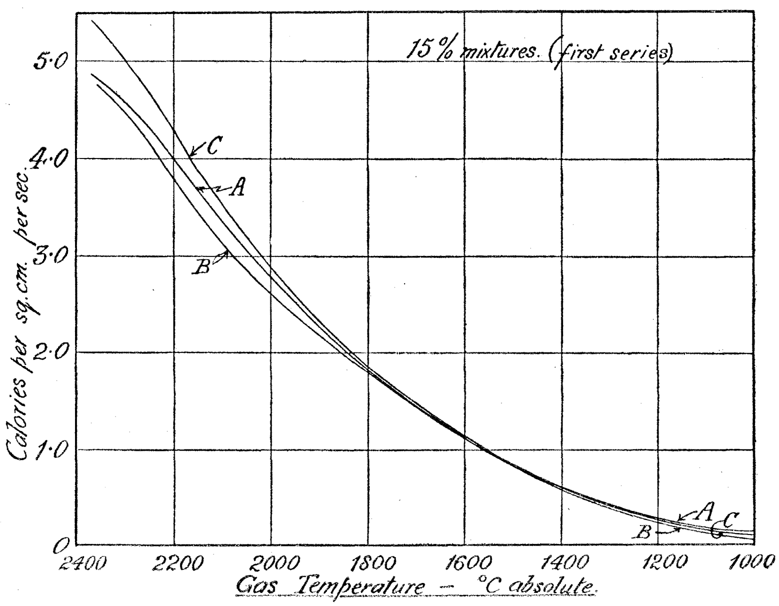

Fig. 7.

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centre of the end cover (position C) is about 5·4 calories per sq. cm. per second, at the top (position A) it is 4·85 calories, and at the bottom (position B) it is 4·75 calories, at a slightly lower maximum temperature. As cooling proceeds the centre still continues to receive more radiation than either the top or bottom parts of the end cover, and the top more than the bottom, until the gas temperature falls to about 1800° C. (abs.), when every part of the end cover seems to be receiving radiation at approximately the same rate and continues to do so until a temperature of something like 1300° C. (abs.) is reached. After this the top receives more radiation than either the centre or bottom and the centre more than the bottom, owing to the hot gas at the top of the vessel emitting more powerfully than the colder gas at the bottom of the vessel.

In fig. 8, Curves I. and III. show the results of later experiments made with 15-per-cent. mixtures and 13-per-cent. mixtures respectively, and Curves II. and IV. show the results of the previous experiments made with 15-per-cent. mixtures and 9·8-per-

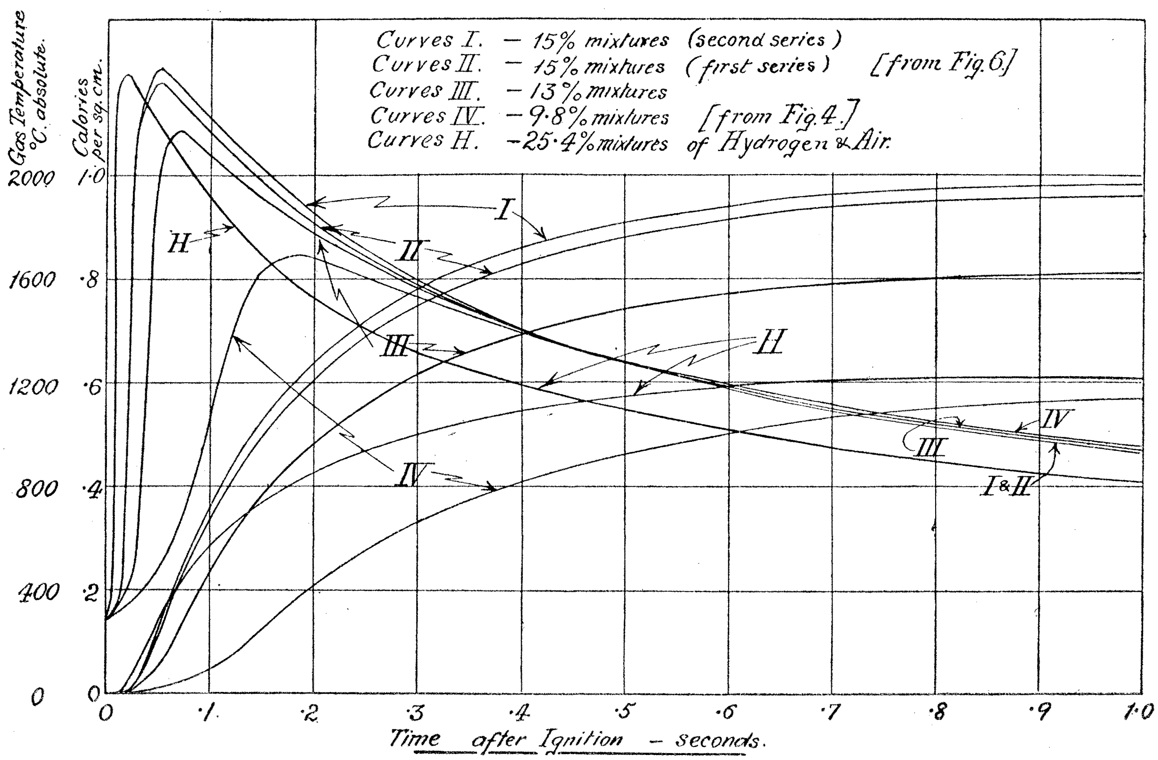

Fig. 8.

cent. mixtures (from figs. 4 and 6). The Curves H refer to experiments made with a 25·4-per-cent. mixture of hydrogen and air (see p. 392). The radiation curves in this figure are the means of those taken with the bolometer in positions A, B, and C. The corresponding gas-temperature curves are also shown. The experiments with the 9·8-per-cent. mixtures and 15-per-cent. mixtures (first series) were made within a week of each other, during which time the calorific value of the coal-gas was probably very nearly the same. Those with the 15-per-cent. mixtures (second series) and 13-per-cent. mixtures were made about a fortnight later, during which time the calorific value of the gas had probably increased slightly.

The following tables have been prepared from the curves in this figure. The third column in each table gives the average loss of heat by radiation per sq. cm. of wall surface (assuming that the mean value of the radiation per sq. cm. measured in positions A, B, and C is the same as that over the entire surface of the vessel) at various times after ignition. The figures in the fourth column show the total heat lost by radiation, at the various times from ignition given in the first column, per cent. of the heat of combustion of the coal-gas present in the vessel.

The calorific value of the coal-gas is taken at 320 pounds—Centigrade units (lower value), equivalent to 145,000 calories—per standard cubic foot.

Volume of vessel, 0·788 cub. ft.

Area of interior surface of vessel, 4380 sq. cm.

TABLE I.—9·8-per-cent. Mixture. Initial Pressure, Atmospheric.

Heat of Combustion of Coal-gas present in Vessel = 10,600 Calories.

Time from ignition.	Mean absolute temperature of gas.	Mean radiation received by walls per sq. cm.	Total loss of heat by radiation per cent. heat of combustion.
	° C.		
0·15	1600	0·12	5·0
0·18	max. temp. 1700	0·17	7·0
0·2	1680	0·21	8·7
0·25	1600	0·28	11·6
0·5	1280	0·46	19·0
0·75	1085	0·54	22·3
1·0	950	0·57	23·6

TABLE II.—15-per-cent. Mixtures (First Set). Initial Pressure, Atmospheric.

Heat of Combustion of Coal-gas present in Vessel = 16,200 Calories.

Time from ignition.	Mean absolute temperature of gas.	Mean radiation received by walls per sq. cm.	Total loss of heat by radiation per cent. heat of combustion.
	° C.		
0·05	2360	0·11	3·0
0·1	2160	0·34	9·2
0·15	1980	0·50	13·5
0·2	1810	0·61	16·5
0·25	1680	0·69	18·7
0·5	1270	0·88	23·8
0·75	1060	0·945	25·5
1·0	930	0·96	25·9

TABLE III.—15-per-cent. Mixtures (Second Set). Initial Pressure, Atmospheric.

Heat of Combustion of Coal-gas present in Vessel = 16,400 Calories.

Time from ignition.	Mean absolute temperature of gas.	Mean radiation received by walls per sq. cm.	Total loss of heat by radiation per cent. heat of combustion.
	° C.		
0·05	2410	0·125	3·3
0·1	2220	0·365	9·7
0·15	2020	0·53	14·2
0·2	1860	0·64	17·1
0·25	1720	0·725	19·3
0·5	1280	0·91	24·2
0·75	1060	0·965	25·7
1·0	930	0·98	26·1

TABLE IV.—13-per-cent. Mixtures. Initial Pressure, Atmospheric.

Heat of Combustion of Coal-gas present in Vessel = 14,230 Calories.

Time from ignition.	Mean absolute temperature of gas.	Mean radiation received by walls per sq. cm.	Total loss of heat by radiation per cent. heat of combustion.
	° C.		
0·07	max. temp. 2170	0·12	3·7
0·1	2080	0·23	7·1
0·15	1920	0·38	11·7
0·2	1780	0·48	14·8
0·25	1660	0·56	17·2
0·5	1280	0·74	22·8
0·75	1070	0·8	24·6
1·0	940	0·81	25·0

After 1 second from ignition the radiation emitted is very little. At this time each mixture has radiated about the same proportion, viz., 25 per cent., of its heat of combustion.

The amount of heat lost by radiation up to the moment of maximum temperature is roughly proportional to the product of the third power of the maximum temperature (absolute) attained into the "time of explosion." This will be seen from the following table, where R_m is the radiation absorbed by the blackened wall per square centimetre up to the moment of maximum temperature, θ_m the maximum temperature (absolute) attained in the explosions, and t the "time of explosion."

TABLE V.

Mixture strength.	t.	θ_m.	R_m.	$\frac{R_m}{\theta_m^3 \times t}$.
per cent. 9·7	0·18	1700	0·17	$1{\cdot}92 \times 10^{-10}$
15·0 (1st series)	0·05	2360	0·11	$1{\cdot}67 \times 10^{-10}$
15·0 (2nd series)	0·05	2410	0·128	$1{\cdot}82 \times 10^{-10}$
13·0	0·07	2170	0·12	$1{\cdot}68 \times 10^{-10}$

The curves in fig. 9 are the differentials of the radiation curves shown in fig. 8 plotted to a gas-temperature base. They show the mean rates at which radiation is received by the black walls of the vessel (in calories per square centimetre per second) from the maximum temperatures attained by the various mixtures after explosion down to 1000° C. (abs.). These curves show that the weaker mixtures radiate much

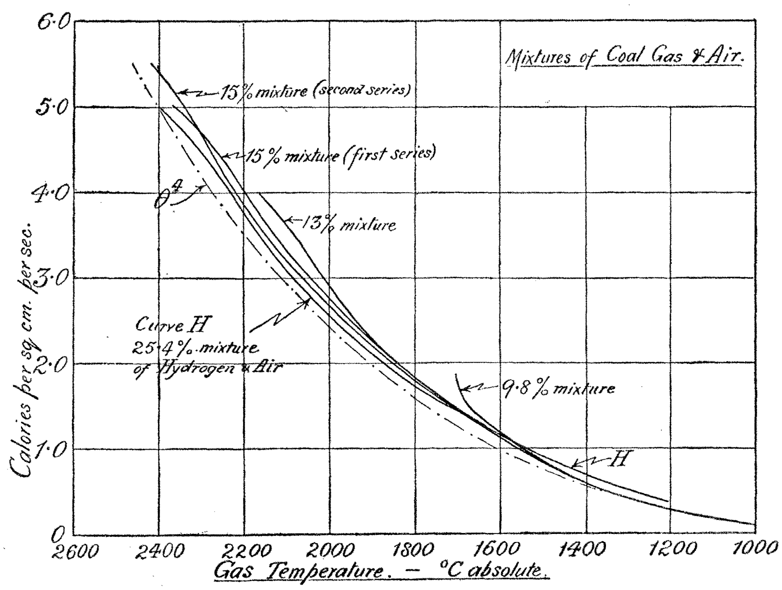

Fig. 9.

more powerfully in the initial stages of cooling than the stronger mixtures do when they have cooled to the same temperatures, although there is very much more radiating gas present in the latter mixtures. Later on in the cooling the radiation from all the mixtures is very much the same at the same gas temperatures. The chain-dotted curve is a θ^4 curve, where θ is the mean absolute temperature of the gas, made to coincide with the radiation curves at the low temperatures.

Mixtures of the Same Strength at Various Densities.

Experiments of the same kind were then made with 15-per-cent. mixtures at various densities. The results of these experiments have been collected into fig. 10. The radiation curves in this figure are the means of those taken with the bolometer in positions A, B, and C on the end cover. Curves I. refer to 15-per-cent. mixtures at one-and-a-half atmospheres density and Curves III. to 15-per-cent. mixtures at half an atmosphere density. Curves II. in the same figure, referring to 15-per-cent. mixtures at atmospheric density, are the same as Curves I. in fig. 8, and are included in this figure for purposes of comparison.

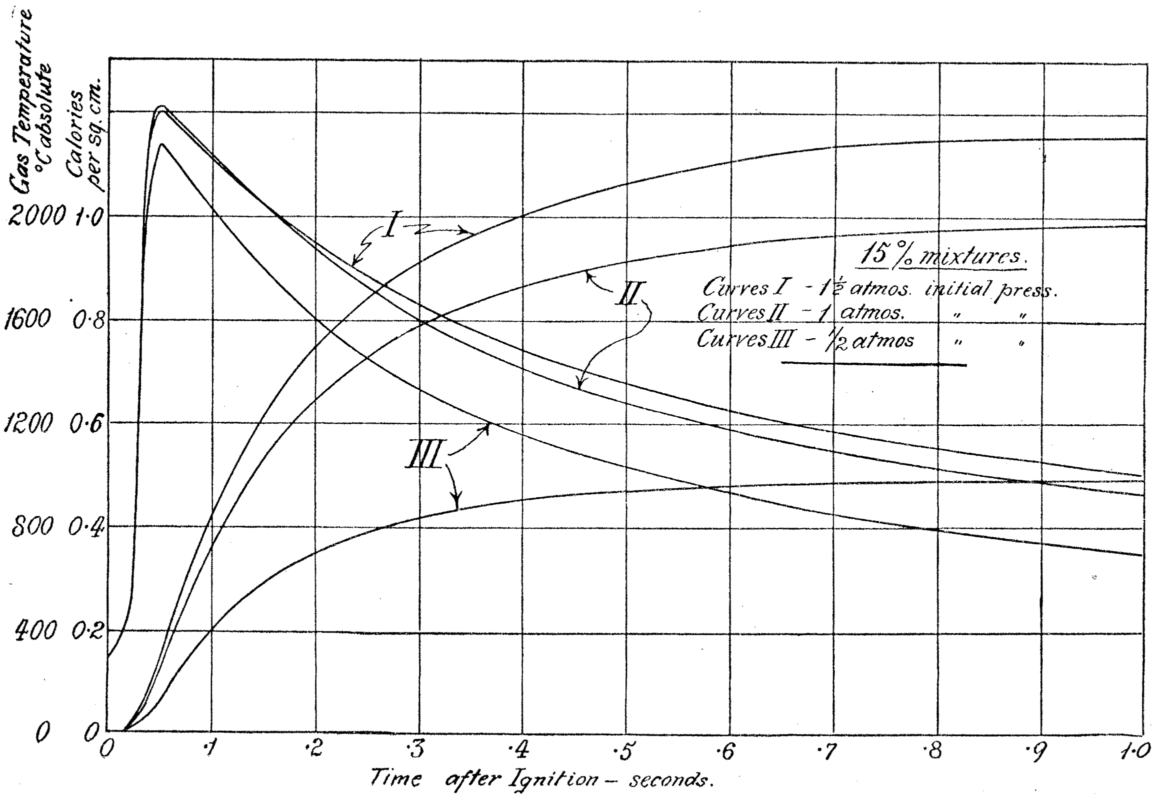

Fig. 10.

Tables VI. and VII. have been prepared from Curves I. and III. in this figure; for Curves II., see Table III., p. 385.

It will be noted that the denser mixtures emit a rather smaller proportion of their heat of combustion up to the moment of maximum pressure than the thinner mixtures do; this is so because the denser mixtures have a slightly greater opacity than the thinner mixtures. In comparing the loss of heat by radiation during cooling it is to be remembered that the rate of cooling of the thinner mixtures is greater than that of the denser mixtures; had the rate of cooling of the mixtures been the same the thinner mixtures would have radiated off a far larger proportion of their heat of combustion than the denser mixtures.

TABLE VI.—15-per-cent. Mixture. Half Atmosphere Initial Pressure.
Heat of Combustion of Coal-gas present in Vessel = 8000 Calories.

Time from ignition.	Mean absolute temperature of gas.	Mean radiation received by walls per sq. cm.	Total loss of heat by radiation per cent. heat of combustion.
	° C.		
0·05	2270	0·061	3·3
0·1	2020	0·2	11·0
0·15	1790	0·29	15·9
0·2	1600	0·35	19·2
0·25	1440	0·39	21·4
0·5	1030	0·47	25·7
0·75	810	0·49	26·8
1·0	700	0·492	26·9

TABLE VII.—15-per-cent. Mixture. One-and-a-half Atmospheres Initial Pressure.
Heat of Combustion of Coal-gas present in Vessel = 24,190 Calories.

Time from ignition.	Mean absolute temperature of gas.	Mean radiation received by walls per sq. cm.	Total loss of heat by radiation per cent. heat of combustion.
	° C.		
0·05	2400	0·14	2·5
0·1	2210	0·425	7·7
0·15	2040	0·615	11·3
0·2	1890	0·75	13·6
0·25	1765	0·843	15·3
0·5	1350	1·065	19·3
0·75	1140	1·143	20·7
1·0	1010	1·158	21·0

The curves in fig. 11 are the differentials of the radiation curves in fig. 10. They give the average rate at which the 15-per-cent. mixtures of the various densities emit radiation during cooling. It will be noticed that the denser mixtures emit much more radiation than the thinner mixtures, especially at the moment of maximum pressure and in the initial stages of cooling. The emission, however, is not in proportion to the density, but varies more nearly as the square root of the density.

Rough Analysis of the Radiation Emitted by the Gaseous Mixture.

The various radiation curves in fig. 12 show the radiation which is transmitted through clear plates of fluorite, quartz, and plate glass, and through $\frac{1}{4}$ in. of water (contained between two plates of glass) in explosions of 15-per-cent. mixtures at atmospheric initial pressure.

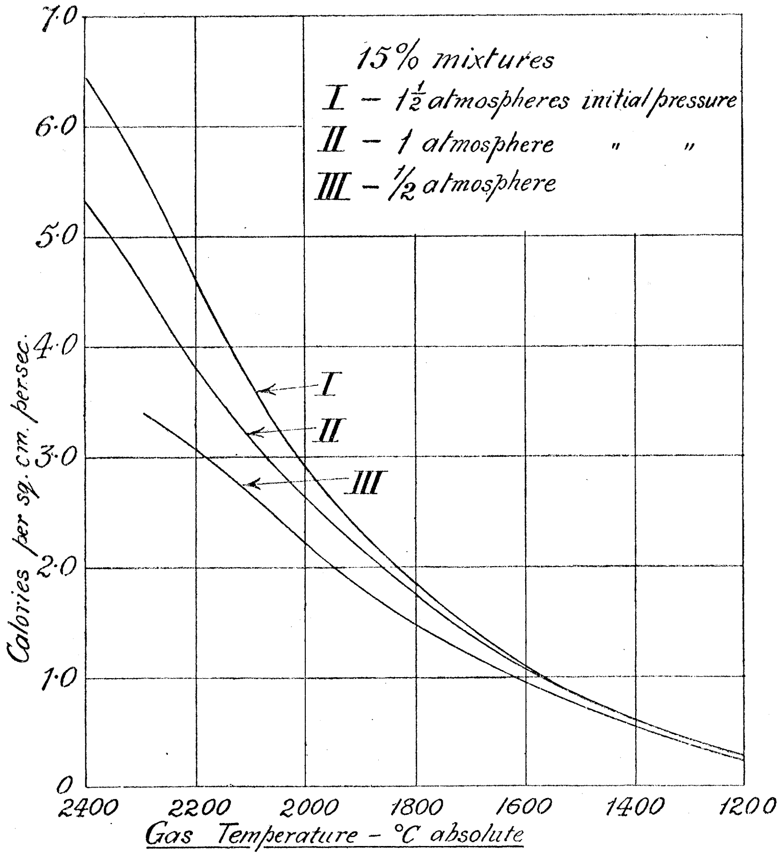

Fig. 11.

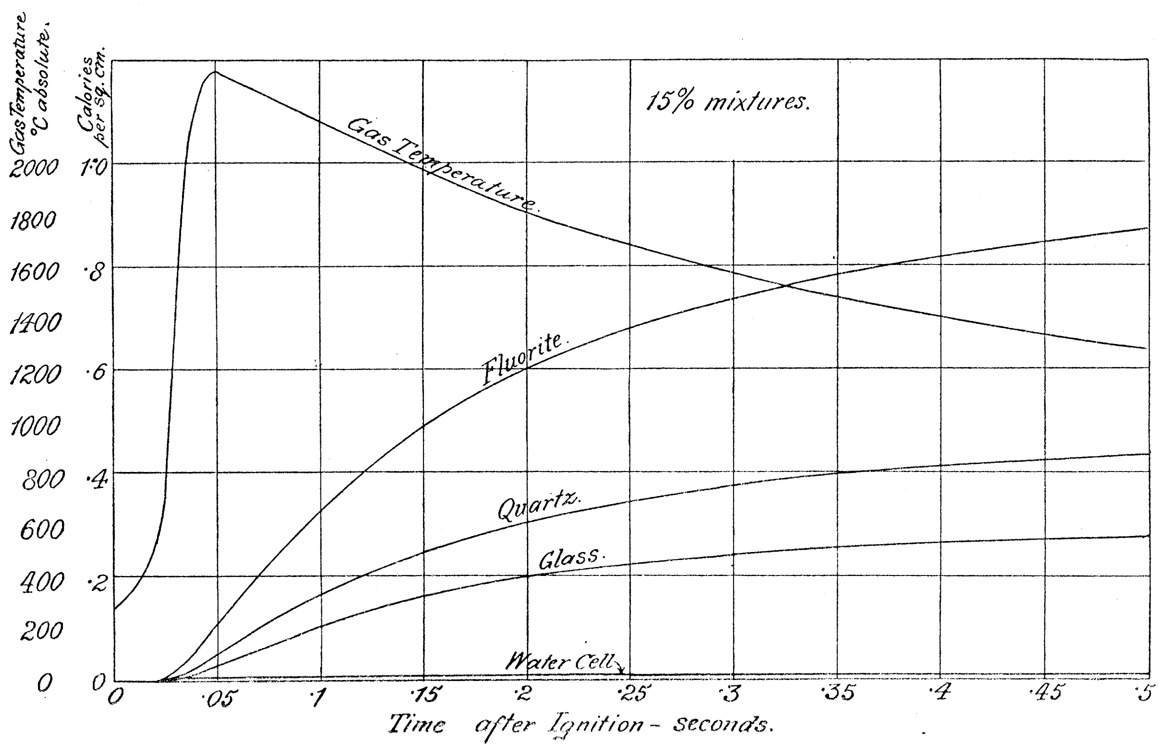

Fig. 12.

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An allowance of 5 per cent. has been made for the absorption of the fluorite, but no allowance has been made for the absorption of the other diathermanous substances.

The quartz plate transmits about 50 per cent. of the total radiation. The Bunsen flame has two strong emission bands whose maxima are at $2{\cdot}8\mu$ and $4{\cdot}4\mu$. The $4{\cdot}4\mu$ band is due to CO_2 alone; the $2{\cdot}8\mu$ band is due to water vapour and also to CO_2. The quartz plate (6 mm. thick) would transmit about 70 per cent. of the $2{\cdot}8\mu$ band and would almost entirely cut off the $4{\cdot}4\mu$ band.* It is highly probable, however, that with the high pressures in explosions the bands broaden out, for SCHAEFER has shown that there is a widening of the *absorption bands* of CO_2 when the pressure is increased. If the emission and absorption bands are similar the quartz will transmit from 10 per cent. to 20 per cent. of the $4{\cdot}4\mu$ bands.† The $2{\cdot}8\mu$ band also broadens out and the quartz transmits about 65 per cent. of it.‡ It is not difficult from these observations to estimate roughly the proportion emitted by the water vapour and by the CO_2. Roughly, one may take it, the hydrogen emits from 50 per cent. to 60 per cent. of the total radiation, the remainder being, of course, emitted by CO_2. There is nearly two and a half times as much water vapour present in the mixture as there is CO_2, so that, speaking somewhat loosely, the CO_2 emits about twice as strongly as the water vapour does volume for volume.§

Bolometric measurements with the window of quartz were also made in the different positions A, B, and C, and also with different strengths of mixtures, and in each case the radiation transmitted through the quartz was always the same proportion of that measured with the fluorite window.

The plate glass ($\frac{1}{4}$ in. thick) transmits about one-third of the total radiation emitted by the gaseous mixture. The glass probably cuts off most of the radiation emitted by CO_2 and transmits about 50 per cent. of that emitted by the water vapour.

The water-cell almost entirely cuts off all the radiation emitted by the gas (see

* See 'Transmission Spectrum of Quartz, Coblentz, Infra-Red Spectra,' Part VI., p. 45.

† See absorption spectrum curves of CO_2 in SCHAEFER'S paper ('Ann. der Phys.,' 16, I., p. 93), and also the transmission spectrum of quartz.

‡ This result was obtained from a comparison of the amounts of radiation from a hydrogen and air mixture received by the bolometer when it was protected first by the plate of fluorite and then by the plate of quartz. This gaseous mixture contained after explosion only steam and nitrogen, so that the radiation emitted was almost entirely of wave-length in the neighbourhood of $2{\cdot}8\mu$.

§ The radiation emitted by the gaseous mixture is almost entirely due to the H_2O and CO_2 which it contains. The mixture contains about $8{\cdot}5$ per cent. of CO_2 and 20 per cent. of H_2O, the remainder being almost entirely N.

It is interesting to compare this result with those of R. VON HELMHOLTZ on the radiation from hydrogen, carbon monoxide, marsh gas, ethylene, and coal-gas flames. He found that the CO_2 produced in the CO flame emitted about $2{\cdot}4$ times as strongly as an equal volume of water vapour produced in a hydrogen flame, and shows that this ratio is preserved in flames whose products of combustion contain CO_2 and steam. The flames in these experiments were just rendered non-luminous by adjusting the air supply, and the temperatures of all of them were probably pretty much the same.

fig. 12). Water 1 cm. thick entirely cuts off all radiation of wave-length greater than 1·2μ or 1·3μ, and is most transparent in the visible part of the spectrum (0·4μ to 0·7μ).* The water-cell therefore cuts off all the radiation peculiar to heated CO_2 and water vapour (which is of wave-length between 2μ and 5μ) and transmits practically only the luminous radiation. The water-cell continues to transmit radiation for about one-tenth of a second after the attainment of maximum pressure, and it seems probable that the mixture is luminous during this period.† The total loss of heat in the explosion of this mixture due to the emission of luminous radiation is about 0·25 per cent. of its heat of combustion.

Table VIII. has been prepared from the Curves H in fig. 8. These curves refer to experiments made with a 25·4-per-cent. mixture of hydrogen and air. The radiation curve is the mean of those taken with the bolometer in positions A, B, and C on the end cover. The hydrogen used in these experiments was supplied by the British Oxygen Company, guaranteed 98 per cent. pure.

TABLE VIII.—25·4-per-cent. Mixture of Hydrogen and Air. Initial Pressure, Atmospheric.

Heat of Combustion of Hydrogen in Vessel = 16,320 Calories.

Time from ignition.	Mean absolute temperature of gas.	Mean radiation received by walls per sq. cm.	Total loss of heat by radiation per cent. heat of combustion.
	° C.		
0·017	2400	0·018	0·5
0·05	2200	0·15	4·0
0·1	1920	0·285	7·7
0·15	1700	0·37	10·0
0·2	1530	0·425	11·4
0·25	1400	0·47	12·6
0·5	1100	0·57	15·5
0·75	910	0·59	15·8
1·0	810	0·60	16·1

The total amount of radiation emitted up to the moment of maximum pressure amounts to 0·5 per cent. of its heat of combustion, the maximum temperature being 2400° C. (abs.) and the time of explosion 0·017 second. A 15-per-cent. mixture of coal-gas and air whose maximum temperature also reached 2400° C. (abs.) emitted up to the moment of maximum pressure rather more than 3 per cent. of its heat of combustion, the time of explosion in this case being 0·05 second.

* For the transmission spectrum of water, see E. F. NICHOL'S paper, 'Phys. Rev.,' I., p. 1, 1896.

† On looking at the explosion of a 15-per-cent. mixture in the same vessel through the window, the bright flash appeared to the eye to last for about $\frac{1}{4}$ second (the "time of explosion" of the mixture in the vessel being only $\frac{1}{20}$ second). Of course if water transmits even a small proportion of radiation of longer wave-length the above statement is not justifiable.

The total amount of radiation emitted by the hydrogen mixture amounts to about 16 per cent. of its heat of combustion. A 15-per-cent. mixture of coal-gas and air having the same maximum temperature emitted 26 per cent. of its heat of combustion; in the latter case, however, the rate of cooling of the gaseous mixture after explosion is much slower than that of the hydrogen mixture.

The Curve H in fig. 9 is the differential of the radiation Curve H in fig. 8. It gives the average rate at which the blackened walls of the explosion vessel receives radiation in calories per square centimetre of surface per second from the hydrogen-air mixture during cooling.

Table IX. compares the emission of the 25·4-per-cent. hydrogen mixture and that of a 15-per-cent. mixture of coal-gas and air in the same vessel and at the same mean gas temperatures. The hydrogen mixture after explosion contains 30 per cent. of water vapour and the coal-gas mixture contains 8·5 per cent. of CO_2 and 20 per cent. of water vapour. The densities of the two mixtures are very nearly the same.

TABLE IX.

Mean absolute gas temperature.	Emission calories per sq. cm. per second.	
	Hydrogen mixture.	Coal-gas mixture.
2400	5·0	5·4
2200	3·75	3·85
2000	2·55	2·7
1800	1·75	1·8
1600	1·15	1·12
1400	0·70	0·62

The hydrogen mixture emits just as strongly at high temperatures as the coal-gas mixture does; at lower temperatures the hydrogen mixture emits rather more powerfully. This, at first sight, seems rather extraordinary, in view of the results given on p. 390, for in the hydrogen mixture there is no CO_2 and the quantity of water vapour is only 50 per cent. greater than that in the coal-gas mixture. We shall see presently (p. 397) that the water vapour is more transparent to the radiation which it emits than is the mixture $CO_2 . H_2O$ to its radiation. This may to some extent account for the equality of the emission in the two mixtures. Probably also there are larger temperature differences in the hydrogen mixture. The much quicker rate of cooling suggests that the temperature gradient in this mixture is greater than that in the coal-gas mixture, so that at the same mean gas temperature the hottest portions of the hydrogen mixture may be at higher temperatures than the same portions of the coal-gas mixture.

PART II.—THE DIATHERMANCY AND EMISSIVE POWER OF THE HOT GASEOUS MIXTURE AFTER EXPLOSION.

After the experiments just described had been made some of them were repeated with an explosion vessel of the same shape and size whose interior surface was silver-plated and therefore reflecting. It at once appeared that the gaseous mixture when exploded in this vessel emitted radiation much more strongly than a mixture of the same strength exploded in the vessel with black walls. Curve A_P, fig. 13, shows the radiation absorbed by the bolometer per square centimetre when it was protected by the plate of quartz* during the explosion and subsequent cooling of a 15-per-cent. mixture of coal-gas and air at atmospheric density in the vessel with reflecting walls. Curve A_B in the same figure shows the same thing when the walls were black. The corresponding gas temperature curves (T_P and T_B) are also shown. The maximum gas temperature reached after explosion is about 3 per cent. greater and the subsequent rate of cooling much slower when the mixture is enclosed in the vessel with reflecting walls than it is when the mixture is enclosed in the vessel with black walls. This is in agreement with Prof. HOPKINSON'S recent experiments.† In the following table the second and third columns give the rate at which that part

TABLE X.—15-per-cent. Mixtures of Coal-gas and Air. Quartz Window.

Bolometer close up to Quartz Window.

Mean absolute temperature of gas.	Rate of absorption of radiation by bolometer in calories per sq. cm. per second.		Ratio Column II. to Column III.
	Walls reflecting.	Walls black.	
° C.			
2300	4·95	2·6	1·9
2200	4·1	2·2	1·85
2000	2·55	1·45	1·75
1800	1·55	0·9	1·7
1600	0·85	0·5	1·7

of the radiation from the gaseous mixture which is transmitted through the plate of quartz is absorbed by the bolometer per square centimetre when the walls of the vessel are reflecting and blackened respectively. These figures are taken from the

* No measurements were made of the radiation transmitted through the fluorite window when the walls of the vessel were reflecting. The platinum bolometer, having only a thermal capacity equivalent to 0·008 gr. of water per square centimetre, would have been heated up to a temperature of over 300° C. with a 15-per-cent. mixture, and the correction to be applied for the loss of heat by the bolometer would have been so great as to make the results unreliable.

† 'Roy. Soc. Proc.,' A, vol. 84, p. 155.

dotted Curves A_P' and A_B' (fig. 13) which are the differentials of the radiation Curves A_P and A_B. The fourth column gives the ratio of the figures in the second column to those in the third column.

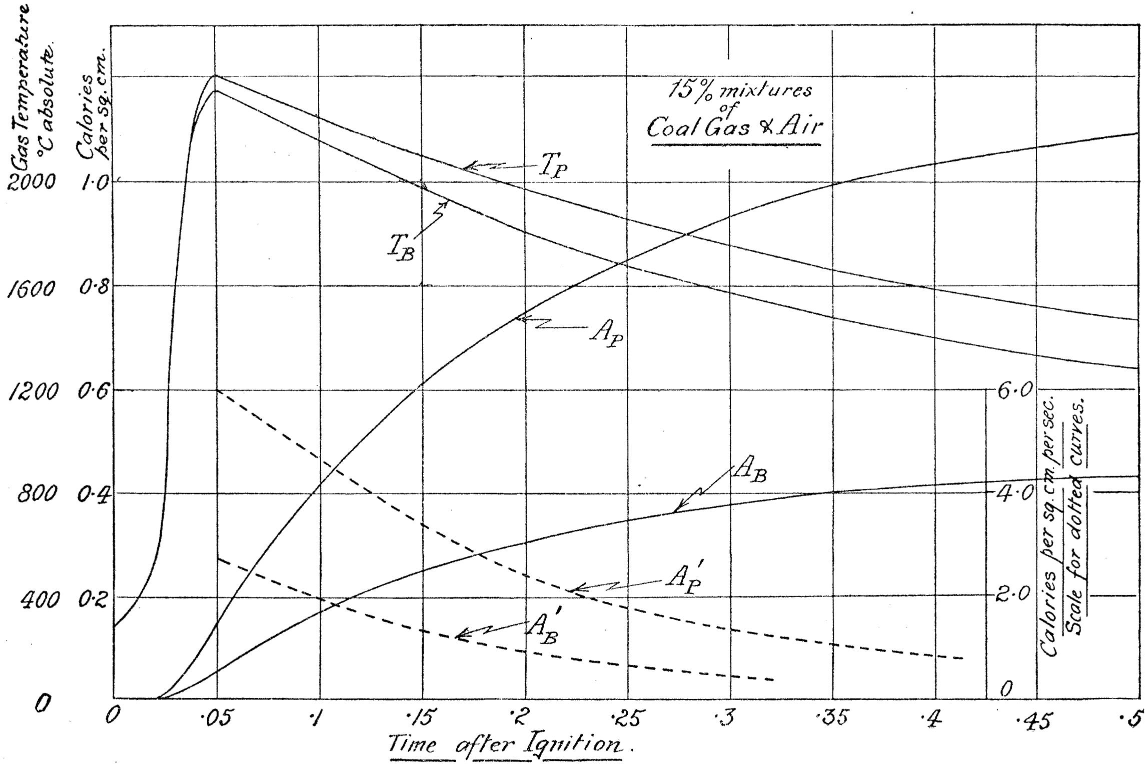

Fig. 13.

From this table it will be seen that the gaseous mixture when enclosed in the vessel with reflecting walls radiates from 70 per cent. to 90 per cent. more strongly than the same mixture does when enclosed in the black-walled vessel.

With the object of analysing this effect measurements were made of the radiation emitted by a small sectioned cylinder (or more correctly a cone of small solid angle) of the gaseous mixture of different (effective) lengths, first, when the walls were made reflecting, and, secondly, when the walls were black.

These experiments were carried out with the silver-plated explosion vessel. The same bolometer holder was used, but the bolometer was placed some distance behind the plate of diathermanous substance, and the interior of the tube, into which the bolometer is pushed, blackened over so as to prevent radiation from any point in the gas outside the cone reaching the bolometer by reflection from its surface.

The emission was measured from two lengths of the gas, viz., 30 cm. and an effective length of 59 cm., these lengths being chosen because they could be conveniently obtained in the vessel. The vessel was 30 cm. in length, and when the walls were black the first length was directly obtained. The second length, which is nearly double the first length, was in effect got by polishing a circular patch of silver of about 6 in. diameter opposite the bolometer on the other end cover, and so reflecting the 30 cm. back upon itself. Were the silver perfectly reflecting a virtual length of 60 cm. would have been obtained by this means, but having regard to its imperfect reflecting power the 30 cm. was increased by about 97 per cent. or 98 per cent.,* this brings the equivalent length down to 59 cm. When the walls of the vessel were reflecting, the 30 cm. length of gas was obtained by blackening a circular patch of about 6 in. diameter on the end cover opposite the bolometer. This made it impossible for radiation from any point outside the cone of gas to reach the bolometer. When this black patch was rubbed off and the silver polished, the 30 cm. was virtually increased to 59 cm. as explained above. In this case, however, it was possible for radiation reflected from the silvered walls surrounding the bolometer to reach the bolometer after again being reflected from the opposite end cover. In order to prevent this a ring of black paint was placed on the walls round the bolometer.

In all the following experiments the bolometer was in position A on the end cover. It was placed at a distance of 12·5 cm. behind the fluorite, so that the solid angle subtended was 0·062.

Records of the pressure of the gas and rise of temperature of the bolometer during explosion and subsequent cooling of mixtures of coal-gas and air were taken in the usual way. From these records curves of mean gas temperature and of radiation emitted by the cone of gas were obtained with times after ignition as abscissæ. In what follows these radiation curves have been differentiated (with respect to time), and the rates at which the cone of gas emits radiation plotted against the mean absolute temperature of the gas.

Fig. 14 gives the results of these experiments for 15-per-cent. mixtures of coal-gas and air with the fluorite window, an allowance of 5 per cent. having been made for the absorption of the fluorite and 5 per cent. for reflection from the blackened surface of the bolometer. The results have been divided by 0·062 so as to give the emission from unit solid angle. Prof. CALLENDAR calls this the "intrinsic radiance."

Curve A shows the intrinsic radiance from 59 cm. of the hot gaseous mixture from the maximum temperature reached in the explosion down to 1300° C. (abs.), when the walls of the vessel were reflecting.

Curve B.—30 cm., walls reflecting.

Curve C.—59 cm., walls black.

Curve D.—30 cm., walls black.†

Curve S.—15 cm., walls black.

* Following the figures given by HAGEN and RUBENS for the reflecting power of silver for radiation of wave-length between 2μ and 5μ ('Z. für Instr. Kunde,' 22 (1902), p. 52).

† The intrinsic radiance from 15 cm. reflected back upon itself, by means of a small polished silvered plate placed opposite the bolometer, was also measured; the results were precisely the same as those shown in Curve D. When this plate was painted black the record giving Curve S was taken.

On comparing Curves A and B we find that when the walls are reflecting, the radiation emitted by 59 cm. is over 30 per cent. greater than that emitted by 30 cm. From Curves C and D we find that when the walls are black, 59 cms. radiate well over 20 per cent. more heat than 30 cm. do until the temperature falls to about 2200° C. (abs.) (*i.e.*, for about $\frac{1}{20}$ second after the attainment of maximum pressure).

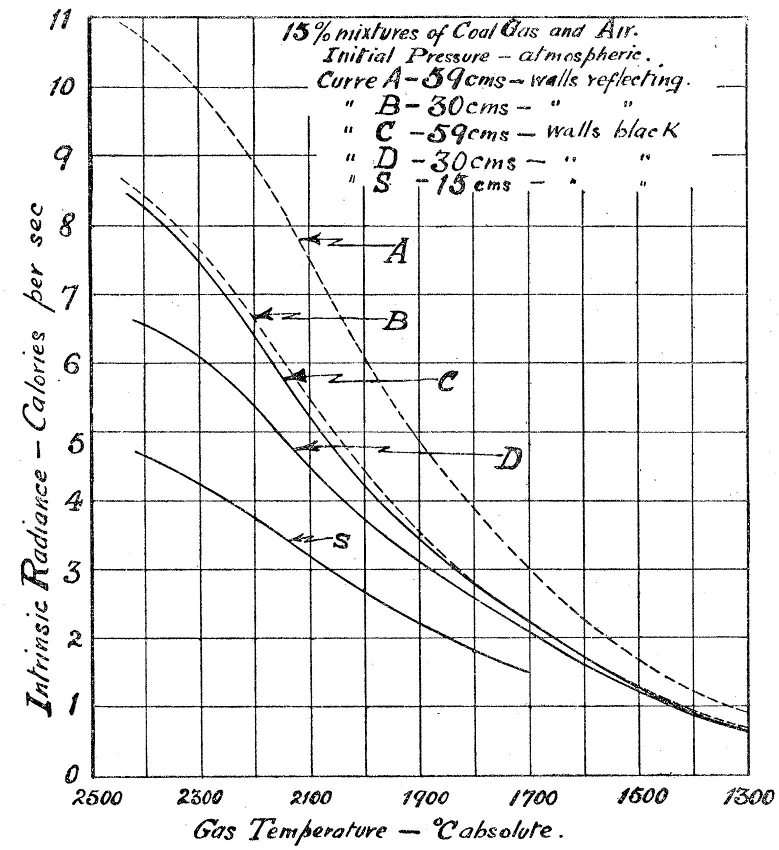

Fig. 14.

After this temperature the radiation from these two thicknesses becomes more and more nearly the same until a temperature of about 1500° C. (abs.) is reached, when it becomes the same. Thus it will be seen that when the walls are reflecting, the gaseous mixture after explosion is highly transparent to its own radiation even after the temperature has fallen below 1500° C. (abs.). It is also very transparent when the walls are black in the initial stages of cooling, although later on, after the temperature has fallen to about 1500° C. (abs.), it has become fairly opaque.

The following table has been prepared from the curves in this figure. The second column compares the radiation emitted from 30 cm. of the hot gaseous mixture when the walls of the vessel are reflecting with that from the same thickness of gas at the same temperature when the walls are black. The third column shows the same ratio for 59 cm. effective length.

TABLE XI.—15-per-cent. Mixtures of Coal-gas and Air. Fluorite Window.

Mean absolute temperature of gas.	Ratio $\frac{\text{Intrinsic radiance from } l \text{ cm. walls reflecting}}{\text{Intrinsic radiance from } l \text{ cm. walls black}}$.	
	l = 30 cm. (from curves B and D).	l = 59 cm. (from curves A and C).
° C.		
2430	1·29	1·29
2400	1·28	1·29
2300	1·25	1·33
2200	1·23	1·4
2000	1·2	1·4

It will be seen from this table that the intrinsic radiance from a certain thickness of the hot gas is about 30 per cent. greater when the gas is enclosed in the vessel with reflecting walls than when it is enclosed in the vessel with black walls.

The same experiments were repeated with the bolometer placed at the centre of the end cover (position C, fig. 1*b*). The results were very much the same as those shown above with the bolometer in position A.

Experiments of the same kind were also made with the window of quartz. The results were very much the same as those obtained with the fluorite window, but the ratios of the intrinsic radiance from 59 cm. of the gaseous mixture to that from 30 cm. were rather greater than those obtained with the fluorite window. This seems to show that the water vapour is more transparent to the radiation which it emits than is the mixture $CO_2 . H_2O$.* to its radiation.

These experiments support those whose results are shown in fig. 13 and Table X. The following table gives the ratio of the intrinsic radiance when the walls are

TABLE XII.—15-per-cent. Mixtures of Coal-gas and Air.

Mean absolute temperature of gas.	$\frac{\text{Intrinsic radiance walls totally reflecting}}{\text{Intrinsic radiance walls totally black}}$.	
	Quartz window.	Fluorite window.
° C.		
2400	1·7	1·65
2300	1·65	1·65
2000	1·6	1·6
1800	1·6	1·55

* The gaseous mixture in the above experiments (15-per-cent. mixtures of coal-gas and air) contains after explosion about 8·5 per cent. of CO_2 and 20 per cent. of H_2O, the remainder being mainly N.

totally reflecting (Curves A) to that when they are totally black (Curves D) both for the quartz and the fluorite windows.

The ratios of the intrinsic radiance when the walls are reflecting to that when they are black, given in this table, are very much the same as those in the fourth column of Table X., which gives the ratio of the emission when the walls are reflecting to that when they are black, measured with the bolometer close up to the quartz plate. In the latter case, however, the ratios are slightly greater. This is because the intrinsic radiance from the gas when enclosed in reflecting walls comes only from an effective length of 59 cm., while the radiation measured when the bolometer is close up to the plate of quartz must be looked upon as coming from a mass of gas of very great dimensions, which would have been infinite had the walls been perfectly reflecting and the ratio of the area of the black bolometer holder and bolometer to that of the total interior surface of the vessel* very small.

In fig. 15 are shown curves giving the intrinsic radiance from 59 cm. (Curve E) and from 30 cm. (Curve F) of the hot gas after explosions of 13-per-cent. mixtures of

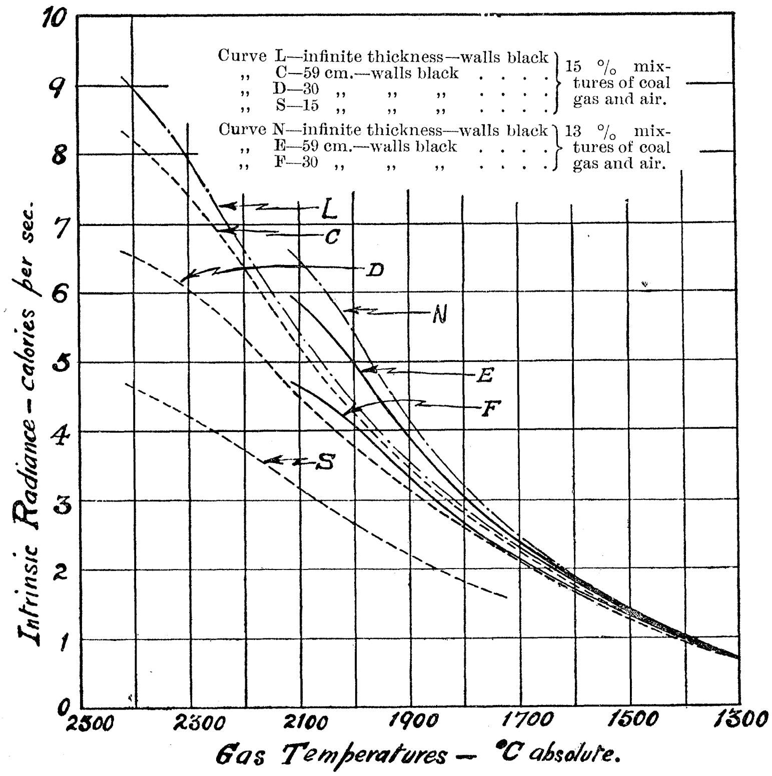

Fig. 15.

coal-gas and air in the vessel when the walls were black. The fluorite window was used in these experiments and, as in the case of those with 15-per-cent. mixtures, an allowance of 5 per cent. has been made for the absorption of the fluorite and 5 per

* The ratio of the area of the black bolometer and holder to that of the total interior surface of the vessel was about 1 to 60 in these experiments.

cent. for reflection from the blackened surface of the bolometer. In the same figure are shown the (dotted) curves C, D, and S taken from fig. 14, which give the intrinsic radiance from 59 cm., 30 cm., and 15 cm. of the hot gas after explosions of 15-per-cent. mixtures in the vessel with black walls. The chain-dotted curves L and N show the values of the intrinsic radiance from an infinite thickness of the gaseous mixture calculated on the assumption that the absorption follows an exponential law (see p. 398).

On comparing Curves C and E, or D and F, we see that the 13-per-cent. mixtures radiate more strongly in the initial stages of cooling than the 15-per-cent. mixtures do when they have cooled to the same temperatures as the 13-per-cent. mixtures have in this epoch, although there is about 15-per-cent. more radiating gas in the latter mixtures. The same result was previously obtained when comparing at the same mean gas temperatures the average rate at which radiation is absorbed by the blackened walls per square centimetre when mixtures of from 10 per cent. to 15 per cent. were exploded in the vessel (see fig. 9).

It will be noticed that Curves C and D (15-per-cent. mixtures) and E and F (13-per-cent. mixtures) show precisely the same peculiarities. At maximum pressure, and also in the initial stages of cooling, 59 cm. emit much more strongly than 30 cm., while, later on, when the gas temperatures have fallen to about 1500° C. (abs.),* the emission from 30 cm. is just as great as that from 59 cm. The following table gives the ratio of the intrinsic radiance from 59 cm. of the hot gas to that from 30 cm. (at the same temperature) up to $\frac{1}{10}$ second after maximum pressure for both the 13-per-cent. and 15-per-cent. mixtures in the vessel with black walls. Gas temperatures and pressures at the same times are also given.

Table XIII.—Mixtures of Coal-gas and Air.

Time from maximum pressure, seconds.	13-per-cent. mixtures. Vessel with black walls.			15-per-cent. mixtures. Vessel with black walls.		
	Pressure lbs. per sq. in. above atmosphere.	Gas temperature, absolute.	$\frac{\text{Radiation from 59 cm.}}{\text{Radiation from 30 cm.}}$	Pressure lbs. per sq. in. above atmosphere.	Gas temperature, absolute.	$\frac{\text{Radiation from 59 cm.}}{\text{Radiation from 30 cm.}}$
		° C.			° C.	
0·0	92·5	2110	1·27	106·0	2430	1·27
0·025	89·0	2040	1·23	100·0	2320	1·22
0·05	85·0	1960	1·20	95·0	2210	1·20
0·075	81·0	1880	1·16	90·0	2110	1·17
0·1	77·0	1810	1·14	86·0	2020	1·14

* The times after maximum pressure taken by the 13-per-cent. and 15-per-cent. mixtures to cool to 1500° C. (abs.) are nearly equal.

The intrinsic radiance from 59 cm. is from 15 per cent. to 25 per cent. greater than that from 30 cm. for both the 13-per-cent. and 15-per-cent. mixtures in the initial stages of cooling. This implies that the gas is very transparent to its own radiation in this epoch. Prof. CALLENDAR, from his recent experiments on the radiation emitted by different thicknesses of flame at atmospheric pressure, finds that in flame the exponential law of absorption is closely obeyed.* He finds practically the same coefficient of absorption, viz., 0·054, for two distinct states of flame (at different temperatures) produced in Mèker burners by varying the air supply. Reducing my results to atmospheric pressure, on the assumption that the radiation and absorption of a layer of gas whose thickness is inversely proportional to the density is constant, I find that at $\frac{1}{20}$ second after the attainment of maximum pressure the coefficient of absorption in the 13-per-cent. mixture is 0·008 (temperature of gas 1960° C. abs.), and in the 15-per-cent. mixture 0·0072 (temperature of gas 2210° C. abs.), whilst at the moment of maximum temperature it is in both mixtures only about $\frac{1}{10}$ of the value found by CALLENDAR for flame. This extremely high transparency of the gaseous mixtures at the moment of maximum pressure, and in the initial stages of cooling, cannot be wholly due to the higher temperatures reached in the explosions, for the transparency of the 13-per-cent. mixture in the initial stages of cooling is much greater than that of the 15-per-cent. mixture at temperatures which the 13-per-cent. mixture has in this epoch, as will be seen from the following table. This

TABLE XIV.—Walls of Vessel Black.

Mean absolute temperature of gas.	Per cent. transmission by $(\frac{15}{13} \times 30)$ cm. of 13-per-cent. mixture.	Per cent. transmission by 30 cm. of 15-per-cent. mixture.
° C.		
2100	22	17
2000	17	14
1800	10	10

table gives the proportion of incident radiation transmitted by $(\frac{15}{13} \times 30)$ cm. of the 13-per-cent. mixture and 30 cm. of the 15-per-cent. mixture; a layer of the 13-per-cent. mixture $(\frac{15}{13} \times 30)$ cm. thick contains the same amount of absorbing gas (CO_2 . H_2O) as 30 cm. of the 15-per-cent. mixture.

The following table gives the observed values of the intrinsic radiance from different thicknesses of the 15-per-cent. mixture after explosion (from Curves C, D, and S), and directly under them are given the values for the same thicknesses calculated by

* Prof. CALLENDAR'S paper on "Radiation from Flames" is given in the 'Third Report of the B.A. Committee on Gaseous Explosions,' Appendix A, p. 19.

means of the formula

$$R_x = R_\infty (1 - \epsilon^{-Kx})$$

where

R_x is the intrinsic radiance from x cm. of gas,
R_∞ is the intrinsic radiance from an infinite thickness, and
K is the coefficient of absorption per cm.

The sixth column in this table gives the value of K at various temperatures, and the last column gives the value K would have were the gas expanded down to atmospheric pressure, assuming, of course, that the transparency of a thickness of gas inversely proportional to the gas pressure is independent of the pressure.*

TABLE XV.—15-per-cent. Mixtures of Coal-gas and Air. Walls black. Fluorite Window.

Mean absolute temperature of gas.	Intrinsic radiance, calories per second. From 15 cm.	From 30 cm.	From 59 cm.	From infinite thickness.	Coefficient of absorption, K.	K, reduced to atmospheric pressure.
° C.						
2300	observed 4·2	6·1	7·45	—	—	—
	calculated 4·18	6·12	7·4	7·75	0·052	0·0069
2200	observed 3·75	5·35	6·4	—	—	—
	calculated 3·7	5·35	6·4	6·66	0·054	0·0075
2000	observed 2·65	3·7	4·25	—	—	—
	calculated 2·66	3·72	4·28	4·4	0·062	0·0095
1800	observed 1·75	2·55	2·85	—	—	—
	calculated 1·88	2·53	2·82	2·86	0·072	0·0122

The close agreement between the observed and calculated values shows that the exponential law of absorption is closely obeyed in the gaseous mixture during cooling.

Table XVI. gives the values which the intrinsic radiance from 1 cm. would have were the gaseous mixture perfectly transparent. The intrinsic radiance corrected for absorption from 1 cm. of the gaseous mixture is the limit of R_x/x when $x = 0$ in the formula $R_x = R_\infty (1 - \epsilon^{-Kx})$; this is equal to KR_∞. The fourth column gives the ratio of the intrinsic radiance corrected for absorption when the walls are reflecting to that when they are black. The figures in the last column are proportional to the radiation

* See, however, p. 404.

TABLE XVI.—15-per-cent. Mixtures of Coal-gas and Air. Fluorite Window.

Mean absolute temperature of gas.	Intrinsic radiance corrected for absorption from 1 cm. of gas.		Ratio Column II. to Column III.	Radiation of wave-length $3\cdot6\mu$ according to PLANCK'S formula.
	Walls reflecting.	Walls black.		
° C.				
2400	0·47	0·43	1·09	0·42
2300	0·44	0·40	1·11	0·39
2200	0·37	0·36	1·03	0·35
2000	0·24	0·27	0·89	0·28
1800	0·16	0·20	0·8	0·22

of wave-length $3\cdot6\mu$ (the mean between $2\cdot8\mu$ and $4\cdot4\mu$, which are the principal maxima of emission and absorption in the Bunsen flame spectrum) emitted by a full radiator at the temperatures given in the first column according to PLANCK'S formula

$$E_\lambda = c_1\lambda^{-5}\left(\epsilon^{c_2/\lambda\theta} - 1\right)^{-1}$$

when c_2 is taken as 14,700.

There is in all probability a considerable error in the values given in the second column of this table and, consequently, in the ratios in the fourth column. It is unlikely that these ratios should ever be less than unity, for it will be remembered that the observed values of the intrinsic radiance from 30 cm. and 59 cm. of the gaseous mixture enclosed in the vessel with reflecting walls were about 30 per cent. greater than those from the same thicknesses of an identical mixture enclosed in the vessel with black walls.

The similarity between the figures in the third and last columns shows that the variation of the radiation from the gas with temperature is very much the same as that given by PLANCK'S formula for a single wave-length of $3\cdot6\mu$, which at high temperatures (1800° C. abs. to 2400° C. abs.) varies approximately as the square of the absolute temperature. The very rapid variation of the total radiation from the gaseous mixture with temperature shown in figs. 9 and 15 (which varies approximately as the fourth power of the absolute temperature*) is in part due to the decreasing transparency of the gaseous mixture as it cools. PASCHEN found that the emission of radiation of wave-length $4\cdot4\mu$ from a thickness of CO_2 greater than 7 cm. was, between the temperatures 150° C. and 500° C., only a little below that of a

* It should be noticed that this is accidental. Had the vessel been much larger (or smaller) the radiation curve would lie far above (or below) the θ^4 curve in the initial stages of cooling (see dotted curves, fig. 15) on account of the high transparency of the gaseous mixture; but after the temperature of the mixture has fallen to about 1500° C. (abs.) it would coincide with the θ^4 curve, the gaseous mixture having by this time become fairly opaque.

black body at the same temperature, so that, if we assume that the width of the CO_2 emission bands do not change with temperature, the total emission would vary approximately according to PLANCK's formula for a single wave-length of $4 \cdot 4\mu$. At these low temperatures, however, the variation of PLANCK's formula for radiation of wave-length $4 \cdot 4\mu$ with the absolute temperature θ is very nearly proportional to the variation of θ^4 with θ, so that it is not possible to say whether at the high temperatures the emission from the CO_2 would vary according to PLANCK's formula or the fourth power law.

Effect of Density on the Transparency and Emissive Power.

The same experiments were repeated with 15-per-cent. mixtures of coal-gas and air at various densities varying from half an atmosphere to one and a quarter atmospheres. The experiments were not carried further for it was questionable whether the fluorite would stand very much higher pressures. These experiments showed that the ratio of the emission by 59 cm. (or 30 cm.) when the walls are reflecting to that when the walls are black decreases as the density increases. For example, at 2200° C. (abs.) this ratio for 59 cm. is 1·48 at $\frac{1}{2}$ atmosphere density, 1·25 at $\frac{3}{4}$ atmosphere, and 1·19 at $1\frac{1}{4}$ atmospheres, and for 30 cm. at the same temperature it is 1·35 at $\frac{1}{2}$ atmosphere, 1·15 at $\frac{3}{4}$ atmosphere, and 1·06 at $1\frac{1}{4}$ atmospheres. It will be noticed that these ratios are always greater for 59 cm. than they are for 30 cm. thickness. This

TABLE XVII.—15-per-cent. Mixtures of Coal-gas and Air. Fluorite Window. Walls Black.

Mean absolute temperature of gas.	$\frac{\text{Intrinsic radiance from 59 cm.}}{\text{Intrinsic radiance from 30 cm.}}$ walls black.			
	$\frac{1}{2}$ atmosphere density.	$\frac{3}{4}$ atmosphere density.	1 atmosphere density.	$1\frac{1}{4}$ atmospheres density.
° C.				
2400	—	—	1·27	—
2300	1·32	1·25	1·22	1·22
2200	1·27	1·20	1·19	1·18
2000	1·22	1·15	1·14	1·12
1800	1·19	1·13	1·1	1·1
1600	1·19	1·13	1·07	1·08

is also true of the experiments made with the gaseous mixture at atmospheric density, as will be seen on comparing the figures in the second and third columns of Table XI. This is partly because the transparency of the gas when enclosed in the vessel with reflecting walls is greater than it is when the gas is enclosed in the black-walled vessel, and probably partly because the measurements of the intrinsic radiance from

30 cm. (walls reflecting) are somewhat too low on account of the reduced radiating power of the gas at the end of the cone owing to its being near the blackened patch opposite the bolometer.

Table XVII. gives the ratio of the intrinsic radiance from 59 cm. to that from 30 cm. of the gaseous mixtures of the various densities when the walls of the explosion vessel were black.

The second column in the following table shows the ratio of the intrinsic radiance from $(\frac{1}{2} \times 59)$ cm. of the gaseous mixture at atmospheric density to that from $(\frac{1}{2} \times 30)$ cm. The third column shows the same ratio for $(\frac{3}{4} \times 59)$ cm. and $(\frac{3}{4} \times 30)$ cm.; the fourth (which is the same as the fourth column in Table XVII. above) for 59 cm.

TABLE XVIII.—15-per-cent. Mixtures of Coal-gas and Air at Atmosphere Density. Fluorite Window.

Mean absolute temperature of gas.	$\frac{\text{Intrinsic radiance from } l_1 \text{ cm.}}{\text{Intrinsic radiance from } l_2 \text{ cm.}}$ walls black.			
	$l_1 = 29 \cdot 5$ cm. $l_2 = 15$ cm.	$l_1 = 44 \cdot 3$ cm. $l_2 = 22 \cdot 5$ cm.	$l_1 = 59$ cm. $l_2 = 30$ cm.	$l_1 = 74$ cm. $l_2 = 37 \cdot 5$ cm.
° C.				
2300	1·47	1·32	1·22	1·15
2200	1·44	1·29	1·19	1·13
2000	1·36	1·22	1·14	1·08
1800	1·30	1·17	1·10	1·05

and 30 cm.; and the fifth for $(1\frac{1}{4} \times 59)$ cm. and $(1\frac{1}{4} \times 30)$ cm. These ratios have been calculated from Curves C, D, and S, fig. 15, by means of the formula given on p. 401.

Were the absorption and transparency of a column of gas whose length is inversely proportional to the density independent of the density the ratios given in the corresponding columns of Tables XVII. and XVIII. should be the same. There is, however, a considerable difference between them. Those in the second and third columns of Table XVIII. are distinctly greater than those in the corresponding columns of Table XVII., while those in the last column of the former table are less than those in the last column of the latter table. This shows that the transparency of a column of gas whose length is inversely proportional to the density increases as the density increases, at least, when the gaseous mixtures are enclosed in vessels of the same dimensions.

The curves in fig. 16 give the intrinsic radiance from the gaseous mixtures of the same strength but of various densities at the same mean gas temperatures. The dotted curves give the intrinsic radiance from a thickness of 59 cm. and the full curves that from 30 cm. It will be seen that the emission from a definite thickness of gas increases greatly as the density of the gas increases. The emission does not vary directly as the density, but rather as the square root of the density,* as will be seen from the following table. This same result was obtained from the experiments made under similar conditions with the bolometer close up to the plate of fluorite (see p. 388).

TABLE XIX.—15-per-cent. Mixtures of Coal-gas and Air. Walls Black. Fluorite Window.

Mean absolute temperature of gas.	Thickness of gas in cm.	$\frac{\text{Intrinsic radiance}}{\text{Square root of the density in atmospheres}} = \frac{R}{\sqrt{D}}$.			
		½ atmosphere.	¾ atmosphere.	1 atmosphere.	1¼ atmospheres.
° C.					
2200	59	6·1	6·45	6·4	6·35
	30	4·8	5·45	5·4	5·36
2000	59	4·25	4·4	4·3	4·3
	30	3·55	3·83	3·8	3·78
1800	59	2·85	2·87	2·82	2·80
	30	2·45	2·55	2·55	2·52

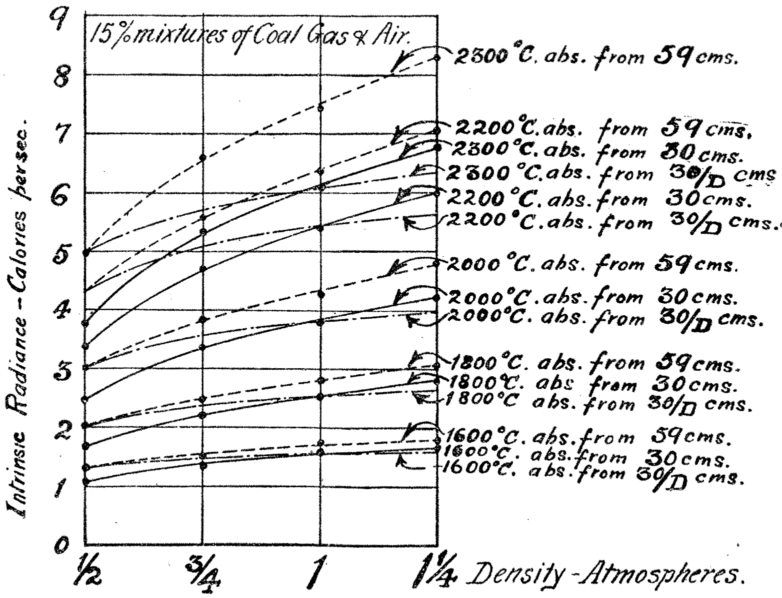

Fig. 16.

* The emission seems to vary more nearly as the density with mixtures of about half an atmosphere density at high temperatures.

The chain-dotted curves in the same figure give the intrinsic radiance from thicknesses of gas inversely proportional to the density. The thicknesses are 60 cm. at $\frac{1}{2}$ atmosphere, 40 cm. at $\frac{3}{4}$ atmosphere, 30 cm. at atmospheric density, and 24 cm. at $1\frac{1}{4}$ atmospheres. In the calculation of the intrinsic radiance from these lengths the formula on p. 401 has been used. The equations to these curves are of the form

$$R = k \, . \, D^{0 \cdot 25},$$

where

R is the intrinsic radiance in calories per second from a thickness of gas = 30/D cm.,

D the density of the gaseous mixtures in atmospheres, and

k a constant for each curve.

The following table gives the value of k at various temperatures:—

TABLE XX.

Mean absolute temperature of gas.	k.
° C.	
2300	6·1
2200	5·3
2000	3·7
1800	2·5

The following table gives the values which the intrinsic radiance from 1/D cm. (where D is the density in atmospheres) would have were the gaseous mixtures perfectly transparent. The intrinsic radiance corrected for absorption from 1 cm. is the limit of R_x/x when $x = 0$ in the formula $R_x = R_\infty (1-\epsilon^{-Kx})$; this is equal to KR_∞.

TABLE XXI.—15-per-cent. Mixtures of Coal-gas and Air. Walls Black. Fluorite Window.

Mean absolute temperature of gas.	Intrinsic radiance corrected for absorption from—			
	2 cm. at $\frac{1}{2}$ atmosphere density.	1·33 cm. at $\frac{3}{4}$ atmosphere density.	1 cm. at 1 atmosphere density.	0·8 cm. at $1\frac{1}{4}$ atmospheres density.
° C.				
2300	0·41	0·42	0·39	0·37
2200	0·38	0·4	0·36	0·32
2000	0·32	0·33	0·27	0·27
1800	0·23	0·21	0·20	0·19

The accuracy of the figures in this table is not insisted upon, since they depend upon K and R_∞ which have been calculated from the observed values of the intrinsic radiance from two lengths of gas only (except in the case of the mixture at atmospheric density). I think, however, they definitely show that were the gaseous mixtures perfectly transparent the intrinsic radiance from a thickness inversely proportional to the density would decrease as the density increases, at any rate within the limits of density in these experiments. The increasing emission from 30/D cm. of the gaseous mixture as D is increased (see chain-dotted curves, fig. 16) must, therefore, be wholly due to the increasing transparency of 30/D cm. as D is increased (*cf.* Tables XVII. and XVIII.). It should be noted that the equation found above, connecting the intrinsic radiance with the density, viz., $R = kD^{0 \cdot 25}$, holds only for 30/D cms. From small lengths of 1/D or 2/D cm. the intrinsic radiance decreases as D increases.

Summary of Results and Short Theoretical Discussion.

The following are the main results obtained from these experiments:—

Part I.—When mixtures of coal-gas and air of various strengths at atmospheric density are exploded in the vessel when its walls are blackened over with a thin layer of dull black paint—

(i.) The total amount of heat lost by radiation to the walls of the vessel up to the moment of maximum pressure is roughly proportional to the product of the third power of the maximum absolute temperature attained into the "time of explosion."

(ii.) The total radiation lost to the walls during explosion and subsequent cooling is about 25 per cent. of the heat of combustion of the gas present in the vessel.

(iii.) The emission of radiation in the initial stages of cooling after explosion is a function of the time from ignition as well as of the temperature. The emission varies very rapidly with the temperature and the time from ignition.

(iv.) In weak mixtures (and probably also in strong mixtures) the rate at which radiation is emitted is a maximum some time before the attainment of maximum pressure, and probably occurs at the moment when the flame fills the vessel.

(v.) Weak mixtures radiate much more powerfully in the initial stages of cooling after explosion than stronger mixtures do when they have cooled to the same temperatures as the weaker mixtures have in this epoch.

(vi.) CO_2 emits radiation about twice as strongly as an equal volume of water vapour at the same temperature does.

In explosions of mixtures of the same strength but of various densities—

(vii.) The total heat lost by radiation per cent. of the heat of combustion of the gas present in the vessel up to the moment of maximum pressure decreases as the density increases.

(viii.) Denser mixtures emit radiation much more strongly than thinner mixtures, especially at the moment of maximum pressure and in the initial stages of cooling. The emission varies approximately as the square root of the density.

Part II.—The following results refer to the experiments made in the vessel whose walls were silver-plated and, therefore, could be made reflecting or absorbent at will. The experiments were made with the bolometer placed at some distance behind the plate of fluorite, so that the emission was measured from a cone of gas of small solid angle:—

(ix.) The intrinsic radiance from a gaseous mixture at any given temperature after explosion depends largely on the reflecting power of the interior surface of the explosion vessel, and also on the size of the vessel. The greater the reflecting power, or the greater the size of the vessel, the greater the intrinsic radiance. This effect is probably due both to greater vibratory energy and to greater transparency of the gas in the larger vessels and in the reflecting vessels.

(x.) (*a*) Gaseous mixtures after explosions in vessels with reflecting walls are very highly transparent to the radiation which they emit at maximum pressure and throughout cooling.

(*b*) Gaseous mixtures after explosion in a vessel with black walls are very highly transparent at the moment of maximum pressure and also in the initial stages of cooling. Later on in the cooling they become fairly opaque.

[(xi.)–(xiv.) refer to coal-gas mixtures of the same strength but of different densities.]

(xi.) The ratio of the intrinsic radiance from a definite thickness of gaseous mixtures of the same strength at any given temperature when the walls of the explosion vessel are reflecting to that when the walls are black decreases as the density increases.

(xii.) When the walls of the explosion vessel are black the transparency of a thickness of gas inversely proportional to the density at any given temperature increases as the density decreases.

(xiii.) (*a*) The intrinsic radiance from a definite thickness of gaseous mixture at any given temperature after explosion in the vessel with black walls varies as the square root of the density.

(*b*) The intrinsic radiance from thicknesses of gas inversely proportional to the density varies as the fourth root of the density.

(xiv.) The intrinsic radiance corrected for absorption from 1/D cm. of the gaseous mixtures at any given temperature in the vessel with black walls seems to decrease as the density (D) increases.

(xv.) The radiation (after correcting for absorption) from the hot gaseous mixture after explosion varies with the temperature approximately as PLANCK's formula for a single wave-length of $3\cdot 6\mu$; this at high temperatures (1800° C. abs. to 2400° C. abs.) varies approximately as the square of the absolute temperature.

These experiments suggest among other things that the radiation from thicknesses of gas containing the same number of radiating molecules does not depend solely on the temperature of the gas, even after correcting the observed values of the radiation for absorption (see, *e.g.*, Tables XVI. and XXI.). The following theoretical explanation of this is suggested. A molecule as it describes its free path loses energy owing to the emission of radiation and gains energy owing to the absorption of energy from the ether, and the vibratory energy of the molecule will increase or decrease according as the absorption is greater or less than the emission. During collision with another molecule there will be a transference of energy between the vibratory energy and the rotational and translational energies, which, as Mr. JEANS has shown, will be very rapid if the duration of collision is comparable with the periods of vibration of the molecule. In the case of CO_2 and steam at high temperatures the duration of collision between the molecules is probably short in comparison with the periods of their low frequency vibrations,* and the vibratory energy of the molecules will therefore tend to take up during collision a value such that the energy in each of the vibratory degrees of freedom equals that in each of the rotational and translational degrees. During collision therefore the vibratory energy of the molecules will tend to take up a value which is proportional to the absolute temperature, but during the free-path there may be considerable departure from this value if the energy density in the ether is above or below a certain value and the time of description of free-path is not very short. From this theory it appears that at any given temperature the greater the gain of vibratory energy during the free-path the greater will be the average vibratory energy of the molecule; and that, *other things being the same*,

* According to JEANS ("Dynamical Theory of Gases," Camb. Univ. Press, 1904, Chap. IX.), transfer of energy from the translational to the vibrational degrees of freedom, and *vice versâ*, can go on at an appreciable rate only when the duration of collisions between the molecules is comparable with the periods of vibration of the molecule. It appears from experiment that the degrees of freedom possessing high-frequency vibrations (which absorption spectra show to be very numerous) are not excited during molecular collisions (at any rate at temperatures which can be commanded in the laboratory), presumably because the duration of collision is not short enough. But in the case of CO_2 we know from PASCHEN'S experiments on the emission of infra-red radiation from the heated gas that at 150° C. the transfer of energy from the translational to those vibrational degrees of freedom possessing frequencies corresponding to radiation of wave-length $2\cdot 8\mu$ and $4\cdot 4\mu$ goes on sufficiently rapidly to compensate for the loss of energy by radiation. The duration of collision is dependent on the velocity with which the molecules approach each other; the higher the velocity the less time they remain in contact on collision. The mean velocity is approximately proportional to the square root of the absolute temperature, and if at 150° C. the duration of collision is short enough to excite the vibrations (infra-red, $2\cdot 8\mu$, $4\cdot 4\mu$, and $14\cdot 1\mu$) in CO_2 molecules, certainly at the high temperatures reached in explosions the duration of collisions will be short enough to allow transfer of energy between the vibrational and translational to go on with extreme rapidity. The same thing applies to the steam molecules, for they also emit infra-red radiation at quite moderate temperatures.

(i.) The greater the energy density in the ether (which depends among other things upon the transparency and the volume of the gas) the greater will be the average vibratory energy of a molecule as compared with its translational energy, though, of course, the average vibratory energy of the molecule will only increase slowly with the energy density in the ether.

(ii.) The smaller the time of description of free-path (or, in other words, the greater the density of the gas) the nearer will the average vibratory energy of a molecule approach a value which is proportional to the absolute temperature of the gas.

The average value of the vibratory energy of the radiating molecules of a gas thus appears to be a function, not only of the absolute temperature of the gas, but also of the value of the energy density in the ether, the rate at which the molecules emit radiation, the time of description of free-path (inversely as the density of the gas), and the rate of partitioning of energy during collisions.

The result given on p. 381, that the rate at which radiation is emitted by the gaseous mixture is a maximum some time before the attainment of maximum pressure, shows that the vibratory energy of the radiating molecules is a maximum some time before the mean temperature of the gaseous mixture attains its maximum value. Prof. HOPKINSON'S experiments show that no portion of the gaseous mixture during explosion has such a high value as at the moment of maximum pressure,* so that it is very probable from this result that the violence of combustion during explosion causes a considerable part of the energy of combination to pass into the form of internal vibrations of the CO_2 and steam molecules. Part of the energy in these vibrations is lost by radiation, but the greater part is transformed into rotational energy and translational or pressure energy.

I desire to thank Prof. HOPKINSON for his kind interest in these experiments and for the encouragement and advice which he has so kindly given me during the progress of the work. The experiments described in this paper were all carried out in the Engineering Laboratory at Cambridge.

* 'Roy. Soc. Proc.,' A, vol. 77, p. 389.

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