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THE RADIATION FROM THE HYDROGEN-OXYGEN FLAME.

By W. E. Garner and K. Tawada.

(*Received 7th October*, 1929.)

The radiation from flames consists in part of primary radiation from the newly-formed products of combustion, and in part of secondary radiation emitted by molecules which are at a high temperature. Since the life of an excited molecule, such as those formed as a result of chemical change, is probably not much shorter than 10^{-7}-10^{-8} second, it is clear that the average molecule undergoes many collisions within its active life. It may be deactivated during any one of these collisions, in which case it emits no primary radiation or chemiluminescence. The quantity of primary radiation emitted will depend therefore on the probability of deactivation by collision.

For the carbon monoxide-oxygen flames, the primary radiation or chemiluminescence is emitted during the process

$$(1)\quad CO_2' \rightharpoonup CO_2 + h\nu,$$

and the deactivation by collision, by

$$(2)\quad CO_2' + X \rightharpoonup CO_2 + X + \text{thermal energy}.$$

In previous papers,[1] it has been suggested that in the dry carbon monoxide flame, the second process is relatively slow compared with the first, especially when X is a molecule of oxygen, carbon monoxide or dioxide. In other words, a large proportion of the radiation from the dry flame of carbon monoxide and oxygen is primary in character. This is inferred from the fact that the presence of minute quantities of hydrogen or water in the carbon monoxide flame materially reduces the radiation emitted. It is concluded that the decreased emission is due to an increased rate of deactivation by collision by (2), where X represents a molecule of hydrogen or water.

The concentrations of hydrogen employed, 0·005 to 0·1 per cent., are so low that the physical properties of the gaseous mixture are not materially affected; thus, the thermal conductivity of the gas, its extinction

[1] Garner and Johnson, *Phil. Mag.*, 1927, iii, 97; *J. Chem. Soc.*, 1928, 281; Garner and Roffey, *J. Chem. Soc.*, 1929, 1133.

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coefficient, etc., are unlikely to be the direct cause of this effect. The decrease in the radiation emitted runs parallel with the effect of hydrogen on the speed of flame movement, discovered by Dixon.

Wohl and Elbe,[2] while admitting the possibility that the explanation of Garner and Johnson can be applied to the radiation from dry hydrogen and oxygen flames, throw doubt on its applicability to the flame of carbon monoxide, and suggest that the diminution of the radiation emitted is due to the shortening of the period of flame which occurs; they maintain that the radiation is thermal and that more radiation is emitted from the dry than from the wet flame because the high temperatures of flame are in existence for a longer time. This interpretation of the experimental results had occurred to us, but was considered not to apply, because any reduction in the velocity of the chemical change will lead to greater losses of heat to the walls during the process of combustion, and hence to lower flame temperatures. Since the radiation emitted varies as the fourth power of the temperature, and only directly as the time, it was considered that in the case of the slow moving flame, the factor of temperature was the more important and that the thermal radiation from the " dry " flame would be less than that from the " wet " flame.

In the hydrogen-oxygen flame, the hydrogen itself or the water produced in the flame may behave in the same way as it does in the flame of carbon dioxide. The concentrations will be so high that it is not improbable that deactivation according to (3) may be slow compared with deactivation by (4),

$$(3)\quad H_2O' \rightharpoonup H_2O + h\nu.$$
$$(4)\quad H_2O' + H_2O \text{ (or } H_2) \rightharpoonup 2H_2O + \text{kinetic energy},$$

that is, the radiation from this flame may be almost entirely secondary in character. If the radiation from the hydrogen flame be thermal, and that from the carbon monoxide flame mainly chemiluminescence, then a comparison of their behaviour when inert gases are added or changes in pressure studied, would be helpful for the understanding of the whole problem of the nature of radiation from flame.

The radiation from the hydrogen-oxygen flame has been studied by firing the gaseous mixture in a cylindrical bomb 2·5 cms. in diameter and 32 cms. long. The bomb was constructed in a similar manner to that used previously, and could be fitted with either a fluorite or quartz window. The results obtained with a fluorite window were published in *Nature*,[3] and those with a quartz window are given below.

Effect of Drying.—The gases were slowly passed through a train of tubes containing phosphorus pentoxide, 150 cms. long. The bomb was dried by evacuation through a tube containing phosphorus pentoxide. A Hyvac and a mercury condensation pump were employed in series. After drying the gases, they could either be passed directly into the dried bomb, through a saturator containing water, or into a bomb saturated with water vapour. The radiation emitted from the flame was measured by the methods described previously. In the earlier experiments, the gases were fired by the ignition of iron wire, but this method of ignition was discarded because mixtures containing 60 per cent. or more of oxygen gave erratic results. The iron wire burnt to oxide more or less completely in such mixtures. Platinum wire was therefore used in all

[2] *Z. physik. Chem.*, 1929, **B5**, 241. [3] 1928, **122**, 879.

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experiments quoted in this paper. This was fused by the application of a potential of 12 to 24 volts. The curve previously published in *Nature* for the radiation through a fluorite window is probably incorrect in the region of 60 to 80 per cent. of oxygen on account of the burning of the iron wire.

The water produced in one explosion could be removed from the walls and window of the bomb within 60 minutes, and an increase in the time of pumping beyond this period had no effect on the radiation emitted. Neither could any change be observed if the bomb were filled several times with dry air and then evacuated after each admission. The results obtained with $3O_2 + 2H_2$ are given below :—

Time of pumping (mins.)	60	120	120	120	1460*
Deflection (cms.)	38·1	37·2	36·4	38·4	38·6

The gas when saturated with water vapour at a temperature 3° below that of the room, gave similar results, *viz.*, deflections of 41·0, 42·5, 39·5, 36·5, 37·7, 38·7 cms.

It was concluded from these results that water vapour had little effect on the emission from the hydrogen flame. They are of importance in view of the conclusions of Wohl and Elbe[2] that the "dry" flame emits chemiluminescence which is suppressed on saturation of the gaseous mixture with water. This deduction was made from the maximum pressure reached in explosions of "dry" and "wet" hydrogen-oxygen mixtures in a 10-litre bomb. The gases were dried to an extent comparable with that in our experiments. In order to account for the lower maximum pressures given by the dry gas, they conclude that for the wet mixtures there is no appreciable loss of energy as radiation before the attainment of maximum pressure, but that there is a 3 to 7 per cent. loss of energy for the "dry" mixtures. In view of the above results, it is doubtful if Wohl and Elbe's deduction is correct. It was thought advisable, however, to examine the effect of drying a mixture containing excess of hydrogen ($3H_2 + O_2$), since these authors have worked with such mixtures. A mixture saturated with water vapour gave radiation equivalent to 15·0 units, and drying for 240 minutes, 15·2 units, and for 1000 minutes, using the diffusion pump, 15·6 units.

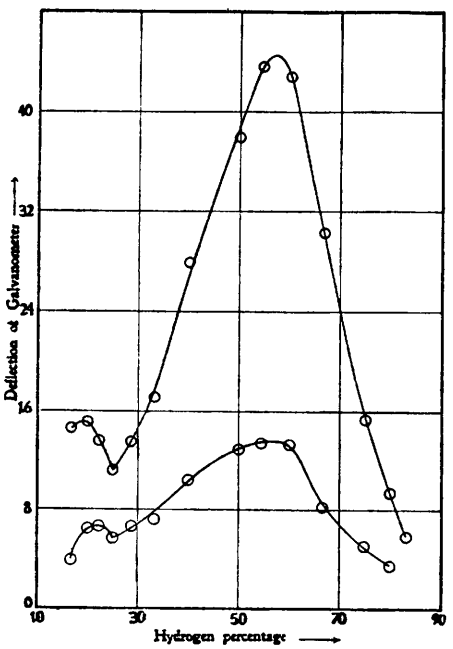

FIG. 1.

* In this experiment the mercury condensation pump was used and the bomb filled with dry air repeatedly.

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There is only a slight increase on drying which is negligible compared with that claimed by Wohl and Elbe.

In all subsequent experiments, the procedure was standardised. The pumps were applied for 1 hour and the " dry " gaseous mixture was used.

Composition of Gases.—Variation in the composition of the gaseous mixture gave the results in Fig. 1. Those for two pressures are given. The upper curve gives those carried out at an initial pressure of 1 atmosphere, and the lower those for ½ atmospheric pressure. The maxima occurring at 55 per cent. and 20 per cent. hydrogen were quite unexpected. A maximum at 66 per cent. hydrogen was most probable for two reasons : (1) this is the composition for which the production of water has its maximum value ; (2) it is the composition which gives the highest flame temperature.

Bonhoeffer and Haber have demonstrated the existence of the hydroxyl radical in these flames,[4] and in discussing the results obtained with a fluorite window, it was suggested that the maximum at 55 per cent. might be due to radiation from the hydroxyl radical (*Nature, loc. cit.*). The production of OH by the equation,

$$H_2 + O_2 \rightharpoonup 2OH,$$

would attain its maximum value for a mixture containing 50 per cent. H_2, and if this radical were the principal emitter of infra-red radiation, the position of the maximum on the curve would be accounted for qualitatively.

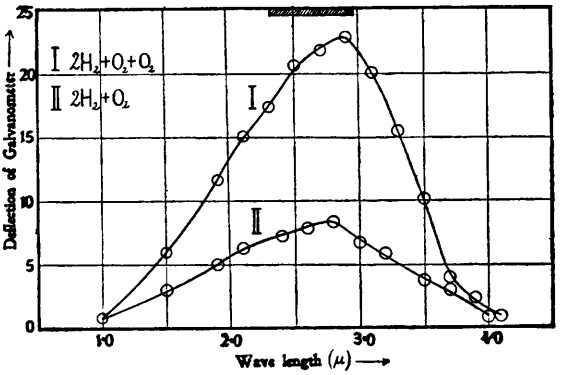

FIG. 2.

The spectrum of the radiation from the OH radical would be expected to differ in some respects from that emitted by water molecules, and the determination of the infra-red spectrum of the flames of mixtures containing 50 per cent. and 66 per cent. hydrogen might throw light on the above suggestion. The spectra for the flames of these mixtures are given in Fig. 2. On account of the small intensity of the radiation, a large slit width was used (see Fig. 2), and it was not possible to separate the maxima usually found in the spectra from the hydrogen flame. There are, however, no obvious differences between the qualities of the radiations from the two flames, that is, there is no direct evidence in favour of the view that the hydroxyl radical is the emitter of the radiation. The shift of the maximum in the curves of Fig. 1 is thus very probably due to the lower thermal conductivity of the mixtures containing excess oxygen (see below).

Effect of Pressure.—The pressure-radiation curves for the mixtures $2H_2 + O_2$ and $2H_2 + 2O_2$ are given in Fig. 3. The curvature is noteworthy. The radiation from the flame decreases more rapidly than the

[4] *Z. physik. Chem.*, 1928, **137**, 263.

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pressure. Were the radiation of the nature of chemiluminescence, a curvature in the opposite direction would be expected, since at low pressures there should be relatively fewer deactivations by collision. Several attempts were made to account for the form of the pressure curves by a mathematical treatment of various deactivation hypotheses, but all were unsuccessful. The cause of the pressure effect is very probably the increase in the average mean free path which occurs on lowering the pressure. This increase favours a more rapid rate of cooling of the products.

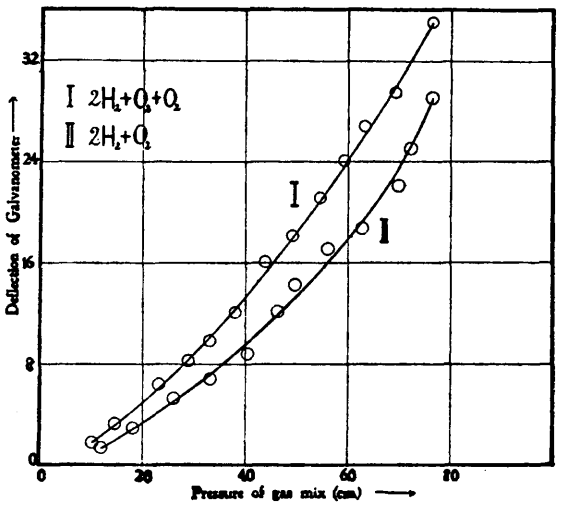

FIG. 3.

Effect of the Addition of Inert Gas.—It was therefore of interest to ascertain what would be the effect of lowering the flame temperature by the addition of inert gases. For additions of equal volumes of gas, the lowering of flame temperature will depend on the specific heat of the gas added. The results are summarised in Figs. 4 and 5 for the gaseous mixture, $2H_2 + O_2$, to which argon, oxygen, nitrogen, helium, and hydrogen, respectively, are added. In Fig. 4, the effect of pressure is given and the form of the curves is similar to that of the curves in Fig. 3. The results on Fig. 5 are those for the hydrogen and oxygen mixtures at $\frac{1}{2}$ atmospheric pressure. Increases in radiation are observed on addition of the first three gases, and a decrease for the last two. The threefold increase which occurs on the addition of argon is surprising if we consider solely the effect which this gas has on the flame temperature due to its specific heat. If, however, its effect on the average molecular velocity, or the conductivity for heat of the products, be taken into account, it will be seen that although the addition of argon will lower the flame

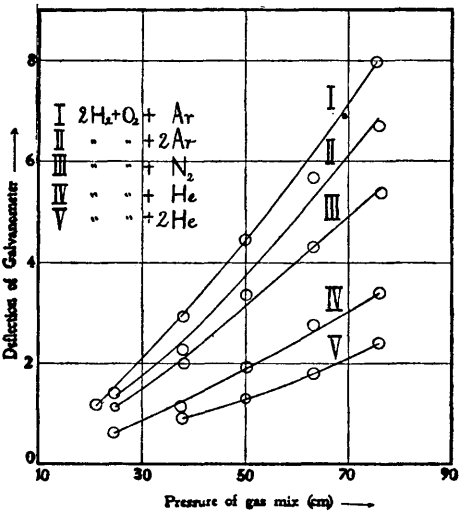

FIG. 4.

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temperature, it will also increase the duration of the high temperature of the flame. The radiation emitted will vary as T^4, and directly as the duration of flame. Thus, the addition of an inert gas will exert two opposing effects on the radiation. It would appear that the predominant effect in metal explosion vessels of the shape and dimensions used in this investigation is that due to changes in the conductivity of the heated products. This masks the anticipated effect due to the lowering of flame temperature. In agreement with this explanation, it will be observed that the effect of the gases is in the order of their densities, which is the same as that of their mean velocities and conductivities, as will be seen in Table I.

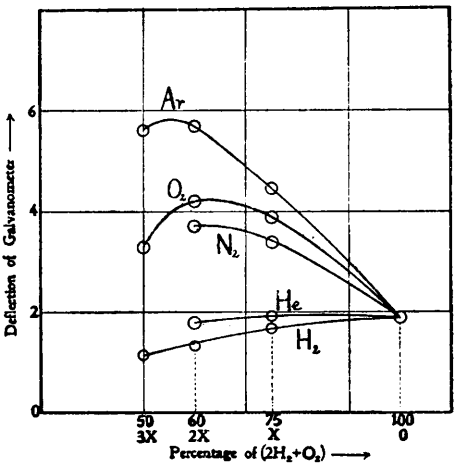

FIG. 5.

The agreement between the intensity of the radiation and the densities and conductivities is only qualitative, for the speed of flame, and the specific heats, will also influence the duration of flame. The order is, however, very different from that of inert gases on the speed of the hydrogen flame.[5] Argon and helium have very similar effects on the speed of this flame. It is thus impossible to account for the differences in the behaviour of the helium and argon mixtures in terms of the effect of the velocity of flame movement on the duration of flame. The thermal conductivity of the gases and its effect on the duration of flame is much the more important. In large spherical bombs this effect would probably be negligible, as Wohl and Elbe point out.

TABLE I.

Mixture.	Radiation. (Area.)	Density of Products.	Conductivity of Inert Gas, 0°C.
$2H_2 + O_2 + 2Ar$	5·69	29	0·039
$2H_2 + O_2 + 2O_2$	4·20	25	0·057
$2H_2 + O_2 + 2N_2$	3·73	23	0·056
$2H_2 + O_2$	1 90	18	—
$2H_2 + O_2 + 2He$	1·79	11	0·336
$2H_2 + O_2 + 2H_2$	1·32	10	0·400

When it is borne in mind that two very similar gases, argon and helium, produce such dissimilar effects on the radiation from the flame, it will be evident that a deactivation hypothesis similar to that put forward previously for the carbon monoxide flame is valueless for explaining the phenomena of the hydrogen flame. Both the pressure-radiation

[5] Bone, Fraser, and Winter, *Proc. Roy. Soc.*, 1927, **114A**, 402.

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curves and the effect of inert gases indicate a thermal origin for the radiation from the flame.

It is hoped that experiments of a similar character on the carbon monoxide flame will help to settle the question of the chemiluminescence from the carbon monoxide flame.

Experimental.

Preparation of Gases.—The hydrogen was prepared from pure zinc and pure sulphuric acid, and the gas was washed through alkaline permanganate and water, and stored over water. It was dried as required over P_2O_5. The oxygen was prepared from potassium permanganate. The argon and helium were freed from other gases by passing through tubes containing (*a*) heated calcium oxide-magnesium, and (*b*) heated copper oxide, the process being repeated until the gases showed that hydrogen and nitrogen were absent when the purity of the gas was

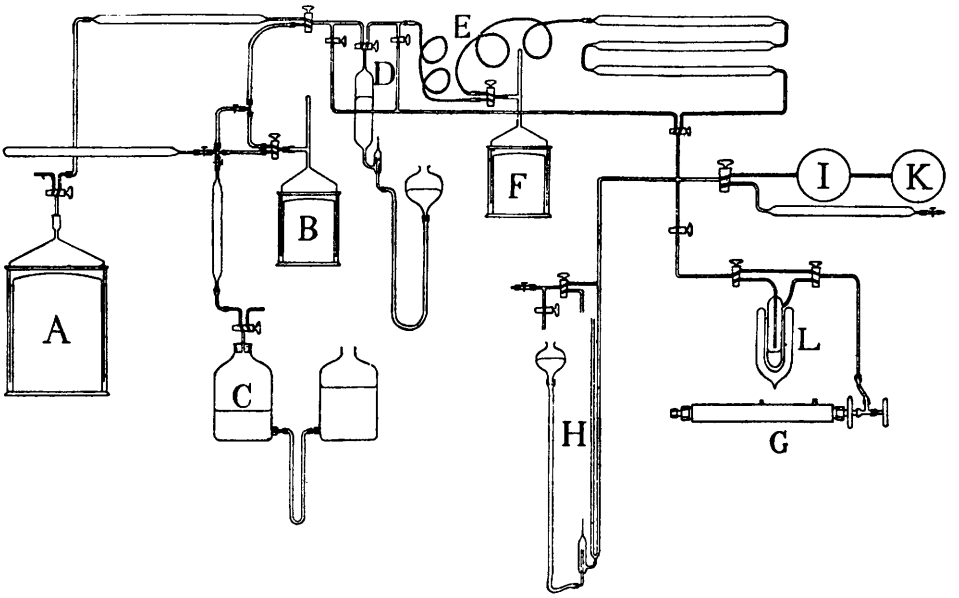

FIG. 6.

tested in a discharge tube. This method was suggested to us by Dr. M. W. Travers.

Experimental Arrangement.—The gas holders A and B were used for storing dry hydrogen and oxygen respectively (Fig. 6). The inert gas was stored in C. The gases were measured in D and passed through a lead tube into the holder F, from which they were led through tubes containing P_2O_5 into the bomb G, either directly or by way of a water saturator L. The initial and final pressures could be read on the manometer H, and the whole system could be evacuated by means of the mercury condensation pump I, and the Hyvac pump K. No rubber tubing was employed for connections between D and L.

The radiation emitted was either (*a*) read visually, or (*b*) photographically recorded by means of the apparatus described previously by Garner

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and Roffey.[1] The ratio of deflections by method (*a*) was identical with the ratio of areas by method (*b*) so that in general the visual method was adopted. In view of the possibility that very marked changes in speed might occur on the addition of inert gases, the experiments in Figs. 4 and 5 were carried out by the photographic method. Both fluorite and quartz windows were employed; these needed special attention and frequent polishing on account of the violence of explosion of some of the mixtures examined.

The replacement of the iron wire used in firing by platinum wire, mentioned above, did not remove entirely the cause of the fluctuation in experimental values, especially in the region of large excess of oxygen (Fig. 7). The cause of the fluctuations has not been traced, nor is the maximum which occurs at about 20 per cent. understood. The mean values are given in Fig. 1.

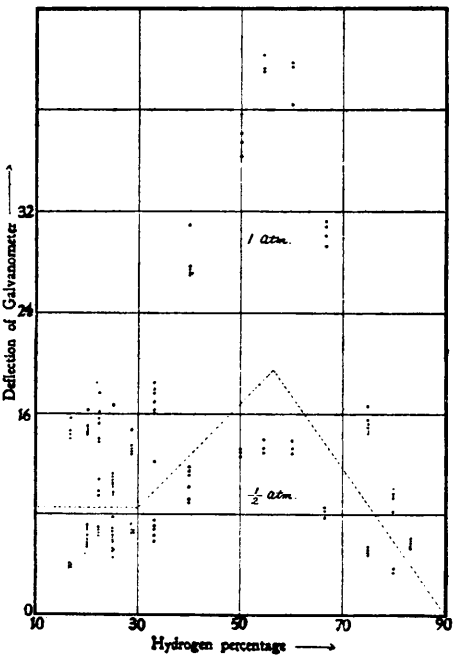

FIG. 7.

Effect of Addition of Water, Nitric Oxide, etc.—Saturating various gaseous mixtures with water vapour, or changing the conditions of drying did not modify the values of the radiation.

Addition of nitric oxide depressed the radiation slightly.

Gas mixture .	$H_2 + O_2$		$H_2 + 2O_2$		$2H_2 + 3O_2$			
Pressure NO, cms.	2·8	0	0·34	0	2·0	0·2	0·054	0
Deflection .	22·15	22·72	15·56	17·5	17·05	17·70	16·15	19·0

The results with nitric oxide are of interest in connection with the curious effect of this gas on the ignition temperature of hydrogen (Dixon).

Experimental Results.—The results shown in the figures were all obtained by employing a quartz window. Fluorite windows were very liable to fracture, and so quartz was mainly employed. The ratio of the radiation emitted through fluorite to that emitted through quartz was about 1 : 1·45. In both cases, the windows were 1 cm. thick. The distance of the thermopile from the window was without effect on the ratios of the radiation from two flames with different percentage composition.*

* The fraction of the energy of chemical change which is emitted as radiation in the case of the $2H_2 + O_2$ mixture at 1 atmosphere pressure using a fluorite window is 2 per cent. This has been determined by comparison with a standard Hefner lamp, and employing the methods described by Johnson, *Phil. Mag.*, 1028, v. 301.

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The results can be read off from the figures with as great an accuracy as that of the results themselves, so that tables of data need not be given.

Residual Pressures.—In measuring the pressures of the cooled products of explosion, care was taken that the gases were saturated with moisture, even after expansion into the manometer. From these pressures, the volume of the bomb, and the glass apparatus between it and the manometer, the volume of the unburnt gas could be calculated. In many cases, this gas was analysed, and the analysis served as a check on the accuracy of admixture of the gases. Also, in some cases, the unburnt mixture was analysed. The combustion did not proceed to completion when excess of hydrogen was present, but in the case of the results at one atmosphere pressure, combustion was complete in excess oxygen. The maximum unburnt gas occurred in the case of the most rapidly moving flame (66 per cent. H_2). The unburnt gas is given as a percentage of that theoretically possible in Table II.

TABLE II.

Gas Mixture.	Per Cent. Gas Unburnt.	
	1 Atmosphere.	½ Atmosphere.
$4H_2 + O_2$	2·0	0·5
$3H_2 + O_2$	2·3	1·9
$2H_2 + O_2$	4·2	2·6
$3H_2 + 2O_2$	0·6	0·3
$H_2 + O_2$	0·1	— 0·1
$2H_2 + 3O_2$	0·3	— 0·9
$H_2 + 2O_2$	0·0	— 1·3
$H_2 + 3O_2$	0·0	— 1·5
$H_2 + 4O_2$	0·1	— 1·9
$H_2 + 5O_2$	0·0	— 2·0

These figures refer to the results given in Fig. 1. Tests were made for hydrogen peroxide and ozone in the liquid deposited after an explosion. Small quantities were shown to be present. Also, explosions were carried out in glass U tubes surrounded by liquid air. There was no difficulty in getting the flame to pass through explosive mixtures at liquid air temperatures. The amount of hydrogen peroxide produced was not materially increased by this method even for the mixture ($3O_2 + H_2$). Also, coating the interior of the tube with ice did not affect the production of H_2O_2.

Summary.

The effect of composition, pressure, and the addition of inert gases on the radiation emitted from the flame of mixtures of hydrogen and oxygen has been measured in a cylindrical bomb, 2·5 cms. in diameter.

The radiation is at a maximum for the mixture containing 55 per cent. of hydrogen. The radiation decreases with reduction of pressure more rapidly than the pressure. Inert gases have an effect on the radiation emitted which is dependent on the density of the gas. Argon, oxygen, and nitrogen increase the radiation and hydrogen and helium decrease it. It is considered that the effects are due to changes in the duration of the high temperature of the flame. When two volumes of argon are added to three volumes of explosive mixture ($2H_2 + O_2$), there is a threefold increase

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in the radiation emitted. Drying the gaseous mixture does not affect the emission of radiation. Wohl and Elbe's conclusion with regard to the chemiluminescence of the " dry " flame is thus probably in error.

The phenomena observed can best be accounted for on the assumption that the radiation from this flame is thermal in character.

Our thanks are due to the Imperial Chemical Industries for a grant which has made possible the carrying out of this research.

The University,
Bristol.

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