CXLIX.—*Effect of the Addition of Hydrogen and Water on the Radiation emitted from the Carbon Monoxide Flame.*

By WILLIAM EDWARD GARNER and F. ROFFEY.

THE flame of carbon monoxide and oxygen emits the major part of its radiation in two bands with maxima at wave-lengths $2 \cdot 8$ and $4 \cdot 4 \mu$, which correspond to the infra-red emission and absorption bands of carbon dioxide gas. On account of this correspondence, it is concluded that the emitters of the infra-red radiation from the flame are molecules of carbon dioxide (compare Garner and Johnson, *Phil. Mag.*, 1927, **3**, 97; J., 1928, 281; Johnson, *Phil. Mag.*, 1928, **5**, 301). The spectrum of the flame in the ultra-violet and visible regions consists of a continuous band ranging from 5500 to 2300 Å., on which are superimposed carbon monoxide bands, the wave-lengths of which have been measured by A. Fowler (" Flame and Combustion in Gases," Bone and Townend, p. 331).

The addition of hydrogen or water to the flame of carbon monoxide causes a diminution in the intensity of emission of radiation over the whole spectrum. The total radiation is reduced to one-eighth on the addition of 2% of hydrogen (see below). Weston (*Proc. Roy. Soc.*, 1925, *A*, **109**, 177, 523) has shown that the visible and ultra-violet spectrum of the carbon monoxide flame practically disappears on the addition of 50% of hydrogen, the place of the carbon monoxide spectrum being taken by the hydroxyl bands in the ultra-violet. Experiments by Johnson (*loc. cit.*) have shown that the emission at both $2 \cdot 8$ and $4 \cdot 4 \mu$ is diminished on addition of water vapour.
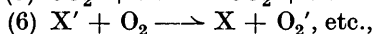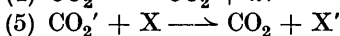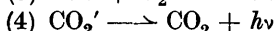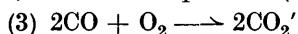
These changes in the character and intensity of the radiation from the carbon monoxide flame on the addition of hydrogen and water are of importance for the study of the catalytic effect on the speed

of flame discovered by Dixon (*Phil. Trans.*, 1884, **175**, *A*, 617), which was explained by him as due to the action of steam :

$$(1) \quad CO + H_2O \longrightarrow CO_2 + H_2$$
$$(2) \quad 2H_2 + O_2 \longrightarrow 2H_2O, \text{ etc.}$$
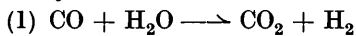
Bone, from the above changes in the ultra-violet spectrum and from the fact that the gas dried for two years over phosphoric oxide can still give rise to flame, concludes that two independent reactions occur in this flame : (1) a dry reaction, and (2) a reaction catalysed by steam.

The mechanism of catalysis suggested by Dixon is based on a chemical explanation of the catalytic effect. There is, however, an alternative interpretation of the increased speed of flame caused by the addition of hydrogen or water vapour, *viz.*, that it is due to physical processes, *e.g.*, to collisions of the second kind. The fact that the radiation from the carbon dioxide molecules produced in the flame is reduced on the addition of hydrogen is suggestive in this connexion. Energy which is emitted as radiation in the absence of hydrogen is retained within the reacting gases when it is present, and this energy must be available in one form or another for facilitating the chemical change. Thus, a physical explanation of the phenomenon is not ruled out by the experimental evidence. A typical mechanism, illustrating a catalytic effect due to collisions of the second kind, is shown in equations (3)—(6) :

$$(3) \quad 2CO + O_2 \longrightarrow 2CO_2'$$
$$(4) \quad CO_2' \longrightarrow CO_2 + h\nu$$
$$(5) \quad CO_2' + X \longrightarrow CO_2 + X'$$
$$(6) \quad X' + O_2 \longrightarrow X + O_2', \text{ etc.},$$

which illustrate the formation of activated molecules of carbon dioxide by the chemical change (3), their deactivation by emission of radiation (4) and by collision with a third substance X (5), and the transference of the energy from X' to one of the reactants (6). This chain mechanism provides an explanation of the decrease in radiation on addition of hydrogen, and is also in agreement with the fact that the addition of substances which do not increase the speed of the reaction, *e.g.*, nitrogen, oxygen, carbon monoxide, carbon dioxide, etc., does not decrease the emission of radiation.

It is not improbable that both the chemical and the physical type of catalytic effect are present in flames. In order to determine the extent to which these two types of effect occur in the carbon monoxide flame, the following investigation was undertaken.

EXPERIMENTAL.

The experimental method employed has been described in previous communications (*locc. cit.*), and only a broad outline of the methods

used is now given. The gaseous mixtures, enclosed in a cylindrical phosphor-bronze bomb, are ignited at one end of the bomb by the fusion of thin iron wire (this may be replaced by a thin platinum wire), a 12- or 24-volt battery being used as a source of current. The radiation from the flame emerges through a fluorite window in the bomb and is measured by a Moll thermopile and a Downing galvanometer. Fig. 1 shows the arrangement for drying and storing the gases. Carbon monoxide was prepared from pure formic acid

FIG. 1.
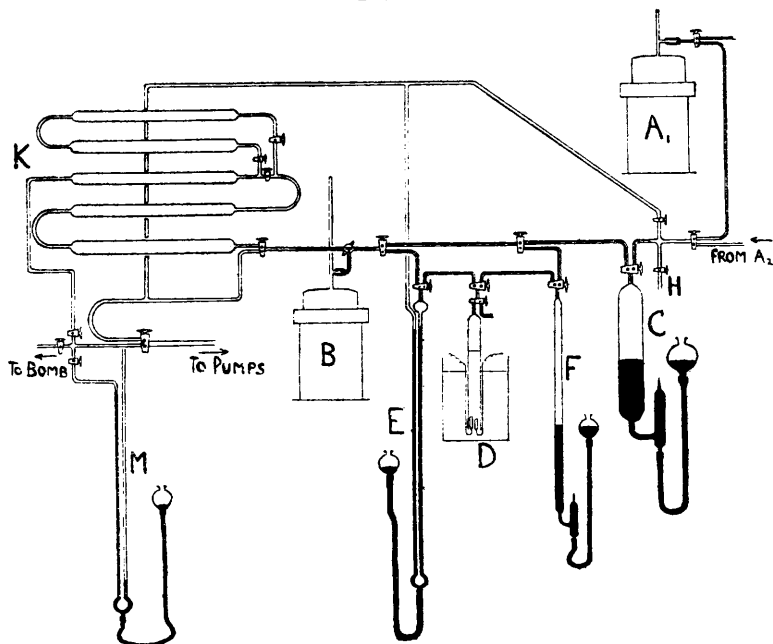
and sulphuric acid, and oxygen by heating pure permanganate. The hydrogen was added in the form of electrolytic gas.

The carbon monoxide was stored in glass vessels over water in the majority of the experiments recorded here (A_2, Fig. 1), it having been found that a metal gas-holder evolved sufficient hydrogen to the gas to vitiate the results for low hydrogen concentrations. The oxygen after drying was stored over mercury (A_1). The dried gases were mixed in the proportion $2CO : 1O_2$, and stored in a gas holder over mercury (B). The gases were further dried by standing for one hour over phosphoric oxide, which had not been distilled in oxygen before use, but was practically free from phosphorous oxide. The pentoxide gave no precipitate with the mercuric chloride test, but gave a positive test for trioxide by the silver nitrate method.

A lengthening of the period of contact of the gases over pentoxide did not affect the radiation emitted or the speed of flame. Contact with pentoxide over-night or for several days had no effect. The water present in the walls of the bomb was troublesome to remove, especially after explosions of mixtures containing hydrogen. Drying for one hour with a Hyvac pump was not sufficient to remove this water, but, by using a Ley bolt condensation pump in conjunction with the Hyvac pump, and pumping for one hour, steady and reproducible values for the radiation and speed of flame were obtained. Further evacuation did not alter the values. After experiments with flames containing large quantities of hydrogen, a longer period of evacuation must be employed before carrying out experiments on hydrogen-free mixtures. Although it is unlikely that the whole of the water vapour in the walls of the bomb was removed by this treatment, the water escaping from the walls into the gases during an experiment of 5—10 minutes' duration must be very small. The percentage of hydrogen present in the gases after this treatment could not be very large, for 0·005% of hydrogen, when added to these gases, practically doubled the speed of flame, and reduced the radiation by 15%. Further experiments are now being carried out in a rustless steel bomb, which can be heated in a vacuum at 300—400°, and this will make it possible to carry the investigation into the region of smaller hydrogen concentration. The method of introducing electrolytic gas is shown in Fig. 1, which is self-explanatory.

The speed of flame movement was measured simultaneously with measurements of radiation by the method described in previous papers. The only modification of note was the replacement of the falling-plate camera by a revolving drum carrying negative paper. This made it possible to measure the speeds of movement of flame with greater accuracy. Considerable experimental difficulties were experienced before the Einthoven galvanometer could be made to yield trustworthy results. The trouble appeared to be a leak of alternating current to the instrument, and was minimised by insulating all of the recording apparatus and by earthing the field magnets through a resistance.

Two bombs were used, both of 2·5 cm. internal diameter, one 40 and the other 80 cm. long. The longer bomb was provided with three pairs of insulated electrodes mounted at intervals of 10, 32·5, and 73·5 cm., respectively, from the firing plug, itself placed 3—4 cm. from the valve end of the bomb. The platinum wires of the insulated electrodes penetrated 3 mm. into the bomb, and the tips of each pair were separated by 2·5 mm. These were used in the measurement of speed of flame.

The deflexions of the Downing galvanometer were sometimes observed visually and sometimes photographically. The error in the visual readings was about 2 mm. on a deflexion of 40 cm.

Preliminary Series of Experiments.—In this series, a metal gas-holder was used for storing carbon monoxide, and hence the explosive mixture may have contained small amounts of hydrogen. The small bomb was used, and the experimental arrangement was practically that of the preceding paper. A Hyvac pump was used in evacuation. No speeds of flame were measured. The results are shown graphically in Fig. 2, each point shown being the mean

FIG. 2.
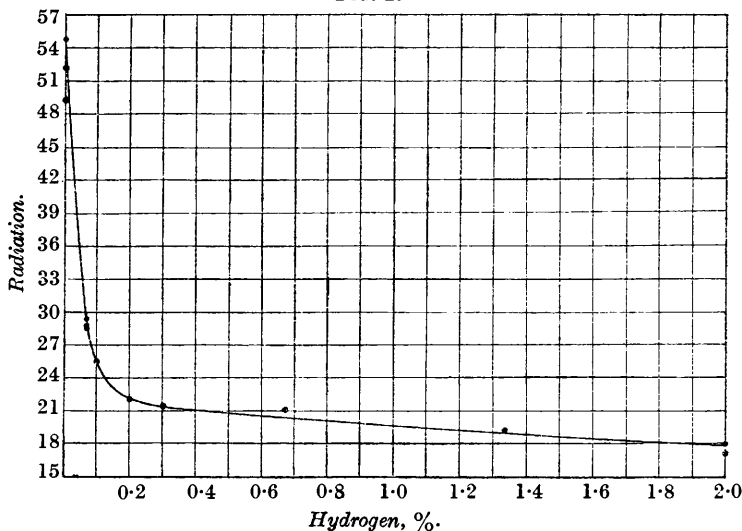
Hydrogen, %.

of a number (4—8) of readings. The fall in radiation on addition of hydrogen is very marked.

Series with the Long Bomb : Speed and Radiation Measurements.— The individual experimental results for this series are all shown in Figs. 3 and 4. The galvanometer deflexions are plotted against the % of hydrogen added in Fig. 3, and against 1/log speed in Fig. 4. For the small percentages of hydrogen (less than 0·02%), the deflexions were not proportional to the radiation received by the thermopile, and this was found subsequently to be the cause of the apparently irregular results with the dried gas mixture. For the slowest speeds of flame, with a galvanometer period of 2 seconds, it is necessary to record the deflexions by a photographic method, and to measure the area below the curve so obtained.

The measurements of the velocity of movement of flame were

usually made between electrodes 63·5 cm. apart.   The time taken for the flame to travel between these two electrodes could be measured accurately.   In a few cases, the speed was also measured between electrodes 1 and 2 which were 22·8 cm. apart.   At this distance, there was sometimes interference between the deflexions
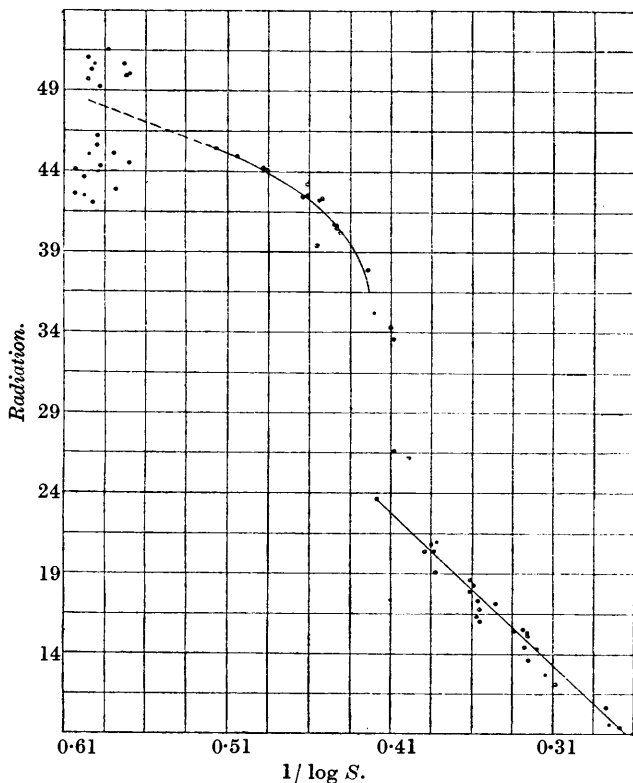
FIG. 3.
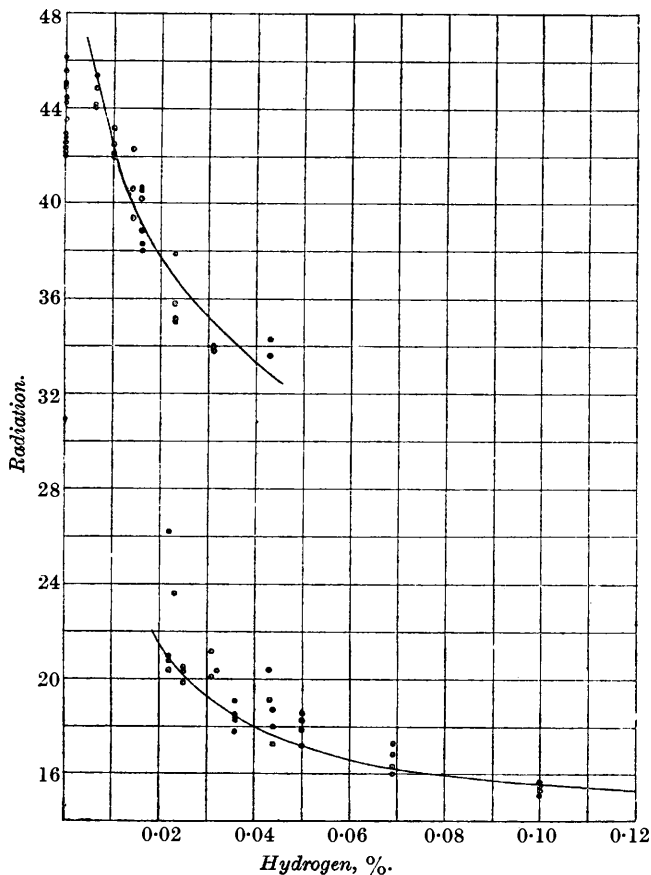
caused by the flame passing the two pairs of electrodes.   The trustworthy results obtained are given below :

Radiation emitted	44·3	42·6	41·3	39·9	23·4	19·0	14·7
Mean speed (cm./sec.) ⎰ 1—2.	49	120	128	180	256	313	1100
between electrodes. ⎱ 1—3.	61	147	149	244	240	423	1140

The average speed of flame between the first and the second electrode is usually somewhat smaller than that between the first

and the third.   There is, however, no very marked increase in the speed of the flame as it moves along the bomb.   This was shown previously to be the case for the smaller bomb (compare Garner and Johnson, J., 1928, 290).   The dry mixture without hydrogen is exceptional; for this mixture the speed between the first and second electrodes is greater than that between the second and third.   The speeds recorded subsequently are in all cases the average speeds between electrodes 1 and 3, placed 63·5 cm. apart.

FIG. 4.

1/ log S.

The main feature of Fig. 3 is the step on the curve; the region between 0·02 and 0·04% of hydrogen is an unstable region in which samples of one and the same mixture give deflexions which lie on one or other of two definite curves.   One or two intermediate points were found.   In this region, there is a sudden change in the nature of the Einthoven records (see later).   The results for quantities of hydrogen greater than 0·10% are not included in Fig. 3; the mean values for all concentrations of hydrogen are, however, given in

Table I, where the deflexion is a measure of the radiation, and u and l refer to the upper and lower curves, respectively.

The step also occurs at the same percentages of hydrogen in Fig. 4. The logarithmic scale is employed for the speeds of flame movement, partly for convenience in plotting, and partly for theoretical reasons. The composition–log speed curve shows evidence of the existence of a slight step which is, however, nearly masked by the experimental error. In a number of experiments (see below) where the emission of radiation varied considerably, nearly identical speeds of flame were obtained. Thus it is improbable that the decrease in radiation at the step at 0·02—0·04% hydrogen is due to changes in the speed of flame movement.

Expt. No.	H_2, %.	Radiation (cm.).	Speed (cm./sec.).
263	0·023	37·9	227
264	,,	23·6	243
268	0·043	33·6	287
269	,,	26·6	282

TABLE I.

Radiation and Speeds of Flame.

H_2, %.	Deflexion (cm.).		Mean speed (cm./sec.).		H_2, %.	Deflexion (cm.).		Mean speed (cm./sec.).	
	$u.$	$l.$	$u.$	$l.$		$u.$	$l.$	$u.$	$l.$
0·006	44·7	—	101	—	0·05	—	18·0	—	597
0·01	42·5	—	150	—	0·07	—	16·4	—	649
0·016	40·6	—	175	—	0·10	—	15·4	—	1150
0·023	36·0 and 22·4		237 and 409		0·20	—	14·1	—	1210
0·025	32·0 ,,	20·3	—	—	0·30	—	13·0	—	—
0·031	33·9 ,,	21·0	—	—	0·50	—	10·3	—	1883
0·036	—	18·4	—	—	0·67	—	9·8	—	4070
0·043	33·9 ,,	19·8	281 ,,	394	1·00	—	8·8	—	—
0·044	—	17·4	—	—	2·00	—	8·9	—	4740

The order of the above experiments was haphazard. Measurements with mixtures with the higher percentages of hydrogen sometimes preceded and sometimes followed those with the lower percentages. The points lying between the two curves are not included in the means. The speed of flame for the dried gases containing no hydrogen was 45—55 cm./sec. Lower speeds of flame have since been obtained by Mr. D. H. Hall with another apparatus.*

Effects of Small Quantities of Hydrogen on the Radiation Emitted.— The upper region of curves (Figs. 3 and 4) was further investigated. In these curves, the deflexions given for the gases containing

* With a new experimental arrangement, the following limiting speeds were obtained for the dried gas mixture :

Dried with commercial P_4O_{10}, 39—41 cm./sec.
,,   distilled P_4O_{10}, 35—37   ,,

The difference is not so great as that which occurs on changing an old phosphoric oxide tube attached to the pump for a new tube.

percentages of hydrogen up to 0·01% require correction on account of departure of the galvanometer deflexions from ballisticity. The necessary correction was obtained by using a photographic method of recording the deflexions. A very accurate clock motor was lent to us by Professor Buckmaster for this purpose. The records taken on this instrument were time-marked in fifths of a second. The areas under the curves, which are proportional to the radiation falling on the thermopile, were measured, and by plotting these areas against the maximum deflexions, a correction curve was obtained. This was used to correct the points in Figs. 3 and 4.

FIG. 5.

$\sqrt{H_2}$.
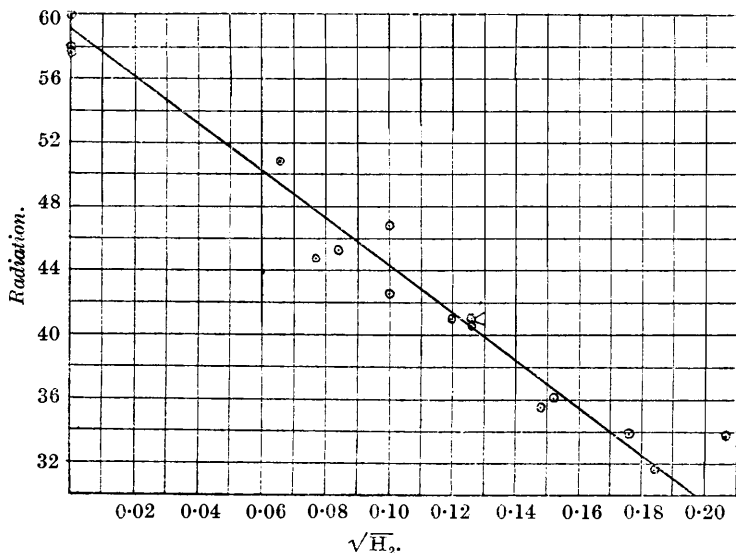
The corrected results, together with the new figures, are given in Fig. 5, the radiation being plotted against $\sqrt{H_2}$.

The corrected values for the radiation are also employed in Fig. 6, where are given the radiation–log speed curves for small percentages of hydrogen (I) and of water vapour (II).

In Table II are given the results of a typical series of experiments in the region 0·00—0·016% of hydrogen, determined by the above method; the value shown against the bracket in each case is the mean of the bracketed values.

Effect of Water Vapour on the Radiation and Speed of Explosion of Carbon Monoxide and Oxygen.—Water vapour, which has a similar effect to hydrogen on the phenomena of the carbon monoxide flame, was introduced into the evacuated bomb from a small bulb containing water at a constant temperature lower than that of the
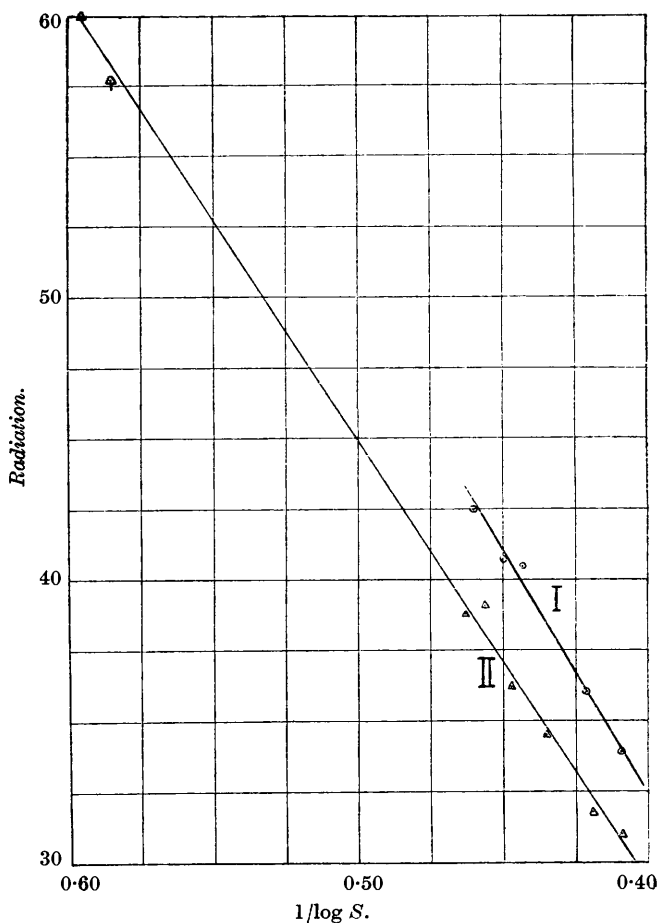
Fig. 6.

TABLE II.

[Expt. No.	H₂, %.	Maximum deflexion (cm.).	Area (in arbitrary units).	Expt. No.	H₂, %.	Maximum deflexion (cm.).	Area (in arbitrary units).
585		6·70 ⎫	29·7 ⎫	579		5·30 ⎫	19·2 ⎫
586		7·00 ⎬6·9	30·7 ⎬30·0	580	0·016	5·35 ⎬5·3	20·0 ⎬19·3
587		6·90 ⎭	29·6 ⎭	581		5·25	18·8
				582		5·20 ⎭	19·2 ⎭
592		6·65 ⎫	28·1 ⎫				
593	0·0014	6·40 ⎬6·3	25·0 ⎬25·4	604		5·40 ⎫	21·4 ⎫
594		6·20	24·6	606	0·016	5·20 ⎬5·3	19·0 ⎬19·7
595		6·05 ⎭	23·9 ⎭	607		5·25 ⎭	19·8 ⎭
596		5·90 ⎫	23·4 ⎫				
597	0·0071	5·80 ⎬5·9	22·6 ⎬22·6				
598		5·85	21·7				
599		5·95 ⎭	22·6 ⎭				

room.   The dry standard mixture was then introduced into the bomb and left for a period of time (one hour) sufficient for complete mixing with the water introduced previously.   The time of saturation with water was increased until reproducible results were obtained.   Erratic results, obtained when the bulb containing ice was kept below 0°, were probably due to the great absorptive

FIG. 7.
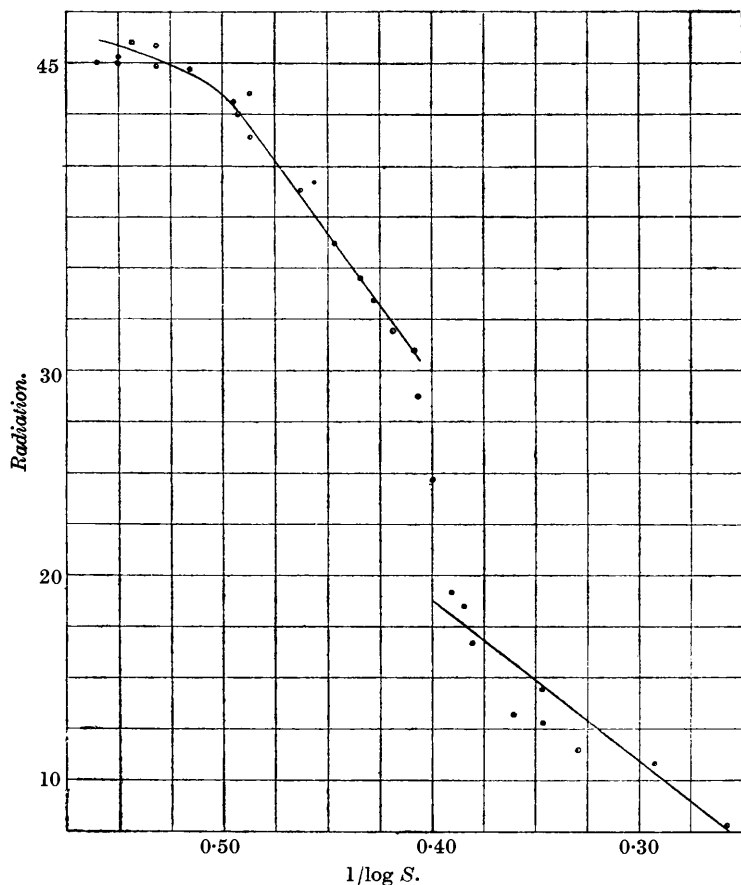
capacity of the walls of the bomb for water vapour.   It was not found possible to complete the composition–radiation curve for water vapour.   The results obtained from mixtures saturated at temperatures above 0° are here compared with those for hydrogen :

H₂O or H₂, %		0·00	0·60	1·02	1·95
Mean deflexion (cm.) {	H₂O	57·7	13·6	10·4	6·8
	H₂	57·7	10·0	8·8	8·8

Johnson (*Phil. Mag.*, 1928, 5, 301) showed that 2·3% of the gross heat of combustion was emitted as radiation for a mixture of $2CO + O_2$ containing 1·95% of water vapour. Taking this figure as a basis for calculation, we find that 19·5% of the heat of combustion is emitted in the case of the gas free from hydrogen.

Fortunately, it was possible to complete the radiation–log speed curve with water, since for this purpose it was not necessary to know the percentage of water vapour in the mixture. The results are shown in Fig. 7. The upper portion of the curve, corrected to values proportional to the radiation emitted, is given in Fig. 6, curve II. These results show that qualitatively the action of water and hydrogen is the same. The curve for water lies a little to the left of that for hydrogen.

Ionisation Phenomena.—The employment of the Einthoven galvanometer in the measurement of the speeds of flame has led to the accumulation of a certain amount of information on the effects of the addition of hydrogen on the ionisation in the flame. The information is qualitative in significance, for no attempt was made to obtain quantitative results. The figures in Table III are the means for a large number of experiments.

TABLE III.

| H_2, %.	Velocity of flame (cm./sec.).	Maximum conductivity (arbitrary units).	Persistence of ionisation (sec.).
0·00	51·0	10	0·25—0·35
0·01	150	50	0·16
0·016	175	80	0·11
	237	90	0·10
0·023	409 *	150 *	0·06 *
	281	130	0·08
0·043	394 *	200 *	0·05 *
0·1	1150	360	0·03
0·5	1883	600	0·02
2·0	4740	1200	0·01

* Lower curve, Fig. 4.

The maximum conductivity increases 120-fold on passing from the dry mixtures to those containing 2% of hydrogen. The effect of the addition of larger quantities of hydrogen has been studied previously by Saunders and Sato (*Trans. Faraday Soc.*, 1927, 23, 254).

The character of the Einthoven records undergoes marked changes as the percentage of hydrogen in the flame increases. With no hydrogen, the deflexions are single and very broad. On the addition of 0·01% of hydrogen or less, double peaks make their appearance at each deflexion, and this character is retained by the explosions represented on the upper curves in Figs. 3 and 4. Below the step on the radiation curves, the ionisation peaks become single

and give much sharper maxima. The experiments giving radiation
values on the lower curve show single maxima of this type without
exception. The typical double maxima of the upper curve suddenly
give way to the sharp peaks of the lower region. Typical curves are
shown in Fig. 8. In the earlier experiments (J., 1928, 280), the
Einthoven records were either of type II or III. The "dried" gas
was not sufficiently freed from water to give the maximum radiation
from the flame, the minimum speeds of flame, or curves of type I.

FIG. 8.
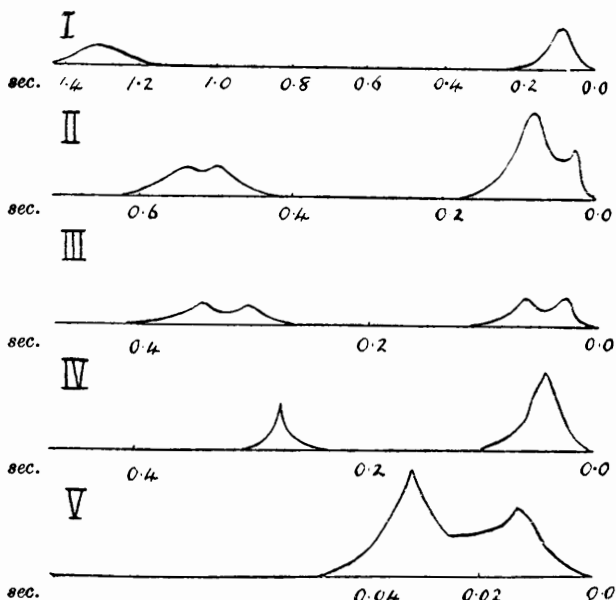
I. 0·00% H$_2$; R = 45·1 cm.; V = 52·9 cm./sec.
II. 0·01% H$_2$; R = 43·2 cm.; V = 148 cm./sec.
III. 0·023% H$_2$; R = 37·6 cm.; V = 227 cm./sec.
IV. 0·023% H$_2$; R = 23·6 cm.; V = 243 cm./sec.
V. 0·5% H$_2$; R = 10·2 cm.; V = 2200 cm./sec.

In the present series, the pump used to remove traces of water from
the walls of the bomb was more efficient than that employed in
previous work.

Combustion of the Gases.—Analysis of the gases left in the bomb
after combustion showed that about 10% of the carbon monoxide
was unburnt. This percentage did not change very much through-
out the above series of experiments, indicating that a definite
fraction of the gas was chilled by the walls of the bomb in all cases :

H$_2$, %	0·00	0·10	2·0
Combustion, %	88·1	90·2	91·9

Radiation from the Hot Gases in the Flame.—The investigations of Paschen (*Ann. Physik*, 1894, **52**, 214) show that carbon dioxide emits its typical radiation at high temperatures, so that some part of the radiation from the flame must be due to thermal causes. The thermal emission will be the greater the slower the cooling of the products of combustion, and for a large mass of burning gas which cools slowly, the thermal emission would be expected to mask any chemiluminescence that may possibly occur. It is clear, therefore, that the chemical effects are best studied under conditions of rapid cooling. The incompleteness of combustion shown by the above figures indicates that in our experiments the cooling is rapid. The phenomena described in this paper could not be observed at all accurately in the larger bombs used by David (*Phil. Mag.*, 1920, **38**, 66). In large explosion vessels, the infra-red emission from the flame will consist mainly of radiation from the hot gases, and the effect of water or hydrogen on the radiation emitted will be very much smaller than in the above experiments.

This appears to be the case from experiments of Bone, Townend, and Scott (*Proc. Roy. Soc.*, 1928, *A*, **120**, 553), where at 64·4 atmospheres initial pressure, the addition of water did not increase the pressure generated in the explosion vessel. This would be expected were the radiation losses the same in the presence of water as in its absence. At high pressures, the increased rate of molecular collision, the increased absorption of radiation by carbon monoxide, and a relatively slow rate of cooling would militate against the observation of the above effect.

The best conditions for the study of chemiluminescence from flames are provided by low-pressure flames under conditions of rapid chilling. The results obtained will throw light on the mechanisms occurring in flame, and the information gained will be of value not only for the interpretation of low-pressure flames, but also for those flames where the conditions are such that the chemiluminescence is masked by the thermal emission.

Discussion of Results.

Chemiluminescence.—The large decrease in the emission of radiation from the flame, which accompanies the addition of small quantities of hydrogen (a reduction of 30% for 0·016% of hydrogen) is a confirmation of the view expressed by von Helmholtz that the radiation from flames is very largely chemiluminescence. The reduction in the emission cannot have been brought about by changes in the extinction coefficient of the gases due to the addition of hydrogen. The percentage of this gas producing the effect is so small that neither it nor the water produced from it can absorb

infra-red radiation to a sufficiently great extent to account for such a marked reduction. Another explanation of the result, *viz.*, that the temperature of the flame is reduced by the addition of hydrogen, is also unsatisfactory. The fact that the flames containing hydrogen lose less radiation than those of the hydrogen-free gases must mean that the former give the hotter flame.

If further confirmation of the view of von Helmholtz be needed, it is to be found in the behaviour of the flame on dilution by inert gases. The emission of radiation during the combustion of carbon monoxide is the greater the lower the temperature of the flame (compare *Ind. Eng. Chem.*, 1928, **20**, 1009).

The emitters of the radiation are the freshly formed molecules of carbon dioxide, which are activated as the result of the chemical change (3) (see p. 1124). These molecules may become deactivated by the emission of this energy as radiation (4), or by collisions of the second kind (5). It is possible to account for the decrease in the radiation on addition of hydrogen by ascribing to this gas, or to one of its products in the flame, a property which is possessed to a smaller extent by other gases, *viz.*, that it can readily remove the internal energy of carbon dioxide molecules by collision. This process is indicated by equation (5), the occurrence of which decreases the number of molecules deactivated by (4). Thus the emission of radiant energy is reduced.

An alternative explanation is that the hydrogen brings about a reduction in the radiation by modifying the mechanism of the reaction, thus :

$$(7)\ CO + H_2 + O_2 \longrightarrow CO_2' + H_2O.$$
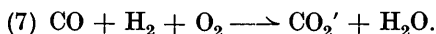
It is conceivable that molecules of carbon dioxide so produced may not be activated to the same extent as when produced by (3). The chemiluminescence from molecules of carbon dioxide when produced by reaction (7) may be quite small. This also applies to the Dixon mechanism [(1) and (2), p. 1124].

General Characteristics of Flames containing Hydrogen.—The Einthoven records indicate that there are at least three distinct processes involved in the combustion of carbon monoxide in the presence of hydrogen. The flame of the hydrogen-free gases differs from one containing up to 0·04% of hydrogen, which in turn differs from one containing above this percentage. The dry flame passes into the second type of flame without discontinuity occurring in the speed of flame movement or in the radiation emitted. These properties change gradually, the former increasing and the latter decreasing as hydrogen is added. The flame containing less than 0·04% of hydrogen differs from that of the gases containing no

hydrogen in that in the former the flame is composite in character, possessing two distinct zones of ionisation.

The second type passes into the third more abruptly. There is a rapid fall in radiation at nearly constant speed of flame, and the two zones of ionisation are replaced by one. The third type is the only flame which occurs with the production of sound.

Interpretation.—At the present time, insufficient is known about the phenomena of flame to make it possible to interpret these results with any degree of completeness. The value of any interpretation suggested to account for the facts will lie mainly in its usefulness as a working hypothesis and in its suggestiveness for further experiments.

It is suggested that the nature of the flame reactions when less than 0.02% of hydrogen is present is different from that at higher percentages. If we designate the reaction occurring at low concentrations of hydrogen by A, and that at high concentrations by B, then the interpretation of the step on the above curves is that reaction A is more rapid at low, and reaction B more rapid at high, hydrogen concentration. At the step itself, it is suggested that reactions A and B possess similar speeds, and, in this region, slight changes in the conditions of firing, etc., lead to the predominance of either reaction in any particular experiment.

In the region where A is dominant, there are two ionisation maxima on the Einthoven records. These maxima are an indication that the flame is divisible into two parts following one another, and that possibly reaction A occurs in two distinct stages. Since the double maxima disappear below the step, these two stages may occur simultaneously in reaction B.

Logarithmic Relationship between Speed of Flame and Radiation.— The logarithmic relationship found to hold between speed and radiation (see Figs. 4 and 6), which resembles that between the velocity coefficient of chemical change and temperature, can be expressed as $1/\log S' = - Nr' + M$, where S' is the speed when the radiation $= r'$, or $\log S' = 1/(M - Nr')$, M and N being constants. When $r' = 0$, $\log S_m = 1/M$, S_m being the maximum speed; and hence

$$\log S_m - \log S' = Nr'/M(Nr' - M) \quad . \quad . \quad . \quad (8)$$

This equation can be derived from the Arrhenius equation, $\log k = C + A/RT$. Stevens (*Ind. Eng. Chem.*, 1928, **20**, 1018) has shown that the speed of flame of mixtures of carbon monoxide and oxygen at constant pressure is given by $S = K[CO]^2[O_2]$, which is of the same form as the velocity equation $dx/dt = k[CO]^2[O_2]$, indicating that there is a linear relationship between K and some

velocity coefficient, k, which controls the speed of flame. The precise significance of k in the flame is not known.   It may be that the velocity coefficients of the reaction change according to the same law across the flame front for all mixtures of carbon monoxide and oxygen, and the value of k for any zone in the wave front may be said to control the speed of flame.

In our experiments with this flame, the concentrations of carbon monoxide and oxygen are constant throughout.   The percentages of hydrogen and the losses of radiation, however, vary.   In each zone in a flame, the loss of radiation is proportional to the amount of chemical change.   The temperature of these zones will also be proportional to the amount of chemical change, so that any variation in the total radiation from the flame will probably affect the temperature of each zone by a constant fraction.   This will be only approximately the case, since the specific heats vary with temperature, and the emission of radiation varies slightly with the temperature.   This fraction will equal cr'/T, where c is a constant, r' is the loss of radiation, and T the temperature at any point in the flame front when there is no loss of radiation.

Now, since $S' = k[CO]^2[O_2]$, where k is the velocity coefficient at any point in the flame front, $\log S' = C' + A/RT''$, where $T'' = (T - cr')$ and C' is a constant.   Hence

$$\log S' = C' + A/R(T - cr'),$$
$$\log S_m = C' + A/RT,$$
$$\text{and } \log S_m - \log S' = Acr'/RT(cr' - T) \qquad . \quad . \quad (9)$$

This is of the same form as (8), but until the result obtained by Stevens is more clearly understood, the similarity cannot be stressed. Also, the speeds given in this paper are average speeds of flame movement, and if any arrest in the speed of flame occurs between the electrodes used in measuring this speed, the applicability of the above argument is weakened.

Summary.

The effect of hydrogen and water on the emission of radiation and the speed of flame of mixtures of hydrogen and oxygen has been studied.   On addition of hydrogen or water the radiation from the flame decreases as the speed of flame increases.   There is little difference between the effects of the two gases.   At 0.02—0.04% of hydrogen, there is a critical region, where the radiation from the flame falls abruptly and the properties of the flame undergo a marked change.   The radiation–composition and radiation–speed curves give a step at this point.

Logarithmic relationships are found to hold between the speed of

flame and the radiation emitted. These apply to mixtures above and below the step respectively. They afford support for the " energothermic " theory of the catalysis.

The step on the radiation curves is considered to be due to a change in the nature of the chemical reaction.