CCLXIII.—*The Catalytic Action of Hydrogen on the Carbon Monoxide Flame.*

By W. E. Garner and D. A. Hall.

The radiation from the "dry" carbon monoxide flame decreases on the addition of hydrogen or water (Garner and Johnson, J., 1928, 281), and the curves obtained by plotting the radiation emitted against the percentage of hydrogen added show a step at 0·03% of hydrogen (Garner and Roffey, J., 1929, 1123). Above and below this step, the radiation falls continuously as hydrogen is added. There are thus two distinct effects of hydrogen: (1) a continuous fall in emission, and (2) an abrupt change at a critical percentage of hydrogen. It was suggested in the previous communication that the continuous fall in radiation was due to quenching of the chemiluminescence of the flame in a manner analogous to the extinction of fluorescence by impurities, and the particular mechanism suggested for the process was $CO_2^* + H_2O \longrightarrow CO_2 + H_2O^*$. The discontinuity was considered to be due to an abrupt change in the mechanism of flame propagation, and the equations suggested for the reactions occurring above and below the step were: For the "dry" reaction, $2CO + O_2 \longrightarrow 2CO_2$; for the hydrogen reaction, $CO + H_2 + O_2 \longrightarrow CO_2 + H_2O$.

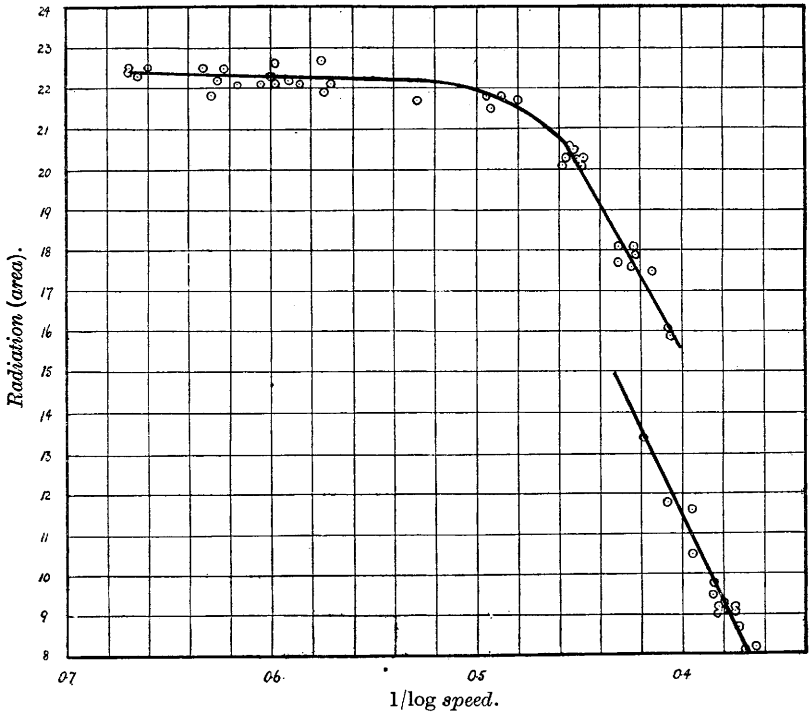
In the present investigation, these ideas have been put to experimental test by examining the effect of changes of pressure on the phenomena observed, and by comparing the results so obtained with predictions based on the above hypothesis. The pressure–radiation curves obtained for hydrogen-containing mixtures supply information with regard to both the continuous and the discontinuous effects. These are discussed later (p. 2045), where it is shown that the new experimental results are in agreement with the mechanisms suggested above.

EXPERIMENTAL.

The apparatus employed did not differ appreciably from that of Garner and Roffey (*loc. cit.*). The following improvements were, however, made: (1) The connexions from the hydrogen reservoir to the bomb were glass and metal throughout, (2) platinum wire was used for firing the gases, (3) phosphoric oxide distilled in oxygen was used for drying them, (4) the time of evacuation of the bomb and the drying of the gas was increased to 2 hours, the pressure being 10^{-4} cm., and (5) the bomb was permanently fixed in relation to the thermopile and to the gas container. The gas was introduced into the dried bomb and fired within 5 minutes. These modifications led to greater reproducibility in the results, and to the attainment of a higher degree of drying than was possible before.

Quartz windows were employed throughout instead of the fluorite windows used by the above authors, in order to minimise the percentage loss of radiation which occurs through absorption by the gases ahead of the flame. The average extinction coefficient of the gases in front of the flame and also of the products of the flame is smaller for the radiation which passes through a quartz window than for that passing through a fluorite window. Thus, corrections for absorption and the errors in their application will be smaller for quartz than for fluorite windows.

FIG. 1.



Radiation through Quartz Window for Gases initially at Atmospheric Pressure.—In this series of experiments, the bomb was that used by Roffey, and as in his experiments, the speed of flame movement and the radiation emitted were measured simultaneously. The radiation was measured by means of a Kipp and Zönen thermopile. This was connected to a Downing galvanometer, the deflexion of which was recorded on photographic paper. The area under the curve so obtained is proportional to the radiation falling on the thermopile. In Fig. 1, the inverse of the logarithm of the speed * is plotted against radiation. The step on the curve occurs at 0·03% of hydrogen, as in the earlier experiments with the same bomb (*loc. cit.*). There is, however, one marked difference between the results with the quartz and with the fluorite window at low speeds of flame. With the latter, the linear portion of the curve immediately above the step extends to the lowest speeds measured; for the former, on the other hand, the radiation approaches a constant value when the speed approaches 50 cm./sec. Thus, a limiting value for the emission of the 2·8 μ band is reached *before* the limit for the speed of flame is attained. The cause of this difference between the results obtained with fluorite and with quartz windows is obscure at present, and further work will be needed before any explanation can be given. The lowest speed measured was 31 cm./sec., which is of the same order as those found by Bone for " dry " gas mixtures, but comparison of speeds in metal bombs and in quartz tubes is perhaps not justifiable.

The results for the continuous fall in radiation above the step (Fig. 1) are of interest in that they permit a test of the theory put forward previously. If the cause of the decrease in radiation is deactivation of activated molecules of carbon dioxide according to the scheme

$$CO_2^* \longrightarrow CO_2 + h\nu \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$CO_2^* + H_2O \longrightarrow CO_2 + H_2O + \text{kinetic energy} \quad . \quad (2)$$

then $dx_1/dt = k_1[CO_2^*]$ and $dx_2/dt = k_2[CO_2^*][H_2O]$. Since $[CO_2^*]$ is the same for both reactions at every stage in the process of combustion, the radiation emitted is given by the equation

$$R = R_0k_1/(k_1 + k_2[H_2O])$$

where R_0 is the radiation of the dry hydrogen-free gas mixture. Therefore

$$k_1/k_2 = R[H_2O]/(R_0 - R) \quad . \quad . \quad . \quad . \quad (3)$$

If this mechanism be correct, then $R[H_2O]/(R_0 - R)$ should be constant. Unfortunately, a very accurate test is precluded by the magnitude of the experimental error, but Table I shows that the

TABLE I.

H_2, %.	R (mean).	$10^5k_1/k_2$.		Mean speed (cm./sec.).
0	22·7			32—50
0·005	21·5	4·0	Mean 3·57	109
0·010	20·2	3·62		157·4
0·019	17·8	3·08		215

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* The speeds were measured as in the previous paper, but the pointed electrodes used in the earlier work were replaced by platinum T-pieces.

theory holds within these limits. The mean value of k_1/k_2, *viz.*, $3{\cdot}57 \times 10^{-5}$, is very approximate. It is employed later in the analysis of the results obtained at lower gas pressures, and is found to be in agreement with the radiation–pressure curves obtained.

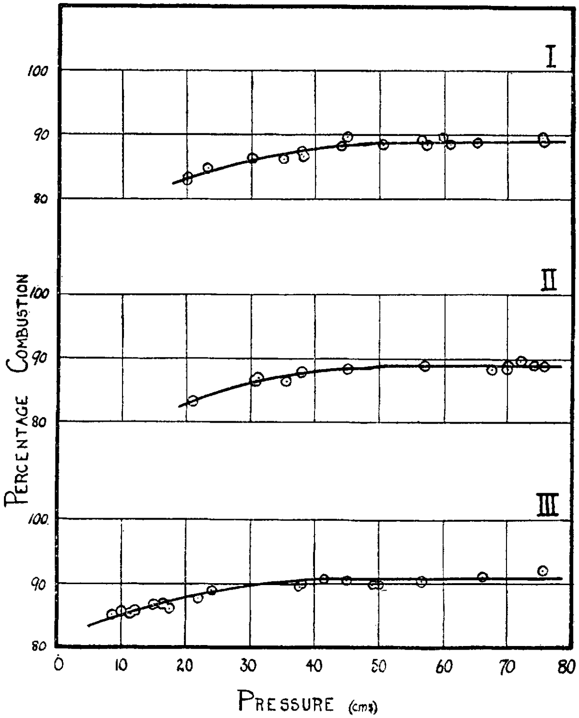
The figures in Table I are of value in indicating the lower limit of concentrations of hydrogen required to produce an appreciable effect on the radiation emitted. It will be seen that 0·005% has a definite effect, and it is of interest to determine whether such an effect is, on the above hypothesis, kinetically possible.

The ratio k_1/k_2 can be calculated if certain assumptions are made with regard to reactions (1) and (2). If, in the case of reaction (2), it be postulated that every collision between a water molecule and a molecule of carbon dioxide is effective for deactivation, then from the kinetic theory, it can be shown that the initial rate of reaction (2), when the carbon dioxide is at atmospheric pressure and contains 0·005% of water vapour, is $1{\cdot}46 \times 10^5$ g.-mols./litre/sec. From this rate, the value of k_2 is $1{\cdot}47 \times 10^{12}$, whence $k_1 = 5{\cdot}24 \times 10^7$. The latter constant gives $1{\cdot}3 \times 10^{-8}$ sec. as the average life of a molecule of activated carbon dioxide, which is somewhat smaller than the normal value for the excited states of atoms (10^{-7}). If, however, only one in ten collisions is effective in deactivating molecules of carbon dioxide, then the calculated life of the excited state would agree with the normal value. Thus, the number of collisions between activated carbon dioxide and water or hydrogen is sufficiently large to make the above hypothesis feasible.

Effect of Pressure of Gas Mixture on the " Step."—In this series of experiments, a smaller bomb, 2·5 cm. in diameter and 32 cm. long, was used (compare Garner and Tawada, *Trans. Faraday Soc.*, 1929, 37). This made it possible to carry out a larger number of experiments with the limited quantity of gas contained in the gas-holders, and a change of bomb was desirable in order to determine if the step was due to purely adventitious circumstances connected with the dimensions of the bomb. The smaller bomb also permitted of placing the thermopile in such a position that it did not " see " any portion of the walls of the bomb. We have never found any effect due to the position of the thermopile, but the above precaution was taken wherever possible. With this bomb, it was, however, impossible to measure speeds.

Extinction Coefficient of Gases in Front of the Flame.—Previously, when corrections were made for absorption of the radiation from the flame by carbon monoxide, use had been made of the figures of Coblentz (" Investigations of Infra-Red Spectra," *Carnegie Institution of Washington*, 1904, **50**, 175) and those of Garner and Johnson (*Phil. Mag.*, 1928, **5**, 301). The method adopted was possibly not very accurate, so it was decided to measure the average extinction coefficients directly. A cell 10·765 cm. long, with fluorite windows, was placed in front of the bomb and between it and the thermopile. The cell was filled with carbon monoxide at a pressure such that the quantity of the gas traversed by the radiation was equivalent to one-half of the gas in the bomb itself when this gas was at atmospheric pressure. The extinction coefficient was calculated from the readings of the radiation (1) from gas at 1 atm. pressure with the cell evacuated, (2) from gas at ½ atm. pressure with the cell evacuated, and (3) from gas at ½ atm. pressure with the cell filled with carbon monoxide to a pressure of 750 mm. The sum of the radiations from (2) and (3) was found to be exactly equal to that from (1). The extinction coefficients were as follows, the thickness of the window being 1 cm. in each case :

FIG. 2.



I. *Dry gas.* III. *Dry gas* + 0·2% H_2. III. *Dry gas* + 2·0% H_2.

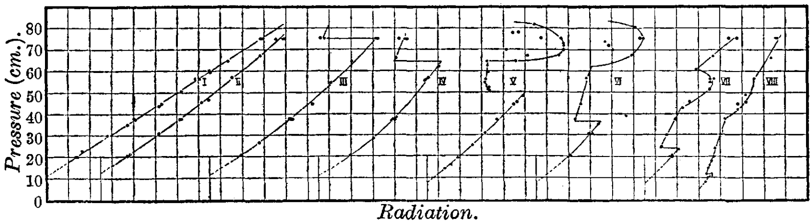
Radiation through quartz (× 10^5) : 8·6 ; 8·8 ; 8·5.

Radiation through fluorite (× 10^4) : 2·4 ; 2·8.

Pressure of Unburnt Gas.—After every experiment, the pressure of the gas mixture was measured. It was found that the percentage of gas burnt varied somewhat with the state of dryness of the gas. Curves in Fig. 2 show the manner in which the percentage of gas burnt varies with pressure for a mixture free from hydrogen, and for those containing 0·2 and 2% of this gas. These percentages were used together with the extinction coefficients in correcting the radiation in the curves of Fig. 3.

Experimental Results.—These are summarised in Fig. 3, which gives the radiation plotted against pressure for the "dry" mixture and for mixtures containing 0·019, 0·0315, 0·0537, 0·101, 0·200, 0·517, and 2·02% of hydrogen. The "step" occurs at 0·03% for 1 atm. pressure, in agreement with the results in the long bomb (Fig. 1). This critical percentage has thus been observed for three different sets of experimental conditions.*

FIG. 3.



I. *Dry hydrogen-free gas.*
II. *Gas* + 0·019% H_2.
III. ,, + 0·0315% H_2.
IV. ,, + 0·0537% H_2.
V. *Gas* +0·101% H_2.
VI. ,, +0·200% H_2.
VII. ,, +0·517% H_2.
VIII. ,, +2·02% H_2.

The step occurs at a greater hydrogen pressure the lower the pressure of the mixture of carbon monoxide and oxygen (Table II). The relationship between p_{H_2} and p_{gas} at the step is such that their product is practically constant. The drift in this value is outside the limits of experimental error, but several factors which may influence such a relationship are difficult to evaluate. Better constants are obtained if the equation $p_{gas} = a/p_{H_2} + b$ is employed, but the consideration of such refinements is not warranted at this stage.

TABLE II.

$p_{H_2} \times 10^4$, cm.	2·36	3·46	5·04	7·2	12·4	24·0
p_{gas}, cm.	75	64·5	50	36	24	12
$p_{gas} \times p_{H_2} \times 10^2$	1·77	2·25	2·52	2·59	2·99	2·88

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* Smithells, Whitaker, and Holmes (this vol., p. 185) also note that this is a critical percentage for the catalysis of the carbon monoxide flame by hydrogen.

The interpretation of the step as the point at which one chemical mechanism replaces another is supported by the fact that it is possible to suggest mechanisms for the two reactions which are in accord with the above relationship. Provided that the dry reaction is a chain mechanism whose velocity is given by

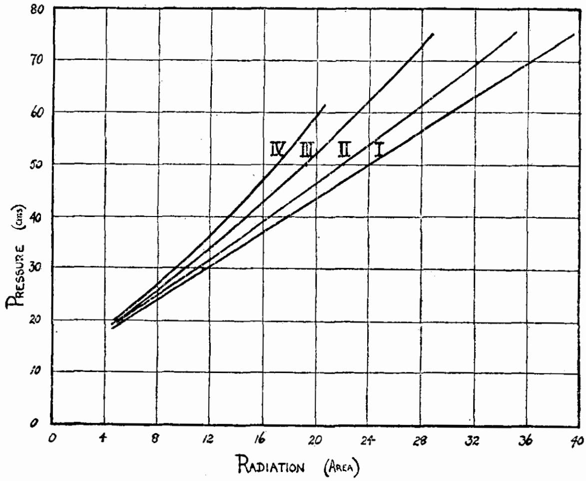
$$dx_1/dt = k_1[O_2^*]$$

and that the mechanism of the wet reaction is given by

$$dx_2/dt = k_2[H_2][O_2^*][CO],$$

FIG. 4.

Calculated effect of hydrogen on the radiation from the "dry" carbon monoxide flame.



I. *Dry gas.* II. *Gas* + 0·02% H_2. III. *Gas* + 0·032% H_2. IV. *Gas* + 0·054% H_2.

then the speeds of reaction, which are equal at the step, give us

$$dx_1/dt = dx_2/dt, \text{ or } k_1 = k_2[H_2][CO],$$

which is the relationship found. If the step is due to the onset of the reaction

$$H_2 + O_2^* + CO \longrightarrow CO_2 + H_2O \quad . \quad . \quad . \quad (4)$$

which replaces the "dry" reaction, then since water is produced simultaneously with carbon dioxide, it is possible that the carbon dioxide formed, owing to the proximity of water at the moment of formation, will give less chemiluminescence than the same molecules when produced by the "dry" reaction. Thus, the fall in radiation at the step may be accounted for.

The fall in radiation at the step, R_S, is proportional to the radiation above the step, R (see Table III), except in the case of curve VII (see Fig. 3) for which there are insufficient experiments. This proportionality is not incompatible with the above interpretation.

TABLE III.

H_2, % ……	0·0	0·019	0·0315	0·0537	0·101	0·200	0·517	2·02
R_S/R ……	—	—	0·33	0·38	0·36	0·39	0·52(?)	0·40
Intercept, p, cm. …	11·5	12·0	11·0	10·5	8·0	5·0	—	1·2

These theoretical conclusions can be readily submitted to further test. For example, since the concentration of oxygen enters into the velocity equations of both the dry and the hydrogen reaction, then the position of the step should not be affected by the addition of excess oxygen. Excess carbon monoxide should change the position of the step to lower pressures. Such tests of the theory are now being made by Mr. F. E. Harvey.

The Slope of the Pressure–Radiation Curves.—If the energo-thermic theory is correct, then the relationship (3), which was found to hold for the radiation from flames initially at atmospheric pressure, should apply also to the results embodied in Fig. 3. Such a relationship will not hold exactly unless the whole of the radiation is chemiluminescence. Neither will it hold if there is appreciable deactivation of activated molecules by the walls of the bomb. An examination of the slopes of the curves in Fig. 3 and a comparison between them and the corresponding curve for the hydrogen flames (Garner and Tawada, *loc. cit.*) will throw light on this matter.

The pressure–radiation curves for hydrogen–oxygen flames are concave to the radiation axis, and the curves pass through the origin. This type of curve would be given by a hypothetical flame, the radiation from which was due solely to its being a hot body. It is called for brevity the " thermal " type of curve, and is concave towards the radiation axis because the cooling of gases is more rapid at low than at high pressures. This is a consequence of the fact that the mean free path of the gases increases with decrease in pressure. If hydrogen–oxygen flames give " thermal " curves, then it is because the radiation from them is in the main thermal in origin. This view is supported by the effects obtained on addition of inert gases to the hydrogen flame (*loc. cit.*).

The hydrogen-free carbon monoxide curve is, however, linear, and does not pass through the origin but intercepts the pressure axis at $p = 12$ cm. Thus it does not show the characteristics of the " thermal " curve. If, however, the radiation were entirely due to the chemiluminescence from molecules whose average life was 10^{-7} sec., and these molecules were not deactivated by collision, then the emission should be simply proportional to the pressure. Thus, a linear pressure–radiation curve would be obtained which would pass through the origin. It is the intercept of the carbon monoxide curve which requires a special interpretation. This intercept diminishes as hydrogen is added to the gas, and practically disappears when the hydrogen percentage is 2% (Table III). Thus it is a characteristic property of carbon monoxide flames containing small quantities of hydrogen.

An explanation of the intercept can be given if the activated molecules possess a life of the order of 1 to 10^{-3} sec. Under these conditions, there will be appreciable loss of energy on account of the fact that within this time the Brownian movement of activated molecules to the walls will be appreciable. This movement will be assisted by turbulence in the flame. On this assumption, at 12 cm. pressure, practically the whole of the activated molecules would be deactivated by the walls. The assumption of a long life for the activated state is not in opposition to any results so far obtained, and it is supported by the fact that the addition of inert gases which reduce the Brownian movement decreases the magnitude of the intercept.*

In view of the fact that there is probably appreciable deactivation by the walls of the bomb, equation (3) would not be expected to hold quantitatively. Qualitatively, however, it would be predicted that on addition of hydrogen the radiation–pressure curve should become concave to the pressure axis, *i.e.*, it should have the opposite curvature to that observed for the hydrogen flame. This will occur because the deactivation process must be bimolecular, and hence will be especially favoured at high pressures. This curvature is actually found, and on calculating the values of R for hydrogen mixtures from values for the hydrogen-free mixture, using equation (3), the curvatures predicted are, within experimental error, the same as those actually obtained (see Fig. 4). The only discrepancy which occurs is the shift of the curves bodily towards greater values of R as the percentage of hydrogen increases, and this is probably due to the same discrepancy as that referred to in the preceding paragraph. (It is interesting to note that, as a consequence of this shift, the radiation from the 20-cm. flames increases as hydrogen is added, and then decreases.)

The general conclusion reached from a consideration of the

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* *Note added in proof.*—No account has been taken of the transference of energy from one carbon dioxide molecule to another by resonance at distances many times the molecular diameter. If this be considered, much shorter times than 10^{-3} second will be needed to account for the intercept (compare Beutler and Rabinowitsch, *Z. physikal. Chem.*, 1930, *B*, **8**, 231, 403).

change in radiation with pressure is that the radiation of the hydrogen-free carbon monoxide flame is in the main chemiluminescence. This explanation is necessary in view of the curvature of the radiation–pressure curves of the hydrogen-containing mixtures.

Other Features of Curves.—As the pressure of the hydrogen increases, there appears a further irregularity on the curves. This is separated from the " step " by a region in which reproducible results are obtained. Curve V was determined in more detail than the others in order to determine the boundary of the irregularity. It is obviously of a different character from the " step," but, like it, the irregularity moves to lower pressures with increasing hydrogen concentration. Whether this is due to a second change in mechanism or not is uncertain. It could probably be investigated better at pressures higher than those used in this work, for the region increases in extent as the pressure is raised. This irregularity was missed in the earlier work with the long bomb, so its magnitude probably depends on the size of the explosion vessel.

Above the irregularity, *i.e.*, at higher pressures, the values of R become reproducible again, but little attention has been paid to the curves obtained.

Summary.

The " step " which was found to occur on the radiation–1/log speed and radiation–hydrogen curves of the carbon monoxide flame has been confirmed. This step, which lies at 0·03% of hydrogen for the gases initially at 1 atm. pressure, occurs at a greater hydrogen pressure the lower the pressure of the mixture of carbon monoxide and oxygen : $p_{H_2}p_{gas}$ is found to be constant at the " step."

The decrease in the emission of radiation which occurs for percentages of hydrogen less than 0·03% is given by the equation $R = R_0k_1/(k_1 + k_2[H_2O])$, where R_0 is the radiation for the hydrogen-free mixture.

The radiation–pressure curve for the hydrogen-free carbon monoxide flame is linear, giving an intercept on the axis at 12 cm. This is different in type from that of the hydrogen flame, which is concave to the radiation axis. Flames of carbon monoxide containing hydrogen give radiation–pressure curves concave to the pressure axis. These results are in agreement with the view that the radiation from the carbon monoxide flame is mainly chemiluminescence.

An irregularity occurs on the radiation–pressure curves above the step, and like it, this irregularity moves to lower pressures with increasing hydrogen concentration.

The extinction coefficients of the gases ahead of the flame have been determined for the radiation that passes through quartz and through fluorite.

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