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

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THE total radiation emitted from a dried carbon monoxide flame in narrow cylindrical bombs, 2·5 cm. in diameter, amounts to 24% of the total energy of combustion (Tawada and Hall, *Trans. Faraday Soc.*, 1930, **26**, 605). On the addition of 2% of water to the flame, this radiant energy is reduced to 2·3% of the total energy of combustion (Johnson, *Phil. Mag.*, 1928, **5**, 301). This marked reduction in the radiation emitted is due, in part, to a gradual fall in the emission as the percentage of hydrogen is increased, and in part to an abrupt fall which occurs at a critical percentage of hydrogen (Garner and Roffey, J., 1929, 1123; Garner and Hall, J., 1930, 2037). This abrupt fall occurs as a step on the curves showing the relation between radiation and the percentage of hydrogen, the amount of the latter corresponding with the step varying with the pressure of the flame. The relationship, $p_{H_2} \cdot p_{gas} = \text{const.}$, was found to indicate sufficiently accurately the connexion between these variables.

Tentative explanations of these phenomena have been advanced in the preceding papers, and with the view of testing these hypotheses, the effects of the dimensions of the explosion vessels, the addition of inert gases, etc., have been investigated.

EXPERIMENTAL.

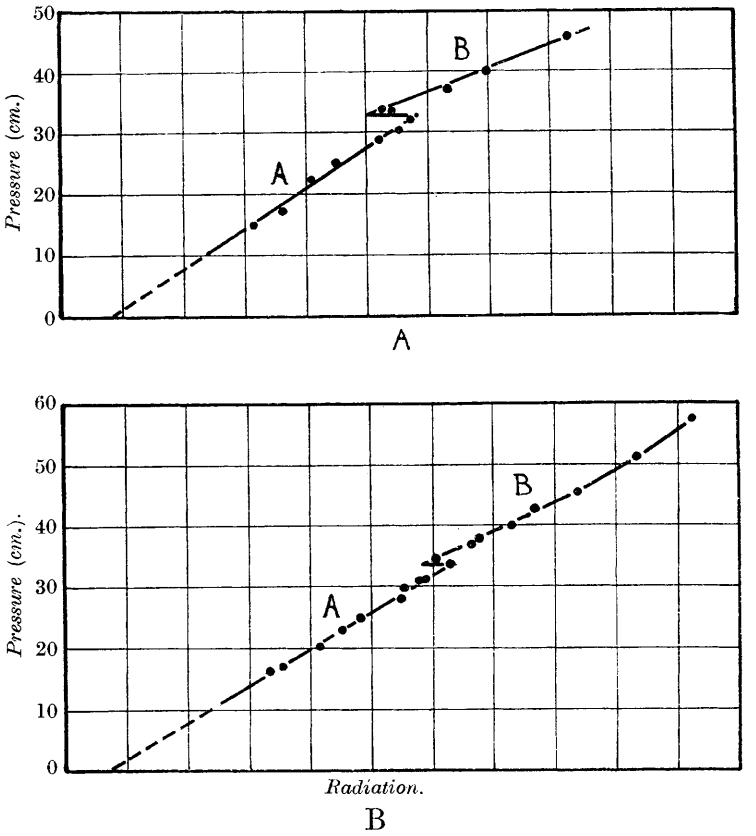
Effect of Dimensions of Explosion Vessels on the Radiation–Pressure Curves.—By using the technique previously described (Garner and Hall, *loc. cit.*), the radiation emitted through a fused silica window 1 cm. thick has been measured for bombs of different dimensions. Four bombs have been used: (1) 1·5 cm. diameter, 32 cm. long; (2) 2·5 cm. diameter, 32 cm. long; (3) 2·5 cm. diameter, 80 cm. long; (4) 6·5 cm. diameter, 67 cm. long. The thermopile was so placed that it could not " see " the walls of the vessels.

Attention was mainly directed to the step which is found on the radiation–pressure curves, with the object of determining whether its position and magnitude would undergo modifications with change in the experimental conditions.

The nature of the step can best be seen by reference to Fig. 1 and Fig. 3, V (J., 1930, 2037). Reference to the latter curve shows that, above the step, there is a region where very variable results are obtained. This region, which is connected by a curve to the step, needs a very large number of experiments to determine its area, and

this has not been attempted in the present work. There are three distinct groups of results on any pressure–radiation curve, (*A*) those below the step, (*B*) those immediately above the step, and (*C*) those in the variable region. The results *A* and *B* lie on two different curves. The regions *A*, *B*, and *C* are indicated on the curves given in this paper. Under certain conditions, *B* occurs over a small

FIG. 1.

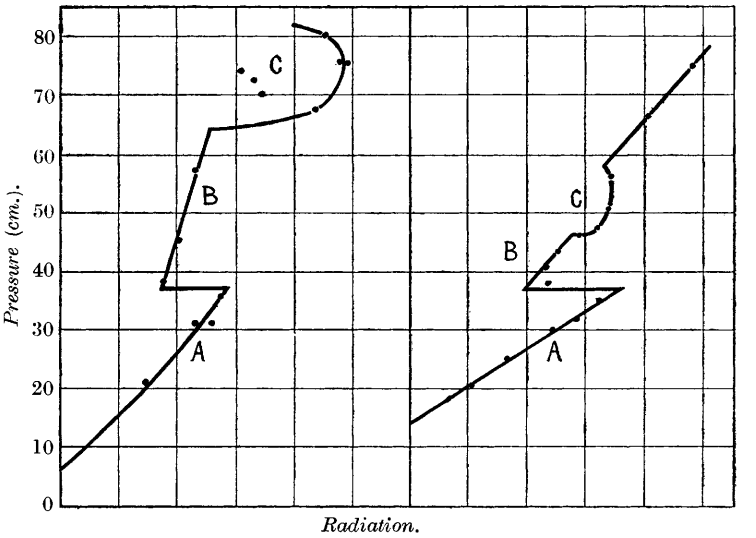


pressure range (Fig. 3). Below and above the step, the results are always reproducible, but in the neighbourhood of the step, values lying on neither of the two curves are frequently obtained. This is most marked with the long explosion vessel (see Fig. 6, and also curves in the paper by Garner and Roffey, *loc. cit.*).

In the earlier work, it was suggested that the chemiluminescence for pressures in the neighbourhood of 1 atm. bears a higher ratio to the total emission the more rapid the cooling of the gases after

explosion. The phenomena of luminescence should, therefore, be more marked in narrow than in wide explosion vessels. In the latter, on account of slow cooling, it would be expected that the luminescence phenomena would be masked by thermal emission from the hot gases. On the other hand, the effect of changing the length of the bomb, which cannot materially affect the rate of cooling, should be without appreciable effect on the radiation–pressure curves. These views have been confirmed (Table I).

FIG. 2. FIG. 3.



It was always possible that some of the effects observed might be due to wave phenomena set up by the flame, and not to the reactions occurring in the gases themselves. Since wave formation is very markedly influenced by the dimensions of the containing vessels, the position of the step, if due to such processes, should vary in these experiments. This is not found to be the case; hence, the view that the step is entirely due to changes in chemical mechanism of the reaction has been considerably strengthened. The step is therefore very probably due to the occurrence of two quite distinct and independent chain mechanisms in the flame. Two possible independent mechanisms are

$$(1)\quad CO + O + O_2 \longrightarrow CO_2 + O_2^*$$
$$O_2^* + CO \longrightarrow CO_2 + O, \text{ etc.}$$
$$(2)\quad CO + OH \longrightarrow CO_2 + H$$
$$CO + H + O_2 \longrightarrow CO_2 + HO, \text{ etc.}$$

The rate of the latter depends on the hydrogen concentration.

It is suggested that the replacement of mechanism (1) by (2) could be the cause of the step. This replacement of one mechanism by another will occur discontinuously on account of the autocatalytic character of explosive reactions. The two reactions will occur simultaneously, but in the flame front one or other will predominate. That reaction will carry on the flame which reaches its maximum rate in the shortest time.

In Table I are given results for the radiation through fused silica windows from two explosive mixtures containing carbon monoxide and oxygen in equivalent proportion and 0·03% and 0·2%H_2 respectively. Experiments 4 and 5 show that increase in the length of the bomb does not materially change the position or magnitude of the step. Experiments 1, 2, and 3 show that an increase in diameter from 1·5 to 6·5 cm. does not change the position of the step, although there is a reduction in its magnitude from 46% to 10%.

TABLE I.

Expt. No.	Diameter of bomb, cm.	Length of bomb, cm.	H_2, %.	Pressure at step, cm.	Size of step, %.
1	6·5*	67	0·198	34	10
2	2·5	32	0·200	36	38
3	1·5	32	0·197	37	46
4	2·5	32	0·03	75·5	38
5	2·5	80	0·03	75·5	41

* A rustless steel bomb; the others were made of phosphor-bronze.

The radiation–pressure curves are given in Figs. 1, 2, and 3. Those of Fig. 1 were obtained with the 6·5-cm. bomb for two different positions of the thermopile. As was expected, the position of the step is not very clearly defined in Fig. 1. The thermopile receives the radiation from a cone of gas in the centre of the bomb which cools comparatively slowly. In these experiments, therefore, the radiation is mainly thermal and there is little evidence of the phenomena due to chemiluminescence. The cone of gas was wider in the case of 1A, and here the step is more clearly defined than in 1B. In Figs. 2 and 3 are given the results with the 2·5- and the 1·5-cm. bomb respectively. Here the step is clearly present, and occurs at the same pressure for the two bombs. The variable region C, however, occurs at different pressures in the two cases.

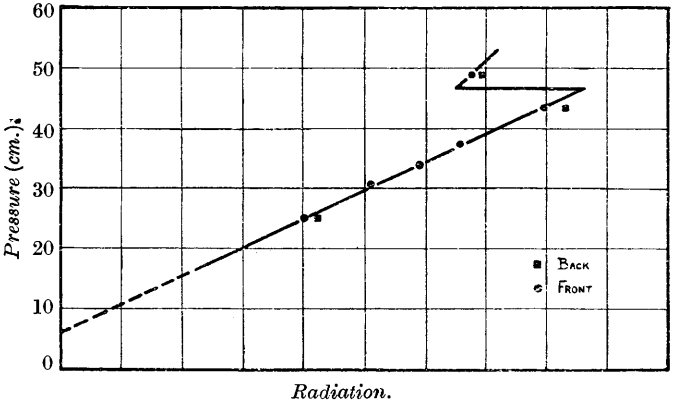
The position of the intercept is interesting. In the 1·5-cm. bomb, the intercept occurs at 13 cm. on the pressure axis, and in the 2·5-cm. bomb at 5 cm. on the same axis, but in the 6·5-cm. bomb, it lies on the radiation axis. This shift in the position of the intercept was anticipated, since the intercept on the pressure axis was considered to be one of the phenomena due to the occurrence of

luminescence, and this must tend to disappear as the relative amount of purely thermal radiation increases.

Transparency of the Flame to its own Radiation.

The optical phenomena of flames have not been investigated very completely. The experiments of Callendar (*British Assoc. Rep.*, 1910), however, show that flames are remarkably transparent to their own radiation, and thus, whether the radiation be measured from the front or the back of the flame, should not affect the nature of the results obtained. It was, however, necessary to check this deduction, if any confidence was to be placed in the result obtained for the radiation measurements of Tawada and Hall (*loc. cit.*). For this purpose, the 32-cm. bomb, 2·5 cm. diameter, was used, and this was filled with the $2CO + O_2$ mixture containing 0·12% of

FIG. 4.



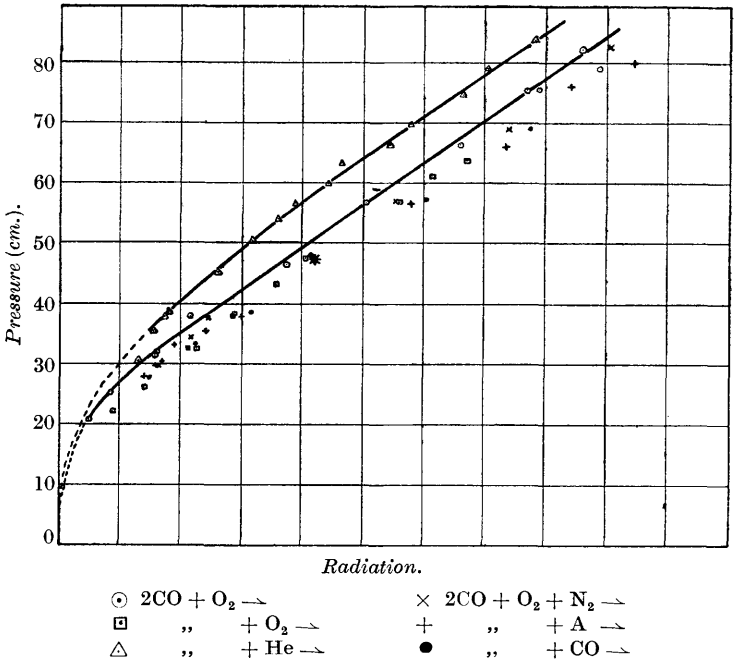
hydrogen. Measurements were made of the radiation emitted through fused silica, both when the flame was travelling away from the thermopile and also when it moved in the contrary direction. In the first case, the radiation travels through a column of carbon dioxide and in the second through carbon monoxide. Since the extinction coefficients of these two gases are small in the near infra-red (2·8 μ), the radiation emitted would not be expected to be markedly affected by the change in the direction of measurement. Fig. 4 shows that this is the case : the luminescence phenomena are independent of the direction in which the radiation is emitted.

Effect of the Addition of Oxygen, Carbon Monoxide, and Inert Gases to the Equimolecular Mixture.

Hydrogen-free Gases.—The value of experiments on diluted flames lies in the information gained on the question as to whether the

emission from the flame is luminescence or thermal emission. Three important properties of the flame are modified by the addition of inert gases, *viz.*, (1) the maximum flame temperature, (2) the thermal conductivity of the products, and (3) the speed and duration of flame. The relationship between these properties and the radiation emitted is very complex, so the interpretation of any experimental results is likely to be a matter of difficulty. By a suitable choice of diluent, however, some useful information can be gained.

FIG. 5.



The flame temperatures will be lowered by the addition of inert gas, and since the radiation emitted varies as T^4, there must in all cases be a reduction in the thermal radiation on dilution. The thermal conductivity of the products of the flame will also be an important factor in determining the magnitude of the emission; any diluent which decreases the thermal conductivity will decrease the rate of cooling and hence increase the thermal emission. The effect of speed of flame on the radiation emitted is difficult to determine on account of the possibility of the production of turbulent motion. It would be expected, however, for slow-moving flames with velocities less than 100 cm. per second, such as those studied, that more

energy would be lost to the walls by collision the slower the rate of flame; hence, less energy would be available for emission of radiation.

Oxygen, nitrogen, and argon, when added to the dry flame of carbon monoxide and oxygen, lower the flame temperature and the thermal conductivity of the product (carbon dioxide), and either reduce or have very little effect on the average speed of flame, as measured by the duration of the radiation emitted (see Table II). They should, therefore, on all counts, reduce the thermal emission from the flame. Actually (see Fig. 5), these gases increase the radiation emitted over a pressure range of 20—80 cm., which, therefore, cannot be entirely thermal in character. This apparent anomaly can, however, be explained if a large part of the energy emitted is luminescence from the newly-formed molecules of carbon dioxide.

Of the diluents added to the dry carbon monoxide flame, helium alone lowers the radiation emitted. This gas has a very high thermal conductivity, and the rate of cooling of the gases is very much enhanced when it is present. This result is readily understandable if the radiation is partly thermal and partly luminescence, for any gas with a high thermal conductivity will reduce the thermal emission.

TABLE II.

Average Speed of Flame, cm./sec.

		Gas mixture.				
Pressure, mm.	$2CO+O_2$.	$2CO+2O_2$.	$2CO+O_2+He$.	$2CO+O_2+N_2$.	$2CO+O_2+A$.	$3CO+O_2$.
600	74·0	80·2	29·6	44·0	54·4	64·0
300	32·0	33·6	21·6	20·8	28·8	33·6

The results in Table II are the average speeds of flame in a bomb 80 cm. long. These values have been taken from smoothed curves.

The radiation–pressure curves showing the effect of the diluents in the 80-cm. bomb are collected in Fig. 5. In order to make the results for each series directly comparable, the radiation is plotted against the pressure of the combustible gas for the mixtures (1) $2CO + O_2$, (2) $2CO + 2O_2$, (3) $2CO + O_2 + He$, (4) $2CO + O_2 + N_2$, (5) $2CO + O_2 + A$, and (6) $3CO + O_2$. The values have been corrected for the radiation absorbed by the gases through which the flame passes and also for the amount of gas unburnt. The corrections are of the order of 10%, and were made as described in previous papers. The corrections for the radiation absorbed are very small and practically the same for each mixture. The magnitude of the correction for percentage combustion can be gathered from Table III. The form of these curves is different from those obtained for any

other type of explosive mixture yet examined. The main difference between these curves and those of (1) hydrogen and oxygen, (2) cyanogen and oxygen, and (3) hydrogen-containing carbon monoxide flames lies in the fact that the radiation–pressure curves for the dry gases give an intercept on the pressure axis, *i.e.*, they are probably hyperbolic. The radiation emitted by the dry gases becomes practically zero at finite low pressures. This, we believe, is due to the fact that a very large part of the radiation in these flames is luminescence, and that, in consequence, energy is lost from the flame in an unusual manner.

A Luminescent Flame.—It is advantageous now to consider what would be the properties of a flame for which the rate of conversion of internal energy of the products into kinetic energy was negligibly small. The activated products would then lose their energy either as radiation, (1) $CO_2^* \longrightarrow CO_2 + h\nu$, or (2) by collision with the wall of the containing vessel. The molecules must move to the walls by Brownian movement, and since the rate of Brownian movement is inversely proportional to the pressure, the rate of loss of energy at low pressures will be proportionately higher than at high pressures. The probability of the occurrence of process (1) will therefore be diminished at low pressures.

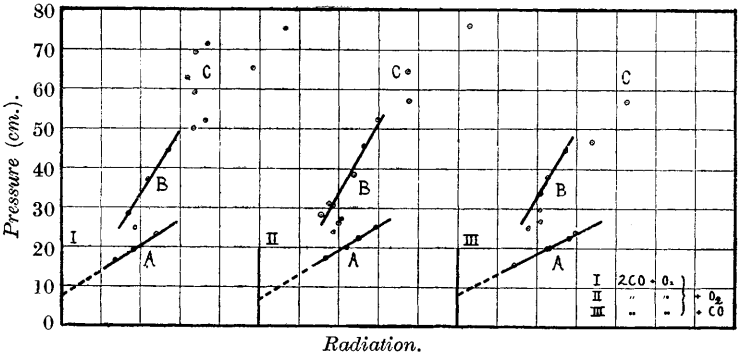
Loss of energy by Brownian movement of activated molecules to the walls in bombs of several centimetres diameter will only be appreciable if the activated molecules can travel several centimetres before losing their energy. This implies a marked stability towards collisions and an average duration of life of the order of 1 sec. (see previous paper, *loc. cit.*). Activated molecules which possess a high stability towards collisions and an average duration of life of this order are not uncommon, as, *e.g.*, those of active nitrogen. Also, resonance between activated and unactivated molecules of carbon dioxide according to (3) $CO_2^* + CO_2 \longrightarrow CO_2 + CO_2^*$ is likely to occur over distances of the order of 1000 times their actual diameter (Beutler and Rabinowitsch, *Z. physikal. Chem.*, 1930, *B*, **8**, 231, 403). These authors call such a process " energy diffusion." If this process has a very high probability, then the rate of deactivation by (1) will be reduced, and so give an apparently high duration of life.

In bombs of the dimensions used in this research, the production of activated molecules with a long life would lead to radiation curves of the type obtained for the dry carbon monoxide flame. In these curves, the radiation will tend to approach zero at finite low pressures. Calculations of the form of the ideal curves are difficult on account of a lack of quantitative knowledge with regard to the above processes. There is, however, available a method of testing the hypothesis of loss of energy by Brownian movement. The presence

of diluents like argon will diminish the rate of Brownian movement and so diminish the energy lost by this process. As a consequence, the emission of radiation by (1) will increase in magnitude. This is actually what does occur on the addition of inert gases to the dry carbon monoxide flame (see Fig. 5).

In flames for which the duration of life is of an intermediate order of magnitude, due to the conversion of the internal energy into kinetic energy, there will be loss of total energy both by conduction and by Brownian movement, because in any exothermic chemical change there must be some increase in kinetic energy of the products, so in any actual luminescent flame there must be some loss by conduction.

FIG. 6.



Addition of Diluents to Gases containing Hydrogen.—It was found in an earlier paper that $p_{H_2} \cdot p_{gas}$ = constant defines the position of the step on the radiation curves. In explanation of this, it was considered that the velocity of the dry reaction between carbon monoxide and oxygen was given by

$$\dagger\ dx/dt = k_1[O_2^*]. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and the hydrogen reaction by

$$dx/dt = k_2[O_2^*][H_2][CO]. \quad . \quad . \quad . \quad . \quad (5)$$

If the velocity of the two reactions be equal at the step, then

$$k_1[O_2^*] = k_2[O_2^*][H_2][CO] \quad . \quad . \quad . \quad . \quad (6)$$

Thus, $p_{H_2} \cdot p_{CO}$ = constant.

If this were the case, the addition of excess oxygen should be without effect on the position of the step, since this substance appears

† The assumption of activation of oxygen is made because there is an oxygen level which is 37 kg.-cals. higher than that of the molecule in the normal state. This level is much lower than that for carbon monoxide, *viz.*, 138 kg.-cals.

on both sides of equation (6). Increase in the concentration of carbon monoxide should, however, cause a shift in position. Experiment shows, however, that neither diluent has any effect (Fig. 6). An equimolecular mixture containing 0·5% of hydrogen was used. These results were obtained with the 80-cm. bomb, and the step is less clearly defined than in the earlier series where the 32-cm. bomb was used.* The results are, however, quite definite.

The " step " is thus independent of the dimensions of the bomb, and the pressure of the oxygen and carbon monoxide. It is, however, determined by $p_{H_2} \cdot p_{gas} = \text{const.}$ A possible explanation, therefore, is that it is the pressure of the products which enters into the equation defining the step, thus :

$$p_{H_2} \cdot p_{CO_2} = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which case, the velocity of the hydrogen reaction is proportional to the amount of carbon dioxide formed. It is proposed to examine this possibility by further experimental work.

Although excess carbon monoxide and oxygen have no effect on the position of the step, yet they increase its magnitude. The curves above the step are superposable, but this is not the case for those below it. Excess oxygen or carbon monoxide causes a shift of the lower curve to the right, just as was found for the hydrogen-free mixtures. The increase in magnitude of the step is thus understandable in terms of the hypotheses put forward in the previous section.

Rate of Emission of Radiation from Dry Flames.—The method of Hartree and Hill (*Proc. Roy. Soc.*, 1921, *A*, **99**, 172) was employed in the analysis of some of the photographs of the galvanometer deflexions, as described previously (Garner and Johnson, J., 1928, 280). Typical analyses are given in Fig. 7. It will be observed that there are two minima in the curves for $2CO + O_2 + He$, indicating partial arrests of the flame in the middle of the tube, which are similar to the visual effects found by Bone and his co-workers (Bone and Townend, " Flame and Combustion in Gases," 1927, p. 350). For the argon mixtures, in which the duration of flame is less, analysis shows that these arrests have practically disappeared. There are considerable variations in the rate of emission of radiation (compare 7 III and 7 IV).

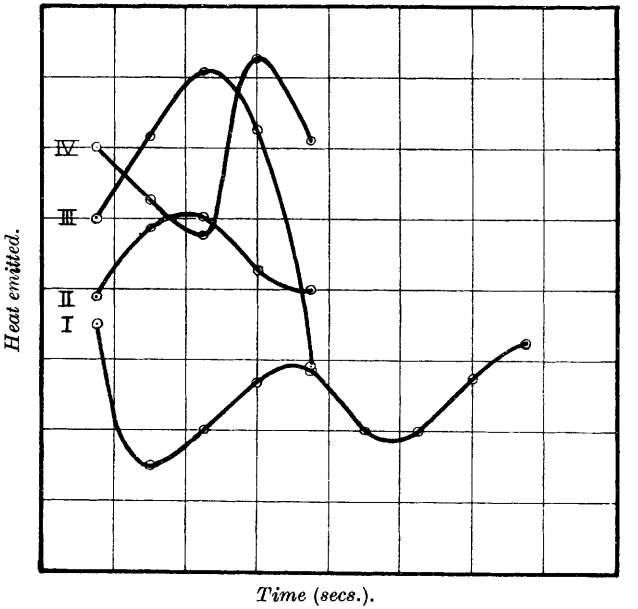
Percentage Combustion in the Flame.

In the course of the above work, data on the manner in which the percentage combustion varies with the pressure and the nature of

* This is due to the occurrence of points lying on neither curve. These are probably due to the flame passing from one mechanism into another as it moves down the explosion vessel.

the diluent have been accumulated. The curves of percentage combustion against pressure are similar to those published previously, so that the values for only a few pressures are given (Table III). It will be noticed that carbon monoxide is more effective in increasing the percentage combustion of the gases than is excess of oxygen, a fact which may have a considerable bearing on the mechanism of the flame (compare Garner and Cosslett, *Trans. Faraday Soc.*, in the press).

FIG. 7.



I. $2CO + O_2 + He$; $p = 746$ mm.
II. $2CO + O_2 + A$; $p = 660$ mm.
III. $2CO + O_2 + A$; $p = 760$ mm.
IV. $2CO + O_2 + A$; $p = 798$ mm.

TABLE III.

Dry gases.	% Combustion. 0·5 Atm.	0·75 Atm.	1 Atm.
$2CO + O_2$	91	93·5	94
$2CO + O_2 + O_2$	89·5	92·5	—
„ „ + He	83·5	88	93·0
„ „ + N_2	83·0	88·5	93·5
„ „ + A	88·6	92·5	96·0
„ „ + CO	92	95·5	98·0
Dry gases + 0·5% H_2.			
$2CO + O_2$	92·0	93·5	95·5
„ „ + O_2	92·0	96·0	99·0
„ „ + CO	96·5	99·5	102·2

Conclusions.

It has been shown that the position of the "step" on the radiation–pressure curves for the carbon monoxide–oxygen flame is not affected by the length or diameter of the bomb or by the direction in which the radiation is measured. Its magnitude, however, decreases as the diameter of the bombs increases, which would be expected if the radiation from the dried flame was partly thermal and partly luminescence.

The effect of addition of inert gases to the hydrogen-free and hydrogen-containing flames has been studied. Helium, which possesses a high conductivity, increases the loss of heat from the flame by conduction, and reduces the radiation emitted. Carbon monoxide, oxygen, nitrogen, and argon increase the radiation emitted, and this fact can be interpreted if we assume that energy can be given up from the flame by the Brownian movement of activated molecules to the walls.

The addition of excess carbon monoxide or oxygen does not affect the position of the step. Thus, the hypothesis put forward previously, *viz.*, that the step is determined by the relationship $k = p_{H_2} \cdot p_{CO}$, must be withdrawn. It is suggested that the equation be replaced by $k = p_{H_2} \cdot p_{CO_2}$, which fits the facts obtained up to the present.

The main conclusions of the earlier work still hold good, but it is possible now to present a more detailed picture of the action of hydrogen-containing substances on the dry carbon monoxide flame. During the combustion of the dry hydrogen-free gases, the product, carbon dioxide molecules, contains a large fraction of the energy of combustion. This forms at least 24% of the total energy set free. These molecules are very stable towards collisions, but can lose their energy either by the emission of radiation or by resonance to other molecules of carbon dioxide. As a result of resonance, the activated molecules possess an apparently long duration of life. Since their internal energy is only slowly converted into kinetic energy, the loss of energy to the walls occurs very largely by Brownian movement of activated molecules.

On the introduction of small percentages of hydrogen, the average duration of life of the activated molecules decreases, and the rate of conversion of internal into kinetic energy increases. Thus, the temperature and the speed of flame are augmented, and at the same time, there is an increase in the loss of energy from the flame by thermal conductivity.

When higher percentages of hydrogen are added, discontinuities appear on the radiation–pressure curves, which can only be explained as due to changes in the mechanisms of the reaction. The nature of

these changes has not yet been determined, although some facts bearing on their mechanisms have been elucidated.

The authors wish to express their indebtedness to Imperial Chemical Industries, Ltd., for a grant towards the cost of this investigation, and Mr. D. A. Hall records his thanks to the Department of Scientific and Industrial Research for a maintenance grant.

THE UNIVERSITY, BRISTOL. [*Received, January 12th,* 1931.]