

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

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IN earlier communications (J., 1928, 280; 1929, 1123; 1930, 2037; 1931, 641), it was shown that the radiation emitted from the carbon monoxide flame undergoes very marked variations on the addition of hydrogen. These have been studied mainly with a view to the discovery of new facts concerning the mechanism of the catalytic action of hydrogen on the carbon monoxide flame. The results obtained concern two main features of the radiation-pressure curves: (1) the intercept, and (2) the step on the curves. The manner in which these two properties are modified by the addition of some inert gases or by changing the dimensions of the explosion vessels has already been investigated. In the present paper, it has been sought to determine the influence of the material of the walls of the bomb and also to extend the list of inert gases studied by investigations on carbon dioxide and sulphur dioxide.

The Intercept on the Radiation-Pressure Curves.

The total radiation from a "dry" carbon monoxide flame in a cylindrical vessel, when plotted against the pressure, gives a straight line which cuts the pressure axis at a value that varies approximately inversely as the square of the diameter of the vessel. This intercept decreases in magnitude as hydrogen is added, and, in fact, disappears if more than 2% of hydrogen is present. The lower part of the

pressure-radiation curve and its intercept for both "dry" and hydrogen-containing gases in vessels of constant diameter are slightly lowered by dilution of the explosive mixture with large volumes of carbon monoxide, oxygen, nitrogen, argon, and carbon dioxide, but the change which occurs is negligible compared with that caused by the addition of hydrogen. It has been shown in the present paper that the materials composing the walls of the explosion vessels, whether made of good or bad conductors, have also little effect on the magnitude of the intercept.

It has been pointed out in the earlier papers that the radiation emitted from the hydrogen-free flame is mainly that from the vibrational energy of the newly formed molecules of carbon dioxide. These molecules can undergo deactivation in three ways: (1) by the emission of radiation, (2) by collision with other gas molecules, or (3) by collision with the walls. The second cause of deactivation, *viz.*, by collision with gas molecules, does not appear to be much in evidence in the hydrogen-free flame, for dilution with large volumes of inert gases does not modify the fraction of the newly formed molecules of carbon dioxide which emit their vibrational energy as radiation. Deactivation on the walls is, however, all important, as is shown by the variation in the magnitude of the intercept as the diameter of the bomb is changed. The vibrational energy is thus distributed mainly between the emission of radiation and deactivation on the walls. There is a very small fraction available for increasing the temperature of the gaseous mixture, so that the vibrational energy can play but a small part in the propagation of the flame.

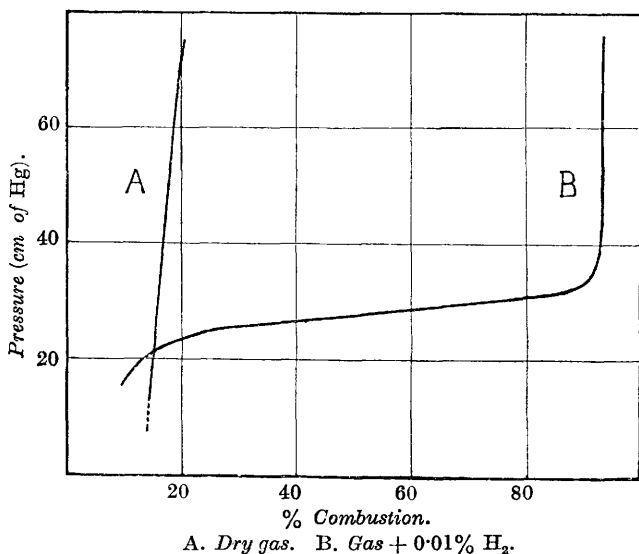
The intercept is a limiting pressure at which, if flame were possible, no radiation would be emitted. It is not identical with the limiting pressure for the propagation of flame as is shown by the experiments described below. The reason for this is that the deactivating influence of the walls is not the same for the two cases. In the former, it is the carbon dioxide molecules which are deactivated; in the latter, it is some component of the reaction chain, very probably oxygen atoms, which are destroyed.

Dry Gases.—A quartz cylinder, 2 cm. in diameter and 32 cm. long, and closed at one end with a plane quartz window, was employed. This carried a firing plug for the ignition of the gases and a tap for their admission. The methods of drying and filling the gases into the bomb have been described previously. A better vacuum can be obtained with the quartz than with metal bombs, so the explosion vessel can be more effectively dried. It was found sufficient to evacuate the bomb for 2 hours with a mercury-vapour pump between two experiments. The use of a liquid-air trap between the

explosion vessel and the gas supply did not increase the dryness of the gas. Firing by the fusion of platinum wire (14 v.) † occurred within 2 or 3 minutes of shutting off the pumps, so that little time was available for the diffusion of the deep-seated water vapour from the quartz into the gas.

No flame and no radiation were observed if the gas pressure lay below 18 cm., and the flames produced above this pressure and up to 1 atm. were not stable: they travelled a short distance down the tube and were then extinguished. The percentage of the gas burnt ranged from 15% at 18 cm. to 20% at 1 atm. (Fig. 1, A). A few cinematograph photographs were taken of these flames. They

FIG. 1.



A. Dry gas. B. Gas + 0.01% H₂.

moved out from the point of ignition to their maximum distance too rapidly for the eye to follow. The illumination from the flame, however, lasted several seconds, and died away in the direction of the firing plug. In its last stages, the illumination consisted of a nearly spherical ball of flame. The most probable explanation of these flames is that the platinum atoms volatilised by the fusion of the wire activate oxygen molecules to their lowest electronic level, which then set up a reaction chain. Since the gases contain negligible quantities of hydrogen, the mechanism is probably:—

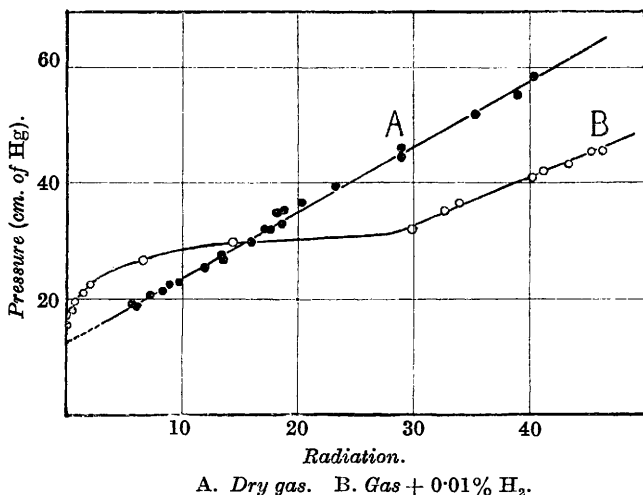
- (I) (1) $O_2 + M \longrightarrow O_2^* + M - 37 \text{ kg.-cals.};$
- (2) $O_2^* + CO \longrightarrow CO_2 + O + 46 \text{ kg.-cals.};$
- (3) $O + O_2 + CO \longrightarrow CO_2 + O_2^* + 90 \text{ kg.-cals.}$

† See previous papers.

Since the flame is unstable, these reaction chains must be of relatively short length under the conditions of our experiments, and thus at least one of the steps in the chain has a high temperature coefficient. When the flame has reached its maximum extension, the combustion in the region traversed by the flame is not yet complete. It is continued behind the flame front at an enhanced temperature, giving rise to the phenomenon of after-burning. At these temperatures, it is probable that mechanism (I) is stable. It will not, however, penetrate further into the cold gases unless hydrogen is present.

One of the causes of the instability of the flame is undoubtedly the retention of a large amount of energy of the reaction as vibrational energy of the carbon dioxide molecules which is not available

FIG. 2.



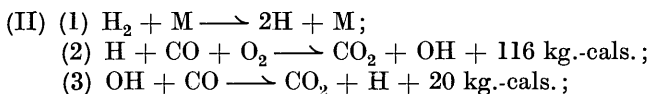
for raising the temperature of the flame. This amounts to at least 25% of the total energy. One of the functions of hydrogen is to make some of this energy available.

The values of the radiation plotted against the pressure are given in Fig. 2, A. A straight line is obtained giving an intercept at 12 cm. This is the limiting pressure for the emission of infra-red radiation, and possesses practically the same value as when there is complete combustion of the gas in a vessel of the same diameter. This limit is less than that for the production of reaction chains in the gas mixture.

Addition of Hydrogen.—If 0.01% of hydrogen is added to the explosive mixture, stable flames can be obtained at pressures above 30 cm. Hg. The flame, however, travels out rapidly to the same

distance as for the hydrogen-free mixtures, and a very slow flame starts from the point of its maximum extension. The values for the percentage combustion are given in Fig. 1, B. Unstable flames are produced between 15 and 30 cm., and no flame at all below the former pressure. The radiation emitted is shown in Fig. 2, B on a scale different from that of Fig. 2, A.

On the addition of hydrogen, the intercept on the pressure axis, and the infra-red radiation emitted, decrease in magnitude. In the presence of hydrogen, therefore, a smaller fraction of the vibrational energy of the carbon dioxide molecules is lost to the walls or as radiation. The speed of the flame increases on this account. The actual mechanism whereby this is brought about is still obscure. There are many possibilities, of which the following are the more important. The hydrogen can react with oxygen atoms thus: (1) $\text{H}_2 + \text{O} + \text{M} \longrightarrow \text{H}_2\text{O} + \text{M}$. The water produced can then deactivate CO_2^* and convert its vibrational energy into kinetic energy. There is no doubt, however, that some hydrogen atoms are produced on collision with rapidly moving platinum atoms or other molecules, and once these are set free, the chance of their recombination to form water or molecular hydrogen becomes remote. These atoms will react according to



that is, an entirely different reaction mechanism is set up. The extent to which mechanism (II) occurs depends on the ratio of the hydrogen converted into atoms to that converted into water. Very little is known about the relative speeds of these processes, but there is evidence in favour of the view that mechanism (II) does not set in until higher pressures of hydrogen are reached, and then mechanism (II) replaces mechanism (I) abruptly.

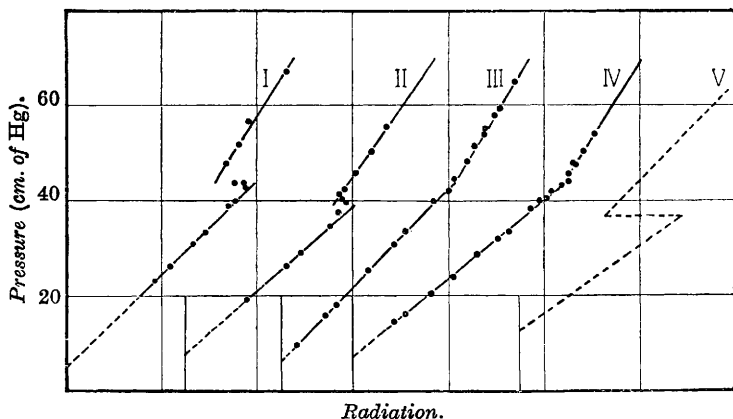
The Step on the Radiation-Pressure Curves.

The radiation-pressure curves of flames of hydrogen-containing mixtures in phosphor-bronze bombs show a discontinuity at a pressure which decreases as the percentage of hydrogen increases. In the earlier papers, this was taken to mean that there were two distinct flame mechanisms in these mixtures, one stable at low [mechanism (I)] and the other stable at high pressures [mechanism (II)]. The pressure at which one mechanism changed over into another was neither dependent on the diameter of the bomb nor affected by the addition of the diluents carbon monoxide and oxygen. It was only determined by the pressure of the hydrogen: $P = k/p_{\text{H}_2}$

approximately, where P is the pressure of the combustible gas. The limiting pressure for mechanism (II) thus appears to vary inversely as the pressure of the hydrogen. This limit will be analogous to the ordinary limiting pressures met with in flames. Since, however, the mechanism is occurring in a gaseous system in which another mechanism is already operating, the factors controlling its lower limit will be more complex than is usual in such cases.

The limiting pressure for mechanism (II) will depend on the product of the rate of production of hydrogen atoms and the chain length. Since hydrogen atoms are readily removed by some surfaces and not by others, it should be possible to change the

FIG. 3.



I. *Copper.* II. *Aluminium.* III. *Quartz.*
 IV. *Silvered quartz.* V. *Phosphor-bronze.*

limiting pressure by the use of various linings to the explosion vessel. Mechanism (II) is more likely to be retarded by wall effects than mechanism (I), on account of the fact that hydrogen atoms possess much higher speeds than oxygen atoms and molecules. Quartz, silvered quartz, and copper and aluminium linings to the quartz tube have been employed to test this point. A mixture of $2\text{CO} + \text{O}_2$ containing 0.2% of hydrogen was used to make the tests. In order to insert the cylinder of metal, a wide ground joint was fused on to the end of the quartz tube. A lubricant with a low vapour pressure was used in the joint. The thickness of the copper was 0.12 mm. and that of the aluminium 0.33 mm., and the length of both tubes was 29 cm.

The radiation-pressure curves are given in Fig. 3, and the broken curve showing the result obtained in the phosphor-bronze bomb of

0.15 cm. diameter is included for reference. The values for the radiation are corrected for the amount of gas burnt, but not for the extinction coefficient by the carbon monoxide.

In the phosphor-bronze bomb, the limiting pressure is 36 cm.; this is raised to 40 cm. in the case of the aluminium tube, and is 44 cm. for each of the other surfaces. Thus, the nature of the surface does exert some effect on the position of the step, as was anticipated. There have been produced very marked differences in the extent of the combustion by varying the nature of the wall material :

Pressure, cm.	Percentage combustion.			
	Quartz.	Silvered quartz.	Copper.	Aluminium.
20	87	95	66	78
40	94	97	77	83
60	94	97	77	84

The percentage combustion increases in the order copper, aluminium, quartz, and silvered quartz. The amount of cooling and deactivation by the walls will be the greater the lower the percentage combustion, so that the above order is that of the effect of the walls in abstracting energy from the flames, that is, in the order of their thermal conductivities. It will be noted that the magnitude of the steps in Fig. 3 decreases in this order. For quartz and silvered quartz, the step has disappeared completely, and the change in mechanism is indicated solely by a change of slope. The step appears when metal liners are introduced into the explosion vessel, but it does not become so great as in a phosphor-bronze bomb. The conclusion is reached, therefore, that limiting pressure is represented as a step on the radiation curves when the surface of the bomb facilitates the transfer of energy from the flame. This must mean that the energy emitted as radiation in the case of mechanism (II) is much more easily abstracted from the flame than in the case of mechanism (I). The obvious conclusion is that the radiation in the former case contains much more thermal emission than the latter. This is in accord with the fact that the magnitude of the step increases in the phosphor-bronze bombs as the diameter decreases. The greater the cooling, the greater is found to be the difference between the radiation emitted by the two mechanisms.

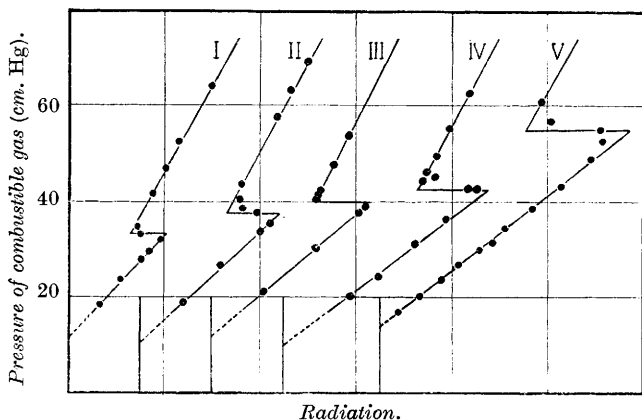
The limiting pressure of mechanism (II) is raised in the case of quartz, silvered quartz, and copper from 36 to 44 cm. This may be due to the abstraction of hydrogen atoms from the gas, which would break the reaction chains of mechanism (II). It cannot be due to the adsorption of hydrogen from the explosive mixture before firing, for the quartz surface was present in all cases. Aluminium appears to be less effective in breaking the reaction chains than copper.

These experiments have, however, thrown more light on the causes of the step than on the mechanism of the reaction.

Effect of Carbon Dioxide and Sulphur Dioxide on the Limiting Pressure of Mechanism II.

Experiments were carried out in a phosphor-bronze bomb, 1.5 cm. in diameter, to determine if the position of the step could be changed by the addition of either of these oxides. Dilution of the explosive mixture with 33.3% of oxygen or carbon monoxide has been shown previously not to affect the position of the step. If mechanism (II) be correct, then it might be expected that carbon dioxide molecules

FIG. 4.



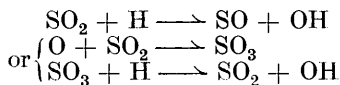
CO_2 contents: I, 0%; II, 10%; III, 14.3%; IV, 18.2%; V, 25%.

would remove hydrogen atoms from the flame and retard the speed of the reaction, thus:



This reaction is endothermic, so that it would only occur within the flame itself.

It was doubtful what would be the effect of sulphur dioxide. It was possible that either



would occur.

The radiation-pressure curves for 0.266% of hydrogen and different percentages of carbon dioxide are given in Fig. 4.* It will

* The percentages of carbon dioxide and hydrogen are given in terms of the volume of $2\text{CO} + \text{O}_2$ present. The figures given in Table I are thus the percentages added to the combustible mixture.

be seen that the step is raised in accordance with expectation (Table I). Experiments III, VI, and VII show the effect of variation in the percentage of hydrogen at a constant percentage of carbon dioxide.

TABLE I.

Expt.	I.	II.	III.	IV.	V.	VI.	VII.
CO ₂ , %	0	10	14.3	18.2	25	14.3	14.3
H ₂ , %	0.266	0.266	0.266	0.266	0.266	0.32	0.10
Step, cm. Hg ...	33	38	40	43.5	54.5	34.5	55

The percentage combustion is given below for several pressures.

Pressure, cm.	I.	II.	III.	IV.	V.
30	88	84	84	85	77
50	89	85	85	85	80
70	89	85	85	85	80

It will be observed that the percentage combustion is lowered by the addition of carbon dioxide, whilst the step is raised. This is contrary to the effect of replacing the phosphor-bronze surface by quartz. In the latter case, both the percentage combustion and the step were raised by a change which increases the temperature. It is clear, therefore, that the effect of carbon dioxide on the step is not connected with any effect it may have on the flame temperature.

Sulphur dioxide gives a curious result: 10% of this gas did not alter the limiting pressure, whereas 25% raised it to 44.5 cm. A possible explanation of this behaviour is that the removal of hydrogen atoms depends on the formation of sulphur trioxide, produced according to the equation $2\text{SO}_2 + \text{O}_2 \longrightarrow 2\text{SO}_3$. The rate of its formation is proportional to the square of the concentration of the dioxide, therefore the capacity of the latter for the removal of hydrogen atoms increases rapidly with its partial pressure.

10% of sulphur dioxide did not lower the percentage combustion, which remained at 89%, but 25% of the gas lowered it to 85%. It would appear from these and the foregoing results that the extent of the combustion is to some extent dependent on the capacity of the gas for nullifying the catalytic effects of the hydrogen gas.

Summary.

Hydrogen-free flames in quartz tubes, 2 cm. in diameter, are unstable. Unstable flames are produced above 18 cm. pressure. The limiting pressure for the emission of radiation is 12 cm.

Flames containing 0.01% of hydrogen give stable flames above 30 cm. Hg, and unstable flames down to 15 cm.

The influence of the material of the wall of the bomb on the step and intercept on the pressure-radiation curves has been studied, quartz, silvered quartz, aluminium, and copper surfaces having been

employed. There is no appreciable change in the intercept with change in the nature of the material of the wall, but the pressure at which the step occurs is modified. This is probably due to differences in the efficiency of removal of hydrogen atoms from the gas phase by different surfaces. The size of the step depends on the thermal conductivity of the walls.

The addition of carbon dioxide and sulphur dioxide to the flame causes the step to move to higher pressures. This is due to the removal of hydrogen atoms from the flame by these gases.

The mechanisms advanced previously for the catalytic action of hydrogen have been discussed in the light of these results.

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