32. *The Catalytic Effect of Hydrogen on the Carbon Monoxide Flame.*

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The recent advances in our knowledge of the kinetics of the *isothermal reactions* between hydrogen and oxygen at the ignition temperature, due chiefly to the researches of Hinshelwood and Semenoff, make it possible to interpret some of the phenomena observed in flames where the conditions are far from isothermal. It is the object of this paper to offer an interpretation of the action of hydrogen on the emission of radiation from the carbon monoxide flame (cf. Garner and Johnson, J., 1928, 281; Garner and Roffey, J., 1929, 1123; Garner and Hall, J., 1930, 2039; Garner, Hall, and Harvey, J., 1931, 641; Bawn and Garner, J., 1932, 129). It has been shown in the above investigations that a step or discontinuity occurs on the radiation–pressure curves of carbon monoxide flames containing hydrogen, which lies at higher pressures the smaller the concentration of hydrogen (Table I). There can be but little doubt that a change in the mechanism of the flame occurs in the neighbourhood of the step, and there are obviously two methods by which such a change of mechanism could be brought about. Either (*a*) the step represents a lower limit for the propagation of a hydrogen flame in a carbon monoxide mixture, or (*b*) it is the pressure at which two mechanisms produce flames that travel with equal speeds. The first hypothesis would provide a ready explanation of the abruptness with which the second mechanism sets in, but it is not in agreement with the fact that there is no appreciable difference between the speeds of the flame above and below the step (cf. J., 1929, 1128; 1930, 2038). On this account, hypothesis (*b*) is to be preferred.

It is well known that in order to initiate a stable flame in cold gases it is necessary to transmit to the combustible mixture, by means of a spark or hot wire, an amount of energy exceeding a minimum value which depends on the nature of the mixture, its pressure, mode of confinement, etc. This must mean that stable flames can be initiated only if a sufficient number of reaction chains are introduced into the gas. Radical or energy chains in combustible gases, such as those under review, do not reach an infinite chain length at room temperatures. Therefore, it is essential that the number of chains penetrating the cold gases ahead of the flame be sufficient to raise the temperature of these gases to that at which the chains become infinite in length, *i.e.*, to raise the temperature to the ignition temperature; if there be two independent mechanisms, then that will be dominant in flame propagation which can achieve this effect in the shortest time.

From Table I it will be seen that the pressure at which the step, p_s, occurs is given by the equation

$$(p_s \cdot p_{H_2} + 0{\cdot}018 p_s)/3{\cdot}28 = 1 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

TABLE I.

$p_{H_2} \times 10^2$, cm.	2·36	3·46	5·04	7·2	12·4	24·0
p_s, cm.	75	64·5	50	36	24	12
$p_s(p_{H_2} + 1{\cdot}8 \times 10^{-2})$	3·12	3·39	3·42	3·24	3·41	3·10

For the interpretation of this equation, there are three relevant experimental observations, *viz.*, (*a*) p_s is not affected by changes in the diameter of the tube between 1·5 and 6·5 cm. (J., 1931, 642, 643), (*b*) the dilution of the combustible mixture with 33% of either oxygen or carbon monoxide has no appreciable effect on p_s (*ibid.*, p. 649), and (*c*) the addition of carbon dioxide raises the step (J., 1932, 136). The first of these observations shows that in tubes of the specified diameters there is no appreciable wall effect, and therefore deactivation of possible chain carriers by the walls can be left out of account. The second observation shows that if equation (1) is to be used to indicate a chemical mechanism, p_s cannot refer either to the pressure of oxygen or carbon monoxide or to the total pressure of the gaseous mixture. It must refer to the pressure of the combustible gas or to some product of the flame which is proportional to it. This suggests that it is the pressure of the newly-formed carbon dioxide which is one of the factors determining the step, and an obvious relationship which fits the experimental results is

$$dx_2/dt = (p_{CO_2^*}p_{H_2}/k_2 + p_{CO_2^*}k_1/k_2) \cdot dx_1/dt \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

where dx_1/dt and dx_2/dt are the rates of penetration of the cold gases in front of the flame by the chain carriers of the first and the second mechanism (I and II) respectively. I and II refer to the mechanisms stable at low and at high pressures respectively. The second term in equation (2) is important only at low hydrogen pressures, so that above 0·1 cm. of hydrogen, the experimental results accord with

$$dx_2/dt = (p_{CO_2^*}p_{H_2}/k_2) \cdot dx_1/dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2a)$$

i.e., the ratios of the speeds of the two mechanisms are proportional to $p_{CO_2^*}p_{H_2}$. This can be interpreted as meaning that the first process in mechanism II is the formation of hydrogen atoms by collision of hydrogen molecules with newly formed carbon dioxide molecules,

$$CO_2^* + H_2 \longrightarrow CO_2 + 2H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3a)$$

The second term in equation (2), however, indicates that there is another process which is effective at low hydrogen pressures in mechanism II. There is much uncertainty as to what this term can mean, since in such complicated processes a term of this sort can have many meanings. A possible interpretation is that it refers to a second type of reaction chain, and that mechanism II is composite in character. If this be accepted as the correct explanation, then the two simultaneous processes of mechanism II can be written as in (3*b*) and (3*c*) :

$$\begin{gathered} CO_2^* + H_2 + O_2 \longrightarrow CO_2 + H_2O_2 \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3b) \\ H_2O_2 \longrightarrow 2OH \\ OH + CO \longrightarrow CO_2 + H \end{gathered}$$

$$\begin{gathered} CO_2^* + O_2 \longrightarrow CO_2 + 2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3c) \\ O + CO + M \longrightarrow CO_2^* + M \end{gathered}$$

These two processes are interlinked, for atomic oxygen can be produced in the reactions of atomic hydrogen and *vice versa*, so that (3*a*) and (3*b*) give two ways of setting into train one mechanism of reaction. Thus, on this view, hydrogen atoms are the carriers mainly responsible for the forward movement of mechanism II : this would be expected on account of their very high mobility.

There is very little information throwing light on the kinetics of mechanism I, except that the velocity of the flame at atmospheric pressure increases linearly with increase in the hydrogen pressure (J., 1930, 2039) ; it is only possible at present to describe its speed in terms of equation (2).

The principal conclusion to be drawn from the above results is that the rate of production of hydrogen atoms is proportional to $p_{CO_2} \cdot p_{H_2} + 0{\cdot}018 p_{CO_2}$, and that the position of the step is mainly determined by the density of the hydrogen atoms penetrating the cold gases ahead of the flame. The hydrogen mechanism takes control of the flame when the density of these atoms in the flame front exceeds a minimal value; this value must increase with increase in pressure of the combustible gases, and also with increase in the hydrogen pressure, since the rate of mechanism I increases in this way.

The breaking of the reaction chains normally occurs on the walls or by collision of two chain carriers, *e.g.*, by $H + H + M \longrightarrow H_2 + M$ and $H + OH + M \longrightarrow H_2O + M$. The first of these processes is not very important in vessels of 2·0 cm. diameter and at gas pressures exceeding 20 cm., and the latter is probably of little importance in the propagation of flame since the hydrogen pressures are small. The extinguishing effect of carbon dioxide on flames is well known, so that this gas, at least in an unactivated state, probably can break the hydrogen chain.

The Action of Carbon Dioxide on the Flame.—On diluting the combustible mixture with carbon dioxide, the pressure of the hydrogen required to make the hydrogen mechanism dominant is increased (Table II). This is in contrast with the effect obtained on dilution with 33% of oxygen or carbon monoxide, which does not change the position of the step. It follows, therefore, that if excess of carbon monoxide and oxygen affects the speeds of the two mechanisms, either by their entering into the reaction or by their presence as inert gases, they must change both to the same degree. The effect produced by carbon dioxide is evidently specific to the chemical nature of this gas.

The reduction in efficiency of the hydrogen by carbon dioxide is given by the equation

$$p_{H_2} - p_{H_2}' = \text{const.} \times p_{CO_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where p_{H_2} is the pressure of the hydrogen at p_s, and p_{H_2}' is that required to produce a step at p_s in the absence of carbon dioxide. The latter is calculated from equation (1). The values are given in Table II (where pressures are in cm.), and it will be seen that $(p_{H_2} - p_{H_2}')/p_{CO_2} = 6{\cdot}9 \times 10^{-3}$ within the error of measuring the step. Hence, the pressure of the step in the presence of carbon dioxide is given by the empirical equation

$$p_s p_{H_2} + (1{\cdot}8 \times 10^{-2}) p_s = 3{\cdot}49 + 6{\cdot}9 \times 10^{-3} p_s p_{CO_2} \quad . \quad . \quad . \quad . \quad (5)$$

TABLE II.

p_s.	p_{CO_2}.	$100p_{H_2}$.	$100p_{H_2}'$.	$\frac{p_{H_2} - p_{H_2}'}{p_{CO_2}} \times 10^3$.
33	0·0	8·77	—	—
38	3·80	10·1	7·40	7·1
40	5·72	10·63	6·92	6·5
43·5	7·91	11·58	6·23	6·8
54·5	13·62	14·50	4·61	7·3
			Average	6·9

The figures in col. 4 are calculated from the equation $p_{H_2}' = (3{\cdot}49 - 0{\cdot}018 p_s)/p_s$, thus making a small allowance for the fact that the step occurs at a slightly higher pressure in the quartz bomb used in the measurements than in the metal bomb used by Hall. This seems to be the most reasonable way of making the correction, which, however, makes little difference to the results in col. 5.

It is suggested that the molecules of carbon dioxide break the reaction chains of mechanism II, thereby diminishing the density of the stream of hydrogen atoms. This stream has a density at the step which is proportional to $p_s p_{H_2} + 0{\cdot}018 p_s = 3{\cdot}49$, and this, according to the theory of chain reactions, will be reduced in the presence of carbon dioxide by the factor $k_1 p_x^n/(k_1 p_x^n + k_2 p_y^m p_{CO_2})$, where $k_1 p_x^n$ refers to the velocity of the process whereby the chains are carried on, and $k_2 p_y^m p_{CO_2}$ refers to the process of breaking the chains. Equation (5) can be derived from this if $p_x^n = 1$ and $p_y^m = p_s$. On making these assumptions, the density of the hydrogen-atom stream in the presence of carbon dioxide becomes proportional to $p_s(p_{H_2} + 0{\cdot}018)k_1/(k_1 + k_2 p_{CO_2} p_s)$, and, providing that there be no other effects of carbon dioxide on the flame than those common to both mechanisms, the pressure of the hydrogen at the step will be given by the equation $p_s(p_{H_2} + 0{\cdot}018) = 3{\cdot}49 + p_{CO_2} p_s k_2/k_1$, which is in accord with that found experimentally.

The action of carbon dioxide can thus be quantitatively interpreted as due to that of breaking the hydrogen chains. It is suggested that the chains are broken by the collisions of hydrogen peroxide molecules with carbon dioxide to give percarbonic acid,

$$H_2O_2{}^* + CO_2 + M \longrightarrow CO_2(OH)_2 + M, \quad \ldots \ldots \quad (6a)$$

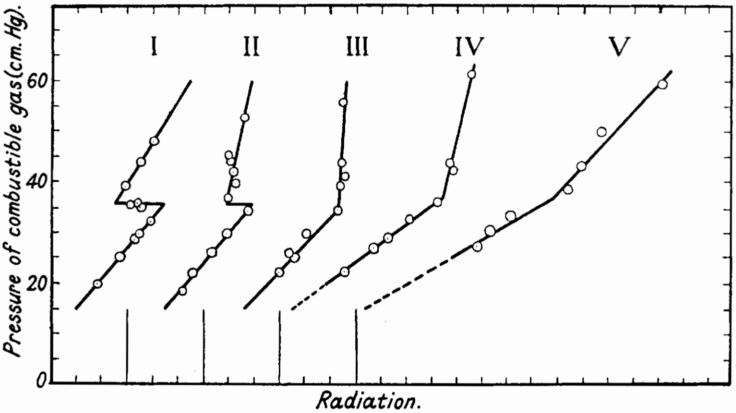
and the chain is carried on by

$$H_2O_2{}^* \longrightarrow 2OH \quad \ldots \ldots \ldots \quad (6b)$$

Provided that the breaking of the chains by carbon dioxide occur much more frequently than by any other similar process, this mechanism is in accord with the facts presented in equation (5).

Fig. 1.

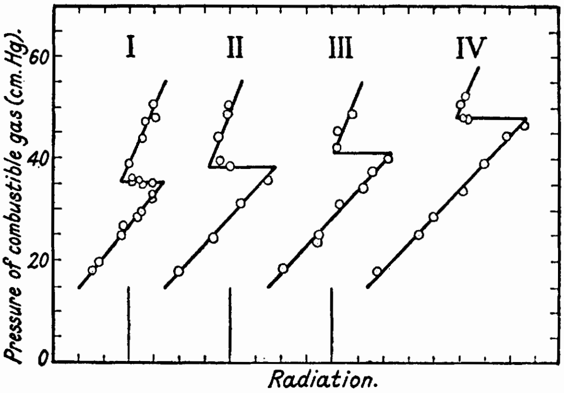
Chlorine contents : I, 0%; II, 1·01%; III, 2·01%; IV, 2·95%; V, 3·93%.



The Action of Halogens on the Flame.—Since the halogens combine with hydrogen atoms, it would be expected that they would exert an appreciable effect on the pressure at which the step occurs. It has been found that both chlorine and bromine do, in fact, caused marked changes in the pressure–radiation diagrams of the equimolecular mixture containing 0·02% hydrogen. Chlorine, however (Fig. 1), has only a slight effect on the position of the step, and therefore affects mechanisms I and II almost equally; it diminishes the speed of the flame, and 4—5% of chlorine causes its extinction. Bromine, on the other hand (Fig. 2), gives a series of diagrams which resemble those obtained with carbon dioxide, the step being raised from 35·5 to 48·5 cm. by the addition of 4% of bromine. As with chlorine, 4—5% of bromine extinguishes this flame.

Fig. 2.

Bromine contents: I, 0%; II, 0·98%; III, 2·02%; IV, 3·92%.



A marked difference between the action of the two gases is shown in the amounts of radiation emitted above the step. As the chlorine percentage increases, the step gradually disappears owing to the fact that the radiation emitted during mechanism II becomes similar in magnitude to that emitted during mechanism I. No such effect is observed with bromine. The radiation is emitted from the gaseous products and its magnitude decreases as the percentage of water increases. Therefore the action of chlorine is probably due to the drying of the gaseous products by the reaction

$$2H_2O + 2X_2 \longrightarrow 4HX + O_2 \quad \ldots \ldots \ldots \quad (7)$$

At the temperature of the flame, this reaction occurs to a greater extent with chlorine than with bromine. A discussion of the radiation phenomena now would tend to confuse the issue, and so is postponed.

The interaction of hydrogen atoms with halogen molecules, which occurs according to the scheme

$$H + X_2 \longrightarrow HX + X \ (8a); \quad X + H_2 \longrightarrow HX + H \quad . \quad . \quad . \quad (8b)$$

has different consequences in the case of the two halogens; (8*b*), although occurring readily in the case of chlorine, possesses a high critical increment in that of bromine, so chlorine atoms possess a shorter life than bromine atoms. Polanyi (*Trans. Faraday Soc.*, **1928**, **24**, 606) found that bromine was an effective breaker of the chain for the reaction between hydrogen and chlorine. Consequently, bromine is likely to be much more effective than chlorine in reducing the density of the hydrogen chains in mechanism II and therefore should be more effective in raising the step, and this is, in fact, found:

Added gas (Cl_2 or Br_2), %	0	1	2	3	4
p_s, cm., for added Cl_2	35·5	35·5	35·5	37·5	—
p_s, cm., ,, Br_2	35·5	38·0	41·3	—	48·5

The action of bromine can be represented by an equation similar to that found for carbon dioxide, *viz.*,

$$p_s(p_{H_2} + 0{\cdot}018) = 3{\cdot}16 + 2{\cdot}8 \times 10^2 p_{Br_2} p_s . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

as will be seen from Table III (pressures in cm.). The errors in measuring the step are, however, so large that the measure of agreement found in col. 5 is better than corresponds to the experimental error. This means that the pressure of hydrogen at the step is raised by the factor $(k_1 + k_2 p_{Br_2} p_s)/k_1$, which indicates that the chains are broken by bromine in a similar manner to that suggested for carbon dioxide. It does not appear that the bromine molecules break the hydrogen chains by collision with hydrogen atoms, for this process requires a very different factor. The chains are probably broken in a termolecular collision with a chain carrier which otherwise decomposes spontaneously. Such chain carriers are HO_2 and H_2O_2, but as there have been no experimental studies of the reactions of such radicals with bromine, it is unprofitable to discuss the action of bromine any further at this stage.

TABLE III.

p_s.	p_{Br_2}.	p_{H_2}.	p_{H_2}'.	$(p_{H_2} - p_{H_2}')/p_{Br_2}$.	p_s.	p_{Br_2}.	p_{H_2}.	p_{H_2}'.	$(p_{H_2} - p_{H_2}')/p_{Br_2}$.
35·5	0·0	0·071	—	—	41·3	0·834	0·0825	0·058	0·029
38·0	0·372	0·076	0·065	0·029	48·5	1·900	0·097	0·047	0·026
									Mean 0·028

The Percentage Combustion of the Gases.—The mixture of combustible gases containing 0·02% of hydrogen undergoes 90—95% combustion in a quartz vessel 2 cm. in diameter. As can be seen from a visual examination of the slow flames, there is a skin of unburnt gases in the neighbourhood of the walls, and this owes its existence to loss of heat from the flame and to the breaking of reaction chains on the walls. That it is very largely due to the latter cause, is shown by the fact that excess oxygen or carbon monoxide in the flame is particularly active in reducing the thickness of this skin of cold gas. When 33% excess of carbon monoxide is added, the combustion is practically complete (J., **1931**, 651). This wall effect, although reducing the percentage combustion, does not affect the position of the step.

When either chlorine or bromine is added to the combustible mixture, the percentage combustion shows a minimum in the neighbourhood of the step (Fig. 3). This shows that the walls exert a greater influence on the chains of mechanism II than on those of mechanism I. This confirms the conclusions reached previously. The carrier for mechanism II, which is broken on the walls, may be a halogen atom, but this is unlikely since similar results are obtained for both halogens. It is very probable that the carriers are hydrogen atoms which, on account of their high mobility, are particularly liable to be removed by the walls.* The minimum on the percentage combustion curve is not found in the combustible gases in the absence of the halogens, probably because the velocity of the flame is too high. When the speed of flame is reduced by the addition of halogens, the wall effect can then appear. The percentage combustion commences to fall within the region of mechanism I, *i.e.*, below 36 cm. This would be expected from the experiments of Roffey on the ionisation of the flame, which showed that below the step there were two successive waves of ionisation (J., 1929, 1135), which were interpreted as indicating that in this region the two reaction mechanisms are successive.

The Effect of Carbon Tetrachloride.—Earlier measurements (J., 1928, 288) had given qualitative indications of the marked effects of this substance on the radiation emitted from the hydrogen-containing flames. In the present research, it is found that carbon tetrachloride has a greater effect than chlorine as a breaker of the reaction chains of mechanism II, 1% raising the step from 35·5 to 39·5 cm. (Fig. 4). The interaction of carbon tetrachloride with hydrogen atoms could result in the breaking of the hydrogen chains by the reaction $CCl_4 + H = CCl_3 + HCl$ (cf. Polanyi, "Atomic Reactions," 1932, for similar processes).

In one respect carbon tetrachloride differs from bromine and chlorine: although it markedly reduces the percentage combustion, it does not show a minimum at the step. A possible explanation of this is that the vapour is adsorbed on the walls to give a multimolecular layer which returns some of the hydrogen atoms to the gas unchanged. In Fig. 4, curve III, the step appears to be reversed, but this is because the flame in the lower region of pressure did not reach the end of the tube.

FIG. 3.

Chlorine contents: I, 0%; II, 1·01%; III, 2·01%; IV, 2·95%; V, 3·98%.

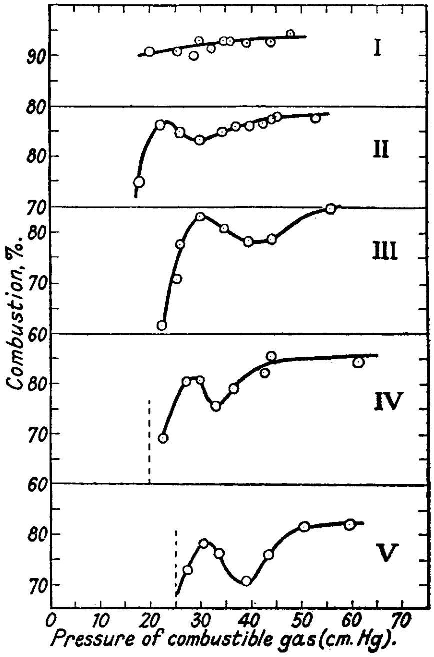
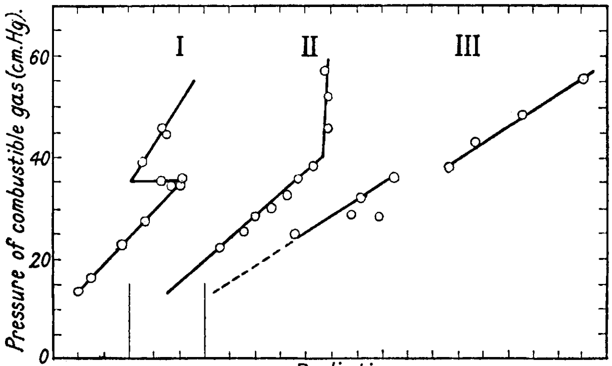


FIG. 4.

Carbon tetrachloride contents: I, 0%; II, 1%; III, 2·15%.



EXPERIMENTAL.

The apparatus employed and the experimental procedure were similar to that described in previous papers. The flames were produced in the quartz vessel previously used by Bawn.

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* Bradford's results (J., 1933, 1557) on the composition of the gases after explosion of mixtures of carbon monoxide, hydrogen, and oxygen can be explained on the same basis.

Chlorine, bromine, or carbon tetrachloride vapour was introduced into the quartz vessel by breaking a glass bulb by a magnetically-released plunger. The tap leading to the quartz tube was closed after allowing 2 mins. for the gas to be evenly distributed, and then the tubes and breaker were re-evacuated. Care had to be taken to prevent contamination of chlorine, etc., with the pump oil and the mercury in the manometers and mercury-vapour pump. Dry air was first admitted to the tubes, etc., and then pumped out by means of an efficient water-pump. More dry air was then admitted, pumped out with the water-pump, and finally completely evacuated with the Hyvac and the mercury pump in series. When a good vacuum had been obtained, the tap to the pump was closed and the carbon monoxide–oxygen–0·2% hydrogen mixture admitted until the pressure was slightly in excess of that required. The tap to the bomb was then opened, and the mixture allowed to flow into it. The pressure was then quickly adjusted to that required, and the tap to the bomb closed. In this way none of the foreign gas, *i.e.*, chlorine, etc., was able to escape back into the tubes. It was found necessary to allow 10—15 mins. for the gases in the bomb to mix before they were ignited and the radiation measured as described in the previous papers. Great care was taken to prevent chlorine attacking the tap grease; it was found satisfactory to grease the central part of the plug of the tap with the chlorine-resisting grease described by Guye (*J. Chim. physique*, 1908, **6**, 756) and Wourtzel (*ibid.*, **1913**, **11**, 31), and the outer part of it with Apieson grease.

Preparation of the Bulbs of Gas.—Constrictions were made in thin-walled glass tubing so that it formed a series of bulbs. After the volume of the bulbs had been calibrated by filling with either water or mercury, they were cleaned with concentrated nitric acid, then distilled water, and finally rinsed with absolute alcohol, and dried by means of a stream of hot, dry air; 30—40 of these bulbs were then sealed on to an apparatus containing the gases to be used in an experiment.

Chlorine. The chlorine, prepared by the action of pure hydrochloric acid on Kahlbaum's potassium permanganate, was passed through solutions of potassium permanganate and copper sulphate, and dried first with concentrated sulphuric acid and then with phosphoric oxide. The bulbs were filled by displacement of air, a rapid stream of chlorine being first passed through them, then a steady stream, a rapid stream again, and finally a steady stream. They were then sealed off at calibrated marks and stored in numbered compartments. The temperature and pressure of filling were noted. All joints in the apparatus were glass to glass.

Bromine. Bromine vapour was obtained from Kahlbaum's pure liquid, which was placed in a bulb and connected through a phosphoric oxide tube to a series of calibrated bulbs. The bromine was immersed in liquid air, and the whole of the apparatus evacuated by means of a Hyvac pump. The tap to the pump was closed and the liquid air removed. When the bromine had reached a suitable temperature, it was surrounded by water contained in a Dewar flask at a temperature slightly lower than that of the room; ½ hour was then allowed for the vapour to fill the bulbs. The temperature of the liquid bromine was recorded, so that the pressure of the vapour in the bulbs could be calculated. The bulbs were then carefully sealed off and stored.

Carbon tetrachloride. A similar method was employed to fill bulbs with vapour from Kahlbaum's carbon tetrachloride.

Results.—The radiation was measured by means of a Moll microthermopile with fluorite window, and a Downing galvanometer, the deflexion of the latter being recorded on photographic paper. The area below the curve obtained is taken to be proportional to the radiation emitted, and this area is multiplied by the reciprocal of the fraction of the gas burned to give the results recorded on Figs. 1, 2, and 4. These are plotted against the pressure of the combustible gas present. This procedure was the same as that adopted in the earlier work. The pressure of the gases after the flame had passed was measured on a mercury manometer, and from these data the percentage combustion was calculated.

CONCLUSIONS.

It is shown that, in the carbon monoxide flame containing hydrogen, there are two independent mechanisms whereby flame is produced. The pressure at which the two mechanisms travel at the same speed is given by $p_s = k_2/(p_{H_2} + k_1)$. It is concluded that the velocity of the mechanism stable at the higher pressures is dependent on the rate at which hydrogen atoms are produced by collision of hydrogen molecules with newly-formed carbon dioxide molecules. Carbon dioxide, chlorine, bromine, and carbon tetrachloride diminish the density of the stream of hydrogen atoms and raise p_s. An interpretation of the results is given in terms of the theory of chain reactions.

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