LII.—*The Propagation of Flame in Complex Gaseous Mixtures. Part V. The Interpretation of the Law of Speeds.*

By William Payman.

The addition of the incombustible gas nitrogen to the mixture of methane and oxygen of the composition $CH_4 + 2O_2$ results in a reduction of the speed of uniform movement of flame in the mixture.

Both methane and oxygen behave similarly to nitrogen in that they also reduce the speed of uniform movement of flame when added to this mixture (T., 1920, **117**, 56).

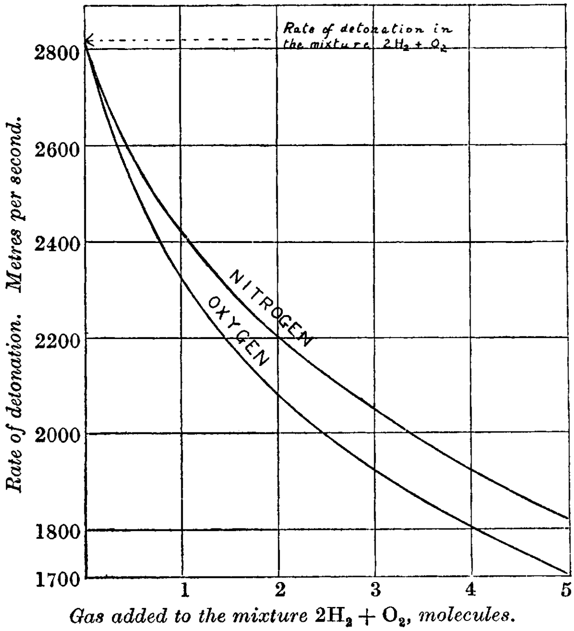
The speed of the uniform movement of flame, under standard experimental conditions, in a mixture of any given inflammable gas with air or oxygen depends on the rate of reaction in that mixture, and is mainly determined, therefore, by the temperature of the burning gases (*loc. cit.*, p. 49). It follows that with a given mixture (such, for example, as $CH_4 + 2O_2$) the greater the cooling effect of a gas added to the mixture the greater will be its retarding effect on the speed of the flame. Thus, methane, having the highest specific heat of the gases methane, oxygen, and nitrogen, is found to have the most marked retarding effect of the three.

If the retarding action of an added gas were dependent solely on its cooling effect, that is to say, on its specific heat, a simple explanation could be offered for the Law of Speeds (T., 1922, **121**, 364). A mixture with a given speed of flame may be obtained by adding a certain volume of methane to the mixture $CH_4 + 2O_2$. A different mixture having the same speed of flame may be obtained by adding a different volume of nitrogen to the same unit volume of $CH_4 + 2O_2$. These different volumes of methane and of nitrogen would, perforce, have the same heat capacity if this supposition were correct; that is to say, they would require the same amount of heat to raise them to the temperature of the burning gases. A complication is, however, introduced by the effect of mass-action. The probable magnitude of this effect will be considered later; in the meantime, it will simplify discussion to neglect it.

Since these two volumes, the one of methane, the other of nitrogen, have the same heat capacity, then a given proportion of the one could be replaced by the same proportion of the other without altering the total heat capacity of either, or altering the retarding effect of either on the speed of flame.

This is in effect what is done when two gas mixtures having the same speed of flame are mixed together. A simple example will help to make this clear. Imagine two mixtures with the same speed of flame produced by diluting the basic mixture $CH_4 + 2O_2$ with either methane or nitrogen, the composition of the one being $CH_4 + 2O_2 + xCH_4$, and that of the other being $CH_4 + 2O_2 + yN_2$. It follows that xCH_4 and yN_2 will have the same heat capacity. Now, if half the diluting gas in the first mixture is replaced by half the diluting gas in the second mixture, the resulting mixture will have the composition $CH_4 + 2O_2 + \frac{x}{2}CH_4 + \frac{y}{2}N_2$. The quantity of diluting gas is now $\frac{y}{2}CH_4 + \frac{y}{2}N_2$; this will have the same heat capacity as either $x\mathrm{CH_4}$ or $y\mathrm{N_2}$, and the new mixture will therefore have the same speed of flame as the original mixture. Exactly the same mixture would be obtained by mixing together equal volumes of the original mixtures, giving a mixture of the composition $\mathrm{CH_4} + 2\mathrm{O_2} + x\mathrm{CH_4} + \mathrm{CH_4} + 2\mathrm{O_2} + y\mathrm{N_2}$, or 2 volumes of $\mathrm{CH_4} + 2\mathrm{O_2} + \frac{x}{2}\mathrm{CH_4} + \frac{y}{2}\mathrm{N_2}$.* From the law of speeds it is known that this mixture will have the same speed of flame as either of the two original mixtures.

FIG. 1.



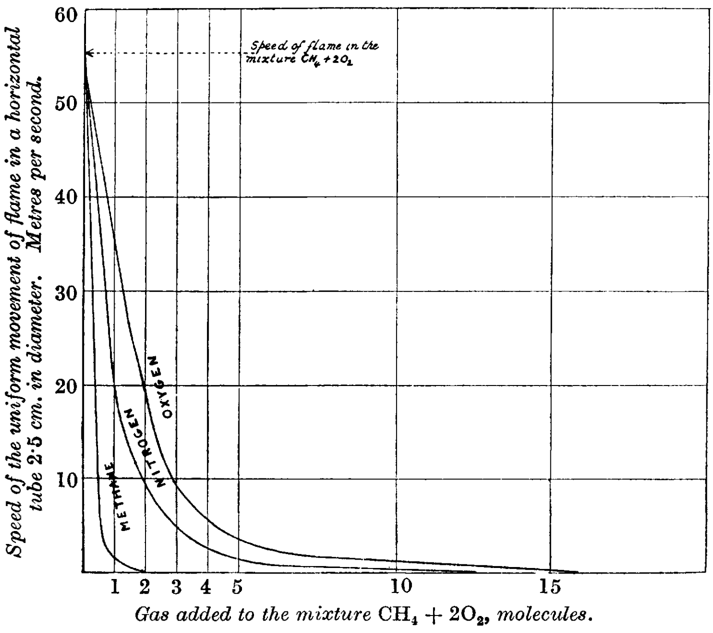
It will be seen that the law of speeds can be explained on the assumption that any addition of incombustible gas, inflammable gas, or oxygen to a mixture of inflammable gas and oxygen in combining proportions has a retarding effect on the speed of the uniform movement of flame proportional to its specific heat.

* It has been emphasised in earlier papers that the law of speeds can only be applied to similar mixtures, containing excess of oxygen or containing excess of inflammable gas. The reason for this will now be apparent, for the mixing together of two unlike mixtures corresponding with, say, $\mathrm{CH_4} + 2\mathrm{O_2} + a\mathrm{CH_4}$ and $\mathrm{CH_4} + 2\mathrm{O_2} + b\mathrm{O_2}$ will result in alteration of the quantity of the basic mixture, $\mathrm{CH_4} + 2\mathrm{O_2}$, present. Some of the added methane of the first mixture would combine with some of the added oxygen of the second, and would no longer act as diluting gas, so that the speed of flame would be increased.

This explanation of a law which was first enunciated as a purely empirical relationship, observed between the speeds of the uniform movement of flame in complex gas mixtures, has proved useful in many ways. One of these is the prediction of the application of the law of speeds to other modes of propagation of flame within certain limits.

The diluting or retarding effect of added gas, both combustible and incombustible, to a given gas mixture has its counterpart in the propagation of the explosion-wave. Dixon has shown (*Phil.*

FIG. 2.



Trans., 1893, **184**, 97) that the addition of either oxygen or nitrogen to electrolytic gas, $2H_2 + O_2$, reduces the rate of detonation in the resulting mixture.* This is shown in Fig. 1, which is reproduced from Dixon's paper (*loc. cit.*, p. 188), and should be compared with Fig. 2, which shows the effect of the addition of methane, oxygen, and nitrogen, to the mixture $CH_4 + 2O_2$, on the speed of the uniform movement of flame.

The diluting or retarding effect of the addition of oxygen and

* The explosion wave differs from the uniform movement in that with the former the addition of hydrogen to the mixture $2H_2 + O_2$, and of methane to the mixture $CH_4 + 2O_2$, increases the rate of detonation, whereas the speed of the uniform movement is decreased in both mixtures.

nitrogen on the rate of detonation of electrolytic gas has been shown by Dixon to be proportional to the respective densities of the gases. Densities are additive properties just as are specific heats; for weights are additive just as are heat capacities. Hence it follows that the law of speeds should hold for the detonation-wave in mixtures of hydrogen, oxygen, and nitrogen in which the oxygen is present in sufficient quantity to burn the hydrogen completely.

In order to test the truth of this conclusion, Professor Dixon kindly allowed a series of experiments to be carried out in his laboratory with a number of mixtures of hydrogen, oxygen, and nitrogen of different compositions, using the original apparatus in which his experiments were carried out. These experiments, which are described in another communication, have shown that the law of speeds holds exactly for the rate of detonation in these mixtures. The fact must be emphasised that the law of speeds applies to these mixtures for a similar, but not the same, reason for which it applies to the uniform movement of flame.

This reason for the application of the law of speeds to the uniform movement of flame also serves to explain certain peculiarities observed in the results of the early experiments that were made to test the truth of the law. It was found that the law did not hold exactly with all gaseous mixtures. Appreciable differences, small, but beyond the limits of possible experimental error, were found between the observed and calculated values for the speeds of flame in complex gas mixtures. There was evidently some other factor which either prevents or assists to a slight extent the retarding effect of the added gas or gases.

We have assumed in the reasoning outlined above that the rate of reaction is dependent entirely on the temperature of the reacting gases, and that in mixtures of one particular gas and air or oxygen the mixture with the highest temperature will also have the highest speed of flame. The rate of reaction, however, will also depend on the concentrations of the reacting gases. It has been shown (T., 1920, **117**, 49) that, for a given combustible gas, the mixture with the highest calorific effect is not necessarily the mixture with the maximum speed of flame, which is sometimes obtained in a mixture of different composition. The difference in composition between these mixtures has been termed the "displacement" of the maximum-speed mixture. The nature of the displacements observed confirms the supposition that they are due to the effect of mass action. In the same way it would appear that the small differences between observed and calculated values for the speeds of flame are also due to the effect of mass action.

Reference to Fig. 2 will show that the retarding effect of oxygen on the speed of the uniform movement of flame in the mixture $CH_4 + 2O_2$ is rather less than that of nitrogen, although the specific heats of nitrogen and oxygen are approximately the same. The reason for this was suggested in Part IV of this series of papers (*loc. cit.*, p. 56). Since the rate of reaction depends not only on the temperature, but also on the concentrations of the reacting gases, the fact that the oxygen can take part in the reaction will cause its retarding effect to be less than that of another gas of the same specific heat which cannot take place in the reaction; because, although the temperature effect may be the same, the mass-action factor is greater when the diluting gas is reactive, and therefore the rate of reaction in this mixture would be greater. If we consider the two mixtures with the same calorific effect, (1) $CH_4 + 2O_2 + xO_2$, and (2) $CH_4 + 2O_2 + yN_2$, the speed of flame in these two mixtures would be the same if it depended solely on the temperature. If the specific heats of oxygen and nitrogen are assumed to be the same exactly, $x = y$. The mass-action factor is given by the expression $C_{CH_4} \times C^2_{O_2}$. If unit quantity of methane * is taken in both mixtures,

$$C_{CH_4} \times C^2_{O_2} = \frac{1}{3 + x} \cdot \frac{(2 + x)^2}{(3 + x)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$C_{CH_4} \times C^2_{O_2} = \frac{1}{3 + y} \cdot \frac{2^2}{(3 + y)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Since $x = y$, (1) is always greater than (2), and therefore the rate of reaction is always greater in mixture (1) than in mixture (2), even although the calorific effect of the two mixtures is the same.

Let us now consider what effect the coming into play of mass action will have on the application of the law of speeds in mixtures of two inflammable gases with air or oxygen. It will simplify explanation if a particular example be chosen. The upper limit of methane in air in a horizontal tube, 2·5 cm. in diameter, was found to be 13·3 per cent. The upper-limit mixture of hydrogen in air under similar conditions was found to contain 71·4 per cent. of hydrogen. If from these values the limit for the mixture $CH_4 + H_2$ is calculated by means of the law of speeds, the value

* The mass-action factor gives a relative measure of the number of fruitful collisions taking place between inflammable gas and oxygen in unit time. Taking unit quantity of inflammable gas affords a measure of the chances of each molecule of the inflammable gas entering into chemical combination with oxygen in that period.

obtained is 22·4 per cent. The composition of the three limit mixtures is as follows :

	1.	2.	3.
Hydrogen	71·4	—	11·2
Methane	—	13·3	11·2
Oxygen	6·5	18·2	16·3
Nitrogen	22·1	68·5	61·3

The value for the mass-action factor is given by the expression $C^2_{H_2} \times C_{O_2}$ for the reaction $2H_2 + O_2$, and $C_{CH_4} \times C^2_{O_2}$ for the reaction $CH_4 + 2O_2$. For unit volumes of methane and hydrogen the factor in each of the three mixtures becomes :

For hydrogen

$(71·4 \times 71·4 \times 6·5)/71·4 = 464$ . . . . in (1)
and $(11·2 \times 11·2 \times 16·3)/11·2 = 182$ . . . . in (3)

And for methane

$(13·3 \times 18·2 \times 18·2)/13·3 = 331$ . . . . in (2)
and $(11·2 \times 16·3 \times 16·3)/16·3 = 265$ . . . . in (3)

That is to say, the factor for each gas is less in the calculated complex mixture than in each of the simple mixtures.* The speed-law calculation is made, however, on the assumption that the rate of reaction in all three mixtures is the same, since their calorific effects are the same. But the rate of both reactions will be less in the complex mixture, on account of the effect of mass action; instead of this mixture being a limit mixture (that is to say, a mixture just able to support combustion), the result will be that it will not be able to do so, and the mixture must have more air added to it before the rate of reaction becomes sufficiently great, owing mainly to increased temperature, for it to allow of complete and independent propagation of flame. The value found experimentally for the limit in this mixture was 20·8 per cent.

Similarly, if two mixtures having the same speed of flame are mixed together, the resulting mixture will have a slightly lower speed, since the rates of the reactions in this complex mixture will be less than in the respective simple mixtures.

In this illustration limit mixtures have been utilised to simplify the wording. Any mixture of two (similar) mixtures having the same speed of flame could have been chosen; for example, the two mixtures of methane in air and hydrogen in air that have a speed of flame of 50 cm. per second. The law of speeds applies to limit mixtures because the speed of flame in limit mixtures of most

* In other words, the number of fruitful collisions of methane with oxygen and of hydrogen with oxygen in unit time will be less in the complex mixture than in the respective simple mixtures.

inflammable gases in air, taken singly, is approximately the same; when some other speed is chosen, other than the speed at the limits, the same result is obtained.

For ease of reference, it is convenient to make use of special mixtures such as "maximum-speed mixtures," "mixtures for complete combustion," or "limit mixtures." Similar calculations with these mixtures indicate that the speed of the uniform movement of flame actually obtained in most of the complex gaseous mixtures which have been examined should be less than that calculated from the law of speeds.

The observed and calculated speeds of flame in maximum-speed mixtures and mixtures for complete combustion are given in Tables I and II, and the differences observed are in agreement with the theory that has been outlined, that is, the actual speeds of flame are less than those calculated.

TABLE I.

Maximum-speed Mixtures.

	Maximum speed of uniform movement of flame. Cm. per second.		
Mixture.	Calc.	Found.	Diff.
$3C_5H_{12} + 2H_2$	100	89·5	− 10·5
$CH_4 + C_5H_{12}$	78·5	78·3	− 0·2
$CH_4 + H_2$	150	135	− 15
$3CH_4 + H_2$	99	85	− 14
Coal gas	164	154	− 10
Producer gas	85	72	− 13

TABLE II.

Mixtures for Complete Combustion.

	Speed of uniform movement of flame.		
Mixture.	Calc.	Found.	Diff.
$H_2 + 3CH_4$	95	85	− 10
$H_2 + CH_4$	149	135	− 14
$3H_2 + CH_4$	246	240	− 6

Any factor which reduces the speed of flame in a limit mixture will render that mixture incapable of self-propagation of flame. Hence we would expect that the upper limit of inflammability of a complex mixture would always be less than the value calculated. An actual comparison is given in Table III.

TABLE III.

Upper-limit Mixtures.

	Upper limit.		
Mixture.	Calc.	Found.	Diff.
$3C_5H_{12} + 2H_2$	8·6	8·6	0·0
$CH_4 + C_5H_{12}$	7·7	7·7	0·0
$CH_4 + H_2$	22·4	20·8	− 1·6
$3CH_4 + H_2$	16·7	15·5	− 1·2
Coal gas	26·4	24·3	− 2·1

It would be expected that the mass-action effect would become less important when the percentage of oxygen is greatly in excess of that required to burn the inflammable gas completely. Calculation supports this view; thus, in the lower-limit mixture of $CH_4 + H_2$ the mass-action factor for unit volume of methane is slightly higher than in the lower-limit mixture of methane alone, and the factor for hydrogen is reduced, but to a much less extent than was seen to obtain with the upper-limit mixtures. Examination of the curves given in earlier papers will show that the agreement between observed and calculated values is quite close when the oxygen is in excess, and the law of speeds has been shown to apply very accurately to lower-limit mixtures.

The law of speeds as applied to the uniform movement during the propagation of flame can therefore be explained on the assumption that the variations in the speed of flame as determined under standard conditions with mixtures of different compositions depends on the rate of reaction between the inflammable gases and oxygen in the flame front. The law of speeds would hold exactly if this rate of reaction was dependent solely on the temperature, so that excess of either inflammable gas, oxygen, or of incombustible gas could be regarded as behaving simply as diluting gas, lowering the reaction temperature, but taking no part in the reaction. The fact that the rate of reaction must also depend on the concentrations of the reacting gases results in small divergences from the law when the oxygen is in deficit. The correction necessary to allow for this cannot be correctly estimated, but the general effect of this factor is to make the speeds of the uniform movement of flame in complex mixtures rather slower than the speeds calculated from the law of speeds.

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