XLVII.—*The Combustion of Complex Gaseous Mixtures.*

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WITH each of the paraffin hydrocarbons the speed of the uniform movement of flame in its limit mixtures with air is approximately the same under standard conditions of experiment. Thus the speeds as determined in a horizontal glass tube 2.5 cm. in diameter are :

	Speed of uniform movement of flame. Cm. per sec.	
	Lower limit mixture.	Upper limit mixture.
Methane	23.3	19.1
Ethane '	18.1	19.7
Propane	20.8	20.3
Butane	20.1	20.3
Pentane	20.2	20.2

Under the same conditions of experiment, approximately the

same speed of uniform movement of flame is obtained with all limit mixtures of methane, oxygen, and nitrogen, and, for example, with an equimolecular mixture of methane and pentane at its limits with air :

Mixture.	Speed of uniform movement of flame in a horizontal glass tube 2.5 cm. in diameter. Cm. per sec.	
	Lower limit mixture.	Upper limit mixture.
Methane with atmosphere containing 13.7 per cent. of oxygen	21.9	19.1
Methane with atmosphere containing 17.0 per cent. of oxygen	22.4	19.0
Methane with air	23.3	19.1
Methane with atmosphere containing 33.0 per cent. of oxygen	23.0	18.9
Methane with atmosphere containing 50.0 per cent. of oxygen	22.8	18.9
Methane with atmosphere containing 66.0 per cent. of oxygen	21.3	19.4
Methane with oxygen	19.9	18.9
Equimolecular mixture of methane and pentane with air	22.3	20.7

In general, if a limit mixture with air of one gas is mixed, in any proportions, with a limit mixture with air of another gas, the speed of propagation of flame in both mixtures being, as it is, approximately the same under the same conditions of experiment, the speed of propagation of flame in the resultant complex mixture (which is also a limit mixture) is unchanged.*

This law, which can be termed the law of speeds of flame in complex gaseous mixtures, can be shown experimentally to hold, with considerable accuracy, for the propagation of flame, not only in limit mixtures, but in all mixtures of inflammable gases with air (or oxygen), provided that the mixtures of the individual gases are of the same type, all containing excess of oxygen or all containing excess of combustible gas. For example, a mixture of methane and air containing 7.35 per cent. of methane, and a mixture of pentane and air containing 1.98 per cent. of pentane, were prepared. In these two mixtures the speed of the uniform movement of flame under the same conditions of experiment is the same, about 40 cm. per sec. in a horizontal glass tube 2.5 cm. in diameter, and they both contain excess of oxygen. The mixtures were combined in varying proportions and the speeds of the uniform movement of flame in the resultant complex mixtures then determined, as follows :

* Provided that the limit mixtures of the individual gases are of the same type, both lower or both upper.

Speeds of uniform movement of flame in a horizontal glass tube 2.5 cm. in diameter with mixtures containing 7.35 per cent. of methane and 1.98 per cent. of pentane, respectively, mixed together.

Methane mixture. Per cent.	Pentane mixture. Per cent.	Speed of flame. Cm. per sec.
100.0	nil.	39.3
75.0	25.0	39.2
50.0	50.0	39.6
25.0	75.0	39.9
21.2	78.8	39.2 *
nil.	100.0	40.1

* Methane and pentane in equimolecular proportions.

It will be seen that the speeds are identical within the limits of experimental error.

Similarly, two mixtures containing excess of combustible gas were examined in the same manner. These mixtures contained 11.00 per cent. of methane and 3.54 per cent. of pentane, respectively, and the speed of the uniform movement of flame in them was about 60 cm. per sec. in a horizontal glass tube 2.5 cm. in diameter.

Speeds of uniform movement of flame in a horizontal glass tube 2.5 cm. in diameter with mixtures containing 11.00 per cent. of methane and 3.54 per cent. of pentane, respectively, mixed together.

Methane mixture. Per cent.	Pentane mixture. Per cent.	Speed of flame. Cm. per sec.
100.0	nil.	59.1
75.0	25.0	59.1
50.0	50.0	60.3
25.0	75.0	59.1
24.4	75.6	59.1 *
nil.	100.0	59.6

* Methane and pentane in equimolecular proportions.

Further examples of the experimental verification of this "law of speeds" with a number of different inflammable gases in admixture with air or oxygen are given in T., 1919, 115, 1446, 1454; 1920, 117, 48. It can be stated as follows: Given two or more mixtures of air or oxygen with different individual gases, in each of which the speed of propagation of flame is the same, all combinations of the mixtures of the same type * propagate flame at the same speeds, under the same conditions of experiment.

It follows that, so far as the propagation of flame is concerned, a mixture of a number of different combustible gases with air

* All containing excess of oxygen or all containing excess of combustible gas.

(for example) can be regarded as the summation of mixtures of each individual gas with air, the proportions of combustible gas and air in each being such that the speed of flame in it, if the mixture were burning alone, would be the same as in the complex mixture.

For example, a mixture of air, methane, and hydrogen containing 9.00 per cent. of the equimolecular mixture $\text{CH}_4 + \text{H}_2$ (or 4.5 per cent. of each inflammable gas) propagates flame, under given experimental conditions, at a speed of 45 cm. per second. Under the same experimental conditions, a speed of flame of 45 cm. per second is obtained with 7.65 per cent. of methane alone in air. In this simple mixture, the 7.65 per cent. of methane is associated with $(100 - 7.65)$ per cent. of air. According to the "law of speeds," therefore, the 4.5 per cent. of methane in the complex methane-hydrogen-air mixture postulated is associated with $\frac{4.50}{7.65} (100 - 7.65)$ per cent. of air. Similarly, under the same experimental conditions, a speed of flame of 45 cm. per second is obtained with 10.90 per cent. of hydrogen alone in air. In this simple mixture, the 10.90 per cent. of hydrogen is associated with $(100 - 10.90)$ per cent. of air; therefore in the complex methane-hydrogen-air mixture the 4.5 per cent. of hydrogen is associated with $\frac{4.50}{10.90} (100 - 10.90)$ per cent. of air. The ratio between (a) the air associated with, or monopolised by, the methane, and (b) the air monopolised by the hydrogen, during the propagation of flame in the complex methane-hydrogen-air mixture, is thus :

$$\frac{100 - 7.65}{7.65} : \frac{100 - 10.90}{10.90} = 12.1 : 8.2.$$

In the mixture chosen for this example there is sufficient oxygen present in the air to burn all the methane and hydrogen completely. Let us consider one in which the oxygen is in defect. A mixture of air with 18.80 per cent. of the equimolecular mixture $\text{CH}_4 + \text{H}_2$ (9.4 per cent. of each inflammable gas) propagates flame under given experimental conditions at a speed of 60 cm. per second. Under the same conditions, that speed of flame is obtained with either 10.85 per cent. of methane alone in air or 71.00 per cent. of hydrogen alone in air. In these simple mixtures the methane is associated with $(100 - 10.85)$ per cent. of air and the hydrogen with $(100 - 71.00)$ per cent. of air. In the complex methane-hydrogen-air mixture, therefore, the 9.4 per cent. of methane is associated with $\frac{9.4}{10.85} (100 - 10.85)$ and the 9.4 per

cent. of hydrogen with $\frac{9.4}{71.0}$ (100 — 71.0) per cent. of air; so that the ratio between the air monopolised by methane to that monopolised by hydrogen during the propagation of flame in the complex mixture is :

$$\frac{100 - 10.85}{10.85} : \frac{100 - 71.0}{71.0} = 8.2 : 0.4.$$

Since in this mixture there is insufficient oxygen to burn the whole of both the methane and the hydrogen, it must be presumed that the relative proportions of oxygen that will combine with the methane and the hydrogen respectively will be determined by the relative amounts of air "monopolised" by each during the propagation of flame at the given speed.

In general, it can be concluded that during the propagation of flame in a mixture of several inflammable gases with air at a given speed, the gas which will monopolise the most oxygen is that which when burning alone with the same speed of flame is associated with the most air.

These are natural deductions to draw from the law of speeds. They have been tested experimentally, in a manner now to be described.

Suppose that flame is allowed to travel through a mixture of methane, hydrogen, and air, the oxygen present being insufficient for the complete combustion of both gases. If the deductions drawn from the law of speeds (which holds remarkably closely for mixtures of methane, hydrogen, and air) are correct, then the products of combustion of the complex mixture should have the same composition as when a methane-air mixture and a hydrogen-air mixture are inflamed separately and the products of combustion of each are mixed together, provided that the speed of propagation of flame in the two separate mixtures is the same as in the complex mixture.

The determination of the distribution of oxygen between different inflammable gases such as methane and hydrogen is complicated by the occurrence of the secondary "water-gas reaction," which modifies the composition of the final products of combustion. An increase or decrease in the volume of carbon monoxide found in the final gases, above or below that formed before the water-gas reaction came into play, is, however, accompanied by a corresponding decrease or increase in the volumes of carbon dioxide and hydrogen found, according to the equilibrium $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$, and calculation can be made of the amount of change.

Three series of experiments can be recorded, as follow.

TABLE I.—Upper Limit Mixtures with Oxygen.

Inflammable gas :—		Methane.		Hydrogen.		Carbon monoxide.	
Analysis of limit mixture.	Per cent.	{ O ₂ CH ₄ }		{ O ₂ H ₂ }		{ O ₂ CO }	
Experiment No.		1a	1b	2a	2b	3a	3b
Analysis of products of combustion (calculated nitrogen-free). Per cent.		{ CO ₂ CO CH ₄ H ₂ }	{ 3.18 36.17 3.25 57.40 }	—	—	{ 13.43 85.72 }	{ 13.40 85.74 }
Ratio p_2/p_1		1.34	1.34	100.00	100.00	0.85	0.86
Partial pressures of individual constituents of products of combustion. Atmospheres.		{ CO ₂ CO CH ₄ H ₂ }	{ 0.0425 0.4846 0.0435 0.7691 }	0.769	0.769	{ 0.945 0.1269 0.8100 }	{ 0.945 0.1266 0.8102 }
			0.7692	0.7690	0.7690	0.0080	0.0081

TABLE II.

Inflammable gases :—

Inflammable gases :—		CH ₄ + H ₂		H ₂ + CO		CO + CH ₄	
Analysis of mixture.	Per cent.	{ O ₂ CH ₄ H ₂ }		{ O ₂ H ₂ CO }		{ O ₂ CO CH ₄ }	
Experiment No.		4a	4b	5a	5b	6a	6b
Analysis of products of combustion (calculated nitrogen-free). Per cent.		{ CO ₂ CO CH ₄ H ₂ }	{ 2.33 26.38 3.38 67.91 }	—	—	{ 6.71 52.06 2.72 38.51 }	{ 30.77 35.18 2.76 38.36 }
Ratio p_2/p_1		1.10	1.10	0.819	0.819	1.13	1.13
Partial pressures of individual constituents of products of combustion. Atmospheres.		{ CO ₂ CO CH ₄ H ₂ }	{ 0.0256 0.2901 0.0372 0.7470 }	0.0343	0.0340	{ 0.0758 0.5881 0.0307 0.4351 }	{ 0.0760 0.5893 0.0312 0.4355 }

I.—Upper Limit Mixtures with Oxygen.

The combustible gases used were methane, hydrogen, and carbon monoxide. The limits were determined, within about 0.5 per cent., for downward propagation of flame in a glass tube 2 cm. in diameter and 40 cm. long, closed at both ends. Each limit mixture was ignited at atmospheric pressure; the pressure of the cooled products of combustion was then determined and analysis made of them, whence the partial pressure of each product could be calculated. The results of duplicate experiments are recorded in Table I.

From these results it should be possible, if our deductions from the "law of speeds" are correct, to calculate what would be the composition of the products of combustion of any mixture of these upper-limit mixtures, for the speed of flame is the same in each. The mixtures were therefore blended, two at a time, the blend chosen in each instance being that which contained approximately equimolecular proportions of the two inflammable gases. These complex mixtures (which were, like the simple mixtures, upper-limit mixtures) were then ignited and their products of combustion measured and analysed. The results are recorded in Table II, whilst in Table III comparison is made between the values for the products of combustion obtained experimentally and those calculated from Table I. In none of the experiments was carbon deposited, nor did more than a trace of oxygen remain unburnt.

It will be seen that there is close correspondence between the "calculated" and "observed" values for the individual products of combustion.

II.—Upper Limit Mixtures of Methane, Oxygen, and Nitrogen.

The "law of speeds" holds, not only with respect to different inflammable gases mixed with oxygen or with the same "atmosphere" of oxygen and nitrogen, but also with respect to the same inflammable gas mixed with different "atmospheres." Experiments were therefore made to determine whether the composition of the products of combustion of any mixture of methane, oxygen, and nitrogen can be calculated, given the composition of the products of combustion of two other mixtures in which the proportions of methane, oxygen, and nitrogen are different but in which the speed of flame is the same.

The mixtures chosen to supply the experimental data from which to make calculations were the upper-limit mixtures (downward propagation of flame) of methane with (1) air and (2) oxygen.

TABLE III.*

Experiment No.	Partial pressures of products of combustion. Calculated.					Partial pressures. Found.		
	From Expt. 1a. 35.23 per cent. CH ₄ yields :	From Expt. 2a. 35.03 per cent. H ₂ yields :	Total.	4a.	4b.	Mean.		
4	CO ₂	2.62	—	2.62	2.56	2.54	2.55	
	CO	29.90	—	29.90	29.01	28.98	28.98	
	H ₂	47.45	26.95	74.40	74.47	74.75	74.61	
	CH ₄	2.68	—	2.68	3.72	3.77	3.74	
5	From Expt. 2a. 47.04 per cent. H ₂ yields :	From Expt. 3a. 45.82 per cent. CO yields :	Total.	5a.	5b.	Mean	(Corrected for "water-gas reaction").	
	—	6.20	6.20	3.43	3.40	6.20		
	CO	39.60	39.60	42.47	42.53	39.72		
	H ₂	38.81	39.20	36.10	35.97	38.81		
6	From Expt. 3a. 35.18 per cent. CO yields :	From Expt. 1a. 34.05 per cent. CH ₄ yields :	Total.	6a.	6b.	Mean.		
	4.76	2.54	7.30	7.58	7.60	7.59		
	CO	30.37	59.35	58.81	58.93	58.87		
	H ₂	0.30	45.31	43.51	43.35	43.43		
	CH ₄	—	2.60	3.07	3.12	3.09		

* The partial pressures in this table are multiplied by 100.

The test mixture, on which to check the calculations, was prepared by mixing these two mixtures in approximately equal proportions. The results are recorded in Table IV and the "observed" and "calculated" values for the products of combustion are compared in Table V. When obtaining the "calculated" values, allowance was made for the fact that for experiments Nos. 8a and 8b exactly equal parts of mixtures 1 and 7 were not taken.

III.—*Mixtures of Several Combustible Gases with Air, Oxygen being in Defect.*

For this series of experiments, mixtures were chosen in which the speed of uniform movement of flame in a horizontal glass tube 2.5 cm. in diameter was 30 cm. per second. The tube used was 150 cm. long and the flames travelled at a uniform speed over a distance of 100 cm. At a distance of 25 cm. from the open end of the tube, at which the mixtures were ignited, a side-tube was fused with a gas-sampling arrangement attached thereto which enabled a sample of the products of combustion to be secured the moment the flame had passed.

The proportions of inflammable gas required to give a mixture in which the speed of uniform movement of flame, under these conditions of experiment, is 30 cm. per second are: for methane and air 12.50 per cent.; for hydrogen and air 70.20 per cent.; and for carbon monoxide and air 66.78 per cent. Each of these mixtures was inflamed in the manner described and the analyses of the products of combustion are recorded in Table VI. The ratios p_2/p_1 given in that table are calculated from the percentages of nitrogen in the mixtures before and after combustion.

Complex mixtures were now prepared by blending these simple mixtures, either two at a time or three at a time, so as to obtain in them approximately equimolecular proportions of the various inflammable gases. The speed of flame in each of these complex mixtures, as in the simple mixtures under the same condition of experiment, was 30 cm. per second. The products of combustion of these complex mixtures are recorded in Table VII and are compared with the calculated values in Table VIII.

There is in each series of experiments close agreement between the "observed" and "calculated" values for the products of combustion of the complex mixtures, showing that our deductions from the law of speeds of flame in complex gaseous mixtures are correct.

So far as the results of the combustion of complex gaseous mixtures with air (or oxygen) are concerned, therefore, the

TABLE IV.—*Upper Limit Mixtures of Methane, Oxygen, and Nitrogen.*

Description :—	Methane-air.		Methane-oxygen.		Equal parts methane-air and methane-oxygen.
	$\left\{ \begin{array}{l} \text{O}_2 \\ \text{CH}_4 \\ \text{N}_2 \end{array} \right\}$	$\left\{ \begin{array}{l} 7a \\ 7b \end{array} \right\}$	$\left\{ \begin{array}{l} 1a \\ 1b \end{array} \right\}$	$\left\{ \begin{array}{l} 8a \\ 8b \end{array} \right\}$	
Analysis of mixture. Per cent					
Experiment No.					
Analysis of products of combustion. Per cent.	$\left\{ \begin{array}{l} \text{CO}_2 \\ \text{CO} \\ \text{CH}_4 \\ \text{H}_2 \end{array} \right\}$	$\left\{ \begin{array}{l} 5.46 \\ 8.69 \\ 0.51 \\ 7.34 \end{array} \right\}$	$\left\{ \begin{array}{l} 3.18 \\ 36.17 \\ 3.25 \\ 57.40 \end{array} \right\}$	$\left\{ \begin{array}{l} 3.46 \\ 24.77 \\ 2.04 \\ 35.57 \end{array} \right\}$	$\left\{ \begin{array}{l} 3.49 \\ 24.75 \\ 2.07 \\ 35.50 \end{array} \right\}$
Ratio p_2/p_1		$\left\{ \begin{array}{l} 0.884 \\ 0.884 \end{array} \right\}$	$\left\{ \begin{array}{l} 1.34 \\ 1.34 \end{array} \right\}$	$\left\{ \begin{array}{l} 1.09 \\ 1.09 \end{array} \right\}$	$\left\{ \begin{array}{l} 1.09 \\ 1.09 \end{array} \right\}$
Partial pressures of individual constituents of products of combustion. Atmospheres.	$\left\{ \begin{array}{l} \text{CO}_2 \\ \text{CO} \\ \text{CH}_4 \\ \text{H}_2 \end{array} \right\}$	$\left\{ \begin{array}{l} 0.0483 \\ 0.0768 \\ 0.0045 \\ 0.0650 \end{array} \right\}$	$\left\{ \begin{array}{l} 0.0486 \\ 0.0764 \\ 0.0045 \\ 0.0649 \end{array} \right\}$	$\left\{ \begin{array}{l} 0.0424 \\ 0.4846 \\ 0.0435 \\ 0.7691 \end{array} \right\}$	$\left\{ \begin{array}{l} 0.0380 \\ 0.2698 \\ 0.0225 \\ 0.3870 \end{array} \right\}$

TABLE V.—*Partial Pressures of Products of Combustion.**

	Found.		
	Calculated.	Expt. 8a.	Expt. 8b. Mean.
CO ₂	4.33	3.76	3.80 3.78
CO	26.78	26.99	26.98 26.98
H ₂	39.77	38.76	38.70 38.73
CH ₄	2.28	2.22	2.25 2.23

* Multiplied by 100.

TABLE VI.

Mixtures with Air in which the Speed of Flame, under the Conditions of Experiment, is 30 cm. per second.

Inflammable gas:—		Methane.		Hydrogen.		Carbon monoxide.	
Analysis of mixture.	Per cent.	{ O ₂ CH ₄ N ₂ }		{ O ₂ H ₂ N ₂ }		{ O ₂ CO N ₂ }	
Experiment No.		9a.	9b.	10a.	10b.	11a.	11b.
Analysis of products of combustion. Per cent.		6.09	6.01	—	—	15.02	15.07
		7.74	7.80	—	—	56.07	55.90
		0.38	0.42	—	—	—	—
		6.70	6.61	71.01	71.05	0.84	0.91
		79.09	79.16	28.99	28.95	28.07	28.12
Ratio p_2/p_1		0.877	0.877	0.813	0.813	0.937	0.937
Partial pressures of individual constituents of products of combustion. Atmospheres.		0.0534	0.0527	—	—	0.1407	0.1412
		0.0679	0.0684	—	—	0.5254	0.5238
		0.0033	0.0036	—	—	—	—
		0.0388	0.0380	0.5773	0.5770	0.0079	0.0085
		0.6937	0.6937	0.2355	0.2355	0.2633	0.2633

TABLE VII.

Inflammable gases:—		CH ₄ + H ₂				H ₂ + CO		CO + CH ₄		CH ₄ + H ₂ + CO	
Analysis of mixture. Per cent.		{ O ₂ CH ₄ H ₂ N ₂ }				{ O ₂ H ₂ CO N ₂ }		{ O ₂ CO CH ₄ N ₂ }		{ O ₂ CH ₄ H ₂ CO N ₂ }	
Experiment No.		12a. 12b.				13a. 13b.		14a. 14b.		15a. 15b.	
Analysis of products of combustion. Per cent.		{ CO ₂ CO CH ₄ H ₂ N ₂ }				{ CO ₂ CO CH ₄ H ₂ N ₂ }		{ CO ₂ CO CH ₄ H ₂ N ₂ }		{ CO ₂ CO CH ₄ H ₂ N ₂ }	
Ratio p_2/p_1		0.845 0.845				0.838 0.838		0.885 0.885		0.837 0.837	
Partial pressures of individual constituents of products of combustion. Atmospheres.		{ CO ₂ CO CH ₄ H ₂ N ₂ }				{ CO ₂ CO CH ₄ H ₂ N ₂ }		{ CO ₂ CO CH ₄ H ₂ N ₂ }		{ CO ₂ CO CH ₄ H ₂ N ₂ }	
		0.0318 0.0324				0.0434 0.0437		0.0830 0.0815		0.0556 0.0556	
		0.0047 0.0051				0.2919 0.2921		0.1184 0.1184		0.1072 0.1076	
		0.0035 0.0043				— —		0.0021 0.0029		0.0072 0.0072	
		0.1075 0.1090				0.2459 0.2446		0.0472 0.0486		0.0858 0.0845	
		0.6360 0.6360				0.2572 0.2572		0.6341 0.6341		0.5816 0.5816	

TABLE VIII.

Experi- ment No.	Partial pressures of products of com- bustion. Calculated ($\times 100$).			Partial pressures. Found ($\times 100$).		
	From Expt. 9a. 10.25 per cent. CH ₄ yields :	From Expt. 10a. 9.90 per cent. H ₂ yields :	Total.	12a.	12b.	Mean (Corrected for "water-gas reaction").
12	CO ₂	4.39	—	4.39	3.18	3.24
	CO	5.57	—	5.57	6.47	5.31
	H ₂	4.81	8.21	13.02	10.75	12.00
	CH ₄	0.27	—	0.27	0.35	0.39
13	From Expt. 10a. 33.84 per cent. H ₂ yields :	From Expt. 11a. 33.39 per cent. CO yields :	Total.	13a.	13b.	Mean (Corrected for "water-gas reaction").
	CO ₂	—	7.03	4.34	4.37	7.03
	CO	—	26.27	29.19	29.21	26.52
	H ₂	27.82	0.39	24.59	24.46	27.20
14	From Expt. 11a. 10.38 per cent. CO yields :	From Expt. 9a. 10.01 per cent. CH ₄ yields :	Total.	14a.	14b.	Mean (Corrected for "water-gas reaction").
	CO ₂	2.18	4.27	8.30	8.15	6.45
	CO	8.14	5.43	11.84	11.84	13.61
	H ₂	0.12	4.70	4.72	4.86	3.02
15	From Expt. 10a. 9.15 per cent. H ₂ yields :	From Expt. 11a. 8.91 per cent. CO yields :	Total.	15a.	15b.	Mean (Corrected for "water-gas reaction").
	CO ₂	—	1.87	5.56	5.56	5.46
	CO	—	6.99	10.72	10.76	10.84
	H ₂	5.28	0.10	8.58	8.45	8.41
	From Expt. 9a. 8.40 per cent. CH ₄ yields :	From Expt. 10a. 9.15 per cent. H ₂ yields :	Total.	15a.	15b.	Mean (Corrected for "water-gas reaction").
	CO ₂	3.59	1.87	5.56	5.56	5.46
	CO	4.56	6.99	10.72	10.76	10.84
	H ₂	3.95	0.10	8.58	8.45	8.41
	CH ₄	0.22	—	0.76	0.72	0.74

combustion can be regarded as involving the simultaneous but independent burning of a number of simple mixtures of the individual gases with air (or oxygen) in which the proportions of inflammable gas and air (or oxygen) are such that each mixture, if burning alone, would propagate flame with the same speed (under the same conditions of experiment) as does the complex mixture.

The "Relative Affinities" of Methane and Hydrogen for Oxygen.

The observations we have made (which, it should be pointed out, have no bearing on the character of the reactions that are taking place in flames, but refer only to the final effects of those reactions), seem to us to offer an explanation of the apparent greater "affinity" of methane for oxygen than either hydrogen or carbon monoxide possesses which Bone has deduced from his experiments on gaseous combustion at high pressures (*Phil. Trans.*, 1915, [A], **215**, 275). In our opinion the methods of calculating the "relative affinities" used in that paper are open to criticism, and we think that the results can be explained in a simpler manner.

In order to make our criticism of the method of calculation clear, it will be necessary to quote the description given in Bone's paper. The theoretical basis for the method of calculation is contained in the following paragraphs (p. 298) :

"The possibility of deducing from our bomb experiments a direct comparison between the relative affinities of methane and hydrogen in explosions arose from the fact that the primary oxidation of methane involves a direct transition from $\text{CH}_4 + \text{O}_2$ to $\text{CH}_2(\text{OH})_2$, which later breaks up into, ultimately, $\text{CO} + \text{H}_2 + \text{H}_2\text{O}$, without any deposition of carbon. Whence it follows that if mixtures $\text{CH}_4 + \text{O}_2 + x\text{H}_2$ be exploded, the division of the oxygen between the methane and hydrogen during the extremely short period of actual combustion (that is, direct oxidation) may be deduced from the proportion of the original methane found intact in the final products, provided always that there is no separation of carbon, which, in fact, is never observed in such circumstances."

"The experimental method consisted, therefore, in exploding a series of mixtures $\text{CH}_4 + \text{O}_2 + x\text{H}_2$, in which the hydrogen and oxygen were initially present in as nearly as possible equimolecular proportions, but in which x (the volume ratio of H_2 to CH_4) was varied between 2 and 8, and determining from the percentage of the original methane remaining intact in each case (1) the oxygen distribution when $x = 2$, and (2) the influence on such distribution of successive equal increments of x up to 8."

The exact steps taken in making the majority of the calculations

from the results of these experiments appear to have been as follows: The partial pressure of the methane burnt is equal to the sum of the partial pressures of carbon monoxide and carbon dioxide found in the products of combustion. These products can only arise, according to Bone, from the interaction of equimolecular proportions of methane and oxygen; therefore, the sum of the partial pressures of carbon monoxide and carbon dioxide found in the products of combustion is a direct measure of the partial pressure of the oxygen used by the methane "during the extremely short period of actual combustion." Since the partial pressure of the oxygen originally present in the mixture was equal to that of the methane, therefore the partial pressure of the methane found unburnt after explosion must represent the partial pressure of oxygen that was prevented from combining with the methane—because it combined with hydrogen.

Two examples of calculations from experiments with the mixture $\text{CH}_4 + \text{O}_2 + 2\text{H}_2$, recorded in Table IV (*loc. cit.*, p. 299), will suffice to show the method:

Experiment No :—		16.	17.
Partial pressures in gaseous products in atmospheres.	$\left\{ \begin{array}{l} \text{CO}_2 \\ \text{CO} \\ \text{H}_2 \\ \text{CH}_4 \end{array} \right.$	0.394 4.470 14.320 0.270	1.164 10.910 35.520 0.555
	Per cent. distribution of oxygen deduced from unburnt CH_4 .	$\left\{ \begin{array}{l} \text{to CH}_4 \\ \text{to H}_2 \end{array} \right.$	94.74 5.26
			95.6 4.4

Our own calculations from these results, made in the manner described in the preceding paragraph, are: From experiment 16,

$$\frac{p \text{ CO}_2 + p \text{ CO}}{p \text{ CO}_2 + p \text{ CO} + p \text{ CH}_4} = 94.74 \text{ per cent. of oxygen combined with}$$

$$\text{methane, and } \frac{p \text{ CH}_4}{p \text{ CO}_2 + p \text{ CO} + p \text{ CH}_4} = 5.26 \text{ per cent. of oxygen}$$

combined with hydrogen; and from experiment 17, calculated in the same manner, the corresponding values are 95.6 and 4.4. The identity of our results with those recorded by Bone indicates that we have correctly followed the method of calculation he used.*

The calculations themselves are open to criticism on the score that the results of them cannot but be inaccurate because, (1) the experimental mixtures rarely contained methane and oxygen in exactly equimolecular proportions, and (2) owing to experimental error, the sum of the partial pressures of carbon dioxide, carbon

* Our calculations give the same results as those recorded in the paper in 15 out of the 17 experiments performed in Bomb A. The calculations from the experiments performed in Bomb B (9 in number) were apparently made directly from the unburnt methane, and not, as in the experiments with Bomb A, indirectly from the other products of combustion.

monoxide, and methane after explosion does not balance the partial pressure of methane in the unexploded mixture. In all but one of the twenty-six experiments of the series under discussion, more carbon compounds appear in the products of combustion than can be accounted for by the original methane; sometimes much more, as in experiment No. 23, in which 12.1 atmospheres of methane produced 14.15 atmospheres of carbon compounds.

We are primarily concerned, however, with the theoretical basis for the calculations, which causes Bone to believe that they disclose the manner in which oxygen divides itself between methane and hydrogen "during the extremely short period of actual combustion." It can be accepted as most probable that the primary oxidation of methane involves the reactions $\text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_2(\text{OH})_2 \rightarrow \text{CO} + \text{H}_2 + \text{H}_2\text{O}$. It is doubtful, however, whether this must needs be the only primary reaction. There is evidence from experiments recorded elsewhere in Bone's paper (Table III), that when methane is exploded with less than its own quantity of oxygen, more methane burns than can be accounted for by the reactions $\text{CH}_4 + \text{O}_2 \rightarrow \text{CO} + \text{H}_2 + \text{H}_2\text{O}$. Bone himself admits the possibility of the primary reaction $\text{CH}_4 + \text{O} \rightarrow \text{CH}_3(\text{OH})$ taking place when mixtures of methane and oxygen in which the methane is in excess are exploded; the possibility of this reaction occurring when the excess methane is replaced by hydrogen must also be admitted.

If this does happen, and there is no proof that it does not, then the sum of the partial pressures of carbon monoxide and carbon dioxide found in the products of combustion does not give a direct measure of the partial pressure of the oxygen used by the methane, for they have not resulted solely from the interaction of equimolecular proportions of methane and oxygen.

We therefore cannot accept the suggestion that Bone's experiments of necessity afford a measure of the "division of the oxygen between the methane and hydrogen during the extremely short period of actual combustion (that is, direct oxidation)." Even if they did, which we do not admit, we cannot understand why Bone should conclude that a measure of the "relative affinities" of methane and hydrogen for oxygen is thereby obtained.

The reactions taking place during "the extremely short period of actual combustion" presumably are not instantaneous. They have a finite speed, and that speed will be dependent on the temperature at which they take place. It cannot be assumed that the reactions proceed at one fixed temperature. As Dixon has pointed out in his study of the combustion of mixtures of carbon monoxide and hydrogen (*Phil. Trans.*, 1884, **175**, 623), not only is the tem-

perature at which the reactions in a given "layer" of a gas mixture are taking place altering continuously, but the composition of the mixture is also altering as the reactions proceed, so that "the final division of the oxygen represents the sum or net result of its dividing itself between the two combustible gases in a series of different ratios during a series of successive moments."

In our view, the results of Bone's experiments follow as a natural consequence of the law of speeds of flame in complex gaseous mixtures as exemplified in the present paper. When a mixture of methane, hydrogen, and oxygen, the oxygen being in defect, is inflamed, the methane must of necessity combine with the major portion of the oxygen because the methane-oxygen association that is required to yield the same speed of flame as the hydrogen-oxygen association is the richer in oxygen.

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