CIII.—*The Burning of Carbon Disulphide. Part II. The Velocity of the Uniform Movement of Flame in Carbon Disulphide–Second Combustible–Air Mixtures.*

By Albert Greville White.

In previous communications (J., 1922, **121**, 2561; 1927, 793) the author has shown that near the limits for the propagation of flame the burning of carbon disulphide is markedly hindered by the presence of any one of a large number of other combustibles, and has suggested that the limit combustion of carbon disulphide is catalysed, probably by some product of its combustion. The abnormal behaviour exhibited by the disulphide is now shown to extend throughout the whole range of inflammable carbon disulphide–air mixtures.

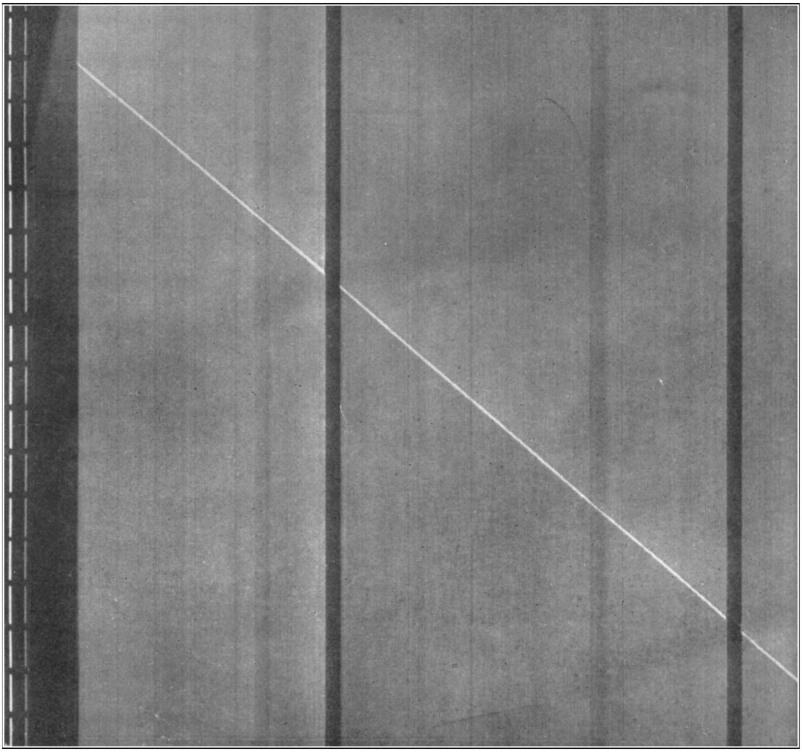
The experimental method employed was to determine the velocity of the uniform movement of flame that often occurs when a quiescent inflammable gas–air mixture is ignited at the open end of a long, horizontal, uniform, cylindrical tube closed at the other end. This glass tube was 2·5 cm. in internal diameter and generally 3·9 m. long, but for certain determinations shorter tubes were used. The purification of the materials and the method of making up the gas mixtures have been described in former communications. The mixtures were made up in separate vessels, and always contained approximately 1·0% of water vapour. The firing tube was filled by displacement, the amount of gas used being always at least 6 times the volume of the tube. Ignition was by means of a gas flame of standard size at a flanged joint from which a cap was gently removed immediately before ignition. The actual flame-speed determination was carried out by a novel photographic method which will be fully described in connexion with the work for which it was evolved. In this the firing tube was traversed by an approximately parallel beam of light falling on a photographic plate or film moving at a known speed. The interception of light by the moving flame was shown on the photographic record by a line of which the inclination to the vertical gave a measure of the speed of the flame. A falling-plate camera made by the Cambridge Instrument Co. was used for most of the work. A powerful source of light was essential for the more actinic flames, particularly those containing about 8% of carbon disulphide in air : a 500-c. p. Pointolite lamp was found to be quite suitable. The type of record obtained is shown in Fig. 1.

For most of the mixtures examined duplicate experiments gave results agreeing to about 1%. Mixtures containing from 7 to 12% of the disulphide in air, however, occasionally gave flame speeds 20% or even more below the values normally obtained, whilst high values were also encountered on rare occasions. For these mixtures the results given are not the mean of all those obtained, but the values around which most of the results appeared to be grouped. One record indicated that the speed of an 8% mixture of carbon disulphide in air had changed while being photographed, and suddenly dropped to about 80% of its original value. An occasional mixture exhibited no real uniformity of flame movement at all, although, so far as was known, no change had been made in the experimental conditions. Instances of this were infrequent, but when they occurred it could often be observed that the flame was subdividing, so that one portion remained behind or even went backwards on occasion. All percentage figures given refer to % by vol.

Carbon Disulphide–Air Mixtures.

The speeds of flame normally given by carbon disulphide–air mixtures are shown in Table I and, for mixtures containing up to 20% of the disulphide, in Fig. 2. The maximum speed of flame observed was greater than that given by hydrocarbons of the paraffin series, but considerably below that given by acetylene or hydrogen. The maximum flame speed is given by a mixture containing approximately 8% of carbon disulphide, whereas the mixture for perfect combustion contains nearly 6·5%. In its general form the curve shown in Fig. 2 is similar to that given by another endothermic compound, *viz.*, acetylene. It was not con-

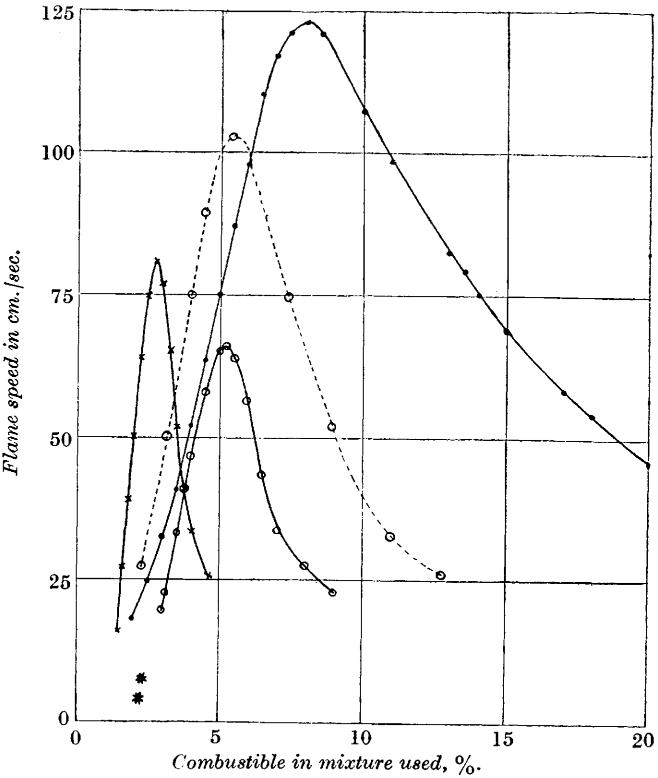
FIG. 1.



Photographic record for $4{\cdot}5\%$ CS_2 *in air.*

tinued to the upper limit owing to the fact that a mixture saturated with the disulphide at the laboratory temperature still propagated flame.

Fig. 2.



Flame speeds for various gas–air mixtures.

* *and* —●—●—●— *Carbon disulphide.*
-×-×-×-×- *Light petroleum.*
-⊖-⊖-⊖-⊖- $3CS_2 + 1$ *light petroleum* (*determined*)
- - o - - - o - - $3CS_2 + 1$ *light petroleum* (*calculated*).

Whilst examining mixtures near the lower limit it was discovered that certain mixtures could propagate flame with either one or other of two widely differing speeds. It has been shown by Bone (*Proc. Roy. Soc.*, 1927, *A*, **114**, 402) that one gas mixture may give speeds of uniform movement of flame differing by as much as 50% in consecutive experiments, and somewhat similar results have been obtained in this work by using carbon disulphide mixtures of fastest speed of flame. In those experiments, however, no means was found of *controlling* the speed to be given by any mixture. In the experi-

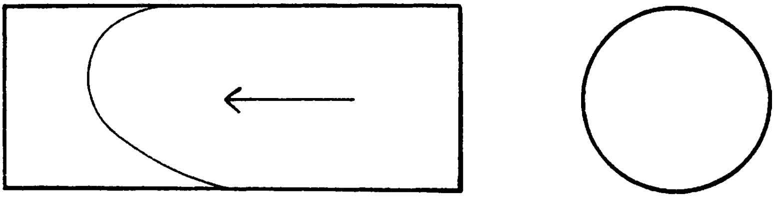
TABLE I.

Speed of uniform movement of flame in carbon disulphide–air mixtures in 2·5 cm. tubes. Original temperature of mixture 17° ± 4°.

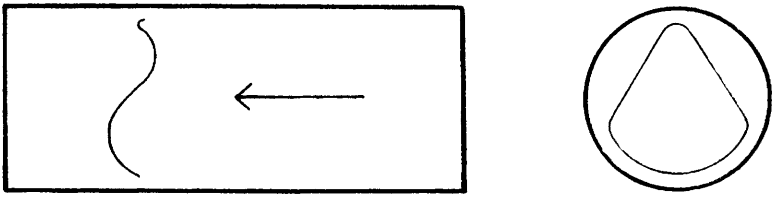
% CS$_2$ in mixture.	Flame speed (cm./sec.).	% CS$_2$ in mixture.	Flame speed (cm./sec.).	% CS$_2$ in mixture.	Flame speed (cm./sec.).
2·00	18·1	5·50	87·0	14·0	74·9
2·10	19·2	6·00	97·8	15·0	68·6
2·15	20·0	6·50	110	17·0	58·1
2·20	21·0 (4·0)	7·00	117	18·0	54·0
2·30	21·8 (7·4)	7·50	121	20·0	45·6
2·50	24·8	8·00	123	25·0	34·5
3·00	32·4	8·50	121	26·0	32·7
3·50	40·6	10·0	107	30·0	27·2
4·00	52·1	11·0	98·2	35·0	23·5
4·50	63·5	13·0	82·4	40·0	21·6
5·00	74·9	13·5	79·1		

The figures in brackets show the speed of a different type of combustion in the same mixture.

FIG. 3.



Normal flame.



Slow (cool) flame.

The two flame types shown by certain carbon disulphide–air mixtures.

ments now being considered, the speed always corresponded fairly closely to one of two values, and the flame could be made to travel with the higher or lower speed at will by varying the means of ignition. Given powerful ignition, the speed of flame was that shown by the full curve in Fig. 2, but with weak ignition the values shown by asterisks were obtained. For a 2·20% mixture one of the speeds is more than 5 times the value of the other. The two flames differed considerably in appearance, as indicated in Fig. 3. The phenomenon could only be observed with a very limited range of mixtures, for with a disulphide content below 2·20% the low-speed flame could not propagate, whilst from 2·35% upwards it appeared to be unstable, changing more or less rapidly into the form giving a higher speed, and at the same time increasing in velocity. The low-velocity flame only occupied a part of the cross-section of the tube, and only burnt a relatively small quantity of the gas mixture. These observations indicate that the passage of a flame through a gas may not be the invariable process it is sometimes assumed to be, and add another to the list of examples of gas mixtures in which the value of the limit obtained depends upon the type of ignition utilised. Another curious observation was made with a mixture containing approximately 43% of the disulphide—in this case the flame travelled along the top of the tube towards the closed end and then returned to the open end as a slower flame filling the whole tube.

Carbon Disulphide–Second Combustible–Air Mixtures.

The effect of other combustibles on the burning of carbon disulphide was originally tested by determining the speed of flame in a mixture containing 4·5% of carbon disulphide in air of which a portion was progressively replaced by various combustibles. The speeds of flame obtained in these circumstances are shown in Table II and in Fig. 4. These at once show that the abnormal burning of the disulphide is not confined to mixtures near the limit, since for the four combustibles tested the speed curves fall below that for added disulphide, whilst for three out of the four a portion of the curve falls below the speed of the original disulphide mixture.

TABLE II.

Showing the effect of replacing some of the air in a mixture containing 4·5% of carbon disulphide in air by various other combustibles. All mixtures contain sufficient oxygen for complete combustion to CO_2, SO_2, and water.

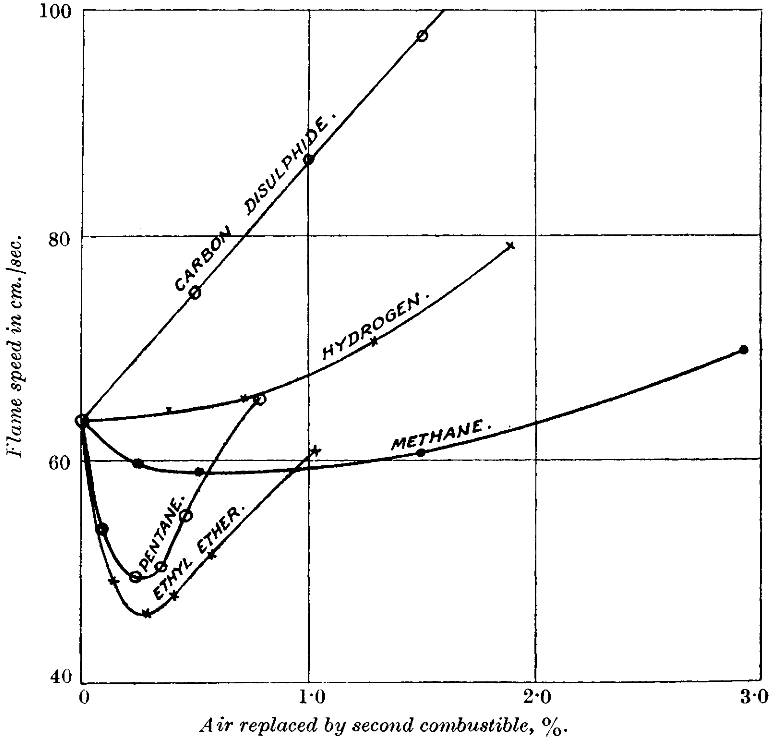
Original temperature of mixtures 17° ± 3°.

Combustible substituted for air.	Flame speed (cm./sec.).	Combustible substituted for air.	Flame speed (cm./sec.).
None	63·5	None	63·5
0·25% of methane ...	59·7	0·39% of hydrogen ...	64·4
0·50% ,, ,, ...	58·9	0·71% ,, ,, ...	65·4
1·50% ,, ,, ...	60·6	1·29% ,, ,, ...	70·5
2·93% ,, ,, ...	69·6	1·90% ,, ,, ...	79·2
0·084% of *n*-pentane	53·7	0·135% of ethyl ether	49·1
0·23% ,, ,,	49·6	0·27% ,, ,,	46·3
0·37% ,, ,,	50·4	0·40% ,, ,,	47·9
0·455% ,, ,,	55·1	0·57% ,, ,,	51·4
0·78% ,, ,,	65·5	1·03% ,, ,,	60·8

The results in Fig. 4 do not enable us to make a sound comparison of the effect of various other combustibles on the burning of the disulphide, for they are affected both by the intrinsic speed value of the added combustible and by its oxygen requirements. The first of these factors is generally the more important. Its effect can be eliminated by mixing carbon disulphide–air mixtures with those of air and a second combustible having the same speed of flame, both mixtures having either an excess or a deficit of oxygen. The results of some of the experiments carried out on these lines are in Table III, together with the results obtained by mixing gas or vapour–air mixtures containing just sufficient oxygen for perfect combustion.

Fig. 4.

Showing the effect of replacing some of the air in a 4·5% mixture of carbon disulphide in air by other combustibles.



The results of the first series are shown graphically in Figs. 5 and 6. These indicate that for mixtures containing carbon disulphide and air : (1) complex mixtures have lower flame speeds than mixtures

TABLE III.

Showing the speeds of flame in cm./sec. given by mixtures obtained by mixing two primary mixtures A and B in various proportions.

Original temperature of mixtures 16° ± 3°.

A =		5·2% CS_2	4·5% CS_2	4·25% CS_2	4·25% CS_2	4·25% CS_2	3·5% CS_2	2·95% CS_2
B =		4·3% C_2H_2	9·0% CH_4	3·86% C_2H_2	3·35% Et_2O	2·29% $n\text{-}C_5H_{12}$	7·35% CH_4	6·6% CH_4
% A.	% B.							
100	0	80·3	63·5	57·9	57·7	57·7	40·6	31·2
95	5				39·3	37·2		23·5
92	8							19·5
90	10	70·8	46·4	44·8	33·1	33·0	27·4	no prop.
80	20				30·8		18·2	,,
75	25	64·7	40·2	37·5	30·6	30·8		
70	30						no prop.	
65	35		39·5					,,
60	40			38·4			,,	,,
50	50	62·7	42·5	41·0	34·9	36·8	21·8	
40	60		46·6	43·6		40·2	24·5	
35	65							,,
30	70							19·5
25	75	68·4	53·1	49·6	45·3	46·4		
20	80							23·0
15	85		57·1		50·4	51·2		
10	90						36·5	
0	100	79·8	63·5	58·5	58·1	58·0	40·5	31·0

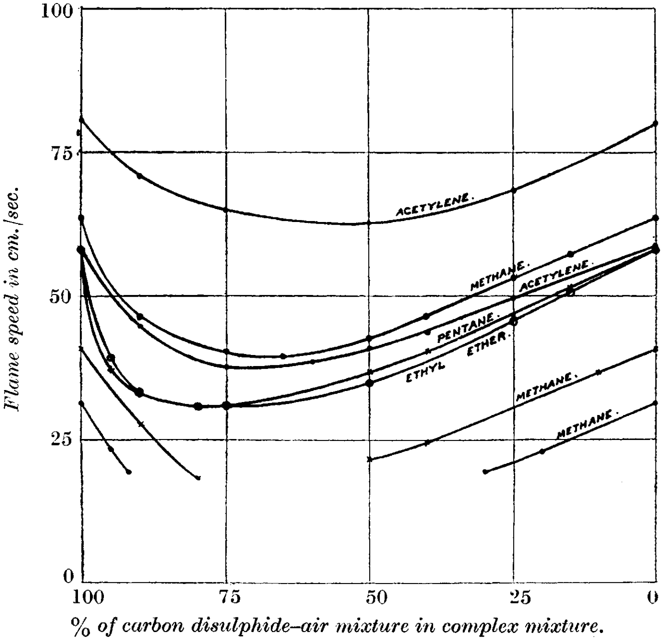
A =		14% CS_2	16·4% CS_2	19% CS_2	23·6% CS_2	6·48% CS_2	6·48% CS_2
B =		3·25% $n\text{-}C_5H_{12}$	10·7% CH_4	11·5% CH_4	12·17% CH_4	9·41% CH_4	2·53% $n\text{-}C_5H_{12}$
% A.	% B.						
100	0	74·6	61·4	49·8	37·0	109	109
95	5	47·2					
85	15	34·6				85·8	
80	20				27·7		
75	25	31·8	35·9	31·9			66·9
70	30				25·0		
69	31					69·6	65·5
50	50	28·8	26·3	24·4	21·6	57·5	60·8
40	60	29·1			19·7		60·6
35	65					57·6	
30	70				no prop.		
25	75	34·4	23·0	20·5		58·0	61·4
15	85	48·3				58·9	
10	90	58·0	27·5	20·8	no prop.		
5	95		38·5	25·5	20·3		
2·5	97·5				23·9		
0	100	74·9	61·0	50·1	37·2	66·0	70·5

containing only one combustible; (2) this effect appears to be rather more pronounced for mixtures containing a deficit of oxygen. For mixtures containing excess of oxygen the effect is best seen when the disulphide–air mixture is in excess, but with deficit of oxygen methane–air mixtures give the lowest speeds when the amount of added disulphide–air is small.

The curves shown for the blending of primary mixtures having flame speeds of about 58 cm./sec. are interesting. For mixtures containing little but carbon disulphide–air, the pentane curve shows lower speeds than that for ethyl ether, whilst the opposite appears to be the case when the complex mixture contains less than 75% of the disulphide–air. This appears to be due to the fact that, whereas pentane hinders the burning of the disulphide more than ether under these conditions, the pentane mixture contains an excess of oxygen, and the ether mixture is balanced for perfect combustion.

Fig. 5.

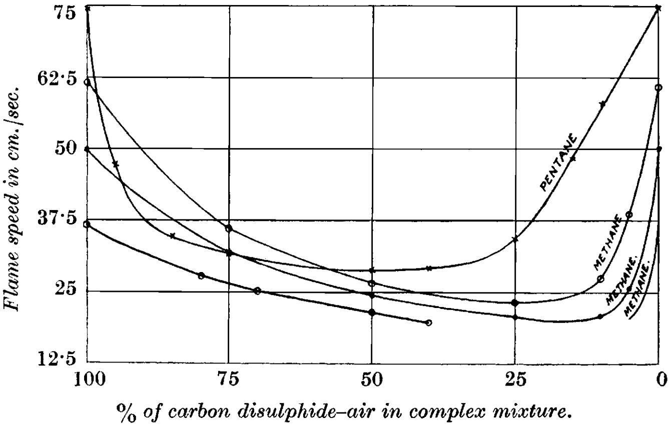
Flame speeds of mixtures obtained by blending CS_2*–air mixtures containing excess oxygen with similar mixtures of other combustibles of the same flame speed.*



The sensitiveness of carbon disulphide mixtures to oxygen content at the lower limit has been emphasised in a previous communication (*loc. cit.*). Experiments still proceeding show that carbon disulphide mixtures appear to be abnormally sensitive to the oxygen content of the mixture. Thus the replacement of 20% of the nitrogen in a 4·5% mixture of the disulphide in air by oxygen caused an increase in flame speed very much greater than that caused in a methane–air mixture of similar oxygen excess under the same conditions. This also explains the relatively small lowering of flame speed caused by the acetylene–air mixture, which contains almost twice as much oxygen as is required for complete combustion. The order of effectiveness of the substances here considered in hindering the burning of carbon disulphide would appear to be : *n*-pentane, ethyl ether, acetylene, methane. This agrees well enough with the author's list for effectiveness in hindering propagation at the lower limit, but disagrees with Dixon's order for effectiveness in raising the ignition temperature of carbon disulphide mixtures, which showed acetylene as being far more effective than ethyl ether (*Rec. trav. chim.*, 1925, **44**, 305). This is possibly due to the fact that Dixon dealt largely with the preliminary phosphorescent combustion of carbon disulphide, a phenomenon far more closely allied to the slow " cool " flames discussed on p. 754 than to the ordinary burning of carbon disulphide, whether at the limit or not. It has been mentioned that these cool flames give rise to ordinary flames under certain conditions. It appears possible that under limiting temperature conditions the slow ignition of carbon disulphide–air or –oxygen mixtures would generally take place through this cool flame, in which the reactions probably differ considerably from those in the ordinary flame.

FIG. 6.

Flame speeds of mixtures obtained by blending CS_2*–air mixtures having a deficit of oxygen with similar mixtures of other combustibles of the same flame speed.*



Carbon Disulphide Mixtures and the Law of Flame Speeds.

Payman and Wheeler have enunciated a generalisation which they have called the " Law of Flame Speeds," and have deduced from it conclusions which, if true, would be of the greatest importance. This law states : " If a complex mixture is made by blending a number of mixtures of air with simple combustible gases all of which have the same speed of uniform movement of flame, then this complex mixture will also have the same speed of flame provided that all the mixtures are of the same type, all containing excess of oxygen or all containing excess of inflammable gas " (*Trans. Faraday Soc.*, 1926, **22**, 304). It is asserted that, by a slight extension of this, all flame speeds in complex mixtures may be calculated from those in mixtures containing only single combustible gases. Le Chatelier's rule for limit mixtures is stated to be a special case of this law (*loc. cit.*, p. 322), and it is also stated that examination of the exceptions to the Le Chatelier formula shows that the limiting speed of one of the inflammable gases is abnormally low. This does not appear to be necessarily so, for the limiting speed for carbon disulphide in air at the lower limit is seen to be the fairly normal value of 18·1 cm./sec., a figure identical with that quoted by Payman for ethane (J., 1919, **115**, 1444); yet in papers previously cited it has been shown that, although carbon disulphide was tested with 15 different combustibles, in no single instance did the mixtures follow Le Chatelier's rule. On the other hand, Payman and Wheeler (*ibid.*, p. 39) give the lower limiting speeds for hydrogen and methane in 9 mm. tubes as 8·3 and 32·6 cm./sec. respectively, and the observed lower limit is quoted as identical with that calculated. It thus appears likely that it is not the limiting speed, but the *type* of combustion occurring at the limit that determines whether a given pair of mixtures obeys Le Chatelier's rule or not.

Bone (*loc. cit.*, p. 420) has criticised some of the experimental work on which the law of speeds is based, and states, with reference to his own experimental work : " In none of the series have the requirements of the supposed ' law ' been fulfilled. . . ." He concludes that Payman and Wheeler's generalisation is not generally applicable to gaseous explosions.

The results in Figs. 5 and 6 form an excellent test of the applicability of the law to combustible–air mixtures containing carbon disulphide. Had the law held, all the curves shown there would have consisted of straight lines joining the speed values for the primary gas mixtures. The speeds of the complex mixtures are seen to be often less than one-half of their calculated values, and by blending primary mixtures of flame speeds less than about 40 cm./sec. it is generally possible to obtain mixtures that cannot propagate flame. The perfect combustion mixtures (last two mixtures of Table III) also give results at variance with speed-law predictions. A final test of the utility of the speed law in connexion with carbon disulphide was made when a complete speed–percentage composition curve was determined for air mixtures containing 3 vols. of carbon disulphide to one of light petroleum as combustible. The results are in Table IV (where L.P. denotes light petroleum) together with similar determinations for light petroleum–air. The results calculated from the light petroleum–air and carbon disulphide–air results by speed-law methods are also given for comparison with those interpolated from the experimental speed–percentage curve. The calculated results are seen to be very different from the experimental values—the error is often over 100%—and an examination of Fig. 2, where the values are plotted for comparison with those of carbon disulphide, shows that the speed law is not applicable to carbon disulphide–air mixtures. As stated by the author (*Nature*, 1927, **119**, 51), the law of speeds must break down when one of the combustibles in a complex mixture interferes with the burning of another. Such interference is certainly partly responsible for the failure of the law of speeds in the case of carbon disulphide.

TABLE IV.

Showing the flame speeds in cm./sec. in mixtures of air with (*a*) light petroleum (L.P.) and with (*b*) a combustible consisting of 1 vol. of light petroleum to 3 vols. of carbon disulphide (gaseous); also (*c*) the speed-law results for the second series compared with interpolated values.

Original temperature of mixtures, 15° ± 2°.

(*a*)		(*b*)		(*c*)		
					Flame speed,	
% L.P.	Flame speed.	% of $3CS_2$ +1 L.P.	Flame speed (determined).	% of $3CS_2$ +1 L.P.	interpolated.	calc. from speed law.
1·45	15·8	3·0	19·5	2·28	—	27·1
1·60	27·1	3·1	22·6	3·15	24·0	50·0
1·70	33·0	3·5	33·1	4·00	46·6	74·8
1·75	36·1	4·0	46·6	4·48	57·4	89·3
1·80	39·0	4·5	57·8	5·43	64·5	103
2·00	50·0	5·0	65·1	7·37	30·4	74·5
2·25	63·7	5·2	66·0	8·93	23·0	51·8
2·50	74·8	5·5	63·7	10·98	—	32·7
2·75	80·8	6·0	56·4	12·75	—	25·8
3·00	76·9	6·5	43·5			
3·25	65·3	7·0	33·6			
3·50	51·8	8·0	27·6			
3·75	41·0	9·0	22·7			
4·00	33·3					
4·60	25·8					

The light petroleum curve in Fig. 2 brings out a defect in the enunciation of the law of speeds. The position of the mixture for perfect combustion (containing 2·32% of the combustible) lies on the straight portion of the curve to the origin side of the maximum.

By blending two mixtures of equal speed, both deficient in oxygen but corresponding to two points one on each side of the maximum, in any proportion whatsoever, the resulting mixture must show a higher flame speed. In the case of light petroleum, this increase may amount to 20% of the value of the speed of the primary mixtures. Again, when one of these primary mixtures is blended with an oxygen-deficient mixture of the same speed containing another combustible, the speed of the blended mixture will evidently depend on which of the two available light petroleum mixtures has been used.

It has previously been shown that at the lower limit, in particular, the effect caused by adding a second combustible to carbon disulphide reached a maximum, after which the vapour behaved quite normally and gave results corresponding closely to those expected from its calorific value. A similar effect can be traced when other combustible–air mixtures are added progressively to those of carbon disulphide. For example (considering the 58 cm./sec.-mixture curves in Fig. 5), the first effect of the added mixture is to cause a pronounced fall in speed, but this effect decreases as more of the second mixture is added, and ultimately gives place to a steady rise to the speed value of the second mixture. The straight portion on the right of the curve becomes less pronounced for mixtures of higher speeds and could hardly be distinguished for the perfect combustion mixtures. It is shown clearly by only one of the curves for mixtures deficient in oxygen. Its presence in those for medium speed mixtures having an oxygen excess, however, indicates that the second combustible has practically attained a steady maximum effect in hindering the burning of the disulphide, and the slope of the line indicates that the disulphide mixtures are behaving as if they possessed a far lower flame speed than that experimentally determined for them. A rough idea of the effective speed of these mixtures in the presence of an excess of another combustible can probably be obtained by producing the sloping straight line to cut the 100% carbon disulphide mixture axis. When this is done, it seems that in the presence of excess of methane mixture having the same flame speed, the disulphide mixture, having a flame speed of 63·5 cm./sec. when burning alone, behaves as if its flame speed were about 21 cm./sec., whereas under similar conditions, one having a speed of 40·6 cm./sec. behaves as if its flame speed were zero. These figures, however, can have little absolute significance, for what may be termed the effective speed in complex mixtures of the 58 cm./sec. carbon disulphide–air mixture seems to vary from about 7 to about 21 cm./sec., depending upon whether the inhibiting combustible is ethyl ether or acetylene. This difference is almost certainly due to the great difference in oxygen content between the two mixtures of these combustibles used. The abnormal sensitiveness of the speed of flame in carbon disulphide mixtures to changes in their oxygen content supplies a second cogent reason for the non-applicability of the speed law to mixtures containing carbon disulphide, and the fact that certain mixtures propagate stable flames at uniform, but widely different, speeds rather tends to discount any law based on flame speeds alone.

The results obtained make it fairly certain that the burning of carbon disulphide in air is catalysed, probably by some product of its combustion, and that this catalysis is inhibited by the presence of material quantities of any one of a large number of other combustibles. It is hoped to extend this work to detonation phenomena in carbon disulphide mixtures.

Summary.

(1) Flame-speed determinations under uniform movement conditions have been made for carbon disulphide–air and carbon disulphide–second combustible–air mixtures.

(2) Certain carbon disulphide–air mixtures have two widely differing flame speeds producible at will by varying the conditions of ignition. These two types of flame, cool and ordinary, give different lower limits.

(3) The presence of certain other combustibles hinders the burning of carbon disulphide in air throughout its propagation range.

(4) Flame speeds in dilute carbon disulphide–air mixtures are far more sensitive to oxygen content than in similar mixtures of normal combustibles.

(5) The law of flame speeds is not applicable to mixtures containing carbon disulphide.

(6) It is concluded that the normal burning of carbon disulphide in air is catalysed.

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