CXVI.—*The Burning of Carbon Disulphide near the Limit for the Propagation of Flame, with some Remarks on the Ignition Point of Sulphur.*

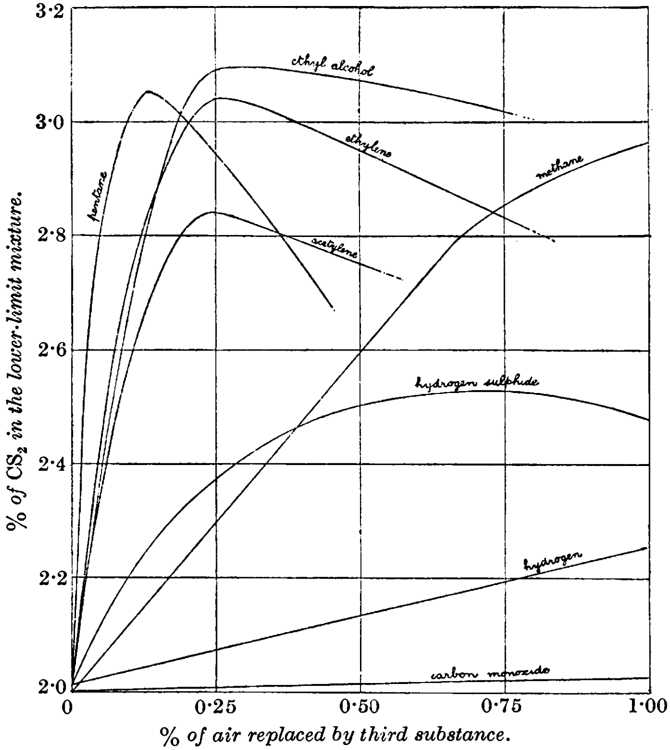
By ALBERT GREVILLE WHITE.

IN a communication on limits for the propagation of flame in mixtures containing air and more than one vapour (J., 1922, **121**, 2561), it was shown that the addition of small quantities of the vapour of ethyl ether, benzene, acetone, or acetaldehyde to carbon disulphide–air caused a pronounced contraction of the propagation range. This was most noticeable at the lower limit, where very small quantities of added vapour *increased* considerably the amount of disulphide present at the limit, although the addition of larger quantities of the vapours reduced the amount of disulphide necessary to give a limit mixture. It was thus found possible to divide the propagation range into two parts, giving four limits instead of the normal two. A similar division for ethyl ether–air is described in the same communication, but this phenomenon relates to the upper limit, near which ether–air mixtures can often propagate a cool flame. It was presumed that propagation at the limit in carbon disulphide–air was catalysed by some product of the combustion, but that this catalysis was inhibited by certain vapours, although not appreciably affected by similar quantities of carbon monoxide, dioxide, or tetrachloride, or of hydrogen.

Phenomena apparently connected with the above were reported on the ignition point of carbon disulphide mixtures by Frankland (*Chem. News*, 1862, **6**, 3), whose work has recently been extended by Dixon (*Rec. trav. chim.*, 1925, **44**, 305), and by Delépine (*Bull. Soc. chim.*, 1922, **31**, 762) for the spontaneous oxidation of certain sulphur compounds in air. Dixon suggests that carbon monosulphide catalyses the phosphorescent combustion of the disulphide, and that the inhibitors act by condensing on the surface of the monosulphide. Delépine found that certain compounds in which sulphur was doubly bound to carbon or phosphorus oxidised in air at the ordinary temperature. This oxidation was apparently stopped by the products of the reaction, and was markedly hindered by traces of ethyl ether or acetaldehyde, and to some extent by ethyl alcohol and benzene. It was promoted by fixed alkali or ammonia, and also by the lower saturated aliphatic acids. He favoured an explanation similar to that advanced by Moureu and Dufraisse to account for the behaviour of " antioxygens " in autoxidation (J., 1925, **127**, 1), in which the compound first produced is assumed to be a peroxide.

FIG. 1.

Showing the value of the lower limit for carbon disulphide–air when part of the air is replaced by a third substance.



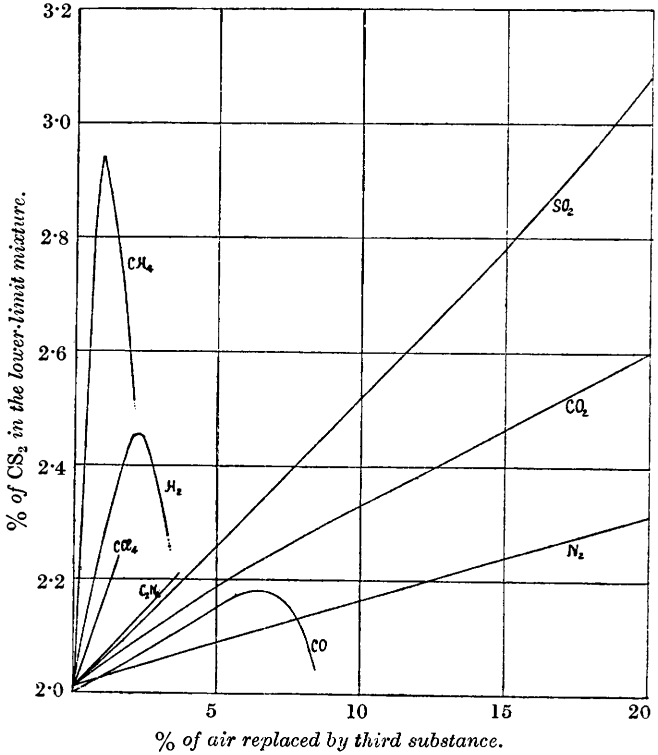
The present work consists largely of an extension of the former results. All limits were determined for downward propagation at the ordinary temperature and pressure in glass tubes 5 cm. in diameter and 150 cm. long. The preparation and ignition of the mixtures were carried out as previously described (J., 1922, **121**, 1244, 2561; 1924, **125**, 2387). Tables I and II show the limits for the propagation of flame in mixtures of various gases and vapours with carbon disulphide and air. All are lower limits except in the one case specified. Compositions are given in percentages by volume.

The calculated limits are those given by Le Chatelier's rule, assuming the values 4·0% and 12·0% for the carbon disulphide limits. The results are shown graphically in Figs. 1 and 2.

The two combustibles present sometimes appeared to burn separately, as two flames were obtained touching only near the axis of the tube. This was well marked for a mixture of carbon monoxide, carbon disulphide, and air containing 7·9% of the monoxide.

FIG. 2.

Showing the value of the lower limit for carbon disulphide–air when part of the air is replaced by a third substance.



The present results are in general agreement with former work, and indicate that the addition of a small quantity of a large variety of substances raises the value of the lower limit for carbon disulphide–air. The large difference formerly noted between the behaviour of gases and that of certain vapours is now seen to have been due in part to the choice of gases, and in part to the small quantities of these that were used. The added substances appear

TABLE I.

Original temperature of mixtures, 15° ± 3°.

Combustible mixture.			Limit (calc.).	Error %.
H_2.	CS_2.	Both.		
—	2·01	2·01		
0·30	2·08	2·38		
0·70	2·18	2·88		
1·31	2·32	3·63		
1·90	2·43	4·33		
2·44	2·45	4·89	5·54.	+13
4·10	2·05	6·15	6·35	+ 3
5·15	1·71	6·86	6·86	0
5·81	1·45	7·26	7·20	− 1
7·49	0·74	8·23	8·09	− 2
9·0	—	9·0		
CO.	CS_2.	Both.		
—	2·00	2·00		
0·95	2·02	2·97		
2·00	2·05	4·05		
4·00	2·11	6·11		
5·60	2·17	7·77	8·6	+11
7·90	2·12	10·0	9·7	− 3
9·1	1·80	10·9	10·6	− 3
10·4	1·33	11·7	11·8	+ 1
11·8	1·00	12·8	12·8	0
13·8	0·50	14·3	14·2	− 1
15·7	—	15·7		
C_2H_4.	CS_2.	Both.		
—	2·01	2·01		
0·04	2·36	2·40		
0·07	2·58	2·65		
0·16	2·92	3·08		
0·25	3·04	3·29		
0·32	3·00	3·32		
0·43	2·99	3·42	3·92	+15
0·96	2·70	3·66	3·83	+ 4
1·54	2·16	3·70	3·74	+ 1
2·23	1·38	3·61	3·62	0
2·72	0·80	3·52	3·54	+ 1
3·42	—	3·42		
EtOH.	CS_2.	Both.		
—	2·01	2·01		
0·06	2·42	2·48		
0·09	2·63	2·72		
0·10	2·65	2·75		
0·14	2·87	3·01		
0·25	3·09	3·34		
0·33	3·08	3·41		
0·46	3·08	3·54	3·99	+13
0·87	2·91	3·78	3·98	+ 5
1·58	2·36	3·94	3·96	+ 1
2·38	1·59	3·97	3·94	− 1
3·90	—	3·90		

Combustible mixture.			Limit (calc.).	Error %.
H_2.	CS_2.	Both.		
(Upper limit.)				
—	34·0	34·0		
3·18	28·6	31·8		
8·3	24·9	33·2		
18·8	18·8	37·6	20·7	−45
33·8	11·2	45·0	32·3	−28
46·4	5·1	51·5	48·8	− 5
74·0	—	74·0		
CH_4.	CS_2.	Both.		
—	2·00	2·00		
0·31	2·43	2·74		
0·65	2·77	3·42		
0·80	2·88	3·68		
0·94	2·94	3·88		
1·21	2·88	4·09	4·45	+ 9
1·58	2·75	4·33	4·58	+ 6
2·40	2·40	4·80	4·84	+ 1
3·08	2·02	5·10	5·05	− 1
4·75	1·02	5·77	5·59	− 3
6·12	—	6·12		
C_2H_2.	CS_2.	Both.		
—	2·01	2·01		
0·08	2·50	2·58		
0·23	2·84	3·07		
0·29	2·83	3·12		
0·42	2·78	3·20		
0·53	2·74	3·27	3·74	+14
1·26	2·02	3·28	3·44	+ 5
1·60	1·60	3·20	3·29	+ 3
2·23	0·74	2·97	3·03	+ 2
2·80	—	2·80		
H_2S.	CS_2.	Both.		
—	2·00	2·00		
0·11	2·22	2·33		
0·28	2·40	2·68		
0·56	2·51	3·07		
0·84	2·52	3·36	4·37	+30
1·22	2·43	3·65	4·51	+24
2·07	2·08	4·15	4·82	+16
2·69	1·79	4·48	5·02	+12
4·27	1·00	5·27	5·51	+ 5
6·05	—	6·05		
n-C_5H_{12}.	CS_2.	Both.		
—	2·01	2·01		
0·013	2·31	2·32		
0·05	2·81	2·86		
0·08	2·95	3·03		
0·13	3·05	3·18		
0·23	2·96	3·19	3·57	+13
0·46	2·67	3·13	3·20	+ 2
0·71	2·18	2·89	2·83	− 2
1·08	1·15	2·23	2·20	− 1
1·34	0·44	1·78	1·77	− 1
1·49	—	1·49		

TABLE II.

Original temperature of mixtures, 16° ± 3°.

N_2.	CS_2.	CO_2.	CS_2.	SO_2.	CS_2.	C_2N_2.	CS_2.	CCl_4.	CS_2.
—	2·01	—	2·01	—	2·01	—	2·01	—	2·01
3·8	2·07	4·0	2·15	1·8	2·09	1·9	2·11	0·75	2·12
7·6	2·13	6·0	2·22	5·5	2·28	3·0	2·16	1·6	2·24
14·2	2·23	8·0	2·28	10·0	2·52	3·7	2·21		
23·3	2·35	12·0	2·38	15·0	2·78				
40·9	2·63	20·0	2·60	20·0	3·08				

to function in three ways : (1) They alter the thermal constants of the mixture ; (2) they alter the percentage of oxygen in the mixture ; (3) they produce what may be termed a specific catalytic effect.

(1) The alteration of thermal constants would affect any mixture of air with a combustible, and is chiefly responsible for such phenomena as the greater extinguishing effect of carbon dioxide as compared with nitrogen.

(2) A small change in the oxygen content of a mixture usually causes only a small change in the lower limit except when the combustible : oxygen ratio is large, as when ammonia burns in air, or when much inert gas is used with a normal combustible. In the case of carbon disulphide (and, to a less extent, of hydrogen sulphide), however, this effect persists even when a large proportion of oxygen is present, as is seen from Table III. The difference between these substances and methane is illustrated in Fig. 3.

TABLE III.

Original temperature of mixture, 16° ± 3°.

% O_2 in mixture.	% CS_2 in lower-limit mixture.	% O_2 in mixture.	% H_2S in lower-limit mixture.
11·8	2·63	15·6	6·60
15·5	2·35	17·6	6·25
17·4	2·23	19·7	6·05
19·7	2·07	28·0	5·56
20·6	2·00	35·4	5·30
37·0	1·59	51·0	5·04
53·2	1·40	66·6	4·93
93·0	1·24		

Table IV shows that ether–carbon disulphide mixtures are similarly affected when 19·7% of oxygen is added. Here the magnitude

TABLE IV.

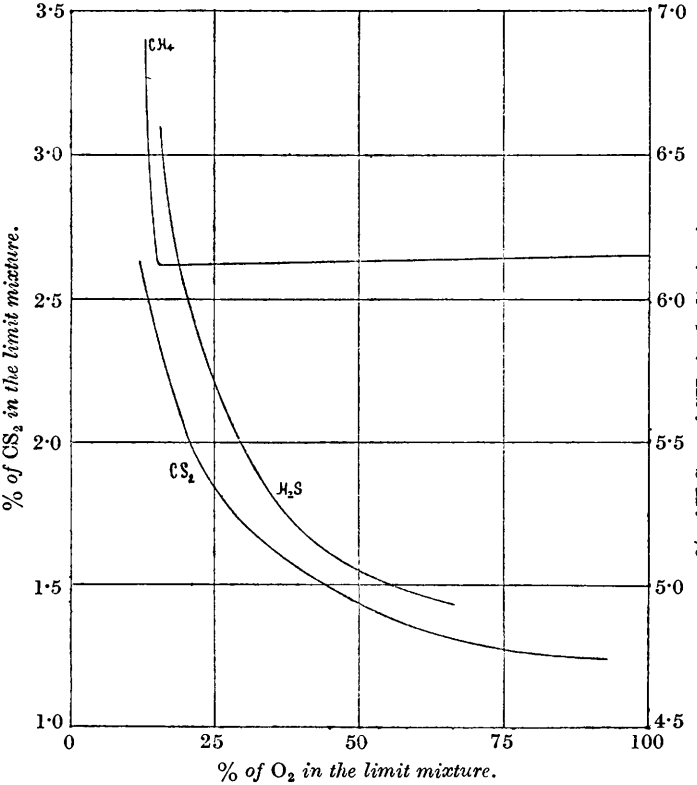
Original temperature of mixture, 15° ± 2°.

% CS_2 in combustible	100	98·5	95·0	85·0	75·0	50·0
% Ether in combustible	—	1·5	5·0	15·0	25·0	50·0
Limit in air	2·00	2·79	3·23	3·30	3·10	2·58
Limit when mixture contained 19·7% of added oxygen	1·61	2·36	2·88	2·98	2·84	2·42

of the effect decreases with decreasing proportion of disulphide, but it is still noticeable when the amount of ether is sufficient to inhibit the specific catalytic effect observed when small quantities of combustible vapours are added to carbon disulphide–air mixtures. This agrees with the fact that the addition of small quantities of several combustible substances to hydrogen sulphide–air was found to reduce the amount of hydrogen sulphide needed to give a limit mixture. This effect of oxygen content on the lower limit appears to be a property conferred by sulphur on certain of its compounds, but does not appear to be intimately connected with the catalytic effect originally observed.

FIG. 3.

Showing the effect of varying oxygen content on the value of the lower limit for carbon disulphide, hydrogen sulphide, and methane.



Except when oxygen is added, any change in the oxygen content of a mixture depends only on the volume of the material added, so that, volume for volume, all substances should produce equal effects from this cause. An upper limit to its value can be obtained from the results given by the addition of nitrogen, since the thermal constants of the mixture are hardly affected thereby. This effect is relatively small, and for most combustibles the rise in the lower limit is far greater than could be attributed to it, even when coupled with any change in the thermal constants of the mixture.

(3) The catalytic effect is the most important and varies tremendously from one substance to another. A comparison of the nitrogen figures with those for carbon monoxide and for cyanogen indicates that in both these cases the residual effect must be small, but for such substances as pentane and ethylene it is overwhelmingly great. This specific catalytic effect seems to be most pronounced for combustibles, although the difference found between carbon dioxide and sulphur dioxide indicates that the effect of the latter substance is greater than would be expected if due to its thermal properties alone. Carbon monoxide and cyanogen, which contain no hydrogen, behave almost as incombustibles; but the effect does not appear to be proportional to the amount of hydrogen in a compound, as may be seen by comparing the amounts of various substances needed to produce the same effect when small quantities are used. The order of efficacy of certain of those tested appears to be : Pentane and ethyl ether, acetaldehyde, ethylene, ethyl alcohol, acetylene, benzene, acetone, hydrogen sulphide, acetic acid, methane, hydrogen, cyanogen, carbon monoxide. This order suggests that ease of oxidation might prove to be an important factor. The relative positions of hydrogen and hydrogen sulphide also seem to point to the molecular nature of the effect, but the high thermal conductivity of hydrogen may be partly responsible for the small effect produced by this gas. Experiments with acetone and hydrogen showed that when used together they produced the effect to be expected from their behaviour when used separately.

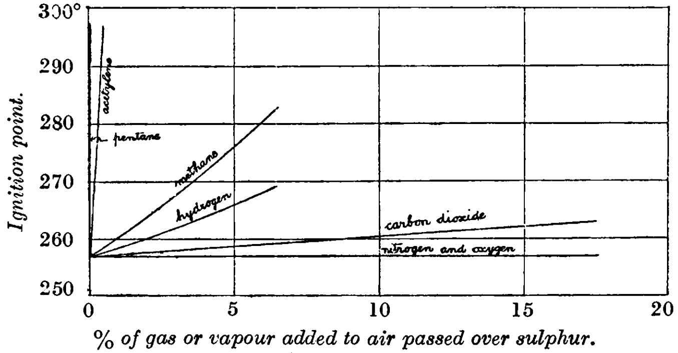
Table I shows that as small quantities of the air in a carbon disulphide–air mixture are progressively replaced by a second combustible, the increase in the amount of the disulphide needed to give a lower-limit mixture becomes smaller, until the amount of disulphide present ultimately reaches a maximum and then diminishes. The maximum is attained more quickly the greater the original effect of the second combustible. The calorific value of the limit mixture containing most carbon disulphide is generally 900—950 Cals., but for hydrogen, hydrogen sulphide, and acetylene the value found is considerably below this. These gases give lower-limit calorific values well below the normal 1100—1200 Cals. when used with air alone, so that the fall in the amount of carbon disulphide in the mixture probably sets in when the second combustible present begins to burn normally. After the amount of disulphide present has begun to diminish, the amounts of the two combustibles can be calculated approximately from Le Chatelier's rule, provided the value of the carbon disulphide lower limit be taken as 4·0%, and agreement with the rule generally becomes closer as the amount of disulphide diminishes. There is a similar tendency shown at the upper limit, but here it is not so well defined. At the lower limit, Le Chatelier's rule is followed fairly well over two-thirds or more of the range of mixtures, as measured by the amount of the second combustible present. In the presence of a minimum quantity of some other combustible, carbon disulphide behaves as though its calorific value at the lower limit was 1060 Cals., a value not very different from that normally found for vapours (J., 1922, **121**, 1244). It is important that this occurs even with carbon monoxide, which has such a very small effect in raising the value of the lower limit of the disulphide. When burning alone, carbon disulphide–air can propagate flame if the calorific value of the mixture exceeds 530 Cals. Carbon disulphide thus appears to possess two different modes of combustion, and there is no reason to doubt the explanation formerly advanced to explain the results then available, *viz.*, that the ordinary limit combustion of carbon disulphide is catalysed, probably by some product of its combustion, and that this catalysis is hindered by a large variety of substances. Of the gases known to be produced when the disulphide burns, the only one found to reduce the value of the limit was carbon oxysulphide, and this had an effect considerably less than that produced by an equal volume of the disulphide. The oxysulphide and oxygen were the only two substances tested which did not hinder the burning of carbon disulphide.

Dixon (*loc. cit.*) suggests that the product catalysing the ignition of carbon disulphide is the monosulphide of carbon. If this is the explanation of the limit results given by carbon disulphide, the phenomenon should be confined to substances containing both sulphur and carbon, such as the disulphide and oxysulphide of carbon. This idea is supported by the behaviour of hydrogen sulphide, which does not exhibit this phenomenon, whilst its lower limit is also calculable from the lower limit for hydrogen and the theoretical (calorific value) limit for sulphur. This might, however, be due to the large amount of hydrogen in the molecule.

To test the monosulphide theory it was decided to examine the effect of certain combustible substances on the ignition point of sulphur itself. To this end sulphur was heated in a glass tube 1·5 cm. in diameter. The temperature of the sulphur was taken by means of a thermometer immersed in it, whilst the necessary air for combustion was introduced by means of a side tube at the surface of the sulphur. The procedure adopted was to introduce a slow stream of air (or air containing the substance under test) through the side tube, after which the stream of gas was gradually cut off. Ignition then took place if the sulphur was just above its ignition point. For comparison, relative values of the ignition temperature of mixtures of 3% carbon disulphide–air with a third substance were determined by evacuating glass bulbs of 12—15 c.c. capacity, and then allowing the appropriate mixture to flow into the bulb. As the figures obtained have no absolute significance, the results are only shown graphically (Figs. 4 and 5), but small quantities of hydrogen sulphide also raised the ignition point of sulphur materially. There is a striking similarity between the general form of the two series of results, despite the greater magnitude of the rise produced in the case of carbon disulphide. The ignition of sulphur is materially hindered by small quantities of various substances, and is thus probably itself a catalysed phenomenon. The ignition and combustion of carbon disulphide may be catalysed by carbon monosulphide, but the occurrence of a somewhat similar phenomenon in the case of sulphur renders it extremely unlikely that the monosulphide is the sole catalysing agent.

Fig. 4.

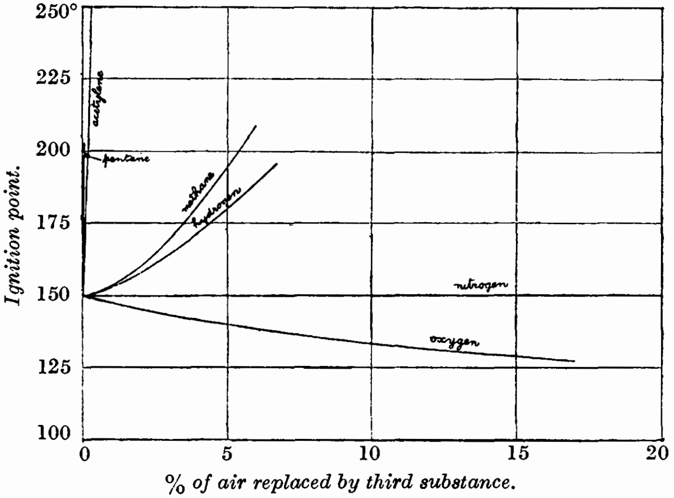
Showing the ignition point of sulphur when the air passed over it contains various substances.



Attention must be directed to certain differences between the results given by the present work and those found by Dixon. The order of efficacy of certain substances as gauged by their power of preventing the propagation of flame at the limit in carbon disulphide–air is given on p. 799. As regards their effect on the ignition of carbon disulphide, Dixon classes ethylene and acetylene as poisonous and pentane, carbon monoxide, methane, and ethyl ether as noxious, whilst hydrogen is grouped with carbon dioxide and nitrogen as inert. Delépine's work (*loc. cit.*) is probably not so closely connected with the present communication, but it is noteworthy that acetic acid, which he found to promote the autoxidation of certain sulphur compounds, has a distinct hindering effect on the propagation of flame in carbon disulphide–air near the limit.

FIG. 5.

Showing the ignition point of a 3% carbon disulphide–air mixture when some of the air is replaced by a third substance.



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