6. *The Upper Limits of Inflammability of Hydrogen–Air and Hydrogen–Nitrous Oxide Mixtures.*

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The compositions of the hydrogen–air and hydrogen–nitrous oxide mixtures at the upper limit of inflammability have been determined for upward propagation in a vertical tube 150 cm. long and 5 cm. in diameter, open to the atmosphere at the lower end. The effect of varying the proportion of air to nitrous oxide on the percentage of hydrogen in the hydrogen–air–nitrous oxide limit mixtures has been determined; and the effects of the addition of nitrogen, methyl alcohol, and methyl iodide on the composition of the hydrogen–air and hydrogen–nitrous oxide limit mixtures, and of ethyl alcohol on the composition of hydrogen–air limit mixtures, have been studied. Some limit flame temperatures have been calculated. It is concluded that the differences in behaviour observed can be related (*a*) to the difference between the hydrogen–oxygen and hydrogen–nitrous oxide chain reactions, the former being branching and the latter non-branching, and (*b*) to the difference between the limit flame temperatures of the two mixtures, which appears to be a consequence of the difference between the chain reactions.

Dixon-Lewis and Linnett (*Proc. Roy. Soc.*, 1951, **210**, *A*, 48) described observations on the effects of small amounts of organic material on the upper limit of inflammability of hydrogen–air mixtures. They found, as had Tanaka and Nagai (*Proc. Imp. Acad. Japan*, 1926, 2, 280, 283, 494, *et seq.*), that the graph of percentage of hydrogen at the limit against percentage of organic vapour added, was not a single straight line; *i.e.*, Le Chatelier's rule was not obeyed. The graphs in fact consisted of two parts: the first small additions caused a large fall in the percentage of hydrogen at the limit, but further addition had proportionately less effect. Thus, the first part of the graph had a greater slope than had the second part. Moreover, the latter obeyed a modified form of Le Chatelier's rule, *i.e.*, it was a straight line. They interpreted their results in terms of the known chain-branching character of the hydrogen–oxygen reaction, and the large effect of the first small additions was regarded as being the result of chain-breaking by the organic molecules. This effect is possible because the upper limit flame temperature of hydrogen–air mixtures is much less than those of most organic vapour–air mixtures, so that the organic molecules are then relatively unreactive. With further addition the limit flame temperature rises to compensate for this chain-breaking effect, and at some point the limit flame temperature of the organic molecule is reached and its oxidation contributes to the combustion. Its lowering effect on the hydrogen percentage at the limit is then much less, so that the slope of the graph for further additions beyond this becomes less.

The object of the present work was to compare the limit of hydrogen–air mixtures with that of hydrogen–nitrous oxide mixtures, and the effect of added materials on these limits. These mixtures were chosen because it is known that the hydrogen–oxygen reaction is a branching-chain reaction whereas the hydrogen–nitrous oxide reaction is a non-branching chain reaction. A comparison of the behaviour of the limits might, therefore, elucidate the factors governing the composition of limit mixtures.

Egerton and Powling (*Proc. Roy. Soc.*, 1948, **193**, *A*, 172, 190) made extensive measurements of inflammability limits including those of hydrogen–air and hydrogen–nitrous oxide mixtures. However, they studied mainly the lower limit. Their results are discussed on p. 41.

Posthumus (*Rec. Trav. chim.*, 1930, **49**, 309) determined the upper limit of inflammability of hydrogen–nitrous oxide mixtures, by using a closed tube of diameter 1·6 cm. We found that mixtures well outside the limit given by him carried a flame. Possible explanations for this will be considered later.

Experimental

The combustion tube in which the inflammability of the prepared mixtures, as regards upward propagation, was tested, was 150 cm. long and 5 cm. in diameter. It was closed initially at both ends by ground-glass plates fitting on the flanged ends of the tube. Platinum sparking electrodes were sealed into side arms at the lower end of the tube by means of vacuum wax, the width of the spark gap being 2—3 mm. Sparking was effected by a 2μF condenser charged to about 4000 volts. Ignition was always at room temperature (17° ± 3°) and atmospheric pressure, the lower ground-glass plate being removed from the end of the tube immediately before ignition. The criterion for flame propagation was that a flame should reach the top of the combustion tube. In some cases the flames were scarcely visible, and propagation was observed by means of a copper–constantan junction waxed into a side tube at the top of the combustion tube and connected to a microammeter.

It is important that the spark should be powerful enough to ignite the mixture being tested. Under our conditions, even when the flame did not propagate to the top of the tube, a diffusion flame of hydrogen in the outside air always burned at the lower end of the tube after the spark had passed. Further proof that the spark was sufficiently powerful was obtained by comparing the limit obtained when ignition was by spark and when it was effected by a small coal-gas flame drawn across the mouth of the tube immediately the plate was removed. The limits obtained by the two methods for mixtures of hydrogen and nitrous oxide containing 1% of methyl alcohol were identical. Two limits for mixtures of hydrogen, nitrous oxide, and methyl alcohol were determined with use of flame ignition, the rest being determined with spark ignition; all fell on a smooth curve. There is, therefore, little doubt that the limits determined were independent of the ignition source.

The gas mixtures were made up in a 5-l. all-glass spherical vessel. Complete mixing was ensured by causing a long glass plate to swing back and forth inside the vessel by means of an electromagnetic device. The hydrogen–air upper limit was determined (*a*) after 300, (*b*) after 500 complete swings of the plate, and (*c*) as in (*b*) but after the mixture had been left overnight. The limits obtained after treatments (*a*), (*b*), and (*c*) were identical. During the remainder of the work procedure (*a*) was adopted.

The partial pressures of the various gases in the mixtures were measured on a mercury manometer. When a small proportion of any material was required, a higher pressure of it was measured in a subsidiary vessel and the gas then expanded into the mixer. The ratio of the initial and the final pressure for this expansion was measured in a separate experiment at higher pressures.

The procedure in determining the inflammability of a mixture was as follows. The 5-l. mixing volume and the 3-l. combustion tube were evacuated by a mercury-vapour pump backed by a rotary oil pump. The gases were then measured in the 5-l. volume and mixed with a Töpler device, they were transferred to the combustion tube until the pressure in the tube was about 5 mm. above atmospheric. The lower plate was removed, and the igniting spark passed. The passage or non-passage of flame up the tube was then noted. This process was then repeated with mixtures of varying composition until the limit had been fixed sufficiently accurately. The following figures demonstrate that it is possible to fix the limit composition, in favourable circumstances, to closer than 0·1%. For hydrogen–air mixtures the following set was obtained (percentages refer to H_2; F = flame propagated in the mixture, NF = no propagation): 74·67, NF; 74·64 NF; 74·52 F; 74·59 F; 74·56 F; 74·69 NF; 74·56 F; 74·67% NF. The limit was therefore taken to be 74·62% of hydrogen. Egerton and Powling (*loc. cit.*) determined this limit in a tube 150 cm. long and 5·3 cm. in diameter and found the upper limit composition to be 74·6% of hydrogen. The agreement is excellent.

Cylinder hydrogen was used; it was freed from oxygen by passage through a silica-tube furnace packed with platinised asbestos and heated electrically to about 800°. The water formed was removed by passing the gases from the furnace through a trap cooled in liquid air. Cylinder nitrogen was used; it was freed from the 1—2% of oxygen it contained by passing the gas up a long tower packed with pumice over which trickled an alkaline solution of sodium dithionite (hydrosulphite) containing sodium anthraquinone-β-sulphonate. The gas was dried by passing it through a trap cooled in liquid air. Nitrous oxide, also from a cylinder, was condensed in a trap cooled in liquid air, then degassed by liquefaction, and resolidified, and the space above it was re-evacuated. This was repeated until no further degassing took place. The nitrous oxide was stored as solid in the trap, and when it was required the liquid air was removed and a portion of the oxide evaporated into the mixer. Mixtures containing nitrous oxide behaved reproducibly even though some were made up with nitrous oxide evaporated from the first and some from the last part of a sample in the trap. This indicates that the nitrous oxide was not contaminated with nitrogen or oxygen. Air was passed into the apparatus through a trap cooled in liquid air so that it was freed from water and other condensable impurities. The methyl alcohol was dried by boiling it with 5% of solid potassium hydroxide; it was then distilled, kept overnight over freshly burnt quicklime, and redistilled; the fraction of b. p. 64·5—65° was used. The ethyl alcohol was dried by the same method, and the fraction, b. p. 78—78·5°, used. The alcohol was stored in a bulb attached to the vacuum line. Before use, it was solidified in liquid air, and the bulb evacuated. It was then allowed to melt and the cycle repeated until no further degassing occurred. The methyl iodide was first shaken with a little mercury to remove iodine, then distilled *in vacuo* into the storage bulb and subjected to the same degassing treatment as the methyl alcohol.

Results.—The upper limit compositions for hydrogen–air and hydrogen–nitrous oxide mixtures are 74·62% and 83·91% of hydrogen, respectively. The limiting compositions for various hydrogen–nitrous oxide–air mixtures are given in Table 1. The calculated flame temperatures of the limit mixtures are also included; these were calculated by using the data of Lewis and von Elbe and of Dwyer and Oldenberg and assuming that the products were at equilibrium at the flame temperature.

TABLE 1.

Air in oxidising gas, %	0	20	40	60	80	100
H_2 at limit, %	83·91	83·40	82·07	80·03	77·39	74·62
Calc. flame temp., °c	1617°	1477°	1368°	1248°	1122°	913°
Diff.		140°	109°	120°	126°	209°

The upper limit compositions obtained when small amounts of methyl alcohol, ethyl alcohol, and methyl iodide, and larger amounts of nitrogen were added to hydrogen–air mixtures, are given in Table 2, those for additions to hydrogen–nitrous oxide mixtures in Table 3.

TABLE 2. *Upper limit compositions of some hydrogen–air–additive mixtures.*

MeOH, %	H_2, %	Air, %	EtOH, %	H_2, %	Air, %	MeI, %	H_2, %	Air, %	N_2, %	H_2, %	Air, %
0·51	71·97	27·52	0·22	70·26	29·52	0·52 *	61·30	38·18	10·90	64·00	25·10
0·97	68·90	30·13	0·51	64·61	34·88	1·00	53·43	45·57	30·00	45·11	24·89
1·71	65·66	32·63	0·72	63·50	35·78	2·03	44·06	53·91	40·04	35·36	24·60
2·92	59·72	37·36	1·47	57·74	40·79	3·48	34·20	62·32			
3·81	54·80	41·39	2·52	50·45	47·03	4·95	26·87	68·18			
5·45	49·40	45·15	4·02	42·00	53·98						
6·90	47·15	45·95									
8·04	44·63	47·33									

* Result obtained by Egerton and Powling (*loc. cit.*).

TABLE 3. *Upper limit compositions of some hydrogen–nitrous oxide–additive mixtures.*

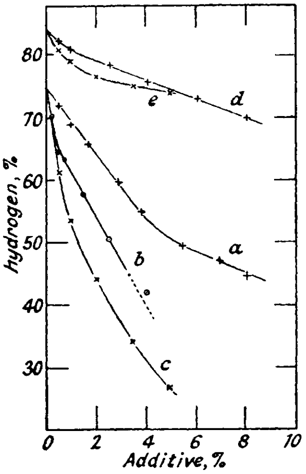
MeOH, %	H_2, %	N_2O, %	MeI, %	H_2 %	N_2O, %	N_2, %	H_2, %	N_2O, %
0·52	82·23	17·25	0·50	80·76	18·74	10·10	73·94	15·96
0·99	80·83	18·18	0·99	78·95	20·06	20·10	64·64	15·26
2·54	78·53	18·93	2·04	76·61	21·35	35·01	50·14	14·85
4·13	75·70	20·17	3·52	75·06	21·42	50·02	35·22	14·76
6·03	72·98	20·99	4·97	73·99	21·04			
8·06	69·95	21·99						

In the figure the results for methyl alcohol, ethyl alcohol, and methyl iodide are shown graphically. These curves show that Le Chatelier's rule fails for these mixtures. The graphs of contents of hydrogen against added nitrogen in the limit mixtures are linear for both hydrogen–air–nitrogen and hydrogen–nitrous oxide–nitrogen mixtures. Other interesting features are the following :

(*a*) As methyl iodide is added to hydrogen–nitrous oxide mixtures the percentage of nitrous oxide in the limit mixtures increases at first, but for amounts of methyl iodide greater than 3% it falls again. Thus over the range 3—5% of methyl iodide the percentages of both hydrogen and nitrous oxide are decreasing as the methyl iodide increases. This result was so surprising that the limit for mixtures containing 4·97% methyl iodide was redetermined, but verified. No such effect is obtained as methyl iodide is added to hydrogen–air mixtures over the range studied.

(*b*) The percentage of air, as well as that of hydrogen, decreases as the percentage of nitrogen added is increased. The same behaviour is observed for hydrogen–nitrous oxide mixtures. For the air mixtures the air content at the limit falls from 25·4 to 24·6 as the added nitrogen is increased from 0 to 40%. For the nitrous oxide mixtures the percentage of nitrous oxide falls from 16·1 to 14·9 over the same range. This may be restated as follows: when the percentage of hydrogen is equal to that of the added nitrogen the limit is at 24·7% of air for the air mixtures (0·7% less than in the absence of nitrogen) and 14·8% of nitrous oxide for the nitrous oxide mixtures (1·3% less than in the absence of nitrogen). It appears that the addition of nitrogen has more effect in reducing the amount of oxidising component with the nitrous oxide mixtures. This is true whether one considers absolute or fractional reduction in the proportions of the oxidising component.

(*c*) Tanaka and Nagai (*loc. cit.*) and Dixon-Lewis and Linnett (*loc. cit.*) determined the effect on the upper limit of hydrogen–air mixtures of the addition of members of homologous series of organic compounds, and found that the slope of the first section of the limit graph increased as the series was ascended and that the graph changed slope at a progressively lower percentage addition as the molecular size increased. Our results for the upper limits of hydrogen–air–methyl alcohol and hydrogen–air–ethyl alcohol mixtures are of the same general form as would be expected from these observations. However, they also found that extrapolations of the second sections of the limit graphs of a given homologous series all intercepted the hydrogen axis at the same point. Tanaka and Nagai also found that the second sections of the limit graphs obeyed a modified form of the Le Chatelier rule, the upper limit of the organic vapour–air mixtures and the intercept made on the hydrogen axis being used as the constants. From the figure it can be seen that the second sections of the limit graphs obtained in this work for hydrogen–air–methyl alcohol and hydrogen–air–ethyl alcohol mixtures do not intercept the hydrogen axis at the same point. On using White's values (*J.*, **1919**, **115**, 1462) for the upper limit compositions of the alcohol–air mixtures (36·5 and 18·95% of the respective alcohols) it is found that the second section of the methyl alcohol graph obeys Le Chatelier's rule as modified by Tanaka and Nagai but the second section of the ethyl alcohol graph does not. On account of these unexpected results the upper limit compositions of mixtures containing 1·5% and 2·54% of ethyl alcohol respectively were redetermined some 8 months after the original observations but were confirmed.



Effect of organic additives on H_2*–air and* H_2*–*N_2O *upper limits.*

(*a*) H_2 + air + MeOH;
(*b*) H_2 + air + EtOH;
(*c*) H_2 + air + MeI;
(*d*) H_2 + N_2O + MeOH;
(*e*) H_2 + N_2O + MeI.

DISCUSSION

It has been possible to check our results against those obtained by Egerton and Powling with a similar tube for hydrogen–air, hydrogen–air–methyl iodide, and hydrogen–nitrous oxide–nitrogen mixtures. In all cases the agreement is good. However, our limit for hydrogen–nitrous oxide mixtures does not agree with that given by Posthumus. He reported that in his closed 1·6-cm. tube, flame was always propagated in mixtures containing less than 75% but never in those with more than 77% of hydrogen. In mixtures containing intermediate amounts flames were sometimes propagated and sometimes not. Because a narrower tube was used by Posthumus it would be expected that his limit would be at a lower percentage of hydrogen than ours. However, the difference is surprisingly large and it may be that his induction coil spark was insufficient to ignite mixtures near the limit.

The lack of reproducibility suggests that this was the case. The limit was entirely reproducible under our conditions.

The calculated limit flame temperature of hydrogen–nitrous oxide mixtures is 1617° while that of the hydrogen–air limit flame is 913°; the difference is surprisingly large. A mixture of hydrogen and nitrous oxide at atmospheric pressure would explode thermally in an isothermally heated vessel at about 700°, while a hydrogen–air mixture would, under the same conditions, explode at about 600°. The former would be a thermal explosion, while the latter would depend on chain branching. The difference of temperature between these explosion limits is much less than that between the calculated flame temperatures of the two limit mixtures. Dixon-Lewis and Linnett concluded from their experiments that the limit was determined by the necessity of reaching a temperature at which a sufficient rate of radical multiplication was allowed. The need for this was supposed to arise because the reaction in any layer must become self-sustaining and at the same time provide a supply of radicals for diffusion into the next layer. Because of its rapid chain-branching mechanism, the hydrogen–oxygen reaction is ideally suited for providing a sufficiently speedy multiplication of radicals in the flame zone at a temperature not much greater than that at which it would explode in a closed vessel. However, the only way in which the number of radicals can increase in the hydrogen–nitrous oxide mixture is by the dissociation of nitrous oxide as a result of a rising temperature. In the hydrogen–oxygen reaction the available energy is used initially to increase the number of radicals, whereas in the hydrogen–nitrous oxide reaction it is initially used to raise the temperature and only secondarily, as a consequence, to increase the number of atoms and radicals. The higher limit flame temperature of hydrogen–nitrous oxide mixtures than of similar hydrogen–air mixtures, therefore, seems to support the view that the multiplication of radicals in the flame front is necessary for the propagation of the flame, and also that the lower the temperature at which this can be achieved at a sufficient speed, the lower will be the minimum temperature necessary for a flame to be maintained (cf. Van Tiggelen, *Bull. Soc. chim. Belg.*, 1946, **55**, 202; 1949, **58**, 259).

Egerton and Powling have shown, by comparing the limits of hydrogen–oxygen–helium and hydrogen–oxygen–argon mixtures, that an increase in the thermal conductivity of the mixture makes an increase in the limit flame temperature necessary. This factor will also be operative in causing the limit flame temperature of hydrogen–nitrous oxide mixtures to be greater than that of hydrogen–air mixtures since there is more hydrogen in the former mixture. This, however, could hardly explain the large difference in the limit flame temperatures.

The calculated limit flame temperatures of hydrogen–nitrous oxide–air mixtures (Table 1) show some interesting features. The rises in flame temperature caused by replacing air by nitrous oxide are 209°, 126°, 120°, 109°, and 140° for 20, 40, 60, 80, and 100% replacement, respectively. The most noticeable effect is the relatively large rise in temperature caused by the first introduction of nitrous oxide. A possible explanation of this is that at about 1000°, nitrous oxide slows up the chain-branching process of the hydrogen–oxygen reaction by providing the non-branching reaction

$$N_2O + H = N_2 + OH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

as an alternative to the branching reaction

$$O_2 + H = OH + O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

This would decrease the rate of radical multiplication so that the minimum flame temperature would have to rise.

The replacement of the first 20% of nitrous oxide by air causes a greater lowering of the flame temperature (140°) than that of the second 20% (109°). This occurs despite the fall in available oxygen (as compared with upper limit hydrogen–nitrous oxide mixtures) and the fact that the percentage of hydrogen is reduced less in replacing the first 20% than the second 20%. This may be related to Melville's kinetic observation (*Proc. Roy. Soc.*, 1933, **142**, *A*, 524; 1934, **144**, *A*, 737) that the addition of oxygen increases the rate of the hydrogen–nitrous oxide reaction, probably because reaction (2) occurs to some extent, causing an increase in the number of radicals.

These comments on the limits and limit flame temperatures of hydrogen–nitrous oxide–air mixtures are necessarily tentative. The main interest in the results lies in the fact that neither the limits nor the limit flame temperatures change regularly with the proportion of air in the oxidising gas. Moreover, the effects of both the first replacements of nitrous oxide by air and of air by nitrous oxide seem to be much greater than the effects of further replacements in either direction.

The effect of nitrogen on both limits was summarised on p. 39. The fact that both graphs are linear is consistent with the conclusion that nitrogen behaves entirely as an inert gas. The greater effect of nitrogen on the hydrogen–nitrous oxide limit than on the hydrogen–air limit remains to be considered. As nitrogen is added to these mixtures one can say that, to a first approximation, the effect of replacing hydrogen by nitrogen in the upper limit mixture is being studied, for the proportion of air or nitrous oxide changes only slightly. The effect of this replacement is that the thermal conductivity decreases greatly and the diffusion coefficient also decreases, but not to proportionally as great an extent. These effects on the thermal conductivity and diffusion coefficient explain why, as nitrogen is added, less of the oxidising component is required in the limit mixture, *i.e.*, the calculated limit flame temperature can be lower. These observations link up with those of Egerton and Powling (p. 41). It seems probable that the reason why the effect on the hydrogen–nitrous oxide limit is greater is that the multiplication of radicals in that system must be essentially thermal in character, since it can only occur as a result of a rising temperature leading to the necessary dissociation of nitrous oxide to give oxygen atoms. This is the reason why the limit flame of hydrogen–nitrous oxide is hotter than that of hydrogen–air mixtures, and it is probably also the reason why changing the thermal conductivity by replacing hydrogen with nitrogen has a greater effect in the former than in the latter mixtures.

The dual nature of the effect of organic materials on the upper limit of hydrogen–air mixtures, observed by Tanaka and Nagai and by Dixon-Lewis and Linnett, is confirmed by our experiments with alcohols. The curves showing the effects of the alcohols (see fig.) are segmented. A possible explanation of this was given by Dixon-Lewis and Linnett (see p. 37). The effect of methyl alcohol on the hydrogen–nitrous oxide limit is rather different; the first segment is much reduced in length and for amounts of methyl alcohol greater than 1% the curve is linear. With hydrogen–air mixtures it is only for amounts of methyl alcohol greater than 5% that the second segment occurs. This difference is presumably to be related to the difference between the two limit flame temperatures and the fact that the limit flame temperatures of methyl alcohol–nitrous oxide and hydrogen–nitrous oxide mixtures are closer than those of methyl alcohol–air and hydrogen–air mixtures. At the hydrogen–air limit stripping reactions, such as $CH_3{\cdot}OH + H = CH_3 + H_2O$ or $CH_3{\cdot}OH + H = CH_2{\cdot}OH + H_2$, probably reduce (or delay) the rate of chain branching because a reactive radical is replaced by another which is much less reactive at the operative temperature. It appears that with hydrogen–nitrous oxide mixtures there is a slight inhibiting effect for small additions of methyl alcohol but this is only noticeable for amounts less than 1%. For amounts greater than this a straight-line plot is obtained, indicating that the two reactions are occurring side by side without any specific interference, *i.e.*, a modified Le Chatelier rule is obeyed.

For hydrogen–air mixtures, methyl iodide has a much greater effect on the proportion of hydrogen at the limit than does methyl alcohol. The most likely explanation of this lies in the large effect of iodine in reducing the rate of the reaction between hydrogen and oxygen, owing to removal of hydrogen atoms by iodine and its compounds. Our observations confirm those made by Dixon-Lewis and Linnett with a narrow tube. However, with hydrogen–nitrous oxide mixtures, methyl iodide has only a slightly greater effect on the limit than has methyl alcohol, perhaps because iodine is less active in the effective removal of hydrogen atoms at the higher than at the lower temperature. Another possibility is that the removal of hydrogen atoms in the hydrogen–oxygen reaction interferes with the branching chain which is necessary for radical multiplication. In the hydrogen–nitrous oxide reaction, radical multiplication only occurs with increasing temperature and consequent dissociation of nitrous oxide. The removal of hydrogen atoms does not, therefore, involve so direct an interference with radical multiplication although, of course, it will have some effect by slowing the non-branching chain reaction and hence the rate of temperature rise.

The strange effect summarised in para. (*a*) (p. 39) appears to indicate that in some way the addition of methyl iodide contributes to the flame propagation when large amounts are added. One possible way in which this might happen appears to be that the reaction $CH_3I + H_2 = CH_4 + HI$ might occur. This reaction is exothermic to the extent of about 10 kcal./g.-mol. and so might increase the heat available to raise the temperature of the gases. It is difficult otherwise to see how the percentages of both hydrogen and nitrous oxide in the limit mixture can fall as methyl iodide is added.

It seems that our results for the effect of ethyl alcohol on the upper limit of hydrogen–air mixtures need extension to higher percentages of ethyl alcohol : this was not possible in our apparatus since the tube could not be heated. The linear segment in the figure, extending from about 1% to about 3% of ethyl alcohol would, if extrapolated, cut the alcohol axis at about 10% of alcohol instead of at the upper limit composition of ethyl alcohol–air mixtures (18·95% of EtOH). It must therefore be presumed that the slope of the graph decreases at some higher percentage of ethyl alcohol : it should be noted that the point representing mixtures containing 4% of ethyl alcohol lies above the line drawn through the points between 1% and 2·5%. Also, evidence for a further change of slope of the graph can be obtained from Dixon-Lewis and Linnett's result, that, in their narrow tube (2 cm.), for methyl alcohol and ethyl alcohol, the segments beyond the bends at about 2% addition extrapolated back to about 60% of hydrogen in both cases. It seems that the bends occur at lower percentages of addition in the narrow tube, *e.g.*, for methyl alcohol, at about 2% in the narrow tube and 5% in the 5-cm. tube. This suggests that the bend observed by Dixon-Lewis and Linnett at about 1·8% of ethyl alcohol in the 2-cm. tube is likely to be beyond the highest percentage (4%) examined by us for ethyl alcohol.

No bend corresponding to that observed by us at about 0·5% in the ethyl alcohol curve seems to be present in the methyl alcohol curve : it may be that the greater probable complexity of the ethyl alcohol curve than of the methyl alcohol curve is a consequence of the greater complexity of the ethyl alcohol molecule. It seems probable that the segment corresponding to that beyond 5% in the methyl alcohol curve has not yet been observed in the ethyl alcohol curve, and that the reason why the straight-line sections in the two graphs do not extrapolate to the same percentage of hydrogen is that they are not corresponding segments. A possible explanation for the sharper initial fall in the ethyl alcohol as compared with the methyl alcohol graph, might be that in ethyl alcohol the C–H bond in CH_2 is weaker than in CH_3 so that a reaction of the type $C_2H_5{\cdot}OH + H = C_2H_4{\cdot}OH + H_2$ can occur more readily with ethyl than with methyl alcohol. In addition, ethyl alcohol, by virtue of its increased size, might be more effective in removing active radicals from the low-temperature hydrogen–air limit flame.

It therefore appears that all the results described can be accounted for in terms of (*a*) the branching and non-branching of the hydrogen–oxygen and hydrogen–nitrous oxide chain reactions, respectively, and (*b*) the higher limit flame temperature of the latter mixtures, which is apparently a consequence of (*a*).

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