123. *The Oxidation of Methane and the Function of Surfaces in Gaseous Reactions.*

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EXAMPLES of thermal chain reactions which exhibit "limit" phenomena are now common. Briefly, such processes are characterised by sudden changes in reaction velocity with minute changes of pressure. This feature, inexplicable in terms of the classical Arrhenius ideas of chemical change, can now be interpreted in terms of the general theory of chain reactions developed mainly by Semenov (*Chem. Reviews*, 1929, **6**, 3) and by Hinshelwood ("Kinetics of Chemical Change," 2nd edtn., Chap. 6).

A typical example of such a reaction in which "limits" are involved is the combination of hydrogen with oxygen (Thompson and Hinshelwood, *Proc. Roy. Soc.*, 1929, *A*, **122**, 610). In the neighbourhood of 500° there exists a critical region of pressure, at lower pressures within which spontaneous inflammation of hydrogen–oxygen mixtures occurs. Below the lower of the two critical pressures bounding this region, the rate of reaction is very small; above the upper one, the rate is also very small but increases steadily with increasing pressure until at higher pressures explosion again occurs.

The mechanisms by which the low- and the high-pressure explosion arise appear to be very different. Whereas the latter is of the ordinary "thermal" type, the former is contrary to classical laws of the rate of chemical change. The concept of branching chains leads mathematically to a satisfactory understanding of it; but in order to visualise the phenomena completely, it would be essential to know how the chains start, how they are propagated, and how they finish. This involves a study of the relationships existing at the two limits.

The investigation of the upper critical explosion limit was made fairly satisfactorily in the original experiments, and has since been repeated (Garstang and Hinshelwood, *ibid.*, 1931, *A*, **130**, 640; **134**, 1). An adequate method for the study of the lower limit was at first not available, but one has recently been discovered.

Some years ago Stavenhagen and Schuchard (*Z. angew. Chem.*, 1920, **33**, 286) noticed that hydrogen–oxygen mixtures ceased to explode with a spark if the pressure fell below a certain value. Alyea and Haber (*Z. physikal. Chem.*, 1930, **10**, *B*, 193) and also Kowalsky (*ibid.*, 1931, **11**, 56) have correlated this limit with the lower limit of Thompson and Hinshelwood (*loc. cit.*), though their arguments cannot be regarded as entirely conclusive. Assuming, however, that the two limiting pressures in the respective series of experiments were the same in principle, an investigation has been made by the sparking method of the influence of various factors such as percentage composition of the mixture, width of vessel, and inert gases upon the pressure limit. The results will shortly be published.

Meanwhile, it became of interest to discover whether other combustible mixtures also exhibited the property of ceasing to explode at a certain limiting pressure. Experiments with methane–oxygen mixtures now show that here too there exists a critical pressure below which ignition with a spark will not occur. This limit varies in position with the percentage composition of the mixture and other factors. This result appeared to weaken the argument that the pressure limit with a spark was the same as that noticed in the other experiments, since in measurements on the reaction velocity of the oxidation of methane no such low-pressure limit and explosion region had been observed. Fort and Hinshelwood (*Proc. Roy. Soc.*, 1930, *A*, **129**, 284), working at relatively high pressures, found a normal measurable reaction typical of a straight-chain process.

Neumann and Serbinoff (*Nature*, 1931, **128**, 1040) have recently stated, however, that the behaviour of methane–oxygen mixtures is precisely similar to that shown by hydrogen and oxygen, there existing at low pressures a critical pressure region for spontaneous inflammation, whilst at higher pressures a measurable chain reaction is observed which ultimately passes into explosion at the highest pressures.

Thus the discovery that there is a critical explosion pressure below which a spark fails to ignite methane–oxygen mixtures seems to fall into line completely, and the suggestion of Haber and Kowalsky, that this is to be identified with the limit observed in measurements on reaction velocity, is substantiated. The experiments now to be reported are of a preliminary nature, but are communicated in view of Neumann and Serbinoff's paper. Meanwhile they are being repeated and extended with great care for reasons which will become obvious in the following; it is hoped from the new data to make calculations which will lead to information about the nature of the chains involved.

EXPERIMENTAL.

The methane used was from a cylinder of natural gas. It contained some hydrogen. Preliminary experiments with this crude sample gave essentially the same results as those with a purified product, obtained by passing the crude gas over heated copper oxide and absorbing in caustic potash solution any carbon dioxide formed by oxidation of the methane. The gases were dried by phosphoric oxide.

Oxygen, nitrogen, argon, and carbon dioxide were obtained from cylinders, and dried as before. Sulphur dioxide was from the liquid, and carbon tetrachloride from a distilled specimen.

The mixtures of known composition were made in a large storage flask. The explosion vessel was a long cylindrical tube, at the upper end of which was fitted a ground joint carrying the platinum electrodes. This joint was so constructed as to fit into tubes of different diameter, thus maintaining the same spark gap in each case. As yet only one tube has been employed. The spark was produced by an induction coil using 6 volts in the primary circuit. In these circumstances it was not entirely reproducible but, as the results showed, it was sufficiently so for the purpose involved, which was not so much to determine the absolute value of the pressure limit as the variation of this with different factors. The experiments of Finch and his collaborators (*Proc. Roy. Soc.*, 1927 *et seq.*) would make it very probable that the absolute value of such a limit depends upon the intensity of the spark used. Explosion could be observed by the progress of the flame or by the movement of a mercury manometer. The limiting pressure for explosion could usually be determined to within 1 mm.

Results.—(1) *Variation of the critical limit with percentage composition.* Table I gives three series of results showing how the total critical pressure (*p* in mm.) varies with the composition of the methane–oxygen mixture. These results are plotted in Fig. 1.

TABLE I.

Series.	CH_4, %.	p.	p_{CH_4}.	p_{O_2}.	Series.	CH_4, %.	p.	p_{CH_4}.	p_{O_2}.
I	49·0	95	46·5	48·5	II	57·7	>270	>156	>14
	33·5	44	14·75	29·25		46·3	81	37·5	43·5
	22·4	32	7·2	24·8		31·8	40	12·7	27·3
	15·7	33	5·2	27·8	III	42·0	58	24·4	33·6
	12·2	38	4·6	33·4		29·6	38	11·5	26·5
	8·2	63	5·2	57·8		25·3	35	8·8	26·2
						10·1	46	4·7	41·3

It is seen that above about 20% of methane, the critical pressure increases with increasing percentage of methane, but below this value the total critical pressure increases with decreasing methane content. This result is similar to that found earlier with hydrogen–oxygen mixtures, except that in the latter case the extreme end of the curve (for low hydrogen concentration) was not determined. The differences in detail which the two series of experiments show are to be explained in a way which will become obvious after the effect of inert gases has been described.

(2) *Effect of inert gases.* The addition of the inert gases nitrogen, argon, sulphur dioxide, carbon dioxide, and of carbon tetrachloride vapour upon the limit has so far been examined. It is natural to suppose that if the inert gases are effective by virtue of some physical property, then methane and oxygen themselves will possess this property to a greater or less extent. For purposes of comparison, therefore, it will be expedient to employ, as far as is possible, such

quantities of methane and oxygen as to give the same inert-gas effect in each experiment, and if possible this should be a minimum. The stoicheiometric ratio $1CH_4 : 2O_2$ was used in these experiments. Table II summarises the results, which are plotted in Fig. 2. The

FIG. 1.

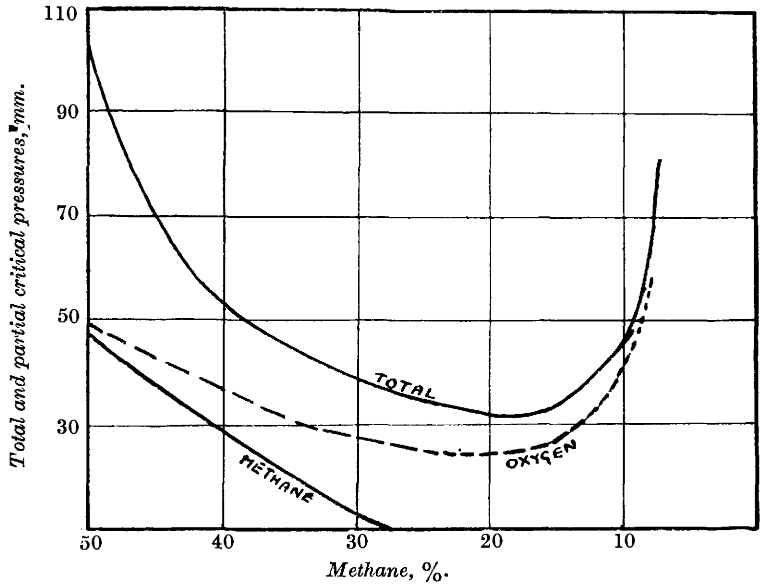


TABLE II.

N_2, %.	p.	p_{CH_4}.	p_{O_2}.	p_{N_2}.
0	43	14·3	28·7	0
8·0	44	13·5	27·0	3·5
15·6	45·5	12·8	25·6	7·1
24·4	47	11·9	23·8	11·3
32·3	49	11·0	22·2	15·8
40·0	52	10·4	20·8	20·8
49·6	61	10·2	20·5	30·3
56	72	10·5	21·1	40·4
67	97	10·7	21·3	65

CO_2, %.	p.	p_{CH_4}.	p_{O_2}.	p_{CO_2}.
0	43	14·3	28·7	0
6·5	43·5	13·6	27·1	2·8
16·0	44	12·3	24·7	7·0
27·0	47	11·4	22·9	12·7
35·8	51	10·9	21·8	18·3
44·4	59	10·9	21·9	26·2
59	85	11·7	23·3	50

SO_2, %.	p.	p_{CH_4}.	p_{O_2}.	p_{SO_2}.
0	43	14·3	28·7	0
15·1	38	10·75	21·5	5·75
28·7	40	9·5	19·0	11·5
35·4	39	8·4	16·8	13·8
45·5	48	8·7	17·5	21·8
52·6	66	10·4	20·9	34·7
57·5	94	13·3	26·7	54

A, %.	p.	p_{CH_4}.	p_{O_2}.	p_A.
0	43	14·3	28·7	0
16·0	47·5	13·3	26·6	7·6
27·5	52	12·6	25·1	14·3
39·7	55	11	22·2	21·8
52·9	58·5	9·2	18·4	30·9
72·6	72	6·5	13·1	52·4

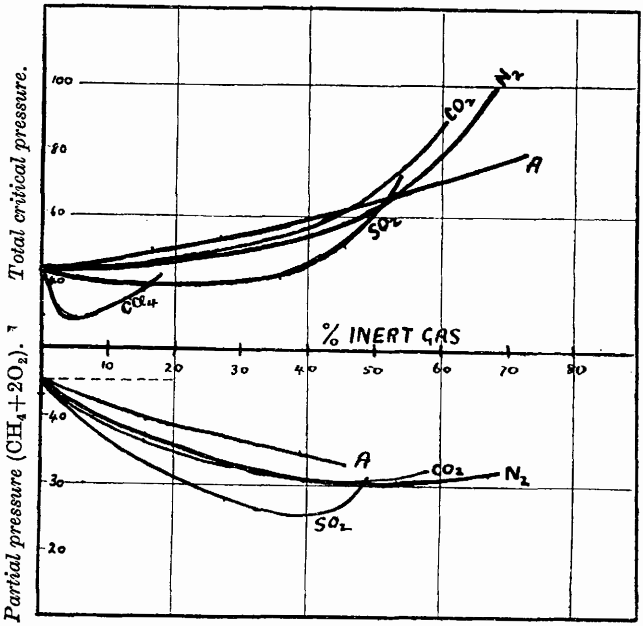
CCl_4, %.	p.	p_{CH_4}.	p_{O_2}.	p_{CCl_4}.
0	43	14·3	28·7	0
2·4	31	10·1	20·3	0·6
3·75	29	9·3	18·6	1·1
8·0	31	9·5	19·0	2·5
13·5	36	10·4	20·75	4·85
27·5	50	12·1	24·15	13·75

upper curves show how the total critical pressure varies with the proportion of inert gas, and the lower ones show the variation of the $CH_4 + 2O_2$ partial pressure. This serves to show clearly how addition of an inert gas can facilitate ignition.

Discussion.

The manner in which the critical pressure limit for ignition is affected by changes in temperature and in the diameter of the explosion vessel has not yet been investigated. Data of this kind will considerably assist in working out the mechanism of the processes involved; but apart from them one important result at least emerges from the above material.

FIG. 2.



Semenov (*Z. Physik*, 1927, **46**, 113) discovered and investigated the low-pressure explosion of phosphorus vapour where ignition occurs between two limiting pressures just as in the case of hydrogen and oxygen. In applying the general theory of branching chains, he derived the following relationship which was actually found to express the conditions at the lower critical limit (d being the diameter of the tube):

$$p_{P_4} p_{O_2} \left(1 + \frac{p_{\text{inert gas}}}{p_{P_4} + p_{O_2}}\right) d^2 = K.$$

In the absence of inert gas, the product $p_{P_4} \times p_{O_2}$ varied approximately inversely as d^2, and in the same tube in the presence of argon the plot of $1/p_{P_4}p_{O_2}$ against $1 + p_A/(p_{P_4} + p_{O_2})$ gave a straight line. Semenov only employed argon as inert gas, and his equation does not provide for quantitative differences in behaviour with other inert diluents.

Melville and Ludlam (*Proc. Roy. Soc.*, 1931, *A*, **132**, 108) have re-examined the problem from this point of view, using many inert gases, with the result that plots of $1/p_{P_4}p_{O_2}$ against $1 + p_{\text{inert gas}}/(p_{P_4} + p_{O_2})$ were straight lines of different slope. The remarkable fact was that the slopes of these lines became progressively greater as the complexity of the inert gas increased. The interpretation suggested was that diffusion of the active products to the vessel walls leads to deactivation and a breakage of the chains. Different inert gases, by virtue of their lower or higher diffusion coefficient with respect to the active centres, are able to a greater or less extent to prevent this diffusion. A complex large diluent molecule will greatly facilitate ignition by preventing diffusion of the active products to the vessel wall. On the other hand, helium will be scarcely effective in this respect. For hydrogen and oxygen identical relationships hold, and the explanation is probably the same.

Here, too, then, in the case of methane–oxygen mixtures, assuming that the pressure limit with a spark is the same in principle as that in the experiments of Neumann and Serbinoff, we can derive an equation $p_{CH_4}p_{O_2}[1 + p_{\text{inert gas}}/(p_{CH_4} + p_{O_2})]d^2 = K$ or, by making the emendation of Melville and Ludlam,

$$p_{CH_4}p_{O_2}[1 + D^{-1}p_{\text{inert gas}}/(p_{CH_4} + p_{O_2})]d^2 = K.$$

Table III gives values of $1/p_{CH_4}p_{O_2}$, represented by x, and of $1 + p_{\text{inert gas}}/(p_{CH_4} + p_{O_2})$, represented as y, calculated from the above data; these values are plotted in Fig. 3.

TABLE III.

Nitrogen.		*Carbon dioxide.*		*Argon.*	
10^3x.	y.	10^3x.	y.	10^3x.	y.
2·439	1·0	2·439	1·0	2·439	1·0
2·747	1·09	2·710	1·07	2·825	1·2
3·049	1·18	3·289	1·19	3·165	1·38
3·534	1·32	3·831	1·37	4·098	1·66
4·098	1·475	4·20	1·56		
4·630	1·67				
4·785	1·99				

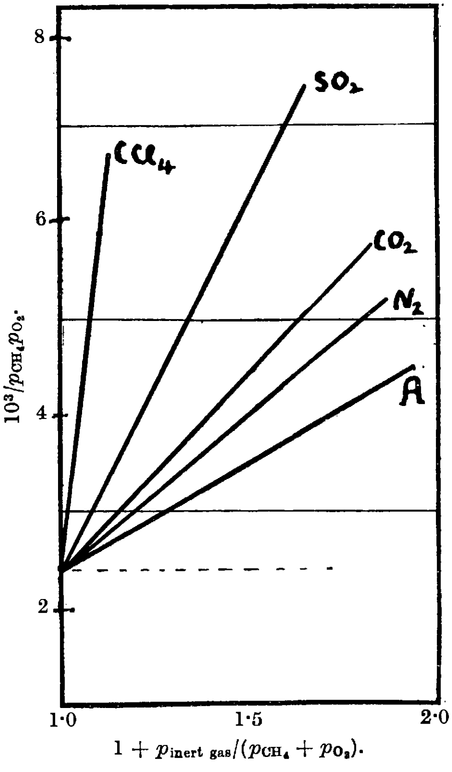
Sulphur dioxide.		*Carbon tetrachloride.*	
2·439	1·0	2·439	1·0
4·329	1·18	4·878	1·02
5·556	1·40	5·78	1·04
7·09	1·55		

It is clear that here again straight lines are obtained, the slopes of which are at any rate qualitatively in the order of the diffusion coefficient for the respective inert-gas molecules. The straight-line relationships break down, however, at higher inert-gas concentrations. This is to be expected, but it is not yet quite clear why the position at which the break begins to appear should be so different for the different cases. This no doubt depends upon more specific properties of the substances concerned. The inert-gas effect of methane and oxygen themselves will also probably assist in making the linearity invalid.

Further experiments will have to decide whether thermal conductivity or some other similar property of the diluent substances is important in determining the limit, but it seems more probable that the original idea here outlined is the correct one.

Conclusions.—The conclusions to be drawn from the above are, accordingly, first, that methane–oxygen mixtures behave like those of hydrogen and oxygen or of phosphorus and oxygen as regards the " low-pressure " explosion; and secondly, that there is direct evidence that the chains (starting in the gas in the spark experiments, at least) are broken at the vessel walls.

FIG. 3.



It should be possible, if the relative slopes of the lines for different inert substances can be determined with sufficient accuracy, to estimate the mass of the respective active centres diffusing through the body of the gas. This may help to decide whether peroxide substances of the type $CH_4{:}O_2$ play any part in the chain.

Summary.

Methane–oxygen mixtures cease to explode with a spark if the pressure is below a certain limit, the value of which depends upon the composition of the mixture and upon the presence of inert gases. In general the inflammability of methane–oxygen mixtures is increased by the addition of an inert gas. The inert gases appear to effect this by preventing the diffusion of active centres to the vessel walls, where deactivation occurs. The discovery of a limiting pressure of methane–oxygen mixtures for explosion by a spark agrees with another recent investigation upon the kinetics of this oxidation process.

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