CCCXXXVI.—*The Ignition of Gases. Part VI. Ignition by a Heated Surface. Mixtures of Methane with Oxygen and Nitrogen, Argon, or Helium.*

By Clement Albert Naylor and Richard Vernon Wheeler.

In Parts II and IV of this research (J., 1922, **121**, 2079; 1924, **125**, 1869), the phenomena of the ignition of methane–air mixtures by heated surfaces are discussed. The work has been continued during the past seven years, the lag on ignition, in particular, being studied with a view to determine the factors that control it. The experimental method was a modification of that used by Mason and Wheeler (*loc. cit.*), wherein the inflammable mixture to be studied was rapidly admitted to an evacuated vessel of quartz, heated to the desired temperature. The lowest temperature of the reaction-vessel necessary to cause the mixture admitted to it to inflame, no matter how long after its admission, is recorded as the "ignition-temperature" of that mixture. The values for different mixtures are relative only, being dependent, for example, on the size of the reaction-vessel. The modification of the method introduced by us enabled the gas mixtures to enter the heated vessel more rapidly than in Mason and Wheeler's experiments, so that zero time was more sharply defined. The "ignition-temperatures" recorded for similar mixtures in the two researches under otherwise identical conditions differ slightly on this account.

The results of the present research show that, under the conditions of experiment, the reactions between methane and oxygen (in admixture with an inert gas) resulting in the production of flame are thermal reactions catalysed by the products of an initial slow and flameless combustion. This appears to be the view held by Egerton (see *Nature*, 1927, **120**, 694).

Two reaction-vessels were used for the experiments with methane and air, both of transparent quartz, the one of 48 c.c. (ratio, surface : volume 1·3) and the other of 440 c.c. capacity (ratio, surface : volume 0·6). The ignition-temperatures for all mixtures of methane and air were lower in the larger vessel. The reason for this has been explained, in the light of knowledge then available, in J., 1922, **121**, 2079.

The heat developed by the oxidation of the products of the initial slow combustion is in part absorbed by the inert gas present, so that the total amount of heat acquired by the reacting gases depends upon the thermal properties of the inert gas. When the nitrogen in methane–air mixtures is replaced by argon, having both a lower specific heat and a lower thermal conductivity, the ignition-temperatures are lowered, whilst replacement by helium, of high thermal conductivity, raises them. The loss of heat to the walls of the reaction-vessel in unit time is considerably greater when helium is present than with either argon or nitrogen. The acceleration of the reactions is therefore checked by the presence of helium, and a higher initial temperature is required to enable them to acquire sufficient speed to produce flame.

Formaldehyde and carbon monoxide are produced during the period of lag. The addition of small amounts of formaldehyde or carbon monoxide to any methane–air mixture lowers its ignition-temperature and shortens the lag on ignition, formaldehyde being the more effective. It can be presumed that the formaldehyde ordinarily produced by the oxidation of methane during the period of lag catalyses the subsequent reactions in the same way as does the added formaldehyde.

The addition of traces of iodine, ethyl iodide, ethyl bromide, carbon tetrachloride or lead tetraethyl to methane–air mixtures raises their ignition-temperatures and decreases the rates of the reactions that occur below the ignition-temperatures. The view held by Egerton (*loc. cit.*) is that, the combustion of hydrocarbons being autocatalytic, " anti-knocks," such as lead tetraethyl, delay oxidation by destroying the catalyst. The inhibiting action of these substances appears to take place on the surface of the reaction-vessel.

With mixtures of methane and oxygen, the slow flameless combustion, according to Fort and Hinshelwood (*Proc. Roy. Soc.*, 1930, *A*, **129**, 284), is a " chain reaction," and the influence of the methane-concentration is great compared with that of the oxygen-concentration. In our experiments with the oxygen diluted by different inert gases, on the contrary, the rate of reaction is influenced mainly by the concentration of the oxygen. Further, a " chain reaction " is characterised by a high temperature coefficient. Although we cannot calculate the temperature coefficient exactly from our results, we can obtain approximate values if we assume the reciprocal of the lag on ignition to be a measure of the velocity of the reaction. The temperature coefficient is low and decreases with increasing temperature, as the following calculations, using the Arrhenius equation, show :

		Small reaction-vessel.		Large reaction-vessel.	
Methane in air, %.	Temp. range.	*K.*	*E.*	*K.*	*E.*
4	700—800°	1·19	35,500	1·15	31,000
	800—900	1·14	34,000		
8	700—790	1·22	41,000	1·14	30,000
	790—900	1·15	34,000		
12	730—800	1·25	48,000	1·13	28,000
	800—900	1·19	44,500		

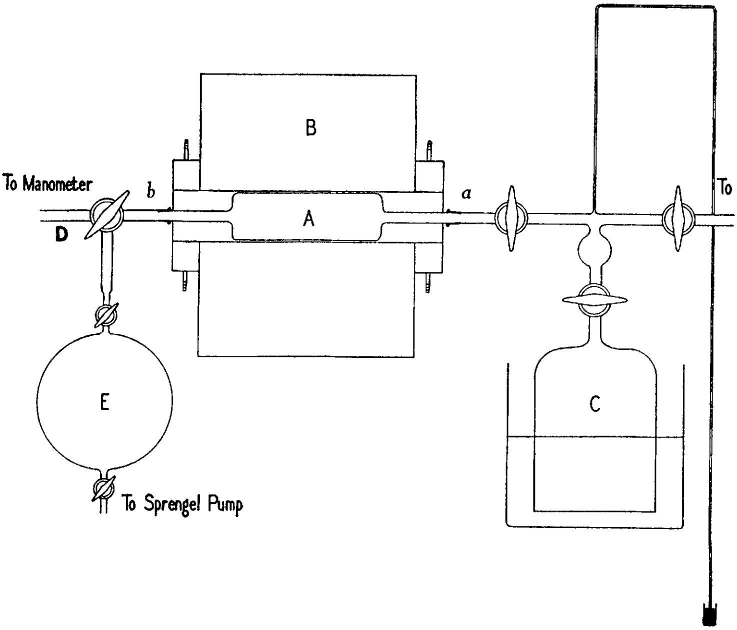
The heats of activation are also given in this table. The average value for the small vessel is 40,000 calories, as compared with 65,000 calories recorded by Fort and Hinshelwood for methane–oxygen mixtures. On the " chain reaction " hypothesis, it can be assumed that the presence of an inert gas breaks the chain. The high concentration of inert gas in our experiments has apparently prevented the propagation of any " chain reaction."

Experimental.

The apparatus used (Fig. 1) consisted of a cylindrical vessel of quartz, A, heated to the desired temperature by a platinum-wound electric resistance furnace, B. The ends of the furnace were water-cooled and the winding was so arranged as to give a uniform temperature over the length occupied by the reaction-vessel. Temperatures were measured by a platinum and platinum–rhodium thermo-couple and a milli-voltmeter. One end, *a*, of the reaction-vessel was attached by a ground joint to a glass gas-holder, C, and the other end, *b*, by a similar joint, to a three-way tap, D. This tap allowed of communication between the reaction-vessel and either a recording manometer or an evacuated glass globe, E, of 4 l. capacity.

In carrying out an experiment, the temperature of the furnace was adjusted with the reaction-vessel filled with nitrogen. To the gas-holder (a bell-glass standing in a mixture of glycerol and water), there was introduced from a storage-holder just sufficient of the required gas-mixture to fill at atmospheric pressure the heated reaction-vessel and its connexions, which were then thoroughly evacuated. The measured quantity of the gas-mixture was allowed to enter the reaction-vessel rapidly by suitable manipulation of the taps on the apparatus. During determinations of the ignition-temperatures and lags on ignition, the three-way tap, D, was in communication with the manometer. If it was desired to sample the gases in the reaction-vessel during the lag period, the tap, D, did not communicate with the manometer, but was in such a position that, after a given interval of time, it could be turned to connect the reaction-vessel with the evacuated globe, E, whence the sample was subsequently removed through a Sprengel mercury pump for analysis. To preserve constancy of condition of the quartz surface, the reaction-vessel was rapidly evacuated after each experiment and filled with nitrogen (see J., 1922, **121**, 2091).

Fig. 1.



The Influence of the Size of the Reaction-vessel.—Taffanel and Le Floch (*Compt. rend.*, 1913, **157**, 469), using a similar method of experiment to ours, which originated with Mallard and le Chatelier (*Ann. Mines*, 1883, **4**, 280), have shown that, for a given mixture of methane and air in two quartz reaction-vessels of 15 and 275 c.c. capacity, the ignition temperature was lower in the larger vessel. We confirm this. Our experiments, with reaction-vessels of 48 and 440 c.c. capacity, are not directly comparable with those of Taffanel and Le Floch, or with our earlier experiments, because of differences in experimental method. The results, which include determinations of the lags on ignition at different temperatures as well as the ignition temperatures, are recorded in Tables I and II.

TABLE I.

Relative Ignition-Temperatures of Methane–Air Mixtures.

	Reaction-vessel, 48 c.c. Ratio, surface : volume 1·3.		Reaction-vessel, 440 c.c. Ratio, surface : volume 0·6.	
CH_4, %.	Ignition-temp.	Lag at ignition-temp., secs.	Ignition-temp.	Lag at ignition-temp., secs.
2·25	—	—	650°	9·5
2·95	682°	10·6	641	13·2
4·55	—	—	636	12·4
5·15	—	—	634	16·5
5·40	679	18·6	—	—
5·80	—	—	632	18·5
6·40	678	16·0	632	16·1
7·65	—	—	634	12·1
8·30	690	13·9	—	—
8·65	—	—	635	12·0
9·00	—	—	636	—
10·00	—	—	638	14·5
10·20	704	9·8	—	—
11·90	—	—	643	13·5
13·75	728	6·3	—	—
14·10	—	—	649	10·2

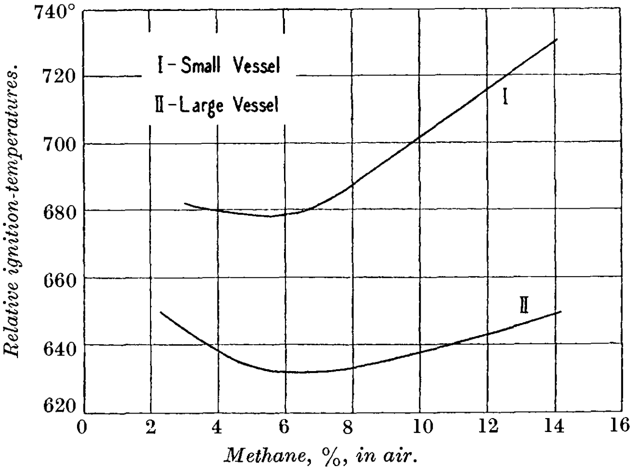
TABLE II.

Lags on Ignition of Methane–Air Mixtures at Temperatures higher than their Ignition-Temperatures.

		Lag., secs.	
Temp.	CH_4, %.	Reaction-vessel, 48 c.c.	Reaction-vessel, 440 c.c.
700°	1·60	—	3·06
	3·90	4·96	3·27
	7·95	8·92	3·71
	9·65	11·75	4·03
	12·65	—	4·33
	15·60	—	5·19
750	1·90	1·33	1·53
	3·90	1·56	1·67
	8·70	2·44	2·07
	13·00	3·56	2·25
	17·65	—	2·67
800	1·65	0·64	0·83
	3·90	0·75	0·85
	7·95	0·93	1·10
	12·65	1·27	1·26
	15·60	1·61	1·36
900	1·90	0·23	0·24
	3·90	0·28	0·29
	8·70	0·32	0·36
	13·00	0·36	0·44
	17·65	0·40	0·51

From the curves in Fig. 2 (ignition-temperatures), it is evident that the rates of the reactions resulting in flame are influenced mainly by the concentration of the oxygen in methane–air mixtures. The same conclusion is to be drawn from the records of lags on ignition at different temperatures (Table II), which are all shorter the higher the concentration of the oxygen. Comparing the results in the two reaction-vessels, the rate at which the heat of the reactions is communicated to the wall of the vessel is proportional to its area, and is lower the less the ratio surface-volume. At low temperatures, therefore, when the lags on ignition are comparatively long, the rate of transference of heat to the wall of the reaction-vessel is a dominant factor, but at high temperatures, when the lags are short, the rate of attainment of thermal equilibrium when the gas-mixture is admitted to the heated reaction-vessel assumes importance. Temperature equilibrium is attained more rapidly in the smaller vessel. The lags, therefore, are shorter in the smaller vessel at high temperatures.

FIG. 2.

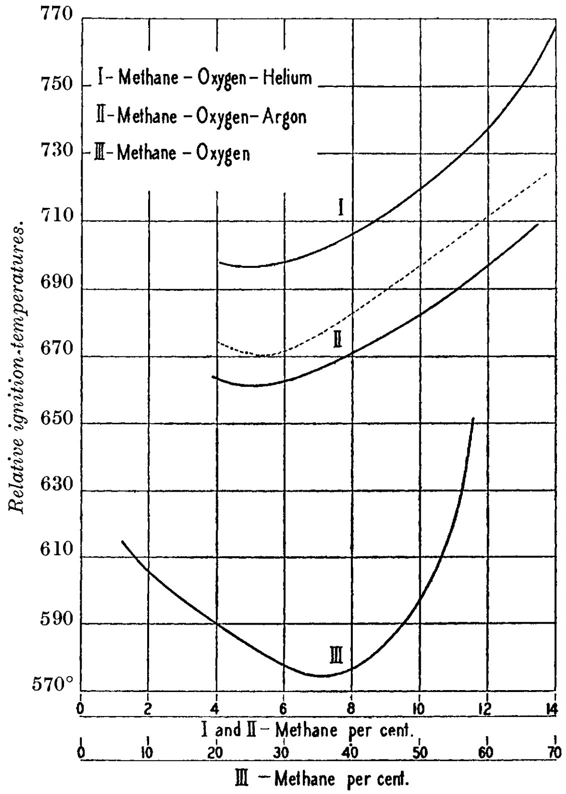


Temperatures higher than 900° could not conveniently be used with the 440 c.c. reaction-vessel. Determinations of the lags have, however, been made up to 1175° in the smaller vessel and the results are recorded in Table III. From these results it is possible to estimate the temperature necessary to cause the ignition of any mixture of methane and air with a given short interval of time of contact between the mixture and the heated surface. For example, to ignite a mixture containing 10% of methane in 0·001 sec. would require a temperature of 1590°.

TABLE III.

Temp.	CH_4, %.	Lag., sec.
925°	2·50	0·16
	4·95	0·19
	8·65	0·25
	12·50	0·26
	16·05	0·30
	21·00	0·37
	26·40	0·36
975°	2·50	0·09
	6·45	0·13
	8·45	0·15
	11·90	0·16
	16·00	0·19
	19·40	0·20
	26·40	0·24
1025°	2·50	0·05
	4·40	0·07
	7·95	0·08
	11·40	0·09
	15·50	0·12
	20·45	0·12
	22·00	0·14
	26·30	0·15
1075°	2·50	0·037
	7·30	0·052
	11·40	0·059
	18·50	0·072
	27·50	0·100
1175°	6·65	0·013
	12·00	0·020
	18·50	0·033
	24·70	0·041

FIG. 3.



The Influence of Chemically Inert Gases.—With mixtures of methane and oxygen, no diluent gas being present, the lowest ignition-temperature is obtained with the mixture for complete combustion, though a curve (see Fig. 3) showing the relationship between the ignition-temperatures and the percentages of methane in the mixtures shows that the rates of the reactions are rather more dependent on the oxygen than on the methane concentration. This observation is confirmed by measurements of the lags on ignition at 650°, for the lags, over a wide range of mixtures, were shorter the higher the concentration of the oxygen (see Table IV).

TABLE IV.

Lag on Ignition of Methane–Oxygen Mixtures at 650°.

(Reaction-vessel, 48 c.c. Ratio, surface : volume 1·3).

CH_4, % ...	22·90	28·25	38·30	39·75	43·65	47·00	50·15	54·40
Lag., secs....	1·16	1·28	1·33	1·51	1·65	1·87	2·18	2·82

With the addition of nitrogen, as in methane–air mixtures, the ignition-temperatures are higher and, as we have seen, their values are markedly dependent on the oxygen-concentration. This suggested that the nitrogen might not be acting merely as a diluent. Comparative series of determinations were therefore made, in a 50 * c.c. reaction-vessel, in which the nitrogen of air was replaced by an equal amount of (a) argon and (b) helium. The results are recorded in Table V, together with those for methane–oxygen mixtures.

TABLE V.

Relative Ignition-Temperatures of Methane–Oxygen, Methane–Oxygen–Argon, and Methane–Oxygen–Helium Mixtures.

Methane–Oxygen.		Methane–Oxygen–Argon.		Methane–Oxygen–Helium.	
Methane, %.	Ignition-temp.	Methane, %.	Ignition-temp.	Methane, %.	Ignition-temp.
4·95	615°	3·95	663°	4·10	698°
14·25	598	5·10	662	4·65	696
17·70	594	5·85	662	5·00	695
21·35	585	6·80	668	5·60	697
27·50	580	7·85	671	6·45	699
33·00	576	9·05	678	7·05	702
36·80	575	9·75	681	7·45	703
41·35	578	11·15	690	7·65	706
48·90	591	12·00	699	9·70	715
56·20	636	13·55	709	12·00	736
58·05	651			14·00	766

The effects of argon and helium are what would be expected from the thermal properties of these gases (see p. 2457), the character of the curves relating percentages of methane to ignition-temper-

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* The 48-c.c. vessel used for the experiments with methane–oxygen mixtures was broken by an explosion.

atures being no different from that for methane–air mixtures (see Fig. 3). An ignition-temperature curve for methane–air mixtures in the 50-c.c. vessel has been added to Fig. 3 (in dotted line) for comparison. Each of the three gases, nitrogen, argon, and helium, therefore, acts merely as a diluent of the oxygen.

The Period of Lag.—A study of the reactions taking place during the pre-flame period was made by analyses of the gases during series of experiments with a 5·8% methane–air mixture in the 440 c.c. reaction-vessel. In individual experiments, the contents of the reaction-vessel were rapidly removed, in the manner previously described, after a measured interval of time. Temperatures of 624°, 634°, and 655° were used. The mixture did not ignite at 624°, whilst at 634° and 655° the lags were 16·3 and 8·32 secs. respectively. The results are recorded in Table VI.

TABLE VI.

Analyses of Gases during Period of Lag on Ignition.

(Methane–air, 5·8% methane.)

Duration of heating.	Analysis of gases, per cent.					
	CO_2.	O_2.	CO.	CH_4.	H·CHO.	H_2O.
			Temperature 624°.			
5 secs.	0·07	18·60	0·11	4·10	1·52	1·88
10 ,,	0·17	14·82	0·45	4·07	1·11	2·35
15 ,,	0·32	15·33	1·19	3·63	0·66	3·67
20 ,,	0·37	15·80	1·39	3·70	0·34	3·86
30 ,,	0·77	15·38	1·73	3·14	0·16	5·16
1 min.	1·82	13·05	1·81	2·12	0·05	7·32
2 mins.	2·96	11·96	1·31	1·52	0·04	8·53
3 ,,	3·29	10·25	0·84	1·11	0·54	8·82
4 ,,	3·68	10·82	0·47	0·74	0·76	9·21
5 ,,	3·84	10·57	0·54	0·58	0·83	9·60
20 ,,	4·82	9·31	0·14	0·34	0·54	10·38
			Temperature 634°.			
1 sec.	0·11	19·13	nil	5·45	0·26	0·48
4 secs.	0·12	18·96	nil	5·38	0·31	0·56
7 ,,	0·09	18·95	0·10	5·27	0·35	0·75
10 ,,	0·18	17·84	0·53	4·57	0·53	1·96
13 ,,	0·53	16·80	0·77	4·13	0·40	2·99
15 ,,	3·59	12·15	nil	2·16	0·06	7·26
16 ,,	5·47	8·17	0·08	0·06	0·21	11·30
			Temperature 655°.			
1 ,,	0·08	19·15	0·07	5·54	0·12	0·42
2 ,,	0·16	18·83	0·05	5·42	0·18	0·60
3 ,,	0·12	19·19	0·09	5·57	0·04	0·43
5 ,,	0·13	18·90	0·16	5·45	0·06	0·65
7 ,,	0·58	17·47	0·43	4·73	0·07	2·09
8 ,,	3·58	12·07	nil	2·16	0·07	7·23

The percentages of formaldehyde and steam are calculated from the carbon and hydrogen balances. Tests for formaldehyde were made during each experiment by confining a portion of the sample of gases over water to which phenylhydrazine hydrochloride, potassium ferricyanide and hydrochloric acid were subsequently added. Positive results were obtained in the majority of the tests and the intensity of the colour produced served as a rough guide to the quantities of formaldehyde present.

With a view to isolate any other intermediate compound that might be formed during the lag period, 40 l. of a 5·8% methane–air mixture were passed slowly through the reaction-vessel heated at 624°, and the products led through a vessel cooled by solid carbon dioxide–ether and thence into water. Both the condensed liquid and the water solution were tested for alcohols, aldehydes, organic acids, peroxides and glycols. Only formaldehyde could be detected.

From the results recorded in Table VI, it will be seen that at 624° a rapid reaction occurred as soon as the mixture entered the heated vessel. This rapid reaction, which is not so marked at the higher temperatures, no doubt occurs at the surface of the vessel as one or other of the reacting gases is adsorbed. It is followed by a comparatively slow reaction. When the temperature of the vessel was below the ignition-temperature of the mixture (*i.e.*, at 624°), the reaction continued to be slow until the methane was consumed, but at or above the ignition-temperature it rapidly accelerated just before flame was due to appear. The beginning of the period of acceleration corresponded with the removal of formaldehyde and carbon monoxide from the gases, suggesting that the heat derived from the oxidation of these intermediate compounds was responsible. If this supposition were correct, it would be expected that the addition of traces of either formaldehyde or carbon monoxide to the mixture initially would influence the rate of reaction. The results of such tests, recorded in Table VII, show that the addition of 0·02% of formaldehyde lowered the ignition-temperature of a 5·6—5·7% methane–air mixture slightly and reduced the lag con-

TABLE VII.

The Effect of Traces of Formaldehyde and Carbon Monoxide on the Lag on Ignition of a 5·6—5·7% Methane–Air Mixture.

Mixture with air.	Temp.	Lag., secs.
5·65% Methane	633°	17·3
	640	13·2
5·7% Methane, with 0·02% formaldehyde	626	6·2
	631	4·4
	640	3·0
5·6% Methane, with 0·25% carbon monoxide	632	10·4
	640	7·4
5·7% Methane, with 0·02% formaldehyde and 0·25% carbon monoxide	627	4·2
	631	3·6
	640	2·7

siderably. Carbon monoxide was not so effective, but the two together had rather more influence than formaldehyde alone.

The Action of " Inhibitors."—The discovery by the late Professor H. B. Dixon that the presence of traces of nitric oxide lowers the ignition-temperature of methane and other inflammable gases (*Trans. Faraday Soc.*, 1926, **22**, 267) led us, in connexion with the work on which each of us was employed for the Explosives in Mines Research Committee, to discuss together the possibility of finding some substance that would act, in the reverse direction to nitric oxide, as an inhibitor of the ignition of methane (see *Trans. Inst. Min. Eng.*, 1930, **80**, 11). A remembrance of early anomalous results for the ignition of methane prepared from methyl iodide suggested that iodine might prove to be such a substance. Parallel experiments were therefore outlined, to be carried out by Professor Dixon with the " concentric tube " apparatus, devised by Dr. H. F. Coward and himself (J., 1909, **98**, 514), and by ourselves with the apparatus described in this paper. The former apparatus has proved more suitable for the work and experiments with it have been continued, under the direction of Dr. H. F. Coward, since Professor Dixon's death.

The results of some of the experiments that we have made, with iodine, halogen compounds, and lead tetraethyl, are summarised in Table VIII. Each of those substances was found to raise the ignition-temperature of a 5·8% methane–air mixture, the degree of elevation varying with the amount present. In Table VIII the maximum elevation is recorded in each instance, together with the amount of the substance that produced it.

TABLE VIII.

The Effect of " Inhibitors " on the Ignition-Temperature of a 5·8% Methane–Air Mixture.

Nature and quantity, %, of inhibitors.	Ignition-temperature.	Lag at ignition-temperature, secs.
Iodine, 0·20	749°	3·6
Ethyl iodide, 0·03	760	2·8
Ethyl bromide, 0·24	744	3·6
Carbon tetrachloride, 0·23	689	3·0
Lead tetraethyl, trace	*ca.* 707	55·0
No addition	632	18·5

For comparison with the results recorded in Table VI, series of experiments were made with a 5·8% methane–air mixture containing traces of (a) ethyl iodide and (b) lead tetraethyl, in the 440 c.c. reaction-vessel at 624°, samples of the products being removed after a given interval of time in each experiment. The results are recorded in Table IX.

TABLE IX.

Analyses of Gases during Combustion of a 5·8% Methane–Air Mixture at 624°. The Effect of Inhibitors.

(*a*) The effect of ethyl iodide (0·14%).

Duration of heating.	Analysis of gases, %.					
	CO_2.	O_2.	CO.	CH_4.	H·CHO.	H_2O.
5 secs.	0·13	18·78	0·28	4·94	0·65	1·27
10 ,,	0·14	18·29	0·45	4·86	0·55	1·13
15 ,,	0·20	17·70	0·65	4·68	0·47	1·61
20 ,,	0·35	17·60	1·14	4·38	0·14	2·56
1 min.	0·61	16·16	1·44	3·50	0·46	4·00
2 mins.	1·16	14·11	1·60	2·50	0·75	5·72
3 ,,	1·36	14·01	1·74	2·32	0·59	6·23
4 ,,	1·51	14·17	1·52	1·56	1·41	6·93
5 ,,	2·22	12·34	1·76	1·48	0·54	7·95
(*b*) The effect of lead tetraethyl (trace).						
20 secs.	0·38	18·87	nil	5·91	*	*
1 min.	0·19	19·00	0·12	5·22		
2 mins.	0·26	18·57	0·31	5·00		
3 ,,	0·36	18·05	0·36	4·74		
4 ,,	0·39	17·77	0·54	4·52		
5 ,,	0·47	16·93	0·71	4·16		

* The exact quantity of lead tetraethyl added not being known, the quantities of formaldehyde and steam formed could not be calculated.

The effect of the ethyl iodide has been to reduce the rate of reaction to about one-half, whilst the lead tetraethyl has reduced it to about one-twentieth. Each substance affects the surface reactions. With lead tetraethyl, or rather, with the lead oxide produced from it, the effect is long-continued, being noticeable in successive experiments with pure methane–air mixtures.

This work forms part of the researches that we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish this paper.

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