304. *Ignition Temperatures of Gases. "Concentric Tube" Experiments of (the late) Harold Baily Dixon.*

By H. F. COWARD.

DURING the last eight years of his life, the late Prof. H. B. Dixon's research was almost entirely concerned with determinations of the ignition temperatures of gases and vapours by two methods: (*a*) ignition by the heat of rapid compression, (*b*) ignition in the "concentric tube" apparatus. A summary of his work with the latter is presented here. It has been compiled, at the request of Prof. R. V. Wheeler, from a series of Reports submitted by Prof. Dixon to the Safety in Mines Research Board, for whom he made the experiments. In addition, an account is given of further work in a direction which Dixon's experiments had clearly indicated, and certain relations between some of his results and current theories of the ignition process are shown.

In his experimental work Prof. Dixon had the assistance of Mr. W. F. Higgins, Ph.D., for seven years, and later of Mr. J. J. Gleadall. Since Prof. Dixon died, Mr. Gleadall and Mr. F. J. Hartwell have continued the work. To these three the writer is indebted for information supplementary to the Reports.

The chief features of the following account are (1) a record of ignition temperatures, especially the "rapid-ignition points" of 0·5 sec. lag, of a number of gases and vapours in air and in oxygen, over a wide range of pressure; (2) the discovery that the presence of small amounts of nitrogen peroxide in the atmosphere (air or oxygen) reduces the ignition points of gases generally, a discovery which Prof. Dixon invited Mr. C. N. Hinshelwood to follow up, with important results in relation to the theory of chain reactions; (3) the discovery that the presence of small amounts of iodine in the atmosphere raises the ignition points of hydrogen, carbon monoxide, and methane, and that various compounds of bromine raise the ignition point of methane; (4) a discussion of the results in terms of current theories.

Much of the commentary on the experiments is derived from Dixon's Reports, and the writer has no reason to think that he would not have accepted the concluding paragraphs of the paper.

EXPERIMENTAL.

The Concentric Tube Apparatus.—This apparatus was originally designed with the help of Mr. G. W. A. Foster. An atmosphere of air or oxygen was passed up through a wide porcelain tube, the temperature of which was slowly raised by an external electrically heated spiral of platinum wire. The inflammable gas was passed up a narrow tube, co-axial with the other, terminating in an orifice at the centre of the wider tube. By these means the gas and the atmosphere were separately heated and continuously renewed, and the products of slow combustion were rapidly removed from the zone of reaction. As the temperature rose, a point was reached at which inflammation occurred; this temperature was recorded by means of a thermocouple, protected by a thin quartz tube, just below the orifice of the inner tube.

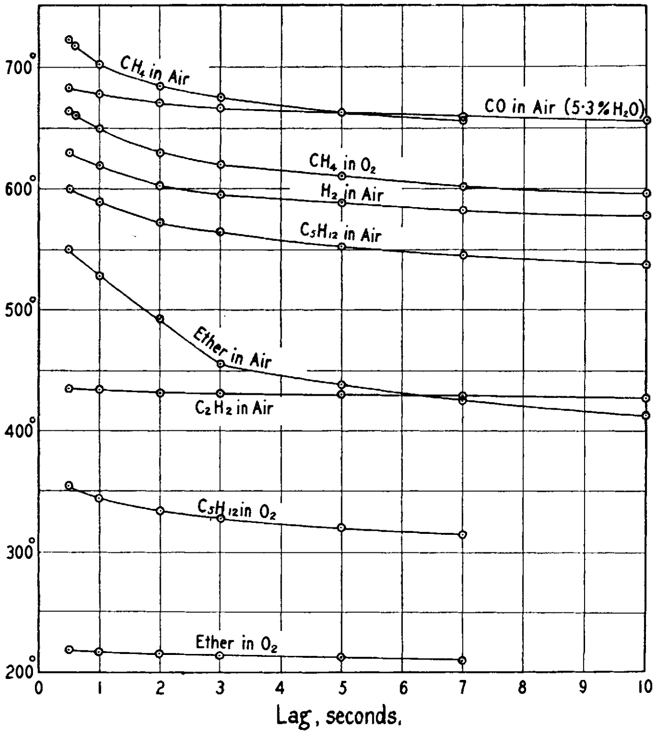
Several gases showed nearly constant ignition points in this apparatus over a considerable range of variation in (1) the rates of flow of gas and atmosphere, (2) the dimensions and (3) the materials of the tubes. Others, notably the paraffin hydrocarbons, were more affected by such variations in conditions (see Dixon and Coward, J., 1909, **95**, 514).

In his subsequent work with this apparatus, during the years 1922—1930, Dixon modified the earlier procedure. Instead of passing continuous streams of gas and atmosphere through the furnace as its temperature was raised, he made the current of gas intermittent, and recorded, for a succession of temperatures, the intervals of time between the sudden turning-on of the gas and the appearance of flame. The temperature at which the gas lit with no more than a 0·5 second interval he regarded as the important figure, for it approximated to his old definition of ignition temperature as that temperature to which the gases must be separately heated so that when brought into contact they will inflame immediately. He usually ascertained the temperatures at which the gas lit after intervals of 0·5, 1, 2, 3, 5, and sometimes 7, 10, and 15 seconds.

Some typical results are shown in Fig. 1. The rapid-ignition points (0·5 sec. lag) are at the left-hand ends of the curves, and are fairly well defined. It is not possible, however, to extrapolate to zero time and thus to deduce instantaneous ignition points, for it is probable from other experiments (cf. Naylor and Wheeler, J., 1931, 2456) that the curves would become steeper towards the left hand and would approach the axis of ordinates asymptotically. Dixon observed that when hydrogen was brought into oxygen, or air, the rapid-ignition points were sharply marked, and concordant results were obtained in different pieces of apparatus. A very few degrees above the temperature at which the lag was 0·5 sec., the inflammation appeared to follow immediately the action of turning on the gas; 0·5 sec., which is easily timed, was therefore taken as the limit for rapid ignition. With methane and air, on the other hand, Dixon at first found it hardly possible to get concordant readings with a 0·5 sec. lag (*Trans. Faraday Soc.*, 1926, **22**, 267), but later he obtained sharply marked ignition points with that lag by improving the arrangements for flushing the inner tube just before each trial.

FIG. 1.

Typical observations showing the relationship of the temperature and the interval of time (“lag”) between starting the jet of gas and its spontaneous ignition.

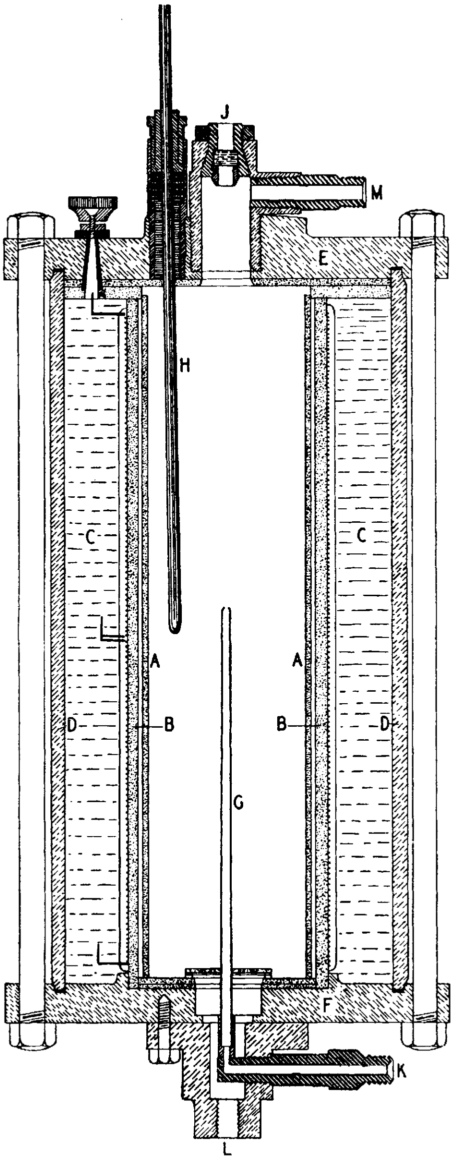


Some of Dixon and Higgins's experimental results of this period have already been published. These are mentioned, but not repeated, in the following. Several sets of published figures were, however, revised by them as a result of improvements in technique; these it has seemed desirable to incorporate. The publications referred to are: Trans. Empire Mining and Metallurgical Congress, 1924, 2304 *A*, p. 38; *Rec. trav. chim.*, 1925, **14**, 305; *Mem. Manchester Lit. Phil. Soc.*, 1925—6, **70**, 31; 1926—7, **71**, 15; 1928—9, **73**, 21; *Trans. Faraday Soc., loc. cit.*

The New Apparatus.—The apparatus represented by Fig. 2 was constructed for experiments over a range of pressures, the extremes used being 50 mm. and 11 atm. The glazed silica cylinder, *A*, was 12 cm. in internal diameter, 65 cm. in length. It was within a clay tube *B*, wound with nichrome wire for electric heating. *C* is kieselguhr, insulating the heating element from the steel case *D*. *E* and *F* are heavy steel end-plates, held against *D* by 12 bolts. The whole casing was tight, and maintained equal pressures inside and outside the silica tube. The central tube, *G*, was of quartz, 4 mm. external diameter, with an orifice of 2 mm. diameter, the rim of which was ground and lightly fused. A resistance thermometer was suspended in a silica cover, *H*. Ignition was observed through a small plate-glass window, *J*, with the aid of a mirror (not shown) above it.

FIG. 2.

Concentric tube apparatus, for experiments under various pressures.



The inflammable gas entered the furnace through *K*, and the atmosphere through *L* and a baffle-plate above *L*. Unconsumed gases and products of combustion passed out through *M*. The supplies of gas and atmosphere and the discharge of products were controlled by suitable valves and measured by flow-meters. Between the gasholder and the furnace, taps (or quick-action valves) were placed so that, when one was full on, the gas could be regulated by the other; thereafter by turning on the first tap rapidly, the gas was admitted to the furnace at the right rate. A rough check on the adjustment of the gas supply was kept by means of a 3-way tap leading to (1) the inner tube in the furnace, or (2) a replica of that tube, standing in the air. The flow of gas was adjusted to give a flame of standard height on the second tube.

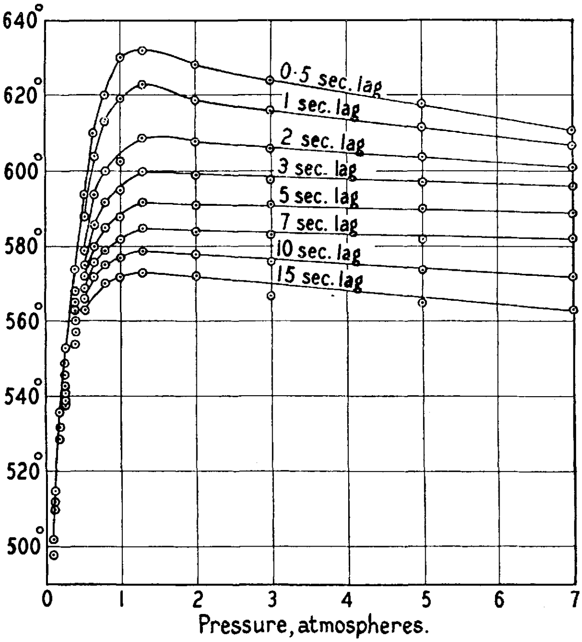
Pressures up to 2 atm. were measured by a mercury manometer, higher pressures by a Bourdon gauge. Temperatures were measured by a platinum-resistance thermometer attached to a Whipple temperature indicator, sensitive to 0·5°. This instrument was checked from time to time, but only small corrections were necessary.

The temperature of the furnace was recorded by one observer as it was slowly raised to the ignition point, while a steady stream of oxygen or air was passing up the wider cylinder. A second observer turned on the tap for a moment to fill the central tube, and then, after 2 or 3 secs., turned on the gas for 15 secs. or until it lit. The small amount of gas flushed out from the central tube did not ignite unless the temperature was close to the rapid-ignition point. The time intervals between turning the gas on and the appearance of flame were estimated, to 0·1 or 0·2 sec., either by a stop-watch or by pendulums set to beat 0·5 and 0·6 sec. The gas was turned off immediately after ignition, to avoid overheating the rim of the orifice. After an interval for the removal of the products of combustion, the operation was repeated at a temperature a few degrees higher, and so on, until the temperature corresponding to 0·5 sec. lag was reached. The observations were repeated with a slowly falling temperature until ignition could no longer be obtained. The ignition points for equal lag periods on the rising and falling temperatures were usually within 2° for the shorter lags. Each ignition point recorded in this paper is a mean, usually of some 4—6 observations which agreed within 2—4° for the shorter and 4—20° for the longer lags.

The apparatus described above was used for each series of experiments in which pressure was a variable, and for some others. When, however, Dixon experimented with nitrous oxide, he found that small amounts of nitrogen peroxide were formed, and that residual traces of the peroxide remained in the apparatus and affected subsequent determinations unless removed by a most laborious process. To meet this difficulty, he selected a smooth silica tube, 5 cm. in diameter, and built a furnace round it; the ends of the tube projected from the furnace, and therefore nitrogen peroxide could not diffuse into the kieselguhr packing and back again, as was possible previously. This apparatus (called below the " narrower apparatus ") was used for all experiments with nitrogen peroxide or inhibitors in the atmosphere. The change from the wider apparatus affected the observed ignition points of hydrogen, carbon monoxide, methane, and ethylene, but only by a few degrees. Other gases were not tested in the narrower apparatus.

Fig. 3.

Ignition points of hydrogen in air (dried by sulphuric acid).



The rates of flow of the combustible gas and the atmosphere are not always stated in the Reports, but it is clear that Dixon satisfied himself, for at least several of the gases tested, that the rates which he used were such that considerable changes did not appreciably affect the results. Had they done so, it is almost impossible that the striking relation between the pressure and the ignition point of hydrogen, and also of carbon monoxide (p. 1405), would have been discoverable. The rates chosen for experiments in the wider apparatus at atmospheric pressure were usually such as would give flames of 25 or 30 mm. height when the gas was burnt at the external jet at room temperature and pressure. For experiments at lower or higher pressures the rates were reduced or increased correspondingly. For experiments in the narrower apparatus the rates were usually such as would give flames from 10 to 21 mm. in height at the external jet. The rate of supply of air or oxygen was usually 3 c. ft. per hour in the wider apparatus, and 1—2 c. ft. per hour in the narrower; at other pressures than normal, the rate was altered in rough proportion.

Hydrogen.—Hydrogen in air. The ignition points of hydrogen in air, dried by sulphuric acid, are given below for pressures up to atmospheric. Below 200 mm. the gas would not usually light with more than 3 secs. lag. These results, together with those obtained at pressures above atmospheric, are shown in Fig. 3. The ignition points at all lags pass through a flat maximum between 1 and 2 atm.; they fall sharply on the low-pressure side, and slowly on the high-pressure side. Some of the results of an earlier series (*Trans. Faraday Soc.*, *loc. cit.*) are high, because the

Ignition points of hydrogen in dry air.

Lag, sec.	Pressure, mm. 75.	100.	150.	200.	300.	400.	500.	600.	760.
0·5	502°	515°	536°	553°	574°	594°	610°	620°	630°
1	498	512	532	549	568	588	604	613	619
2	—	510	529	546	565	579	594	600	603
3	—	—	—	543	563	575	586	592	595
5	—	—	—	541	560	572	580	585	588
7	—	—	—	539	557	569	576	579	582
10	—	—	—	538	554	566	572	575	577
15	—	—	—	—	—	563	—	570	572

air was moist. The effect of the moisture was hardly appreciable at atmospheric pressure, but increased as the pressure was reduced.

In the narrower apparatus, at atmospheric pressure, the ignition point was somewhat lower for the shorter lags, but higher for the longer lags : 623°, 0·5 sec. ; 614°, 1 sec. ; 605°, 2 secs. ; 601°, 3 secs. ; 597°, 5 secs.

Hydrogen in moist air (5·3% H_2O). The ignition points of hydrogen in air, determined under the same conditions as for dry air, except that the air contained 5·3% of water vapour, are shown below. These ignition points were higher by about 10° at normal pressure; the increase was more marked at lower pressure, being, *e.g.*, *ca.* 30° at 100 mm., although the *percentage* of vapour was unchanged. It is thus evident that this charge of water vapour in the air, which confers on carbon monoxide its lowest ignition point (see below), serves only to retard the ignition of hydrogen under the conditions of these experiments.

Ignition points of hydrogen in moist air (5·3% H_2O) *under different pressures.*

Lag, sec.	Pressure, mm. 100.	200.	300.	400.	500.	600.	760.
0·5	546°	579°	595°	608°	620°	628°	638°
1	542	575	589	602	614	621	629
2	540	572	586	594	604	609	613
3	539	570	583	591	598	602	605
5	538	568	580	587	592	596	598
7	—	566	577	583	587	589	591
10	—	564	573	579	582	584	585

Hydrogen in oxygen. The ignition points of hydrogen in oxygen, not specially dried, are shown in the following table. At 75 mm. pressure, hydrogen ignited in oxygen immediately at 500°; below this temperature it did not ignite. It is not unreasonable to compare these results with those for ignition in air dried by sulphuric acid (p. 1385), and to conclude that the substitution of oxygen for air reduces the ignition temperature of hydrogen very slightly; for, although the oxygen was not specially dried, it was used direct from a cylinder of the compressed gas and can have contained much less than 1% of water, an amount which, had it been present in the experiments with air, would have raised the ignition temperature very slightly.

Ignition points of hydrogen in oxygen.

Lag, sec.	Pressure, mm. 75.	100.	150.	200.	250.	400.	550.	760.	1000	2260.
0·5	500°	512°	533°	550°	563°	591°	611°	625°	627°	618°
1	—	510	531	547	558	585	604	618	620	610
2	—	508	528	544	552	575	598	606	—	595
3	—	—	526	541	550	569	587	596	—	580
5	—	—	—	539	548	566	578	588	—	565
7	—	—	—	538	—	563	—	582	—	555
10	—	—	—	536	—	561	—	575	—	546

In the narrower apparatus, at atmospheric pressure, the ignition point with 0·5 sec. lag was slightly lower than in the wider apparatus, *viz.*, 622° and 619° when the rates of flow of the hydrogen were such as to give flames of 13 and 16 mm. height respectively when burning in air at room temperature and pressure.

Hydrogen in nitrous oxide. The ignition point of hydrogen in nitrous oxide was determined in the narrower furnace at atmospheric pressure. Care was taken to remove all traces of nitrogen peroxide after each ignition, for if this was not done, the observed ignition points were much too low. With 0·5 sec. lag the ignition point was 621° and 618° when the rates of flow of the hydrogen were as stated in the preceding paragraph. The ignition point of hydrogen in nitrous oxide is, therefore, very nearly the same as in oxygen (*Mem. Manchester Lit. Phil. Soc.*, 1928—9, **73**, 21).

Carbon Monoxide.—The ignition of carbon monoxide was studied at some length, in view of the recurrent interest in its mode of burning and in the influence of steam and hydrogen on its combustion. The gas used was 99·7% soluble in ammoniacal cuprous chloride, the rest being nitrogen.

Ignition both in air and in oxygen was preceded by a well-marked phosphorescent beam of pale blue haze extending upwards from the orifice of the central tube. This was particularly so at low pressures. Usually, except in the longest lags, the beam appeared very soon after the gas stream had been turned on, though the true flame might not develop until several seconds later. When the normal flame appeared, it formed in the luminous beam usually about half way up, and ran down it to the orifice. The flame generally appeared abruptly in the beam but did not always run down to the central tube quickly. If the gas were sent in under sufficient pressure, it was sometimes possible to maintain the normal flame as a ball of flame half way up the phosphorescent beam. As the lags increased, the beam formation became less well defined, but a bluish haze always appeared. The gas might begin to glow and continue to do so for a

FIG. 4.

Ignition points of carbon monoxide in air containing various amounts of water vapour.

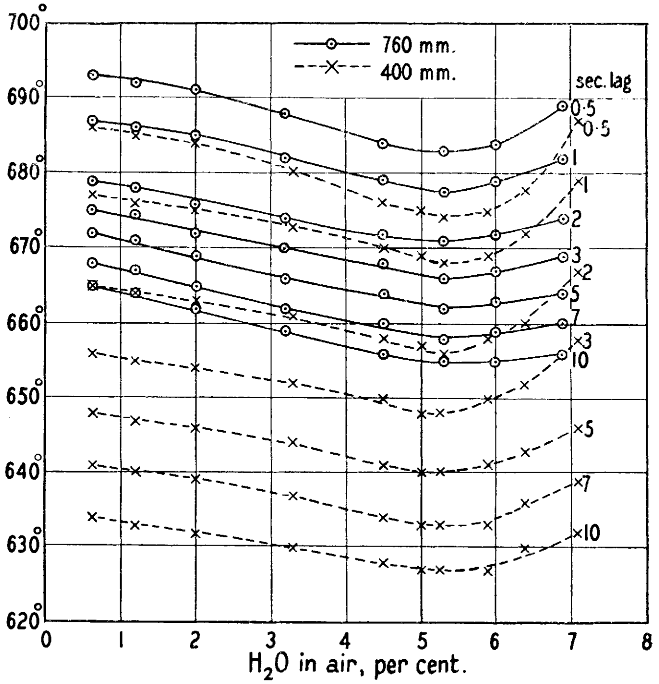


TABLE I.

Ignition points of carbon monoxide in moist air.

Lag, sec.	Pressure, mm.								
	100.	200.	300.	400.	500.	550.	600.	760.	1000.
				(*a*) With 0·63% of moisture in the air.					
0·5	594°	636°	668°	686°	693°	—	696°	693°	683°
1	586	626	661	677	687	—	690	687	678
2	577	615	648	665	679	—	684	679	672
3	—	608	641	656	673	—	680	675	667
5	—	—	631	648	665	—	673	672	661
7	—	—	—	641	657	—	666	668	—
10	—	—	—	634	651	—	659	665	—
				(*b*) With 5·3% of moisture in the air.					
0·5	588*	628	656	674	686	688	689	683	674
1	583*	623	651	668	681	684	685	678	669
2	578*	613	640	656	670	675	676	671	662
3	575*	606	634	648	665	670	671	666	—
5	—	596	621	640	658	662	663	662	—
7	—	589	614	633	648	652	654	658	—
10	—	—	609	627	640	644	647	655	—

* At 110 mm.

minute or more, but the phosphorescence would not develop into a normal flame. Other gases exhibited a similar phosphorescence but, except with carbon disulphide, it was less well defined.

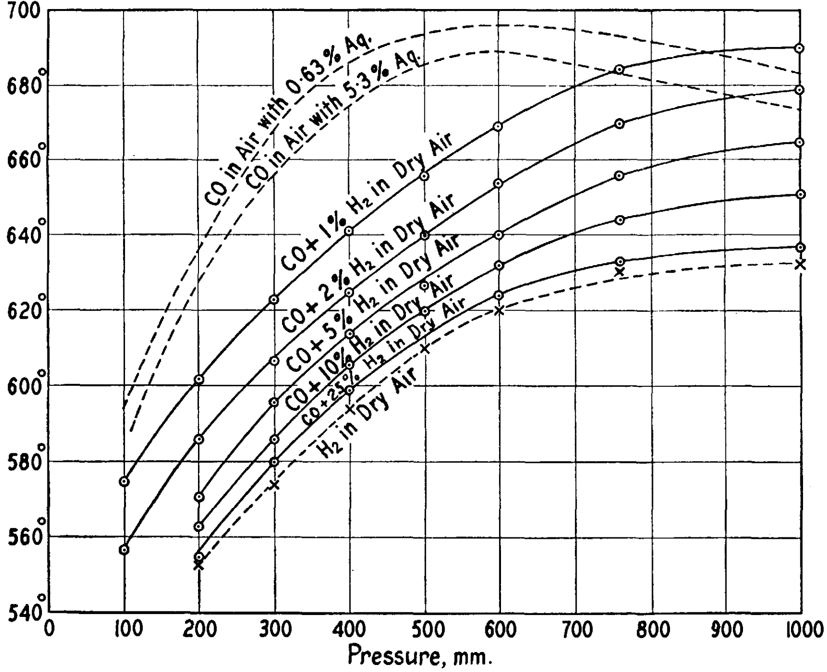
The ignition points and lags recorded below are those for the true flame, not the phosphorescent flame. As is shown in a later section (p. 1405), the relation between these ignition points and the pressure follows a different law from that shown by Hadman, Thompson, and Hinshelwood (*Proc. Roy. Soc.*, 1932, *A*, **138**, 297) to apply to the appearance of the phosphorescent flame.

Carbon monoxide in air. The ignition points of dried carbon monoxide were first determined in air containing various proportions of aqueous vapour.

The ignition points observed at 760 and at 400 mm. are shown in Fig. 4. Flat minima occur in all the curves at about 5·3% of aqueous vapour, and when this is increased beyond 6% the rise in the ignition point is rapid. Concordant results were not obtained when moistened carbon monoxide was used, for the monoxide and the steam reacted in the central tube before issuing from the jet.

FIG. 5.

Ignition points of certain mixtures of carbon monoxide and hydrogen in dry air.



Ignition points at various pressures from 100 to 1000 mm. were determined (*a*) with 0·63%, (*b*) with 5·3% of moisture in the air (see Table I).

In each series the rapid-ignition point (0·5 sec.) reached a maximum at about 600 mm., and for the long lags the maximum shifted towards higher pressures. It is evident from these experiments and from those with oxygen instead of air (see below) that carbon monoxide resembles hydrogen in regard to the effect of pressure, but that its maximum ignition point is at a lower pressure.

Carbon monoxide, containing different percentages of hydrogen, in dried air. As a contribution towards the elucidation of the mechanism by which moisture affects the combustion of carbon monoxide, Dixon determined the effects of small percentages of hydrogen added to carbon monoxide. The rapid-ignition points (0·5 sec.) at different pressures when hydrogen was added in increasing quantities to carbon monoxide and the dry mixture was brought into dry air are shown in Fig. 5. These curves are unlike those for the corresponding ignition points of carbon monoxide in moist air, but correspond with the hydrogen curve, to which they approximate more and more as the proportion of hydrogen is increased.

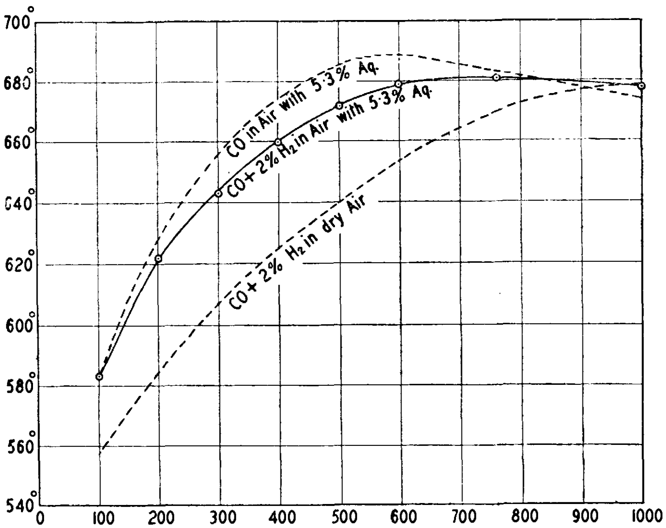
It is seen that below atmospheric pressure carbon monoxide containing 1% or more of hydrogen is more readily ignited in dry air than is the pure gas in moist air (0·63 or 5·3% H_2O), but that the positions tend to reverse with increase of pressure, and at 1000 mm. the pure gas ignited in moist air more readily than the mixture of carbon monoxide with 1% of hydrogen in dry air.

Carbon monoxide, containing a small quantity of hydrogen, in moist air. As the presence of small amounts of hydrogen in the carbon monoxide, and of water in the air, separately, lowered the ignition point of carbon monoxide, it was of interest to ascertain whether the two catalysts would have a cumulative effect if present in the same experiment.

Experiments with dry and with moist hydrogen (see above) had shown that the presence of 5·3% of water vapour in the air, an amount which confers on carbon monoxide its lowest ignition point, served only to retard the ignition of hydrogen under the conditions of these experiments. Determinations were then made in the same apparatus of the ignition points of a mixture of carbon monoxide containing 2% of hydrogen, in air containing 5·3% of moisture. The rapid-ignition points (0·5 sec.) observed at various pressures are shown in Fig. 6, together with two series required for comparison and obtained in the same circumstances. It is evident that the effect of the two catalysts is not cumulative; for the combined effect of the hydrogen and the water vapour never reduced the ignition point lower than the more effective of the two reagents acting alone at a given pressure. At 400 mm. the rapid-ignition point of the CO + 2% H_2 mixture in dry air is 625°, while that of the monoxide in the moist air is 674°, a difference of 49°. At this pressure the rapid-ignition point of the CO + 2% H_2 mixture in the moist air is 660°, the water vapour appearing to retard the action of the hydrogen. In no such case in moist air can the effect of the 2% of added hydrogen be attributed to the mere presence of ordinary molecules of steam formed by its combustion, for the addition of steam molecules above the 5·3% present in the air would raise the ignition point of the carbon monoxide. The result would appear to be due to the process of burning by which the hydrogen is turned into steam, and this burning effect is hindered by the presence of steam in the air. On the other hand at 1000 mm. pressure, when the rapid-ignition point of the pure carbon monoxide in moist air is 674°, below that of the CO + 2% H_2 mixture in dry air, which is 679°, the latter mixture ignites in the moist air at 678°. The result might be explained on the assumption that the action of the water vapour, the more effective of the two catalysts at this pressure, is hindered by the presence of the hydrogen.

FIG. 6.

Ignition points of carbon monoxide, containing 2% of hydrogen, in moist air.



Carbon monoxide in oxygen. Ignition points at various pressures were determined in parallel experiments to those with air, (*a*) with 0·63%, (*b*) with 5·3% of moisture in the oxygen (see Table II). The results are almost the same as those for air, except that the temperatures were

TABLE II.

Ignition points of carbon monoxide in moist oxygen.

Lag, sec.	Pressure, mm. 100.	110.	200.	300.	400.	500.	550.	600.	760.	1000.
	(*a*) With 0·63% of moisture in the oxygen.									
0·5	587°	—	626°	655°	672°	685°	—	689°	687°	675°
1	580	—	618	649	668	681	—	684	682	671
2	572	—	608	639	660	674	—	678	676	667
3	566	—	602	634	654	670	—	675	673	664
5	—	—	598	626	647	662	—	669	668	661
7	—	—	—	622	640	655	—	664	665	658
10	—	—	—	618	634	650	—	658	662	655
	(*b*) With 5·3% of moisture in the oxygen.									
0·5	579	583	622	651	669	682	684	685	680	671
1	575	579	617	647	664	678	680	681	674	667
2	570	574	606	635	652	666	671	672	668	664
3	—	—	600	627	648	662	667	668	664	662
5	—	—	590	616	637	655	659	660	660	659
7	—	—	586	612	632	647	651	653	657	656
10	—	—	—	609	627	640	643	646	653	652

a few degrees lower, in oxygen, for the shorter lags, and that concordant readings were obtained for the longer lags at 1000 mm., which was not so in the experiments with air.

Methane.—Methane in air. A more detailed study was made than that referred to on p. 1383. The chief differences in experiment were the use of a narrower central tube and a new valve, both designed to improve the flushing of the inner tube just before each experiment. Ignition points with 0·5 sec. lag were then obtained regularly.

The effect of varying the rate of flow of the methane was first examined, with the results shown below. The gas used was fire-damp from Cymmer, freed from carbon dioxide; it contained 97·5% of methane, the rest being nitrogen. The rate of flow was adjusted with the aid of the external jet (p. 1384).

Mean ignition points of methane in air at 760 *mm. with various rates of flow of methane.*

Lag, sec.	External flame height, mm. 16.	20.	30.	40.	50.
0·5	738°	731°	722°	722°	722°
0·6	734	726	718	718	718
1	716	711	702	702	701
2	691°	690°	684°	685°	684°
3	680	680	674	675	674
5	—	—	663	664	663

It was evident that increasing the height of flame from 16 to 30 mm. lowered the ignition points, but a further increase had no effect. The ignition at 0·5 sec. lag was sharply marked. A similar series at 400 mm. showed that raising the flame height from 10 to 16 mm. lowered the rapid-ignition point, but a further rise to 20 mm. had no effect.

The ignition points at both 760 and 400 mm. are lower by some 25° than those previously reported (*Trans. Faraday Soc., loc. cit.*). Apart from the small alterations in the mode of experiment, which would not be expected to affect any but the short-lag ignition points, the chief difference was the removal of carbon dioxide from the fire-damp; for the thermometer was checked, the furnace was heated strongly in a vacuum without altering the results, and a redetermination of the ignition point of hydrogen gave the same results as before for that gas. Experiments in which small amounts of carbon dioxide were added to the methane (see below) showed that the presence of such amounts of this gas (somewhat variable) as are present in fire-damp from Cymmer would in large part account for the higher results formerly published (*ibid.*). Nitrogen, also, affects the ignition points, but much less than carbon dioxide.

A redetermination of the ignition points of methane containing 2·5% of nitrogen and no carbon dioxide was made over a range of pressures from 150 to 1000 mm. (Table III and Fig. 7). From experiments described later, it may be assumed that pure methane would give rapid-ignition points about 10—20° lower than those of the gas containing 2·5% of nitrogen.

The ignition points of methane in air could not be determined with accuracy below 150 mm. pressure, but the curves suggest that a maximum would be reached at about 100 mm. A maximum followed by a fall was found, at about 200 mm., for the ignition points of methane in oxygen (*q.v.*).

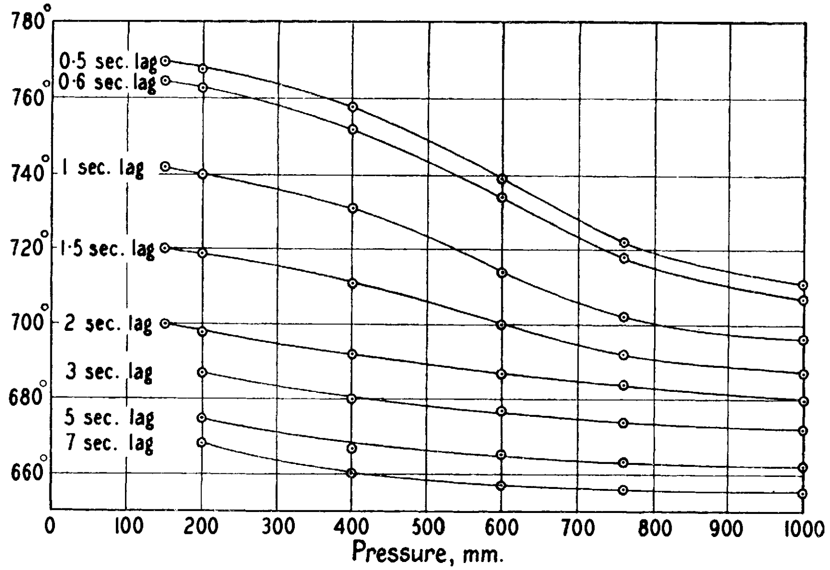
TABLE III.

Ignition points of methane (CH_4, 97·5; N_2, 2·5%) *in air.*

Lag, sec.	Pressure, mm. 150.	250.	400.	600.	760.	1000.
0·5	770°	768°	758°	739°	722°	711°
0·6	765	763	752	734	718	707
1	742	740	731	714	702	696
1·5	720	719	711	700	692	687
2	700°	698°	692°	687°	684°	680°
3	—	687	680	677	674	672
5	—	675	667	665	663	662
7	—	668	660	657	656	655

FIG. 7.

Ignition points of methane (*containing* 2·5% *of nitrogen*) *in air.*



Over the range 2—11 atm. the ignition points were determined with a natural fire-damp which contained : CH_4, 97·0; N_2, 2·5; CO_2, 0·5%; for 0·5 sec. lag, they were :

Pressure, atm.	2	3	5	7	9	11
Ignition point	700°	684°	658°	639°	623°	608°

In these experiments the methane pressure had to be adjusted to give a large flame (60—80 mm. high) in the ordinary air in order to give a proper flame (25—30 mm.) in the compressed and heated air of the cylinder. The lowest temperature at which methane ignited at 11 atm. was 555°, after a lag of 10 secs., but on one occasion it ignited at 550° after a lag of 30 secs. at 9 atm. pressure. Many trials were made at 11 atm. at temperatures between 555° and 550° without getting ignition, although the gas was admitted up to 30 secs.

Effects of small amounts of carbon dioxide, nitrogen, and air in the methane. In parallel experiments it was found that the removal of the 0·5% of carbon dioxide present in a natural fire-damp reduced the ignition point at all lags. The effect was greatest at low pressures; *e.g.*, at 200 mm. the carbon dioxide raised the rapid ignition point by 19°, but at 1000 mm. only by 5°. The effects of various amounts of carbon dioxide, up to 5%, on the ignition points, at 1 atm., of a gas which contained 97·5% of methane and 2·5% of nitrogen are shown in Fig. 8. The effects of nitrogen were shown by experiments in which successive quantities of that gas were added to the sample of Cymmer fire-damp from which the carbon dioxide had been removed. The results are shown in Fig. 9.

A few experiments were made in a similar manner with air instead of nitrogen added to the Cymmer gas. The effect of a small volume of air was larger than that of an equal volume of nitrogen, presumably because some carbon dioxide was formed in the gas before it issued from the jet; but with further additions of diluent, the air did not maintain its greater effect. As the air is increased in the mixture, it is probable that the flameless combustion taking place in the issuing jet heats the gas beyond the furnace temperature, and so begins to facilitate ignition in spite of the dilution.

FIG. 8.

Ignition points of methane, containing 2·5% of nitrogen and small amounts of carbon dioxide, in air.

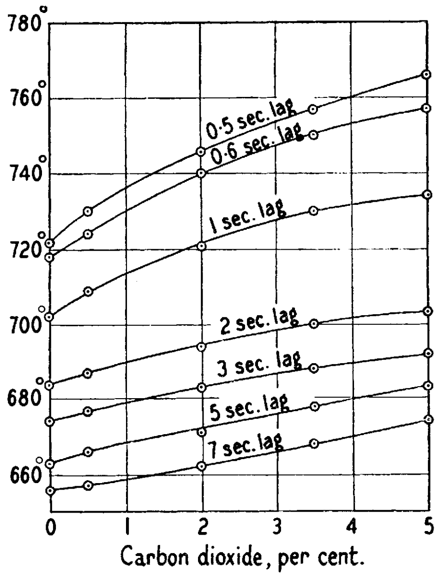
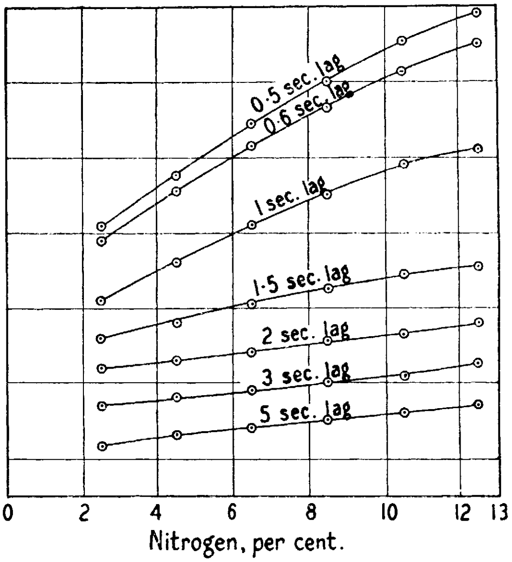


FIG. 9.

Ignition points of methane, containing small amounts of nitrogen, in air.



Methane in oxygen. The ignition points of methane, containing 2·5% of nitrogen, in oxygen are as follows :

Ignition points of methane (containing 2·5% of nitrogen) in oxygen.

Lag, sec.	Pressure, mm.				
	100.	200.	400.	600.	760.
0·5	716°	721°	707°	684°	664°
0·6	708	714	702	678	660
1	684	690	682	666	650
1·5	659	664	660	648	638
2	645	650	645	637	630
3	633°	638°	634°	626°	620°
5	623	627	624	617	611
7	—	618	617	609	602
10	—	—	610	603	595

These results are some 6—12° lower than those formerly published (*Trans. Faraday Soc., loc. cit.*), the reason for which is probably to be found in the greater impurity in the methane used in the older experiments. Curves of these results show that, for each lag, maximum ignition points occurred at about 200 mm. pressure.

Mixtures of Methane and Hydrogen.—Ignition points of the whole range of mixtures of these two gases were determined, both in air and in oxygen, at an early stage of the investigations. The results for the rapid ignitions (0·5 sec. lag) are shown in Fig. 10. The oxygen curve shows that some 25% of hydrogen may be added without an appreciable fall of ignition point; with further additions the fall is fairly regular. As a result of this predominance of the methane, the ignition points of the mixtures all lie above the straight line joining the two extremes. On the other hand, the ignition points of the same mixtures in air are symmetrical about the straight line joining the extremes. Small additions of hydrogen lower the ignition point of methane, but not proportionally to the volume added; similarly, small additions of methane raise that of hydrogen, but not proportionally.

Ethane.—Ethane, prepared by the interaction of diethylzinc and water, in the absence of air, was purified by passage successively over soda–lime, through caustic soda solution and fuming sulphuric acid, and over solid caustic potash. No olefin or higher hydrocarbon could be detected in the gas. The ignition points in air and in oxygen are shown in Figs. 11 and 12 respectively.

The graphs show a gradual alteration of shape as the lags increase. It is only when the ethane ignites fairly quickly that the ignition points reach a maximum within the pressure range investigated. In parallel circumstances, ethane ignites more readily in oxygen than in air, more especially at **300—400** mm. pressure with the shorter lags.

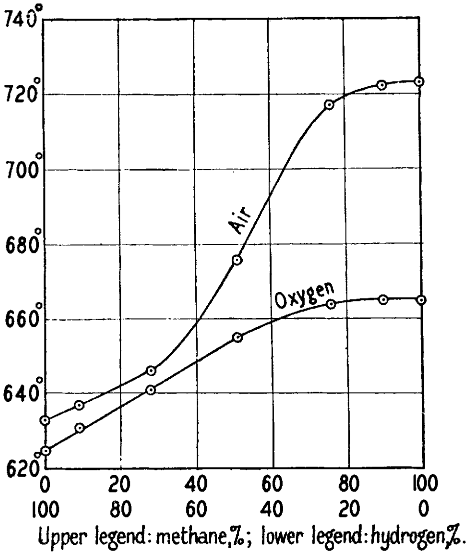
Pentane.—Liquid *n*-pentane was confined in a steel bottle immersed in an air-bath at constant temperature, the vapour passed through two control valves and through a metal pipe to the central tube in the ignition apparatus, all the connexions being heated above the temperature of the air-bath. By adjustment of the control valves a constant rate of flow of vapour was maintained.

Pentane in air. The ignition points of pentane in air are shown in the table below.

At pressures up to 1 atm., the ignitions were fairly regular except at the long lags. A dark blue luminous beam was observed before ignition, and frequently the normal flame was seen to form in the beam, but sometimes the beam disappeared without normal ignition following. The ignitions at higher pressures were not as regular, the vapour burnt with a smoky flame, and concordant results could not be obtained after 2 seconds' lag.

FIG. 10.

Ignition points of mixtures of methane and hydrogen in air and in oxygen.



Ignition points of pentane in air.

Lag, sec.	Pressure, mm. 50.	100.	200.	400.	600.	760.	1000.	1200.	1520.	1770.
0·5	685°	686°	680°	661°	630°	600°	568°	544°	510°	495°
1	672	671	665	646	615	589	557	533	497	477
2	655	653	643	625	595	572	541	518	486	—
3	—	644	632	615	585	564	—	—	—	—
5	—	634	623	600	575	552	—	—	—	—
7	—	624	612	588	566	545	—	—	—	—
10	—	—	—	—	557	537	—	—	—	—

FIG. 11.

Ignition points of ethane in air.

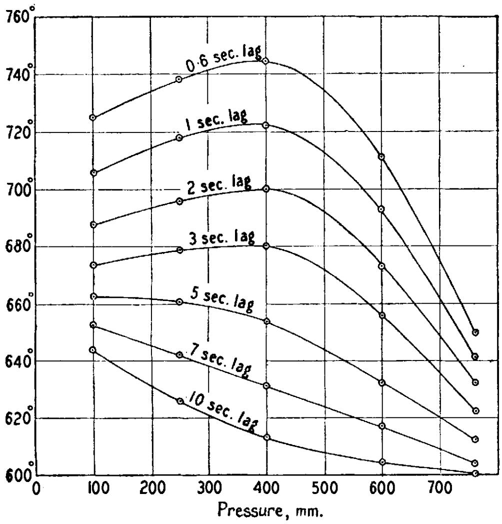
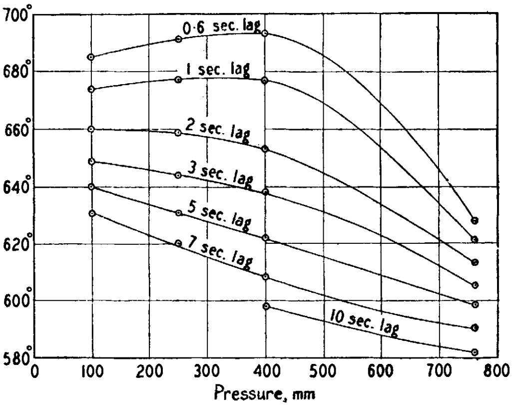


FIG. 12.

Ignition points of ethane in oxygen.



The high ignition points observed at low pressures led to the suspicion that pentane might be appreciably decomposed during its passage to the orifice. Experiments in which pentane was dropped into the nitrogen-filled silica bulb of a Victor Meyer apparatus showed that, whilst at 528° the decomposition was very slow, at 650° there was an increase of 8% in volume in the first 5 secs., and 45% in 30 secs. From a series of such experiments, Dixon concluded that some decomposition of the pentane vapour would occur in the central tube at the higher temperatures employed, and the products of such decomposition might alter the ignition point of the issuing jet. The rapid ignition point found at atmospheric pressure might therefore be too high, and the error would increase at lower pressures and higher temperatures. On the other hand, it did not appear that decomposition affected the results at 1200 mm. pressure and upwards.

Pentane in oxygen. The data are shown in the appended table.

Ignition points of pentane in oxygen.

Lag, sec.	Pressure, mm.							
	100.	200.	400.	600.	670.	760.	1000.	1200.
0·5	677°	641°	620°	542°	430°	355°	339°	330°
1	658	619	595	509	410	345	333	326
2	624	569	544	468	390	334	326	324
3	604	558	521	439	380	328	322	322
5	587	—	493	419	365	320	317	320
7	—	—	475	410	357	314	313	317

It will be observed that the ignition point fell unusually rapidly as the pressure was raised from about 500 to 700 mm., in marked contrast to the parallel observations for pentane in air. At 760 mm. the rapid-ignition point in oxygen was 245° lower than in air, at 600 mm. 88° lower, at 400 mm. 40°, and at 100 mm. only 8°.

Graphs of the figures in the foregoing table are sinuous, as illustrated by the curve for the 0·5 sec. lag in Fig. 25. Similar curves have been given by Neumann and Estrovich (*Nature*, 1934, **133**, 105, 463) for the inflammation of the mixture $C_5H_{12} + 8O_2$ in contact with the walls of a heated iron, or gilded iron, bomb.

Benzene.—An early series of experiments gave the ignition points of benzene in air and in oxygen, at 1 atm., for a lag of 0·5 sec., as 710° and 685° respectively. The lowest ignition points observed were 650° (30 secs. lag) and 621° (28 secs. lag) respectively.

Mixtures of Pentane and Benzene.—The ignition points of the whole range of these mixtures fell on symmetrical, but flat, S-shaped curves, the maximum divergence of the curve from a straight line being 4°.

Ethylene.—Ethylene, prepared by the action of phosphoric acid on ethyl alcohol, was passed through a cooled catch bottle, followed by calcium chloride spirals surrounded by ice and salt, caustic soda solution, and concentrated sulphuric acid. It was collected over mercury. For the high-pressure experiments a sample of commercial gas was used. Neither by analysis nor by ignition tests could any difference be found between the two samples.

Ethylene in air. The ignition points are shown in Table IV (*a*). A maximum is reached at about 400 mm., and is more pronounced with the shorter lags. The lowest ignition point observed at 760 mm. was somewhat higher than that given by Dixon and Coward (*loc. cit.*), which was 543°. When, however, the diameter of the outer tube was reduced to 46 mm., almost the same as that of their experiments, the former figure was obtained for a lag of 10—15 secs.

Ethylene in oxygen. The data are in Table IV (*b*). The maximum ignition point is at about the same pressure as in air, or a little lower. The ignition points are throughout a few degrees lower than in air. The inflammations were more violent, and only two experiments had been made at 3040 mm. when the inner tube was broken. The lowest ignition point observed at 760 mm. was higher than Dixon and Coward's figure, 510°. When the diameter of the outer tube was reduced to 30 mm., a very violent explosion occurred when the temperature had just passed 470° after a lag of 10 secs. The experiments were not continued.

Ethylene in Nitrous Oxide.—Ignition points of ethylene in nitrous oxide and in oxygen were determined in the smaller furnace with the following results for the 0·5 sec. lag :

External flame height, mm.	8	13	16
Ignition point in nitrous oxide	626°	616°	609°
,, ,, oxygen	628	618	611

All traces of nitrogen peroxide were carefully removed after each ignition. It is evident that the ignition point of ethylene in the two gases is almost the same.

TABLE IV.

Lag, sec.	Pressure, mm. 100.	150.	250.	300.	400.	550.	600.	760.	1000.	1200.	1520.	2280.	3040.
	(a) *Ignition points of ethylene in air.*												
0·5	—	646°	665°	—	675°	649°	643°	627°	614°	606°	594°	565°	—
1	—	629	644	—	656	634	629	616	604	596	583	553	—
2	—	610	622	—	632	615	610	599	589	583	570	542	—
3	—	592	602	—	612	601	597	589	578	572	562	532	—
5	—	583	589	—	594	589	587	580	567	560	553	525	—
7	—	575	578	—	580	578	577	571	558	549	546	518	—
10	—	—	567	—	567	565	564	562	548	539	538	513	—
15	—	—	—	—	—	—	—	557	—	—	531	508	—
	(b) *Ignition points of ethylene in oxygen.*												
0·5	594	617	650	659	660	624	—	604	—	—	580	557	535
1	581	600	634	644	646	613	—	593	—	—	572	549	—
2	563	580	614	622	625	601	—	584	—	—	562	539	—
3	555	567	597	603	606	592	—	577	—	—	554	530	—
5	—	558	585	589	590	580	—	569	—	—	546	522	—
7	—	553	574	577	578	570	—	561	—	—	540	515	—
10	—	—	563	566	567	562	—	554	—	—	532	508	—
15	—	—	—	—	—	—	—	—	—	—	—	501	—

Propylene.—Propylene was obtained by passing the vapour of *n*- or *iso*-propyl alcohol over pumice and phosphoric oxide heated in an iron tube to 260—340°, and condensing the liquid products by strong cooling. A commercial sample of compressed propylene was also used. This was stated by the makers to contain some 5% of *iso*propyl ether. At first, it had a lower ignition point than the laboratory preparation, but after standing over water it gave the same results.

Propylene in air and in oxygen. The ignition points are given below. Propylene ignited somewhat more readily in oxygen than in air. In parallel experiments it ignited more easily than ethylene.

Lag, sec.	Pressure, mm. 50.	150.	250.	400.	550.	760.
	Ignition points of propylene in air.					
0·5	—	657°	663°	658°	642°	618°
1	—	642	649	642	628	608
2	—	628	630	624	610	592
3	—	—	617	607	594	580
5	—	—	609	597	584	570
7	—	—	602	591	578	562
	Ignition points of propylene in oxygen.					
0·5	585	608	620	623	605	586
1	574	595	605	608	594	574
2	—	567	574	572	564	556
3	—	552	554	552	549	546
5	—	—	—	541	539	537
7	—	—	—	534	—	—

Acetylene.—Acetylene, obtained from an acetone solution, was cooled, well washed with a strong solution of sodium hydrogen sulphite, dried by calcium chloride, and stored over mercury. For a few experiments, it was prepared from cuprous acetylide, and gave the same ignition point.

Acetylene in air. The ignition points at pressures from 50 to 760 mm. are shown in the accompanying table. A maximum is apparent at about 100 mm. At low pressures (below

Ignition points of acetylene in air.

Lag, sec.	Pressure, mm. 50.	75.	100.	150.	200.	250.	400.	760.
0·5	567°	578°	580°	564°	530°	504°	464°	435°
1	556	562	562	543	514	492	460	434
2	536	538	536	522	498	482	458	432
3	—	—	503	—	496	480	456	431
5	—	—	—	—	495	478	455	430
7	—	—	—	—	492	476	454	429
10	—	—	—	—	—	—	453	427

400 mm.) the ignitions were irregular when the lag exceeded 2 secs. Often a phosphorescent combustion took place near the orifice, over which a faintly luminous blue disc appeared. This disc fluctuated, sometimes growing in size and luminosity until normal ignition occurred, but more often rising and falling in intensity and then going out.

Ether.—A stream of pure ether vapour was obtained by means of the same apparatus as that used for pentane vapour.

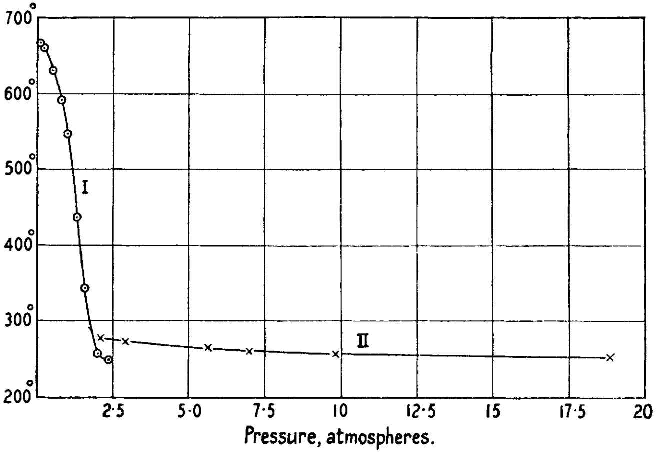
Ether in air. The ignition points are tabulated below. The decrease of more than 400° between 75 and 1770 mm. is remarkable. This series is specially important, for, owing to the low ignition point of ether under moderate pressure, it was possible to compare, *at equal pressures*, the ignition points of ether observed in the concentric-tube apparatus with those observed when ignition was caused by sudden compression, by a piston, of ether–air mixtures contained in a cylindrical vessel. The results of experiments by the two methods are shown in Fig. 13. The ignition point calculated from compression is higher than the true temperature, for cooling must have taken place by contact with the walls, so that it is not surprising that the calculated value is higher than that found in the concentric-tube furnace at the same pressure; but it is satisfactory that there is only 20° difference between the two determinations.

Ignition points of ether in air.

Lag, sec.	Pressure, mm.									
	75.	100.	200.	400.	600.	760.	1000.	1200.	1520.	1770.
0·5	665°	666°	661°	631°	592°	549°	437°	344°	258°	248°
1	646	645	634	607	575	528	420	322	237	231
2	617	610	598	573	544	493	388	296	215	—
3	602	599	585	550	516	456	—	—	—	—
5	586	582	567	534	496	438	—	—	—	—
7	—	—	—	523	484	425	—	—	—	—
10	—	—	—	512	472	413	—	—	—	—

FIG. 13.

Ignition points of ether in air, as found (I) *by the concentric tube apparatus* (0·5 *sec. lag*), (II) *by adiabatic compression.*



Ether in oxygen. The ignition points of ether in oxygen were as follows :

Ignition points of ether in oxygen.

Lag, sec.	Pressure, mm.			
	400.	500.	600.	760.
0·5	242°	225°	221°	219°
1	234	221	218	217
2	226	216	215	215
3	217°	213°	213°	214°
5	213	212	211	212
7	—	210	209	210

The differences between these and those in air are much larger than is usual. It was not surprising, therefore, that when ether vapour carried in a stream of nitrogen was used, the ignition points were sometimes much higher than those of pure ether; *e.g.*, although at 760 mm. pure ether ignited at 219°, and a 1 : 1 ether–nitrogen mixture at 222°, yet at 600 mm. the corresponding figures were 221° and 430° (all for 0·5 sec. lag). In air the differences were 9° at 760 mm. and 23° at 400 mm.

Ether in nitrous oxide. The rapid-ignition point of ether in nitrous oxide, observed in the narrower furnace, was 715° at normal pressure; this is far higher than for oxygen (above) (*Mem. Manchester Lit. Phil. Soc.*, **1929**, **73**, 21).

Carbon Disulphide.—The ignition of carbon disulphide, which presents several special features, was fully described in *Rec. trav. chim.* (*loc. cit.*) and no later investigation was made. The results are, however, summarised. The following table gives the ignition points of carbon disulphide alone and mixed with equal volumes of certain other gases, in air and in oxygen. The experiments brought out clearly the power of carbon disulphide when mixed with certain other gases to maintain the ignition point of the mixture at a low temperature approximating to its own.

Lag,	CS_2.		$CS_2 + N_2$.		$CS_2 + CO_2$.		$CS_2 + H_2$.	
sec.	Air.	Oxygen.	Air.	Oxygen.	Air.	Oxygen.	Air.	Oxygen.
0·5	156°	132°	161°	140°	163°	144°	171°	161°
1	151	128	155	134	157	139	167	157
2	145	123	147	126	148	132	161	149
3	138	118	139	120	139	125	153	140
5	130	114	132	116	132	120	145	131
7	124	110	127	112	127	116	138	122
10	120	107	122	109	122	113	134	116

The rapid-ignition points (0·5 sec. lag) of a wider range of mixtures are collected in Table V. The poisoning action of ethylene (first observed by E. Frankland in 1862) and of acetylene is in contrast with the small effects of other gases, including methane and sulphur dioxide.

TABLE V.

	Air.	Oxygen.		Air.	Oxygen.
$100CS_2$	156°	132°	$50CS_2+50CH_4$	195°	173°
$50CS_2+50N_2$	161	140	$20CS_2+80CH_4$	485	191
$50CS_2+50CO_2$	163	144	$19{\cdot}5CS_2+78CH_4+2{\cdot}5O_2$	—	183
$50CS_2+50H_2$	171	161	$5CS_2+95CH_4$	No ignitions up to 400°	
$50CS_2+50C_2H_4$	608	535			
$50CS_2+50C_2H_2$	520	434	$5CS_2+95H_2$	215	—
$50CS_2+50SO_2$	183	—	$5CS_2+95H_2+1C_2H_4$	410	—
$47{\cdot}5CS_2+47{\cdot}5CO_2+5SO_2$	165	—	$5CS_2+95H_2+0{\cdot}5C_2H_4$	405	—

Attention may be directed to the fact, which Dixon had no opportunity to examine further, that the ignition point of a mixture of equal volumes of carbon disulphide and acetylene in air (520°) was higher than that of either carbon disulphide in air (156°) or acetylene in air (435°). Egerton and Gates (*J. Inst. Pet. Tech.*, **1927**, **13**, 256) made a similar observation with carbon disulphide–petrol.

The Influence of Traces of Nitrogen Peroxide on the Ignition Points of Hydrogen, Carbon Monoxide, Methane, and Ethylene.—Dixon and Higgins (*Mem. Manchester Lit. Phil. Soc.*, **1928**—**9**, **73**, 21) observed that when hydrogen and other gases were ignited in nitrous oxide, some nitrogen peroxide was formed. Some of this was absorbed by the silica walls and by the packing of the furnace, and was only eliminated after long heating and evacuation. The presence of minute quantities of nitrogen peroxide, slowly evolved from the contaminated silica, was found to reduce the ignition points of various gases.

Systematic determinations of these effects were made in the narrower apparatus, which, with a specially selected, smooth, silica tube, proved to be much more easily cleaned than the wider apparatus. The required mixtures of nitrogen peroxide and air were made by passing streams of roughly dried nitric oxide and air separately through meters, and mixing them thoroughly just prior to their admission to the furnace. Each inflammable gas was roughly dried.

Hydrogen in air containing nitrogen peroxide. Before any nitric oxide was admitted to the apparatus, the ignition point of hydrogen was determined in air. The rapid-ignition point was about 7° lower than in the large furnace. Frequent redeterminations of this point served to test the effective scouring of the apparatus from nitrogen peroxide of previous tests. The rapid-ignition points of hydrogen in air containing various small amounts of nitrogen peroxide are shown in Fig. 14. At the optimum concentration of nitrogen peroxide, about 0·5%, the ignition point of hydrogen was 166° lower than in pure air.

Carbon monoxide or ethylene in air containing nitrogen peroxide. See Fig. 14. At the optimum concentrations of nitrogen peroxide, about 0·75% and 1% for carbon monoxide and ethylene respectively, the ignition points were 88° and 128° respectively lower than in pure air.

Methane in air containing nitrogen peroxide. The ignition of methane was examined in some detail, in connexion with a practical point. Among the products of detonation of some solid explosives used in coal-mining are small amounts of nitrogen peroxide. Such products may, therefore, be more liable to ignite fire-damp than has been supposed hitherto, for, as shown below, the presence of 0·1—1·1% of nitrogen peroxide in the air reduces the ignition point of methane by more than 100°.

FIG. 14.

Ignition points (0·5 sec. lag) of carbon monoxide, ethylene, and hydrogen, in air containing small amounts of nitrogen peroxide.

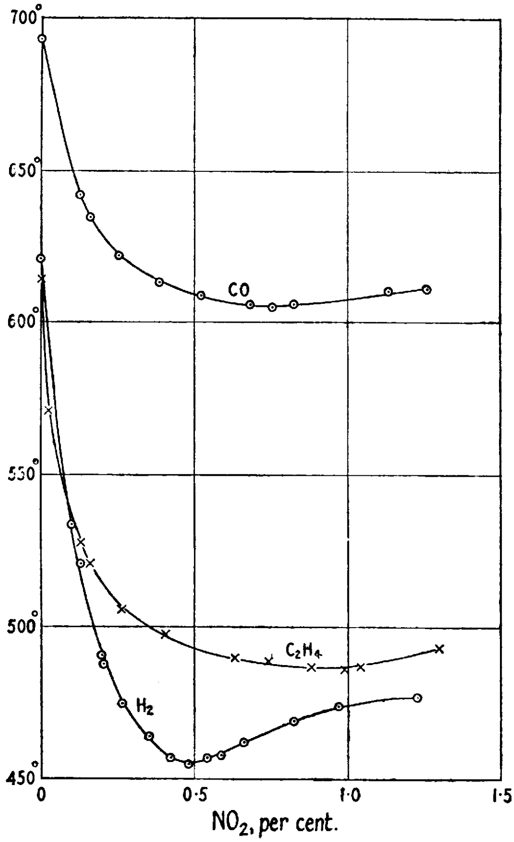
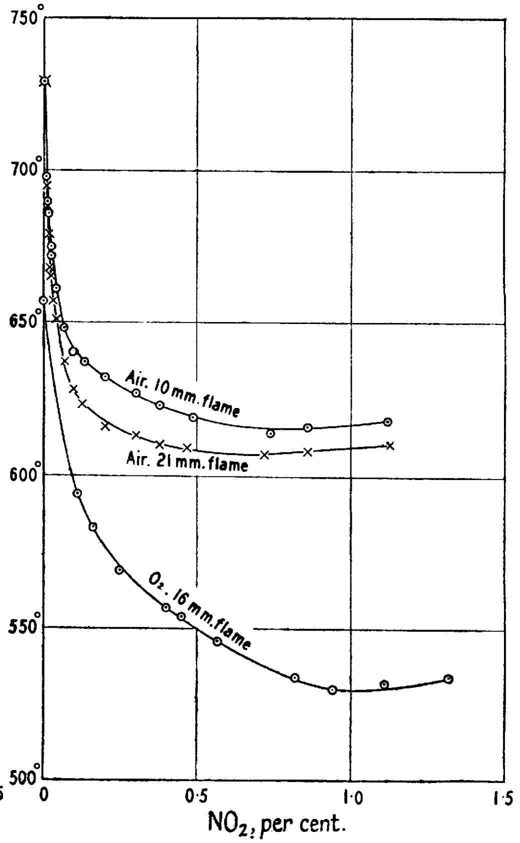


FIG. 15.

Ignition points (0·5 sec. lag) of methane in air and in oxygen containing small amounts of nitrogen peroxide.



Two curves in Fig. 15 show the effect of small amounts of nitrogen peroxide on the rapid-ignition point of methane in air, when the rate of flow of the methane was such as to give (1) a 10 mm., (2) a 21 mm. flame in normal air. It will be observed that the curves coincide when no peroxide was present. In its presence, however, the ignition point was lower with the 21 mm. flame, but no further change occurred when the flame was increased to 27 mm. The maximum lowering of ignition point was 122°, in the presence of 0·7% of nitrogen peroxide.

Methane in oxygen containing nitrogen peroxide. The results of a similar series of experiments, with oxygen in place of air, are also shown in Fig. 15. The optimum concentration of peroxide was just under 1·0%, with which amount the ignition point of methane was 127° lower than in pure oxygen.

The presence of much less than 1% of nitrogen peroxide in the atmosphere lowers appreciably the ignition temperature of each of the four gases tested. The ignition points pass through a minimum when 0·5—1·0% of the peroxide is present. To Dixon's list may be added butyl alcohol and *m*-xylene, the ignition points of which were found by Mardles, independently and at about the same time, to be much reduced by the addition of some 2—5% of liquid nitrogen peroxide (J., 1928, 872).

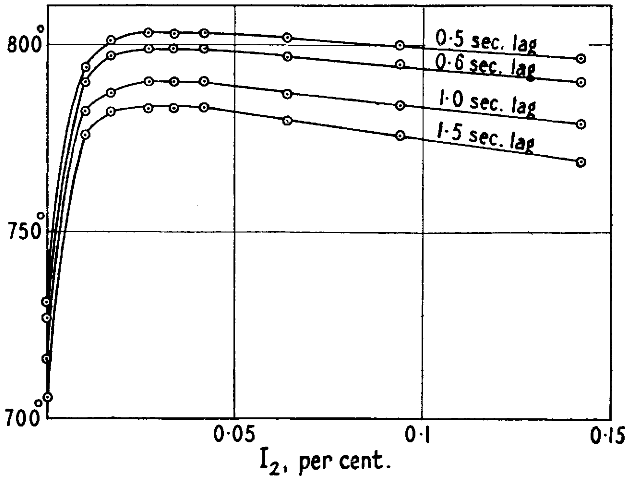


FIG. 16.

Ignition points of methane in air containing small amounts of iodine.

The Effects of Various Inhibitors on Ignition Points.—The discovery of a sufficiently active inhibitor of ignition might have important applications, *e.g.*, in reducing the danger of fire-damp explosions in coal-mines. Since nitrogen peroxide had proved to be a highly active promoter of ignition, the possibility of finding an agent with the opposite property did not seem remote. The first to be tried was iodine, at the suggestion of Prof. R. V. Wheeler, who remembered that high results had been obtained, some years previously, for the ignition temperature of samples of methane prepared from methyl iodide. The effects of bromine and some bromides, of phosphoryl chloride, and of tetraethyl-lead were also examined.

The narrower apparatus was used for all the experiments with inhibitors. The whole, or a measured part, of the air supplied to the furnace was passed through a saturator containing the solid or liquid inhibitor at a controlled temperature. The leads from the saturator to the furnace were maintained at a temperature a little higher than that of the saturator. The concentrations of the inhibitors were calculated from the known vapour tensions, and are probably slightly high, for analysis of the air passing over iodine at the maximum rate used in ignition experiments showed only 92% saturation at 18° and at 40°. The results tabulated below are not corrected for incomplete saturation.

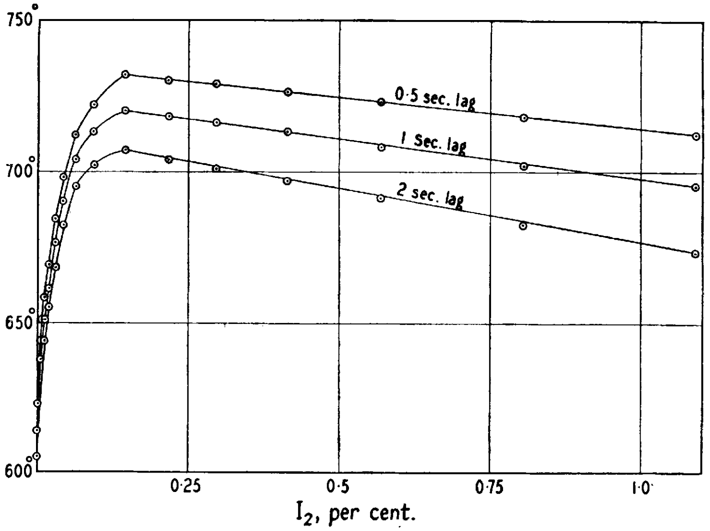


FIG. 17.

Ignition points of hydrogen in air containing small amounts of iodine.

Iodine.—The effects of small amounts of iodine, in the air, on the ignition points of methane are shown in Fig. 16. It will be seen that the optimum concentration of iodine was about 0·03%, but that 0·01% was nearly as effective.

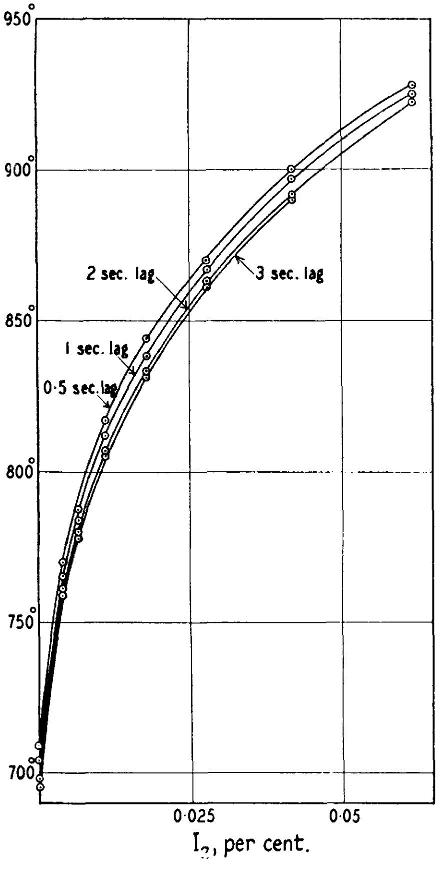
In all these experiments the pre-flame period was marked by a golden glow which, however, did not seem to touch the walls. This glow became more intense the greater the quantity of iodine, and was visible both when the gas was turned on momentarily to flush out the central tube and also at lower temperatures when the gas was left on for 2 or 3 secs. without lighting.

A second important effect of the iodine was the prevention of any ignition of the methane after 1½ secs.' lag. It would appear that the iodine inhibited the normal action of the heated walls in promoting combustion—possibly by forming a layer of condensed vapour on the silica surface.

The effects of iodine on the ignition points of hydrogen are shown in Fig. 17. The effect of 0·01—0·03% was less marked than in the case of methane, but further additions up to 0·15% raised the ignition point by a maximum of over 100°; after this, as more iodine was added, the ignition points declined again. When the iodine exceeded 0·1% a red glow became visible before the flame was formed. It was noticeable that the hydrogen ignited up to a lag of 2 secs., but did not light after that interval.

FIG. 18.

Ignition points of carbon monoxide in air containing small amounts of iodine.



The effects of iodine on the ignition points of carbon monoxide (dried by solid potassium hydroxide) in air (dried by sulphuric acid) are shown in Fig. 18. The rise in the ignition point was more rapid than with hydrogen, and the observations could not be carried to the maximum because the limit of the furnace temperature was reached when the gas lit at 928° in an atmosphere containing 0·062% of iodine.

Dixon observed that for some time after the furnace was first filled with the iodine-laden air the ignition points of carbon monoxide continued to rise, and only became constant when the air and iodine vapour had been passing for more than an hour. That the silica walls were able to condense iodine from the vapour-charged air when the iodine was freshly introduced, and so to reduce the amount of iodine in the atmosphere surrounding the gas jet, afforded the simplest explanation of these observations. When the surface was saturated, the normal (*i.e.*, high) ignition points would be observed. This conclusion seems to be confirmed by the following experiments made to test the combined influence of nitrogen peroxide and iodine on the ignition of methane. When 1 vol. of nitrogen peroxide (NO_2) was added to 200 vols. of air, a jet of methane gave the following mean ignition points in this atmosphere, and when a trace of iodine was added the ignition points were raised for the short lags and *lowered* for the longer lags as shown in the table. It would appear that, during the longer lags, the iodine had the opportunity to displace the nitrogen peroxide attached to the wall, and the liberated peroxide further reduced the ignition point of the methane.

Ignition points of methane in air.

Lag, sec.	With 0·5% NO_2. i.	ii.	Plus 0·028% I_2. i.	ii.	Difference. i.	ii.	Lag, sec.	With 0·5% NO_2. i.	ii.	Plus 0·028% I_2. i.	ii.	Difference. i.	ii.
0·5	606°	605°	615°	615°	+ 9°	+ 10°	1·5	543°	542°	541°	540°	– 2°	– 2°
0·6	592	591	600	600	+ 8	+ 9	2	531	530	527	526	– 4	– 4
1	566	564	570	569	+ 4	+ 5	3	521	521	516	516	– 5	– 5

Ethyl Iodide and Iodoform.—The ignition points of methane in air containing free iodine vapour and ethyl iodide separately did not show strong resemblances except in two particulars.

The highest ignition point was nearly the same with the two inhibitors, and occurred at the same concentration of iodine. When the air was passed over crystals of iodoform at 20°, 30°, and 40°, the maximum effect was observed at 30°, at which the ignition point was the same as the maximum observed with ethyl iodide.

Ethylene Dibromide, iso*Amyl Bromide,* and *Bromobenzene.*—The effects of small amounts of these substances in the air on the ignition points of methane therein are shown in Figs. 19, 20, and 21 respectively. The three substances are powerful inhibitors. Their effects were nearly equal for equivalent concentrations of bromine up to about 0·1%, at which the rise of ignition point was about 100°. Bromine is therefore more efficient than iodine. Further small additions of bromine compounds to the air produced a small rise of ignition point, but with greater amounts the three inhibitors differed in that ethylene

FIG. 19.

Ignition points of methane in air containing small amounts of ethylene dibromide.

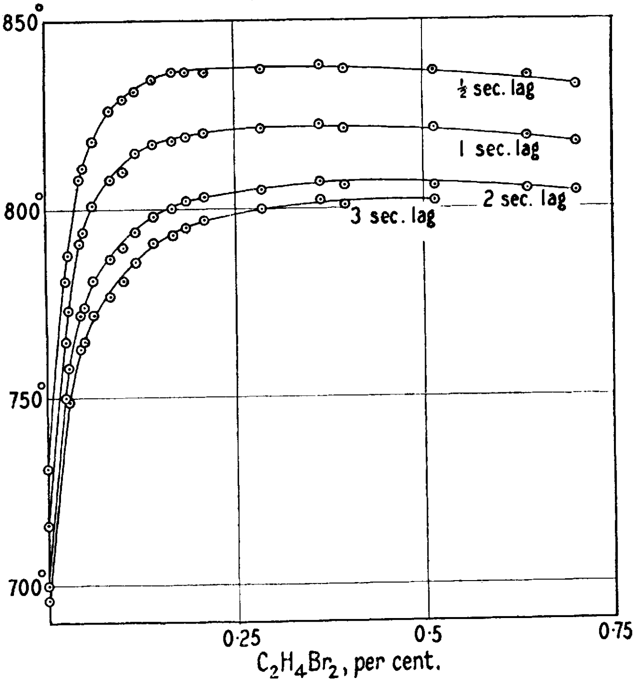


FIG. 20.

Ignition points of methane in air containing small amounts of isoamyl *bromide.*

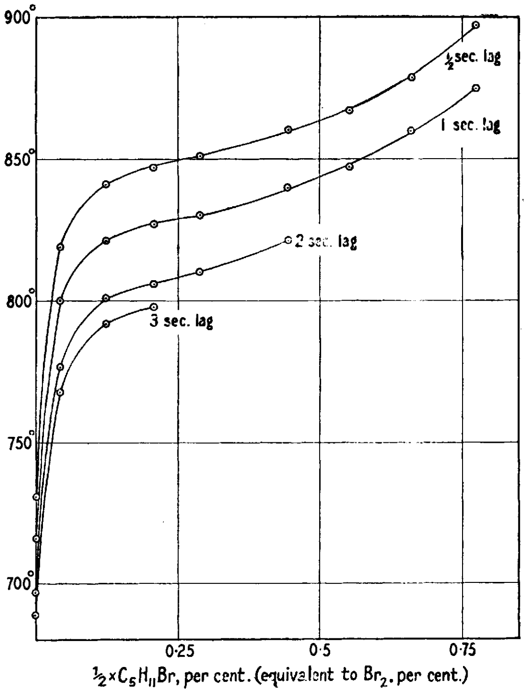
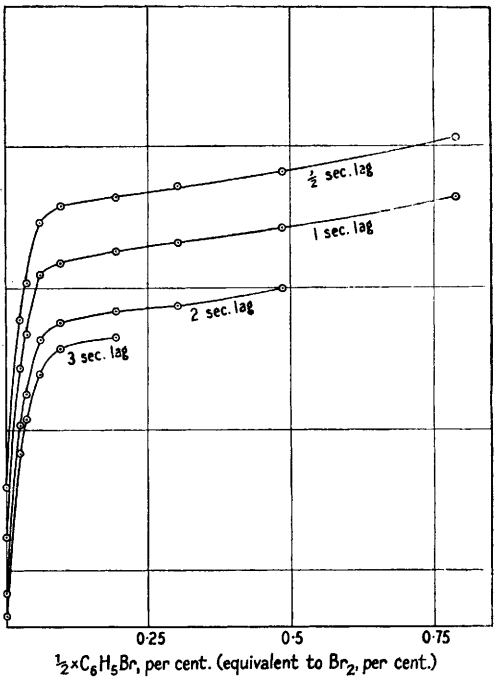


FIG. 21.

Ignition points of methane in air containing small amounts of bromobenzene.

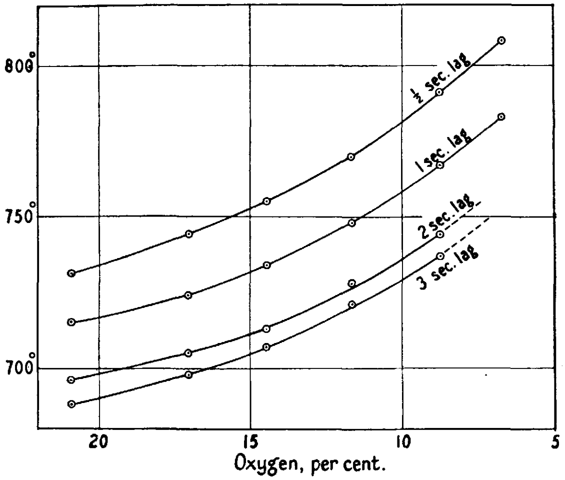


dibromide had a maximum effect at a concentration of about 0·3—0·4%, whereas the other two continued to show an increasing effect. The difference is explained by the interaction of the inhibitor with the oxygen of the air before the " atmosphere " reached the jet.

At the higher concentrations of the inhibitors, more especially those with 5 and 6 atoms of carbon, the reduction of the oxygen content of the " atmosphere " was sufficient to account for a considerable rise in the ignition point; the results of a special series of experiments which prove this are shown in Fig. 22, which records the ignition points of methane in atmospheres containing less than 20·9% of oxygen. The large rise of ignition point when only 0·1 or 0·2% of the bromide is present in the air must, however, be almost entirely due to the bromine.

FIG. 22.

Ignition points of methane in air deficient in oxygen.



In the presence of any but small amounts of bromine (less than about 0·15%) ignitions were not obtained after intervals of more than 3 secs. As the amount of bromine was increased, the possibility of ignition became more and more confined to the shorter intervals of time.

Mixtures of Ethylene Dibromide and Iodine.—The maximum effect of ethylene dibromide on the rapid-ignition point of methane was to raise it to 838° (Fig. 19). Atmospheres composed of air with the optimum amount of ethylene dibromide (0·37%) and various amounts of iodine from 0·0026 to 0·042% did not produce a further rise, but, from about 0·005% upward, produced a small decrease.

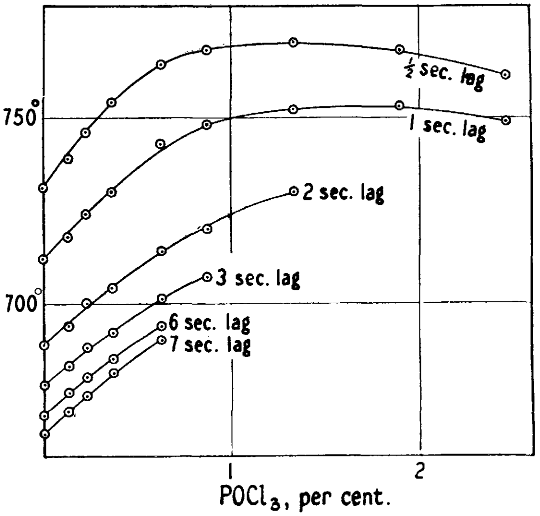
When only 0·08% of ethylene dibromide was present, the rapid-ignition point of methane, 826°, was at first raised by the addition of iodine, until with about 0·012% a maximum was attained at 838°, the same temperature as that observed with the optimum amount of ethylene dibromide alone. A mixture of these inhibitors may, therefore, be more effective than either, but only if the amount of the more effective is less than the optimum.

Phosphoryl Chloride.—The effect of this substance was examined because it had been stated (Jorissen, Booy, and van Heiningen, *Rec. trav. chim.*, 1932, **51**, 868) that the presence of less than 1% of it rendered all mixtures of methane and air non-inflammable at laboratory temperature and pressure.

The air was dried by sulphuric acid before admixture with phosphoryl chloride. Fig. 23 shows that the ignition points of methane were raised, but that the inhibitory effect of the optimum concentration of phosphoryl chloride was less than half that of bromine. With the higher concentrations of phosphoryl chloride, ignition was not obtained with the longer lags.

FIG. 23.

Ignition points of methane in air containing small amounts of phosphoryl chloride.



Tetraethyl-lead.—The effect of tetraethyl-lead on the ignition of methane is shown in Fig. 24. The curves are of the same type as those of *iso*amyl bromide and bromobenzene, and may be interpreted in the same way. The inhibitory effect is about half that of the bromine compounds.

GENERAL DISCUSSION AND SUMMARY.

Rapid-ignition Points at Atmospheric Pressure.—Table VI contains the rapid-ignition points, at atmospheric pressure, of the individual gases when issuing as a jet into atmospheres of oxygen or air. They are the minimum temperatures to which gas and atmosphere must be raised, prior to admixture, so that the gas inflames 0·5 sec. after turning on the jet (cf. p. 1383). They are always higher, sometimes considerably so, than the minimum temperature required to ignite such a jet when it is flowing continuously. Dixon and Coward's figures for the latter appear also in Table VI.

FIG. 24.

Ignition points of methane in air containing small amounts of tetraethyl-lead.

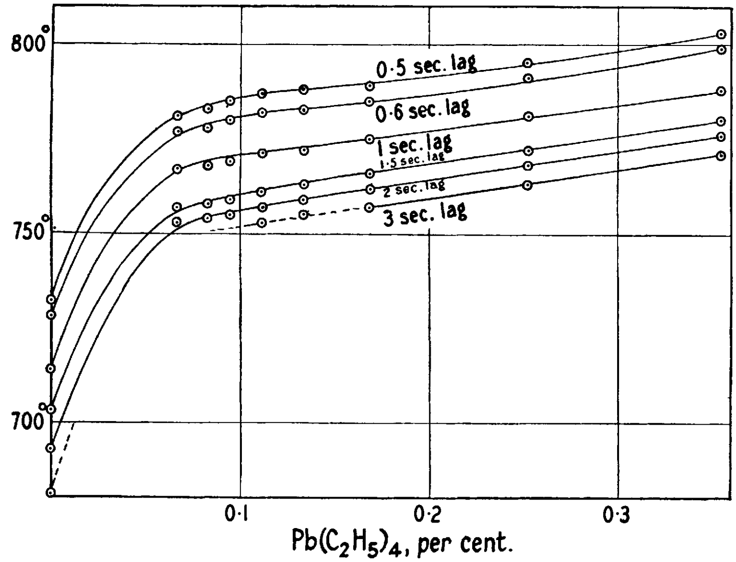


TABLE VI.

Rapid-ignition points (0·5 sec. lag), and ignition-points of a continuous stream of gas, at atmospheric pressure.

	In oxygen.		In air.	
Gas.	Rapid-ignition point.	Ignition point of stream.	Rapid-ignition point.	Ignition point of stream.
H_2	625°	585°	630°	585°
CO	687 [1] 680 [2]	650 [3]	693 [1] 683 [2]	651 [3]
$(CN)_2$	—	811	—	856
CH_4	664	556—700	722	650—750
C_2H_6	628	520—630	650	520—630
C_3H_8	—	490—570	—	—
C_5H_{12}	355	—	600	—

	In oxygen.		In air.	
Gas.	Rapid-ignition point.	Ignition point of stream.	Rapid-ignition point.	Ignition point of stream.
C_2H_4	604°	510°	627°	543°
C_3H_6	586	—	618	—
C_2H_2	—	428	435	429
C_6H_6	685	—	710	—
Et_2O	219	—	549	—
CS_2	132	—	156	—
H_2S	—	227	—	364
NH_3	—	700—860	—	—

[1] 0·63% H_2O in atmosphere.

[2] 5·3% H_2O in atmosphere.

[3] 2% H_2O in gas and in atmosphere.

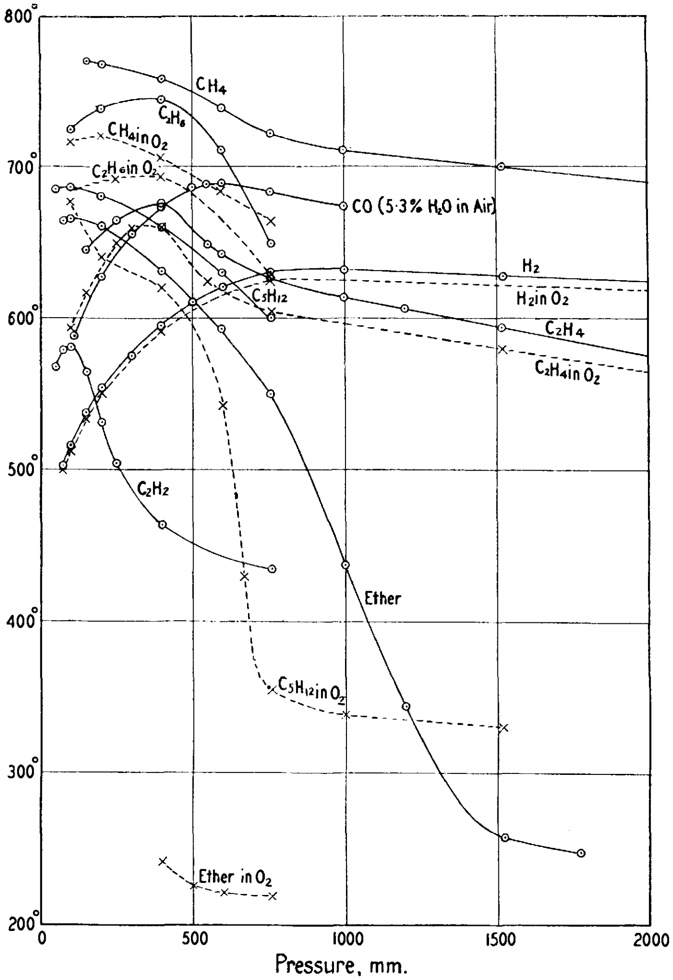
The Relation between Ignition Point and Pressure for Various Periods of Lag.—For most of the gases, the general form of the curve connecting ignition point with pressure is the same for all periods of lag. Reference may be made to Figs. 3 and 7, for hydrogen and for methane respectively in air, as typical of the results for most gases, whether the atmosphere be air or oxygen. An exception is found in ethane, as may be seen in Figs. 11 and 12, in which the curves for the shorter lags show maxima but those for the longer lags do not.

Carbon monoxide is exceptional in that the maxima tend to shift towards higher pressures as the lags increase.

The Relation between the Rapid-ignition Point (0·5 *Sec. Lag*) *and Pressure, for Various Gases.*—Fig. 25 shows a comparison of the rapid-ignition points of most of the gases examined, over a range from 50 to 2000 mm. pressure. The only omissions are three curves for carbon monoxide (in air with 0·63% of water vapour, and in oxygen with 0·63 and 5·3% of water vapour) which would be close to the one curve given for that gas, and the curves for propylene in air and in oxygen, which are similar in type to the corresponding curves for ethylene. Several of the curves might be extended to higher pressures by using the data in the text, but no new feature would be shown. The following general conclusions may be drawn :

FIG. 25.

Influence of pressure on the rapid-ignition point (0·5 *sec. lag*) *of various gases.*



(*a*) In general, each gas has a maximum ignition point, but the pressure at which this is observed ranges from about 100 mm. for acetylene, pentane, and ether, to 1000 mm. for hydrogen. The ignition point of methane in air rises continuously as the pressure is decreased to 150 mm., but appears to be approaching a maximum; that of pentane in oxygen rises continuously with falling pressure, as far as observations were made.

(*b*) The rate of change of ignition point with change of pressure varies considerably with different gases.

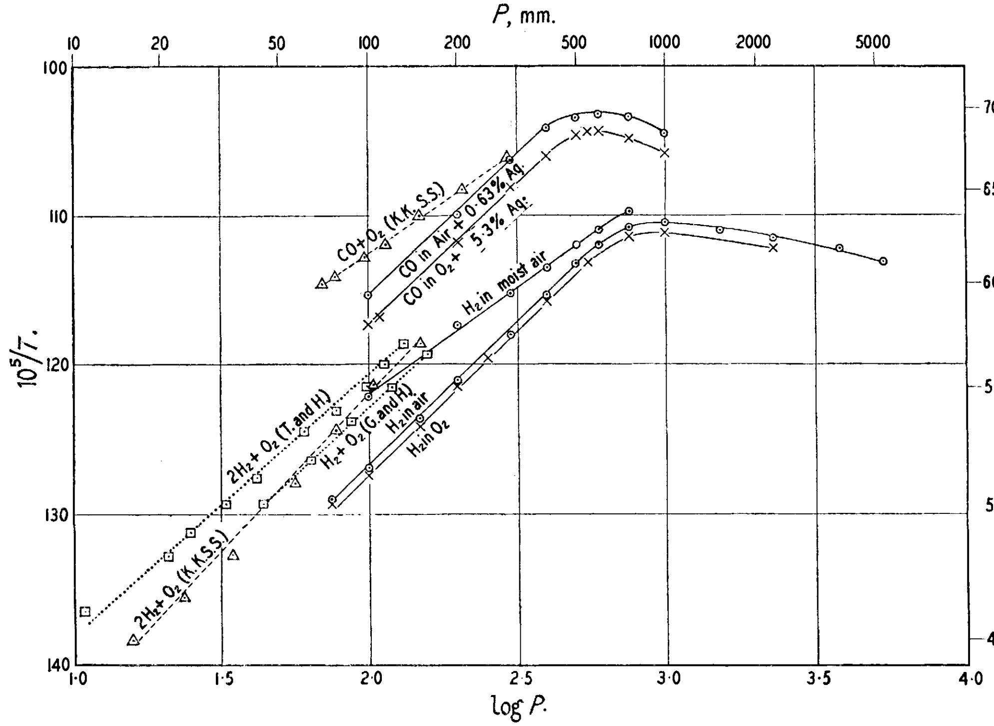
(*c*) In consequence of (*a*) and (*b*) above, the order of ignition points of the gases at any one pressure is no indication of the order at another pressure.

(*d*) The ignition point of any one gas in oxygen is never higher than in air, at the same pressure. It may be only slightly lower (*e.g.*, hydrogen, carbon monoxide), lower (*e.g.*, methane, ethane, ethylene), or considerably lower (*e.g.*, ether). Pentane may belong to each of these categories in turn, according to the pressure.

An Exact Relation between the Rapid-ignition Point and Pressure for Hydrogen and for Carbon Monoxide.—Semenoff (*Z. Physik*, 1928, **48**, 571) deduced a relationship between ignition point and pressure, for thermal reactions, of the form log $P/T = A/T + B$, and Sagulin (*Z. physikal. Chem.*, 1928, *B*, **1**, 275) supported it by the experimental evidence of several reactions. Semenoff (*ibid.*, 1929, *B*, **2**, 161) later adopted the form log $P = A/T + B$, and showed it to be applicable to a chain reaction as well as to a thermal reaction, and to both upper and lower pressure limits of spontaneous ignition.

FIG. 26.

Relation between the inverse of the rapid ignition point (degrees absolute) and the logarithm of the pressure.



It is interesting to find several examples in Dixon's results in which the latter relationship is followed exactly, within the small errors of experiment. Fig. 26 shows straight-line graphs for the rapid-ignition points (0·5 sec. lag) of hydrogen in air and in oxygen between 75 and about 600 mm. pressure, of hydrogen in moist air between 100 and about 600 mm., of carbon monoxide in air (0·63% of water) and in oxygen (5·3% of water) between 100 and about 400 mm. Curves similar to the last two may also be drawn for carbon monoxide in air (5·3% of water) and in oxygen (0·63% of water); they are nearly coincident, and lie between the two curves given for carbon monoxide.

Previous measurements upon the relation between ignition point and pressure, for hydrogen and carbon monoxide, are shown by broken lines in the same figure. These observations were made with homogeneous mixtures in contact with the walls of the container (Thompson and Hinshelwood, *Proc. Roy. Soc.*, 1929, *A*, **122**, 610; Grant and Hinshelwood, *ibid.*, 1933, *A*, **141**, 29; Kopp, Kowalsky, Sagulin, and Semenoff, *Z. physikal. Chem.*, 1930, *B*, **6**, 307), and thus differ from Dixon's, in which the object was to avoid contact between the *mixed* gases and the walls of the container. It seems from the curves that the general character of the phenomenon observed was the same, for Hinshelwood's curves for mixtures of hydrogen and oxygen are nearly parallel to Dixon's, for the roughly dried gases; moreover, Hinshelwood's curves represent the two mixtures $2H_2 + O_2$ and $H_2 + O_2$, whereas Dixon's represent that mixture, whatever it may be, of minimum ignition point in the circumstances. Grant and Hinshelwood did not determine the curves for weaker mixtures than $H_2 + O_2$, but did give single points for a series of mixtures down to $H_2 + 4O_2$ and these points progressively approach Dixon's curve. It is satisfactory that the experimenters agree, on entirely different lines of argument, that the straight-line curves represent a homogeneous reaction. Semenoff and Hinshelwood agree in describing it as a gas-phase deactivation of chain carriers by ternary collisions which, at the ignition point, is just balanced by the formation of new chain carriers by binary collisions. The most recent analysis of this part of the pressure–ignition point curves, which has become known as the upper-pressure limit, is that of Grant and Hinshelwood (*loc. cit.*).

At higher pressures than those of the " upper limit " the ignition points decrease with increasing pressure. This may represent a " thermal explosion," but it does not appear to conform with Semenoff's simple formula : it has not, as yet, been fully interpreted.

Promoters and Inhibitors of Ignition.—The ignition points of hydrogen and carbon monoxide are but slightly raised (3° to 6°) by the substitution of air for oxygen; other gases show greater differences, attaining 245° for pentane and 330° for ether vapour at normal pressure; but these are outstanding, for the difference is more commonly 20—60°. The difference for methane was nearly 60°, and the further reduction of the oxygen of the atmosphere caused a further increase in ignition point. The addition of carbon dioxide or of nitrogen to the methane also caused an increase in ignition point (Figs. 8 and 9). The effects of such changes were, however, small in comparison with the reduction of ignition point when traces (less than 1%) of nitrogen peroxide were added to the atmosphere, or in comparison with the increase of ignition point when traces of bromine or iodine were added. The examples investigated show that nitrogen peroxide is, in general, a powerful promoter of the combustion of hydrogen, carbon monoxide, methane, and ethylene; that small amounts of iodine tend strongly to inhibit the ignition of these three gases; that bromine and its compounds behave even more effectively as inhibitors of the ignition of methane, but that tetraethyl-lead and phosphoryl chloride are less effective.

The writer thanks the Safety in Mines Research Board for permission to publish this communication.

SAFETY IN MINES RESEARCH BOARD LABORATORIES,
SHEFFIELD.

[*Received, June 12th,* 1934.]