XIV—Estimation of the Combustion Products from the Cylinder of the Petrol Engine and its Relation to "Knock"

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CONTENTS

PART I—METHOD AND PRELIMINARY INVESTIGATION

PART II—ESTIMATION OF NITROGEN PEROXIDE

PART III—ORGANIC PEROXIDES

PART I—METHOD AND PRELIMINARY INVESTIGATION

By A. EGERTON, *F.R.S., and* F. LL. SMITH

1—INTRODUCTION

As a result of a variety of experiments* it was suggested in 1928† that engine "knock" "appears to be due to inequality in the condition of the charge (in the engine cylinder) set up, particularly in regions of high pressure and temperature as in the neighbourhood of hot exhaust valves. This inequality provides regions of high energy containing molecules in high energy states where reaction can spread more quickly." This view was a little vague, and was arrived at from indirect experimental evidence. It was with a view to obtaining more precise evidence that knock was occasioned in the flame as the result of processes of slow combustion occurring in the gaseous charge prior to its arrival that the present work was undertaken.

CALLENDAR‡ and those working with him had simultaneously arrived at the conclusion that "knock" was occasioned in much the same manner, but they adopted the more definite view that peroxides of the hydrocarbons were formed and stored in the gas, and then suddenly detonated, so igniting a whole region of the gas simultaneously. This view had also been advanced by MOUREU and DUFRAISSE.§

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* EGERTON and GATES, 'Rep. Aero. Res. Comm.,' Lond., No. 1079 (Dec. 1926) ; 'Proc. Roy. Soc.,' A, vol. 114, pp. 137, 152 (1927) ; vol. 116, p. 516 (1927) ; 'J. Inst. Pet. Tech.,' vol. 13, p. 244 (1927).

† EGERTON, 'Nature' (Suppt.), vol. 122, p. 20 (1928).

‡ 'Rep. Aero. Res. Comm.,' Lond., No. 1062 (Dec., 1926) ; 'Engineering,' vol. 123, pp. 147, 182, 210 (1927).

§ 'C.R. Acad. Sci., Paris,' vol. 184, p. 29 (1927), *also* MOUREU, DUFRAISSE, and CHAUX, 'Ann. Nat. Comb. Liquides,' vol. 2, p. 253 (1927).

The difference at that time between the views* as to the nature of the process adopted by Egerton and Gates on the one hand, and by Moureu and by Callendar on the other, was that the former considered that an accumulation and decomposition of the primary products of reaction caused a larger number of chains of reacting molecules to be started in a given time, so accelerating the combustion, whereas the latter considered that the accumulation of the peroxides was sufficient in itself to give rise to their sudden detonation *en masse*.

Since the time when those investigations were made, a large amount of work has been done, and various summaries of the position have been given.† Of the theories which have been propounded to account for the phenomenon of engine "knock," only those which postulate the existence of centres of high reactivity in the combustible gases just prior to ignition have survived the researches of the last five years. A quantity of evidence has been gained from experiments on slow combustion of gaseous mixtures in tubes, but the experimental difficulties involved have tended to preclude the extension of the work to direct observations of the behaviour of the combustible charge in the engine cylinder. Nevertheless, despite the difficulties, much success has attended such investigations, particularly those carried out in the laboratories of General Motors, Ltd., and some of the results of that work are summarized in the following review.‡

(*a*) Withrow, Lovell, and Boyd§ devised a sampling mechanism by means of which they could collect the gases from the cylinder, and by analysis showed that the knock was confined to the burning of the last part of the charge, and that combustion was complete in the flame front.

(*b*) Some beautiful photographic studies by Withrow and Boyd|| of the travel of flame in an engine cylinder supplied with a quartz window along the head, confirmed that " knock " only occurs in a region of the gas at the end of travel of the flame across the combustion space. It is suddenly set up in this region, and is accompanied by rapid increase in the rate of rise of pressure, and by a great increase in the rate of combustion. A compression wave is set up similar to that observed in bomb experiments by Maxwell and Wheeler¶ and others, and no doubt this is the origin of the knocking sound.

" Auto-ignition, ' *i.e.* ignition in a region of the gas prior to the arrival of the flame front, was observed both in the knocking zone and elsewhere, but does not necessarily give rise to the knocking type of combustion, though it was supposed

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* Mardles, ' Rep. Aero. Res. Comm.,' Lond., No. 1374 (Nov. 1930).

† Egerton, 'J. Inst. Pet. Tech.,' vol. 14, p. 656 (1928). Lafitte, 'J. Chim. Phys.,' vol. 26, p. 391 (1929). Egloff, Schaad, and Lowry, 'J. Ind. Eng. Chem.,' vol. 21, p. 785 (1929).

‡ *Cf.* Cummings, ' Aero. Eng.,' p. 65 (1933), for a more complete *résumé*.

§ 'J. Ind. Eng. Chem.,' vol. 22, p. 945 (1930).

|| 'J. Ind. Eng. Chem.,' vol. 23, p. 539 (1931). *Cf.* Ricardo, 'Automobile Eng.,' vol. 17, p. 149 (1927). Glyde, 'J. Inst. Pet. Tech.,' vol. 16, p. 756 (1930). Marvin and Best, ' Nat. Adv. Comm. Aero.,' Washington Rep., p. 399 (1931). Schnauffer, ' Nat. Adv. Comm. Aero.,' Washington Tech., Memo. No. 668 ; (*see also* ref. p. 451).

¶ 'J. Ind. Eng. Chem.,' vol. 20, p. 1041 (1928).

that the high rate of combustion in the knocking zone was due to auto-ignition within it. The records show that " knock " may occur in more than one place ; a dual knock sometimes occurs. The actual combustion appears to complete itself in the narrow flame front, the afterglow, which may extend for 40° of crank angle or more for benzene, being due to processes associated with the cooling of the reaction products.

(*c*) WITHROW and RASSWEILER* have investigated the spectroscopic character of the flame in non-knocking and knocking engine explosions using various fuels, and showed that the C–C, C–H, and OH bands are prominent in the former ; but in the knocking zone, and only during " knock," these bands do not appear and only continuous emission is observed. By separating the radiation from the combustion flame-front from that of the afterglow, they have shown that the latter is due to molecular products of reaction in an active state, and not to incomplete reaction in the combustion front ; from the similarity with the bands in the CO flame, they ascribe this afterglow to active CO_2 molecules.†

(*d*) The same authors‡ have recently succeeded in obtaining spectrographic evidence of intermediate combustion products just before the passage of the flame, in the last portion of the engine charge to burn, such combustion being much more pronounced when the engine is knocking than when not. It is possible that these intermediate products which cause absorption of the light may play the role of reaction centres, but their precise nature has not been identified.§ This work is allied to some investigations by EGERTON and PIDGEON|| on the absorption spectra of burning hydrocarbons which are still being continued in this laboratory.

RICARDO and THORNYCROFT¶ were able to detect aldehydes in the engine gases immediately prior to combustion, and found that the presence of lead tetraethyl appeared to inhibit the formation of these compounds, but have not conducted a detailed investigation into the precise stage of the engine cycle at which they occur, nor did they extend the work to examine the possible formation of earlier oxidation products. DUMANOIS, MONDAIN MONVAL, and QUANQUIN** have passed the exhaust gases of an engine running on hexane through Schiff's and KI reagents immediately after cutting out the ignition, the engine meanwhile being motored. They found that when the engine was knocking aldehydes and " peroxides " (*i.e.* substances reacting with KI) were present in profusion, but not otherwise. No figures are given for the actual concentration of these compounds, nor is direct evidence given of the

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* ' J. Ind. Eng. Chem.,' vol. 23, p. 769 (1931) ; vol. 24, p. 528 (1932).

† A. FOWLER, ' Proc. Roy. Soc.,' A, vol. 142, p. 362 (1933). KACZYNSKA, ' Bull. Int. Acad. Polonaise,' A, vol. 1A, p. 16 (1931).

‡ WITHROW and RASSWEILER, ' J. Ind. Eng. Chem.,' vol. 25, p. 923 (1933).

§ In a further communication (' J. Ind. Eng. Chim.,' vol. 25, p. 1359 (1933)) the bands of formaldehyde were identified in these spectrograms, and it was shown that this vapour is present in the gases in the region of " knock " just prior to the arrival of flame in knocking explosions.

|| ' Proc. Roy. Soc.,' A, vol. 142, p. 26 (1933).

¶ ' Trans. Fuel. Conf. World Power Conf.,' vol. 3, p. 662 (1928).

** ' C.R. Acad. Sci., Paris,' vol. 192, p. 1158 (1932).

manner in which the compounds are formed in the engine running under its own power. STEELE* has passed gases sampled from an engine cylinder at different points in the cycle through potassium iodide and titanous sulphate, and concludes that whereas no true peroxide is formed at any stage in the cycle, a certain amount of "oxidizing agent," to which KI is sensitive, is present in the gases at the end of the exhaust stroke, and at the beginning of the inlet stroke. The experience gained during the present work suggests that the experimental arrangements were hardly suitable for obtaining precise results ; for one thing, the valve operated over too large a crank angle.

The view that the initial combustion product of certain fuels may take the form of a "peroxide," and that high local concentrations of such a compound in the last portion of the engine gases to burn, may constitute or produce the reaction centres which propagate the enhanced combustion characterizing "knock," has certain attractive features. In support of this theory, reactions with potassium iodide have been observed during combustion experiments by several workers,† but in view of the fact that potassium iodide reacts with many substances other than "peroxides," the presence of these latter compounds has not yet been proved. On the other hand, BONE, in his extensive researches on combustion of hydrocarbons, has never detected the occurrence of peroxides by the titanous reagent prior to the aldehyde stage, and insists that combustion proceeds according to the "hydroxylation" theory, and not by any process of "peroxidation."

The uncertainty regarding the nature of the early stages of combustion in a petrol engine led the authors to attempt a more detailed investigation into the matter than had previously been effected. To this end apparatus was constructed whereby samples of the cylinder gases could be extracted at various points during the cycle, and analysed, not only for initial and terminal components, but also, by special methods, for aldehydes and "peroxides." The outcome of the preliminary work described in this part was to show that oxidation occurs prior to the arrival of the flame front, and that oxidizing substances to which potassium iodide was sensitive were formed in the earliest stages of combustion, while the greater the intensity of "knock," the greater, in general, was the quantity of such products obtained.

2—APPARATUS

(*a*) *Engine*

The engine used throughout the present work was a Delco Knock Rating Engine, presented to one of the authors by the Anglo-American Oil Co. The engine was provided with a single water-cooled cylinder of dimensions $2\frac{1}{2}$ ins.

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* 'J. Ind. Eng. Chem. (Anal.),' vol. 5, p. 202 (1933).

† BONE, 'Proc. Roy. Soc.,' A, vol. 137, p. 243 (1932) ; *see also* 'J. Chem. Soc.' p. 1599 (1933) ; *also* MONDAIN MONVAL and QUANQUIN, 'C.R. Acad. Sci., Paris,' vol. 189, p. 917 (1929).

diameter × 5-in. stroke. The piston was of aluminium and flat topped. Fig. 1 illustrates the design of the cylinder head. At the side remote from the sparking plug a $\frac{7}{8}$-in tapped hole enters the combustion chamber. This hole, which was originally provided for the " bouncing pin " indicator, was used to take the sampling valve in the present experiments. The distance between the centre of this hole and the sparking plug was $3\frac{1}{2}$ ins.

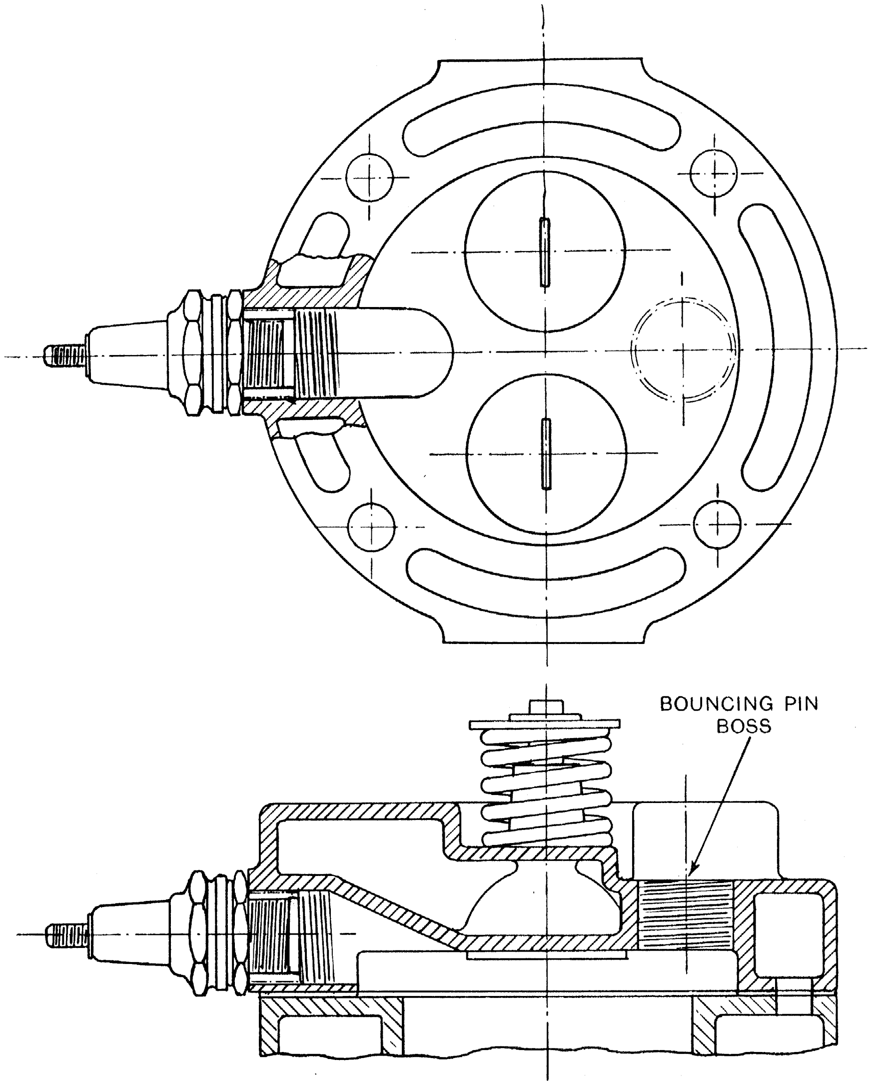

FIG. 1—Cylinder head

Evaporative cooling was employed to ensure a constant jacket temperature. The carburettor was of the single jet venturi type, and the mixture strength of the charge could be adjusted by altering, with the aid of a fine-threaded screw, the height of the float chamber with respect to the jet. A duplicate fuel-feed system was provided to facilitate comparison of fuels. The engine was started up by means of an electric motor which was built integral with it. This motor was arranged to do service as a dynamo and as such to provide the load for the engine, the electrical output being absorbed by the starting battery and/or a large resistance. The load, which was measured by the inclusion of an ammeter and voltmeter in the external circuit to the dynamo, could be adjusted by controlling this resistance. An electrical tachometer was provided for speed measurements. The lever actuating the throttle valve in the induction pipe moved over a graduated quadrant to which it could be clamped in any desired position.

A neon tube fixed radially on a graduated disc mounted on the crank-shaft, and connected by means of a slip-ring to the sparking plug terminal on the induction coil, enabled the igniting timing to be determined with accuracy.

Throughout these experiments a compression ratio of 6·75 to 1 was maintained. The volume of the combustion space was 70 cc. With this value, and with a spark advance of $22\frac{1}{2}$° before top dead centre, a violent " knock " ensued when the engine was run at the maximum possible load, and at a speed of 600 r.p.m., the fuel being Shell No. 1. As will be shown later, this speed was the one selected for the gas-sampling experiments. The compression ratio chosen permitted a wide range of knocking conditions.

(*b*) *Sampling Gear*

The apparatus constructed for withdrawing the samples of gas from the cylinder was essentially similar to that developed by WITHROW, LOVELL, and BOYD* except that it had to be operated by a push-rod from the lay shaft of the engine and that a different phasing mechanism was employed. The gas was extracted through a water-cooled poppet valve, closed by a strong spring of about 12-lb loading, fig. 2. The water-jacket was carried well down to the foot of the valve. The cooling water left the valve at a temperature of 40° C, this being a compromise between the desirability of a high temperature in order to prevent the condensation on the walls of the valve of the less volatile products on the one hand, and of a low temperature in order to prevent further combustion once the gases

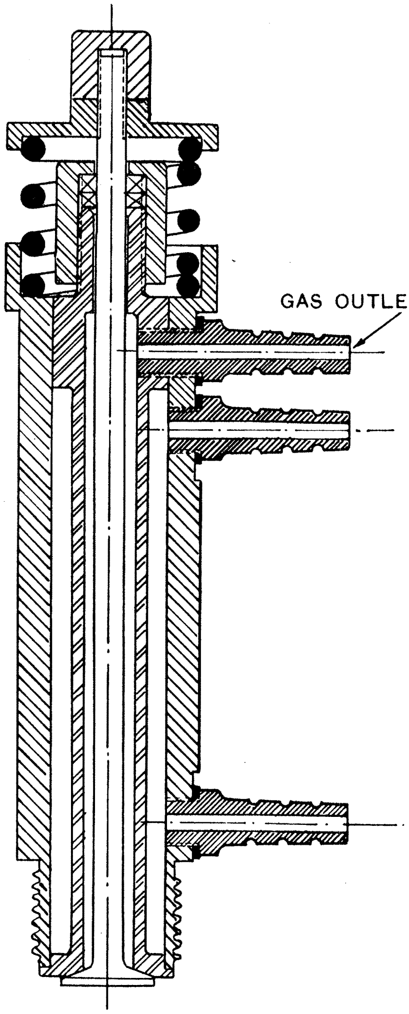

FIG. 2—Sampling valve

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* 'J. Ind. Eng. Chem.,' vol. 22, p. 945 (1930).

had left the cylinder on the other. In practice, no noticeable difference in the analysis of the sample resulted when the flow of cooling water was varied considerably in either sense from that giving the above temperature at outlet.

The gland of the valve was packed with tallow packing, and no difficulty was experienced in preventing leakage into or out of the valve. No lubrication was applied save that provided by the packing. The valve lifted a distance of about 1/100th inch only. The valve was so proportioned that the foot of the body of the valve lay flush with the surface of the combustion chamber.

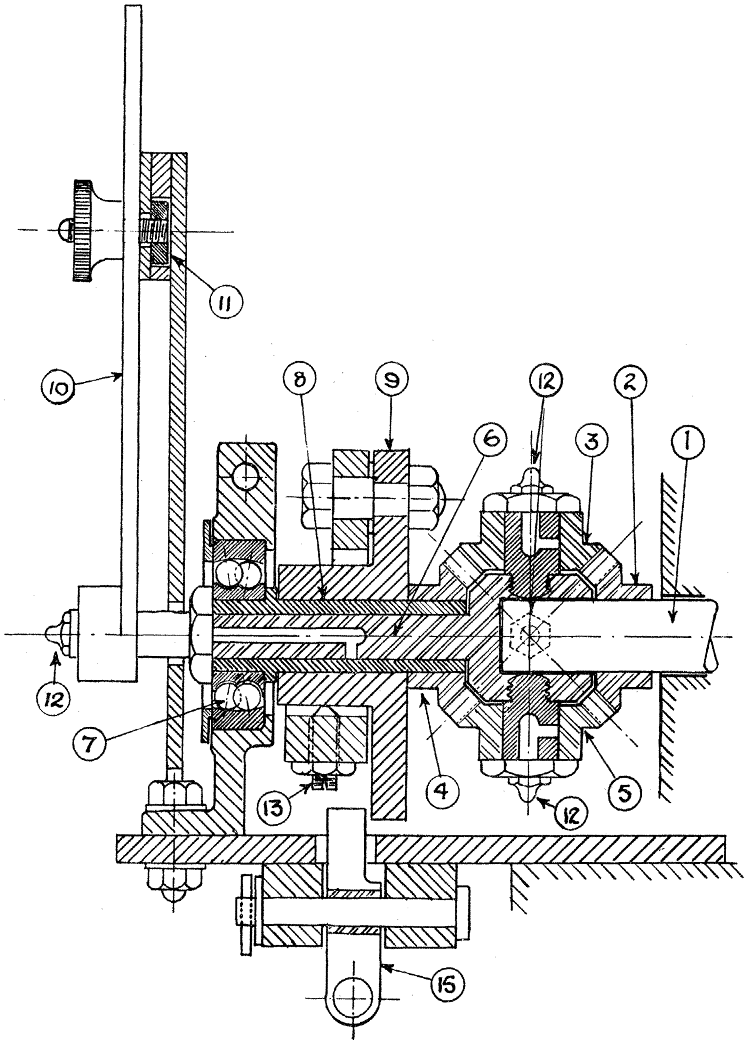

Fig. 3—Phasing gear

The general arrangement of the gear may be gathered from the diagrammatic representation given in fig. 4. A sectional plan of the phasing mechanism is shown in fig. 3. On an extension to the engine-camshaft (1) is fixed the bevel wheel (2), which, together with the equal bevels (3), (4), and (5), form a differential chain. The bevels (3) and (5) idle on spindles fixed in the central phosphor-bronze shaft (6), which is machined to receive the end of the camshaft extension as indicated. The wheel (4) is fixed on a steel sleeve which turns about the central shaft (6) and is supported by the ball-bearing (7). The whole system is adequately supported without the provision of any further bearings. The sleeve (8) carries the trigger disc (9). To the central shaft is attached the arm (10) which may be clamped at any angle against the graduated semicircular slide (11). The effect of giving this arm an angular movement is to impart to the trigger disc twice the displacement with respect to the crankshaft and hence four times the displacement with respect to the cam shaft, irrespective of the movement of these shafts. Thus the trigger-plate is moved through an angle corresponding to a complete engine cycle, as the controlling arm is rotated through two right angles. Referring to fig. 4, it will be seen that the clearance between the valve cap and the rocker slipper could be adjusted by rotating the arm (16), and that by making this clearance sufficiently large, the push-rod could be removed, thus obviating unnecessary working of the mechanism when the sampling apparatus is not required. When the mechanism was functioning, the clearance was always adjusted so that the small rocker (15) could be turned until it was just clear of the trigger (14) without opening the valve, the push-rod being in position. In this manner it was ensured that the heavy valve rocker attained its maximum velocity before striking the valve, and that there was no positive transmission of the trigger blow to the valve, but only by means of the "inertia" of the valve rocker and push-rod. The clearance necessary for this condition was usually about 0·05 in. The intensity of the blow imparted to the

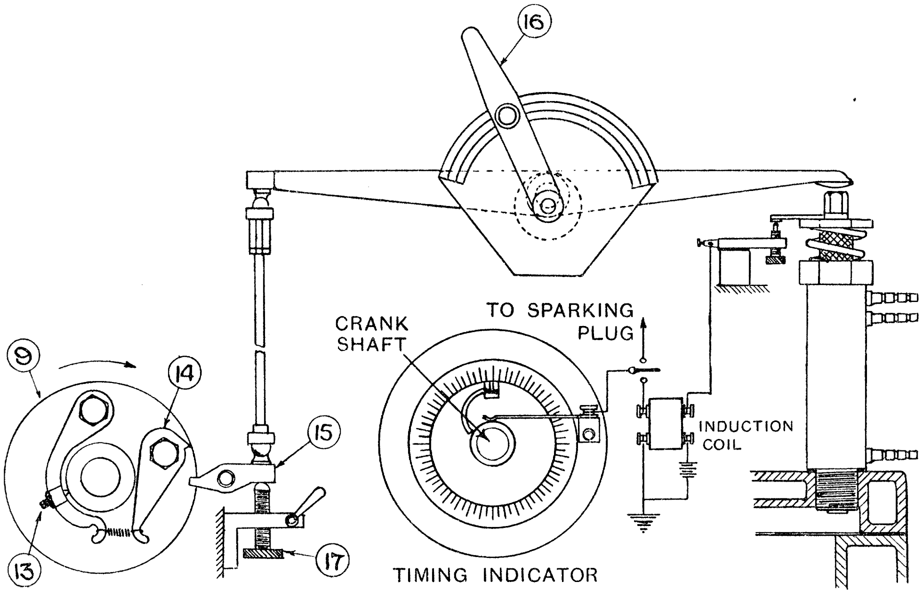

Fig. 4—Arrangement of sampling apparatus

valve gear by the trigger (14), and hence the height of the valve lift, was regulated by adjusting the thumb-screw (17).

The time and duration of the valve opening was indicated by the arrangement illustrated in fig. 4. On the underside of a stiff metal projection on the valve cap was silver-soldered a small bar of platinum-iridium which, on the valve opening, made electrical contact with a light platinum-pointed plunger projecting from a thumb-screw, and within which it slides against a strong spring. The thumb-screw, which was insulated from the earth, was connected through a switch to one of the primary terminals of an induction coil, the other terminal being connected to a six-volt battery and thence to earth. A two-way switch allows the neon tube, previously mentioned, to be disconnected from the sparking plug, and connected to the secondary terminal of the induction coil. The thumb-screw was screwed up until the plunger was on the point of making permanent contact with the projection from the valve cap. The neon tube lighted up both when the valve opened and when it closed, and two corresponding lines of light could be seen against the graduated scale against which it revolved, indicating both the timing and the duration of the valve opening. So long as the contacts were kept clean, the device worked extremely well, and gave conclusive indication of the regular manner in which the valve gear worked, each line of light fluctuating by less than a degree on either side of the mean.

A standard rate of sampling of 80 cc per minute (or 0·27 cc per cycle) was adopted whenever possible. Until wear of the phasing mechanism occurred, the valve provided an extraordinarily even flow of gas. For any given duration of valve opening, the higher the pressure in the cylinder at the moment of sampling the greater would be the amount of gas extracted. On the other hand, the greater the pressure on the underside of the valve foot, the smaller would be the lift of the valve, and hence the duration of the opening for the same impulse from the rocker. This last effect offsets the former to a certain extent, and thus between successive samples extracted at adjacent points of the engine cycle, no very large adjustment of the thumb-screw (17), fig. 4, was necessary to maintain constant gas flow. Furthermore, since the rapid chemical reactions undergone in an engine cylinder occur at a moment of high pressure, the decreasing duration of valve opening as the pressure rose proved a fortunate circumstance, because it was in the region where rapid changes in the composition of the gases occur that it was important to minimize the time during which the valve was open, so that successive points of sampling might be close together without overlapping.

In practice the duration of the valve opening varied from 10° to 15° of crank angle at early stages of the compression stroke and the later stages of the expansion stroke, to about 2° at the point of maximum pressure, corresponding, at 600 r.p.m., to a time of 1/1800 sec from opening to shutting of valve. When the engine was running under heavy load it was impossible to obtain a gas flow from the valve of more than 30 cc per min at the point of maximum pressure, the mechanism not being sufficiently robust to withstand the stresses that a greater valve lift would involve. Except for a narrow region of about 5° in the vicinity of this point of the cycle, the flow was usually maintained at 80 cc per min. The flow was measured by a differential flow meter, surges in the gas stream being eliminated by a vessel of suitable capacity placed between the valve and the meter.

3—Analysis of Gases from Cylinder

Many investigations have been made on the composition of the exhaust gas from internal combustion engines, but only one serious attempt has been made to sample the gases during different stages of the cycle.

Lovell, Coleman, and Boyd* fitted a sampling valve to a single-cylinder engine, and analysed the gases for CO_2, CO, O_2, H_2, paraffins, and unsaturated hydrocarbons, giving curves for the CO_2, CO, O_2, and H_2 percentage at various parts of the stroke. It was found, however, that the valve was open over too long an interval to provide results from which reliable information could be obtained. Withrow, Lovell, and Boyd† designed another valve, which opened over a much smaller crank angle (2° to 4°). They only gave curves for oxygen consumption, the samples were taken from various points, a number of cylinder heads being available with the valve socket arranged in different positions. They showed that oxygen commenced to disappear 2° from t.d.c., and steep curves were obtained only in the region where "knock" occurred. In fact, for a given mixture strength and engine speed the rate of combustion was only found to be affected to any considerable extent by detonating conditions in the last part of the charge to burn.

(*a*)—*Fuels Used in Experiments and Range of the Engine Conditions Investigated*

Three characteristic engine fuels have been investigated, namely Shell No. 1 petrol, winter grade; a mixture of Shell No. 1 and 8·0 cc of ethyl fluid per gallon (*i.e.* 4·4 cc lead tetra-ethyl per gallon); and Pratt's pure commercial benzole. For each of these fuels the gas samples were analysed with the engine running under four different conditions.

Experiments have also been conducted on other fuels in order to elucidate certain facts revealed during the course of this work; those results are recorded in Part II.

The hydrogen and carbon contents of these fuels were determined and found to be as follows:—

	Shell No. 1	Benzole
	% by weight	
Carbon	85·68	91·30
Hydrogen	14·32	8·70

Each of these fuels was investigated with the engine running at four different openings of the throttle valve, the speed and ignition timing being constant. These

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* 'J. Ind. Eng. Chem.,' vol. 19, p. 373 (1927).

† 'J. Ind. Eng. Chem.,' vol. 22, p. 945 (1930).

throttle openings were selected as giving a wide range of knocking conditions when using Shell No. 1, and were as under :—

Throttle 6° open . . .	No " knock."
Throttle $7\frac{1}{2}$° open . . .	Slight occasional detonation (s.o.d.).
Throttle 9° open . . .	Continuous moderate detonation (c.m.d.).
Throttle $10\frac{1}{4}$° open . .	Exceedingly violent detonation (v.d.).

The engine ran quietly at the first three throttle openings when using Shell No. 1 plus ethyl fluid, or benzole ; but both these fuels gave rise to slight roughness at the largest opening.

For each throttle opening and fuel the mixture strength of the charges was set to give maximum power. The electrical output from the dynamo was measured for the various engine conditions and is given in Table I.

TABLE I—POWER OUTPUT

Throttle degrees open	Shell No. 1 Watts	Shell No. 1 ethyl fluid Watts	Benzole Watts
6	204	205	207
$7\frac{1}{2}$	281	286	290
9	335	340	345
$10\frac{1}{4}$	352	399	400

The fall in power with undoped Shell with respect to the other fuels, as detonation increases, is very marked.

(*b*) *Collection and Analysis of Samples for Oxygen, Carbon Dioxide, and Carbon Monoxide*

The analyses of the samples for O_2, CO_2, and CO were completed before proceeding to the more difficult problem of measuring the concentrations of aldehydes and " peroxides " in the gases. For this purpose 15 gas-collecting tubes, each of some 40 cc capacity, were constructed so that a complete set of samples for any one fuel and throttle opening could be collected during one run on the engine, thus assuring constancy of engine conditions. The samples were collected over brine, as it was found, for the accuracy required in these preliminary experiments, to be unnecessary to collect over mercury. They were obtained in succession each 5° of crank angle without altering the engine setting, allowing sufficient time to ensure that all the gas in the interior of the valve in the previous setting had been dispelled. When a position was reached at which no appreciable change in composition was occurring, the samples were extracted at 20° or 30° interval until half the working stroke was completed.

The gases were present in the valve for not more than 4 seconds, but were very rapidly cooled as soon as they entered it, both by their expansion and by the water-jacket, so that the combustion which occurred in the valve itself was unlikely to alter their composition appreciably. Condensation of water did not occur in the valve, and the gases were therefore not altered in composition by absorption in condensed water.

After all the samples had been collected, the gases were analysed in a type of Orsat apparatus, modified for the purpose and designed to provide rapid absorption of the gases, and to give better accuracy than the ordinary type. (EGERTON and SMITH.*)

(*c*)—*Experimental Results*

The results of these experiments are shown graphically in figs. 5, 6, and 7, in which the percentage compositions of the dry cylinder gases are plotted against the crank angle.

The oxygen content is maintained at its maximum value for some time after the passage of the spark, the time increasing as the throttle opening is reduced. As the engine cycle proceeds, the oxygen content at first decreases slowly, but at an increasing rate for 5° or 10° of the crank angle, after which a rapid combustion occurs during which some 80% or 90% of the oxygen is consumed in a period varying from 5° to 25° of the crankshaft, according to the throttle opening. Some 10° after this phase is completed, the oxygen content assumes a value of the order of 1% of the dry cylinder gases, which concentration is maintained for the remainder of the working stroke. The carbon dioxide and the carbon monoxide curves are the inverse of the oxygen curve, but, of course, on a different scale. There was a very noticeable irregularity in the CO_2 and CO contents of the gases during and after the combustion, even between samples extracted from the engine in immediate succession. Invariably a relatively high CO_2 content was accompanied by a low CO content and *vice versa*. This was found to be due to some slight irregularities in the mixture strength at the large carburettor jet, which were, however, insufficient to make appreciable difference to the power output or the tendency to "knock."

The volumes of oxygen accounted for, on the basis of the empirical formula of the petrol being $CH_{2\cdot0}$, in certain selected analyses were :—

$$\begin{array}{lllll}
 & & (O_2) \;\; (CO_2) \;\; (CO) \;\; (H_2O) & & \%\,O_2 \\
\text{t.d.c.} - 90^\circ \;\ldots\ldots & & 17\cdot8 + 1\cdot4 + \dfrac{0\cdot8 + 2\cdot3}{2} & = & 20\cdot7 \\
\text{t.d.c.} + 90^\circ \;\ldots\ldots & \left\{\begin{array}{l}\text{either} \\ \\ \text{or}\end{array}\right. & \begin{array}{l} 0\cdot8 + 9\cdot8 + \dfrac{4\cdot5 + 14\cdot3}{2} \\ \\ 0\cdot7 + 12\cdot0 + \dfrac{0\cdot6 + 12\cdot6}{2}\end{array} & \begin{array}{l} = \\ \\ = \end{array} & \begin{array}{l} 20\cdot0 \\ \\ 19\cdot3\end{array}
\end{array}$$

The results at + 90° are in tolerable agreement, but, as they stand, indicate an under-estimation of the oxygenated gases in the exhaust products, from which it may be inferred that the latter contain little hydrogen or hydrocarbon. A series of gas samples was analysed for hydrogen and revealed that, for the engine conditions used, the hydrogen content of the exhaust products increased with the CO content, and

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* EGERTON and SMITH, 'J. Sci. Instr.,' vol. 11, p. 28 (1934).

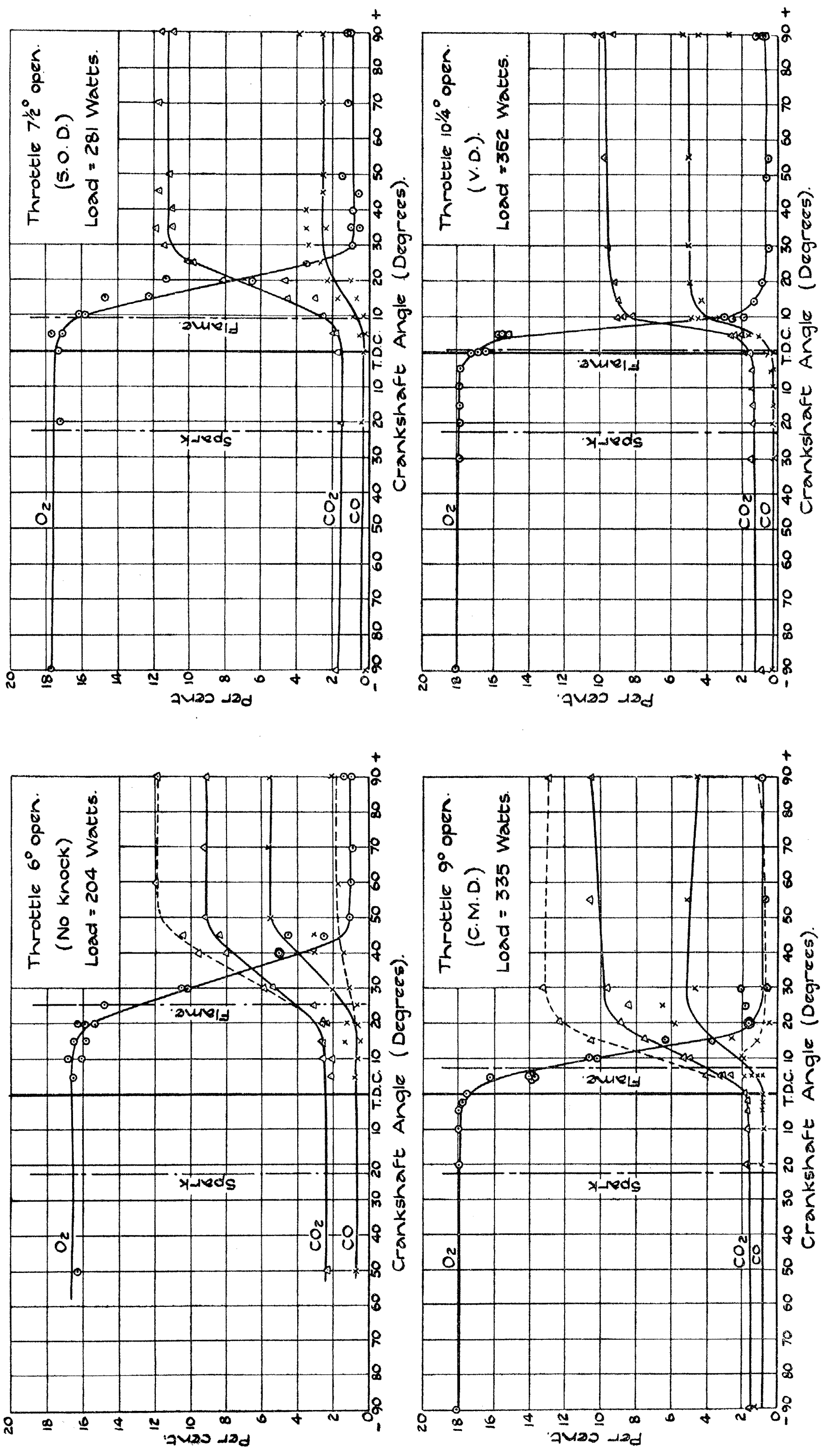

FIG. 5—Fuel : Shell No. 1, composition of cylinder gases

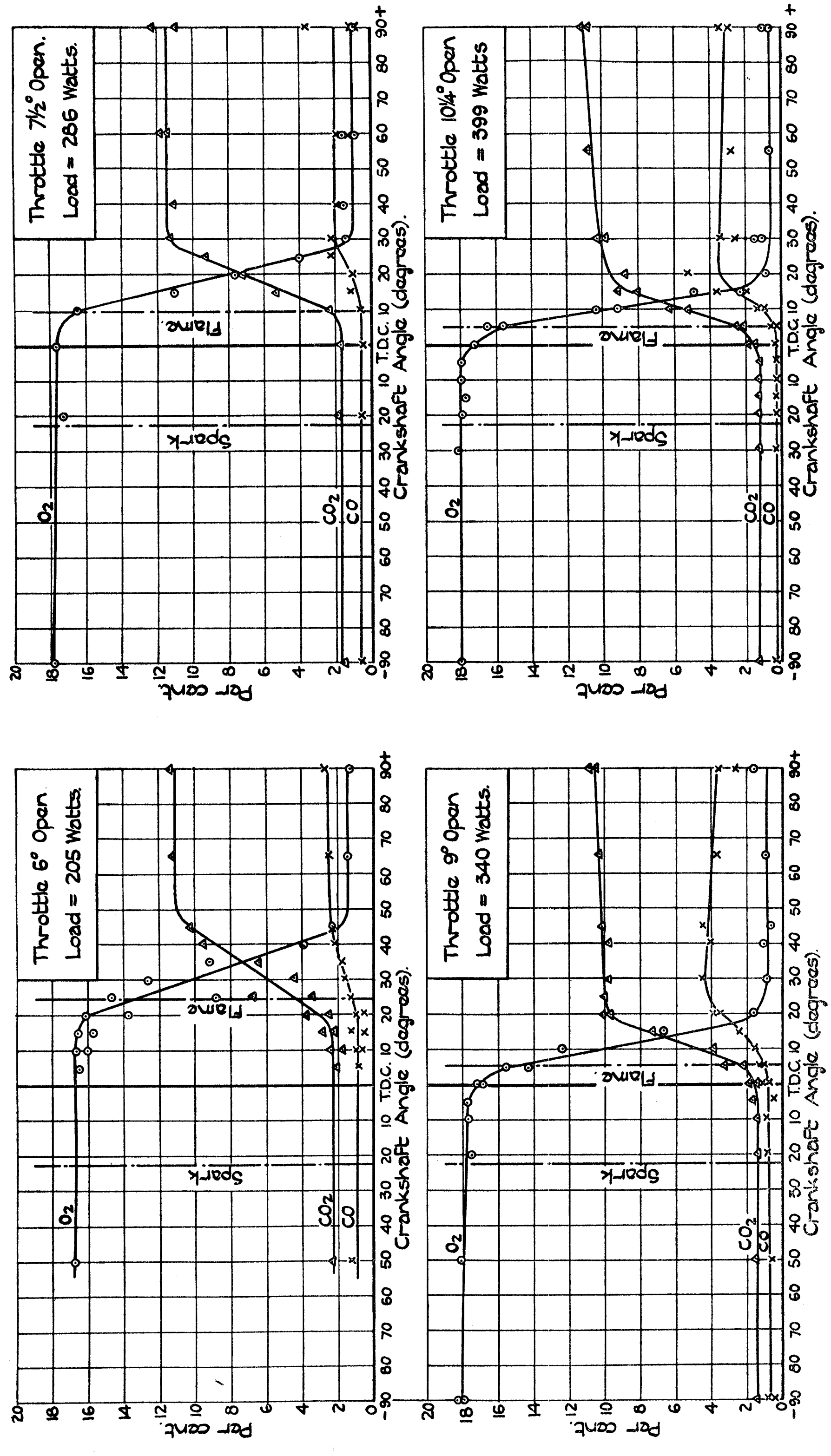

FIG. 6—Fuel : Shell No. 1, + 8 cc ethyl fluid per gallon, composition of cylinder gases

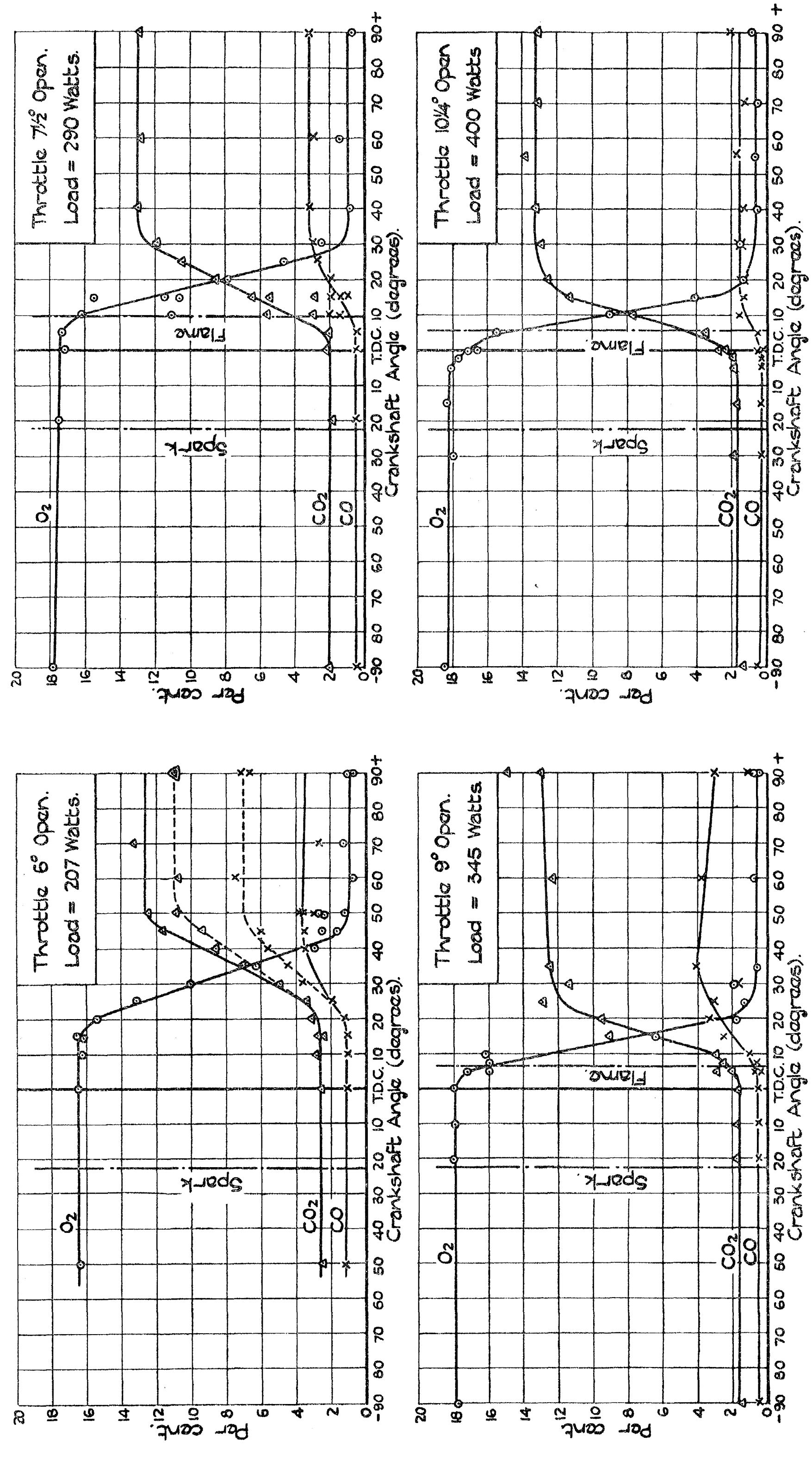

FIG. 7—Fuel : Benzole, composition of cylinder gases

varied between 0·7% and 2·4%. (These analyses for hydrogen were carried out on the residues from the ordinary analysis which contain nitrogen, hydrocarbons, hydrogen, etc. ; all but the hydrogen was absorbed in silica gel cooled in liquid air, a correction previously determined was made for the amount of hydrogen absorbed by the gel. The method was direct, any residual gas being pure hydrogen ; the volume was measured in an apparatus similar to a McLeod gauge.) Gas analyses of samples drawn from the exhaust pipe agreed with those obtained at the end of the expansion stroke, except for a small loss of oxygen.

The tests have shown that the CO/CO_2 ratio is very sensitive to very slight changes in the setting of the height of the float chamber of the fuel feed system. Excess fuel may influence the quantity of active molecules (OH and particularly of CO_2) available which help to sustain the afterglow, and so may alter the temperature at which the water-gas equilibrium tends to be frozen,* and therefore the composition of the exhaust gas. It has not been possible with the present type of fuel feed to get sufficiently accurate measurements to study these possibilities, but the point is obviously of considerable importance, and further investigation is being undertaken.

(*d*)—*Effect of Throttle Opening*

The curves show that the greater the throttle opening, the sooner after the passage of the spark does combustion occur in the neighbourhood of the sampling valve, and the steeper is the slope of the curve depicting the disappearance of O_2. It cannot be assumed that the steepness of the curve is a direct measure of the speed with which the flame passes across the seat of the sampling valve ; not only because the flame front is not a perfectly sharply defined surface in front of which no combustion has occurred and behind which the reaction is complete, but also because the progress of the flame across the cylinder head varied to some extent from cycle to cycle, as was revealed by the stroboscope experiments to be described later.

It is, however, permissible to regard the slope of the oxygen curve as related to the flame velocity. At the largest throttle opening, when the engine knocked violently with undoped Shell petrol, the oxygen curve for this fuel is considerably steeper than for the other two. In Table II are given the slopes of the oxygen curves for the various experimental conditions, calculated as the loss of oxygen

TABLE II—SLOPE OF OXYGEN CURVE.

Throttle opening, degrees	Slope of oxygen curve		
	Shell	Shell + ethyl fluid	Benzole
6	0·616	0·616	0·600
7½	0·848	0·848	0·800
9	1·167	1·120	1·037
10¼	1·930	1·170	1·073

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† *Cf.* LOVELL and BOYD, 'J. Ind. Eng. Chem.,' vol. 17, p. 1216 (1925).

(expressed as a percentage of the total gas) per degree of crankshaft angle. The slope of the benzole curve is consistently less than that of Shell plus ethyl fluid.

The ratio

$$\frac{\text{Slope of oxygen curve for Shell petrol alone}}{\text{Slope of oxygen curve for Shell + ethyl fluid}}$$

has the following values for the four different throttle openings

	Value of ratio
Throttle 6° (no " knock " with Shell petrol)	1·00
Throttle 7½° (s.o.d. ,, ,,)	1·00
Throttle 9° (c.m.d. ,, ,,)	1·04
Throttle 10¼° (v.d. ,, ,,)	1·65

These results are in agreement with the work of WITHROW, LOVELL, and BOYD,* who found a marked increase in the steepness of the oxygen curve as detonation increased in severity. In the present experiments, there is little doubt that the sampling valve is situated in the zone of " knock."

An approximation to the average speed with which the flame travels from the sparking plug to the sampling valve may be obtained by assuming that the flame front has reached this point when half the oxygen, which disappears in combustion, is consumed. On this assumption, the figures given in Table III for the average flame velocity, inclusive of delay at the start, were obtained.

TABLE III—FLAME VELOCITY

Throttle opening	Fuel	Position at which half O_2 is consumed : degrees after spark	Average flame rate (metres per second)	Time of appearance of flame	
				Degrees after spark	Degrees after t.d.c.
6°	Shell Petrol	55	5·81	48	25½
	Shell plus ethyl fluid	54½	5·86	47	24½
	Benzole	54½	5·86	—	—
7½° . . .	Shell Petrol	41	7·84	33	9½
	Shell plus ethyl fluid	41	7·84	32	9½
	Benzole	41	7·80	32	9½
9°	Shell Petrol	33	9·68	30	7½
	Shell plus ethyl fluid	34	9·40	28	5½
	Benzole	35½	9·00	29	6½
10¼° . . .	Shell Petrol . . .	29½	10·83	23	½
	Shell plus ethyl fluid	33	9·76	27½	5
	Benzole	32½	9·84	28	5½

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* 'J. Ind. Eng. Chem.,' vol. 22, p. 945 (1930).

If now, as was done for the slopes of the oxygen curves, the ratio :—

$$\frac{\text{Average flame rate for Petrol Alone}}{\text{Average flame rate for Shell + ethyl fluid}}$$

be calculated, the following values are obtained :—

	Value of ratio
Throttle 6°	0·99
„ $7\frac{1}{2}$°	1·00
„ 9°	1·03
„ $10\frac{1}{4}$°	1·11

The value of this latter ratio does not increase at a rate comparable with that of the former as the throttle opening is increased, whence it may be inferred that detonation is associated with a considerably accelerated flame velocity but only in the last portion of the gases to burn. This fact has several times been conclusively demonstrated by direct experiment.*

(*e*)—*Stroboscopic Observation of Flame*

It is important to know at what stage in the chemical processes revealed by the analysis of the cylinder gases flame appears. In order to obtain evidence on this point, a stroboscope was made through which to observe the passage of the flame across a quartz window fixed in the cylinder head.

The stroboscope took the form of a light hollow cylinder which was rotated by the engine through a suitable chain of gears. The shell of the cylinder was pierced by two diametrically opposed rectangular openings, 2 in. long by $\frac{1}{2}$ in. wide, between which were fixed a series of parallel blades. As the cylinder rotated, a momentary glimpse was obtained between these blades of a quartz window which was mounted in a plug, and screwed into the " bouncing pin " boss of the engine. The shutter was vertically above the window, with its axis parallel to the diameter on which lay the sparking plug and the " bouncing pin " boss. The instrument was designed to give a glimpse of duration of 1° of crank angle, which object was achieved by making the rotor cylinder 1 in. diameter with the blades 1 mm apart. The rotor shaft was geared up to a speed of $4\frac{1}{2}$ times that of the crank-shaft. The shutter and walls of the window plug were painted a dead black to obviate reflections.

The drive for the stroboscope was taken from the shaft which carried the trigger disc when the sampling apparatus was in use, and the same phasing mechanism was employed.

The stroboscope was timed by placing a neon tube, connected in parallel with the sparking plug, over the quartz window and rotating the arm of the phasing gear until the light, given by the neon tube as the spark occurred, was visible through the shutter. The position of the arm on the graduated scale corresponded then

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* *Cf. ibid.*; *also* WITHROW and BOYD, 'J. Ind. Eng. Chem.,' vol. 23, p. 539 (1931); *also* SCHNAUFFER, 'Z. Ver. deut. Ing.,' vol. 75, p. 455 (1931).

with the ignition timing, as indicated by the neon tube device previously described. The quartz window was $\frac{3}{16}$ in. thick and of a diameter $\frac{3}{8}$ in. intermediate between the internal diameter of the sampling valve and the outer diameter of the bevelled valve seat.

The range of engine conditions examined in the experiments was repeated with the stroboscope in position. There was an inter-cyclic irregularity of some 2° or 3° in the time at which the flame was first visible through the window. Since the time taken for the flame to travel across the window is much of the same order as this divergence, no permanent and clearly defined flame front was apparent through the stroboscope.

The figures given in Table III, on p. 450, are the times at which the flame first made an occasional appearance, and are probably some 1° or 2° earlier than the average time at which flame reached the inner edge of the window. These readings are indicated on the analysis curves. With petrol and Shell plus ethyl fluid the flame became invisible after a period of some 20° to 25° had elapsed since the first appearance. It has already been stated that the stroboscope rotated at $4\frac{1}{2}$ times the engine speed. Since two glimpses through the shutter are obtained for every revolution of the instrument, the window is sighted every 40° of the crankshaft, as a result of which events taking place in the cylinder at intervals of 40° are sighted simultaneously. The luminosity persisted with benzole for more than 40° after the flame first appeared, which rendered the determination of the exact timing of this latter event a matter of more difficulty. Only three readings were at all reliable with this fuel.

The first appearance of luminosity always coincided approximately with the instant when rapid combustion began, as indicated on the gas analysis curves, but there was a certain amount of alteration in the composition of the gases for 5° or 10° before this time, during which the oxygen content suffered a decrease of some 5% or 10%. It was thus indicated that, in advance of the flame front, there was a non-luminous zone in which the temperature attained by compression and by contact with the surface of the hot exhaust valve was sufficient to give rise to a relatively slow combustion. Admittedly the effect may have been due in some measure to turbulent admixture with the gas from behind the flame front.

As regards the appearance of the flame with Shell alone, whilst the colour was bluish when the engine was not knocking, detonation* was accompanied by a characteristic yellow white flame of intense brilliance. In general as the throttle opening was increased the flame colour changed from a distinct blue to bluish white with Shell plus ethyl fluid, and to a pinkish blue with benzole. With Shell under conditions of violent detonation, the later stages of the flame were accompanied by frequent reddish flashes, which were not present to the same extent when the fuel was doped with ethyl fluid. The benzole flame became redder as the working

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* The term "knock" is more suitable to the phenomenon, for it is necessary to distinguish it from the initiation and propagation of a detonation wave in a detonating gaseous mixture.

stroke proceeded. Occasional yellow flashes, presumably caused by incandescent particles of carbon, were evident during all the flame observations.

All these observations were repeated six months later after the experiments detailed in Part II : the appearance of the flame at the window occurred at the same time as previously measured within 2° or 3°. Some observations were also made with hydrogen as fuel; under knocking conditions (c.m.d.), flame occurred at the valve about 30° after the spark. The flame was yellow white, with occasional whiter flashes at maximum intensity. There were far fewer red flashes in the afterglow than with petrol.

4—ESTIMATION OF ALDEHYDES AND "PEROXIDES"

(*a*)—*Conditions necessary*

The detection of intermediate products in the engine cylinder, and the estimation of the quantities in which they are formed, necessitated a method of analysis which had to be sensitive, rapid, and convenient. The reagents had to be sensitive to about one part in a million, and at such low concentrations other influences easily mask detection.

Preliminary tests on the engine showed that it would be unsatisfactory to bubble the gas issuing from the sampling valve through the reagents, since the time required for coloration was rather too long to maintain constant engine conditions.

(*b*) *The "Droplet" Method.*

A method was adopted which had been used by EGERTON* for the measurement of small concentrations of NO_2 from explosives. The gas was passed over a small quantity of reagent held in a suitable container such that its volume and exposed surface were of standard proportions. The exposed surface of the reagent was kept small in proportion to the area of the chamber in which absorption was effected. It was thus ensured that the reagent did not deplete the gas in the chamber to such an extent as to lower appreciably the concentration of the compound therein. The time required for coloration of the droplet depends inversely on the rate at which the compound comes into contact with the absorbing surface, and thence the rate at which it diffuses through the mass of the reagent, and on the rapidity with which the compound and the reagent react to produce colour. Since the number of molecules which come into contact with the exposed surface in a given time may be assumed to be a linear function of the concentration, the time of coloration of the reagent and the concentration of the compound in the gas are related according to a law of the hyperbolic type. The method is only accurate over a fairly small range of concentration, but some accuracy can be sacrificed for convenience of operation. The container for the reagent took the form of a disc of vitreosil glass

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* 'J. Soc. Chem. Ind.,' vol. 32, p. 331 (1913).

1 cm in diameter and 6 mm thick with a cavity 3 mm deep and 4 mm diameter. The small cavity thus formed was filled with reagent so that the surface of the "droplet" was flush with the top of the disc and quite flat. A standard absorbing surface was thus obtained. The disc was held in a T-shaped vessel, fig. 8. This was of slightly larger diameter than the disc, which latter rested on an opal glass table at the end of a brass rod, and was pushed into the tube until a fixed mark was reached. Out of the gas space above the disc were led two nozzles, one of which was connected to the exit nozzle of the sampling valve, and the other to the flow-meter which indicated the rate of sampling. A second similar disc was filled with a liquid of a standard colour, and was held against the side of the disc holder. The time required for the reagent " droplet " to attain this colour was measured.

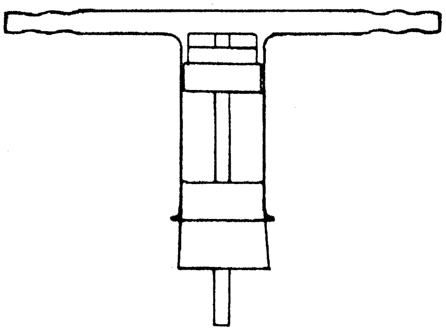

FIG. 8

Schiff's reagent (0·04% rosaniline hydrochloride solution just decolorized by the addition of sulphurous acid) was used for the estimation of aldehydes ; a magenta solution was used as standard tint. The " droplets " were standardized by drawing air at various rates over various aldehydes at a definite temperature in a bath of CO_2 and alcohol. The air containing a small quantity of aldehyde passed over the " droplet " and then into a solution of potassium bisulphite. The time of coloration of the "droplet" was noted, and the bisulphite titrated with iodine to obtain the aldehyde concentration. The time of coloration of the " droplet " was shown to be independent of the rate of flow except at very small flows, and provided it was not so rapid as to cause a rippled surface. A typical standardization curve is given, fig. 9 ; measurements were made, using butyraldehyde and also 40% formalin solution. These standardizations were checked by attaching the disc holder and bisulphite to the sampling valve of the engine, and as the points obtained lay on the standardization curve, the latter could be applied with confidence to other engine experiments in which the " droplet " method was used.

For the estimation of " peroxides " a solution of acid and starch was used (2 cc 5% KI solution, 4 cc 2N H_2SO_4, 1 cc 1% filtered starch solution, 18 cc distilled water) ; a dye solution of suitable tint acted as standard. A 30% H_2O_2 solution replaced the aldehydes in the vapourizer ; after passage over the " droplet " the vapour was absorbed in KI solution which was titrated with thiosulphate. With the necessary precautions, it was possible to achieve a satisfactory standardization curve. This was likewise checked by means of the gases taken from the engine sample valve, the " peroxide " content of which was estimated by absorption in KI solution and titration with thiosulphate.

Special experiments were made to test the simultaneous effect of peroxides, butyric aldehyde, and acetaldehyde on the rate of colouring of the Schiff and KI droplets. For concentrations of aldehyde about 100 times the hydrogen peroxide concentration, the rate of colouring of the KI was about 10% less, and about equal concentrations of hydrogen peroxide and aldehyde very slightly increased the time of colouring of the Schiff reagent. Acetaldehyde and air (concentration about 5%) passed over the KI "droplet" did not colour it appreciably save after a long time. These experiments showed that so far as the detection of hydrogen peroxide and of aldehydes are concerned, the " droplets " would provide results of reliability with mixtures.

Without making any assumption as to the nature of the " peroxides," the behaviour of the KI " droplet" towards H_2O_2 vapour could be used as an approximate

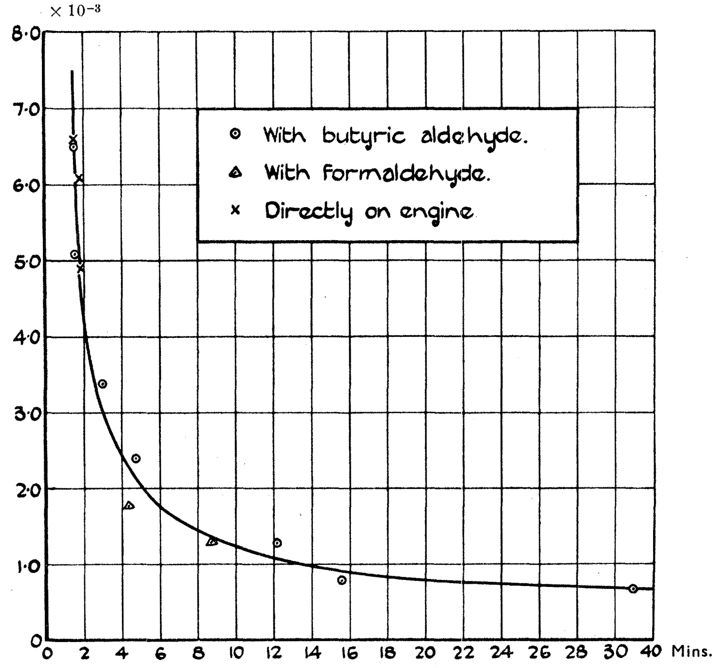

FIG. 9—Calibration of " droplets " of Schiff's reagent.

measure of the " peroxide " content of the engine gases, provided the rate of reaction of the " peroxide " with the KI was more or less similar to that of hydrogen peroxide, *see* Part II, p. 471.

(*c*)—*Aldehyde and " Peroxide " Analyses on the Gases from the Engine*

The series of engine conditions investigated during the analyses for O_2, CO_2 and CO was re-examined in turn for aldehydes and " peroxides."

During the aldehyde tests, care was taken to make sure that the end of the disc-holder nozzle came close up to the nozzle on the sampling valve, the short rubber connection was renewed for every " droplet " reading. To prevent condensation of the aldehyde, etc., in the connecting tube between the valve and disc, a close coil of small metal piping was wrapped round the tube and connected in series with the warm-water outlet from the valve jacket. The results of the aldehyde analyses were consistent and reproducible.

In view of the small amounts of " peroxides " present, it was hardly expected that the analyses for these compounds would reveal the same consistency ; but with scrupulous attention to details (such as boiling out of the discs, frequent cleaning of the sampling valve, etc.) it was possible to obtain satisfactory reproducibility.

During the tests both for aldehydes and " peroxides," the readings for Shell petrol and Shell plus ethyl fluid were alternated, so as to ensure identical engine conditions for the two fuels.

The results of the tests are shown graphically in figs. 10, 11 and 12. On the same figures are shown the oxygen curves reproduced from figs. 5, 6, and 7.

The following facts are outstanding.

Aldehydes.—With Shell petrol alone the aldehydes reach a maximum concentration at a time coinciding approximately with the moment at which flame reaches the sampling valve, the occurrence of the maximum being more retarded with respect to this moment as the throttle opening is increased. This maximum concentration is of the order of 5 parts in 1,000 when the throttle is 6° open, and of 7 parts in 1000 for the three larger throttle openings. During the greater part of the last half of the *compression* stroke the aldehyde concentration is practically constant, and of the order of 1 part in 1000. This quantity increases slightly as the throttle opening is increased. When the crankshaft has reached a position of some 10° before t.d.c. the concentration begins to increase, and rapidly reaches the maximum. Then as combustion proceeds, the concentration decreases until a value of about 2 parts in 1000 is attained, after which no further change is evident up to the completion of half the working stroke.

The results of the aldehyde experiments with Shell plus ethyl fluid are similar to those with Shell alone, save that the maximum concentration is always considerably less, and of the order of 4 parts in 1000. An interesting feature of the curve relating to the 6° throttle opening is that the aldehyde curve for Shell plus ethyl fluid crosses that for Shell petrol alone during the last stages of combustion. This would indicate that the maximum temperature of the cylinder gases is less when lead tetraethyl is present, causing more gradual decomposition of the aldehyde. The concentration at t.d.c. + 60° was found to be the same with both fuels. With benzole, no peak in the aldehyde concentration occurs. Practically up to the end of the compression stroke the concentration is constant to about 1 part in 1000, after which it gradually rises during the " peak " period of the other two fuels, to attain a steady level which is higher the more open the throttle, the greatest value for this being 2 parts in 1000.

The high aldehyde content during the compression stroke cannot be accounted for by the aldehydes in the residual exhaust gases, and must be due to aldehyde formation as the petrol in the fresh charge comes into contact with the hot exhaust valve. If we assume (*see* Part II) that all the aldehydes in the engine are formaldehyde a concentration of 7 parts in 1000 by volume is equivalent to some $\frac{7 \times 30}{28} = 7 \cdot 5$ parts in 1000 by weight. The fuel represents some 70 parts in 1000 by weight, so that

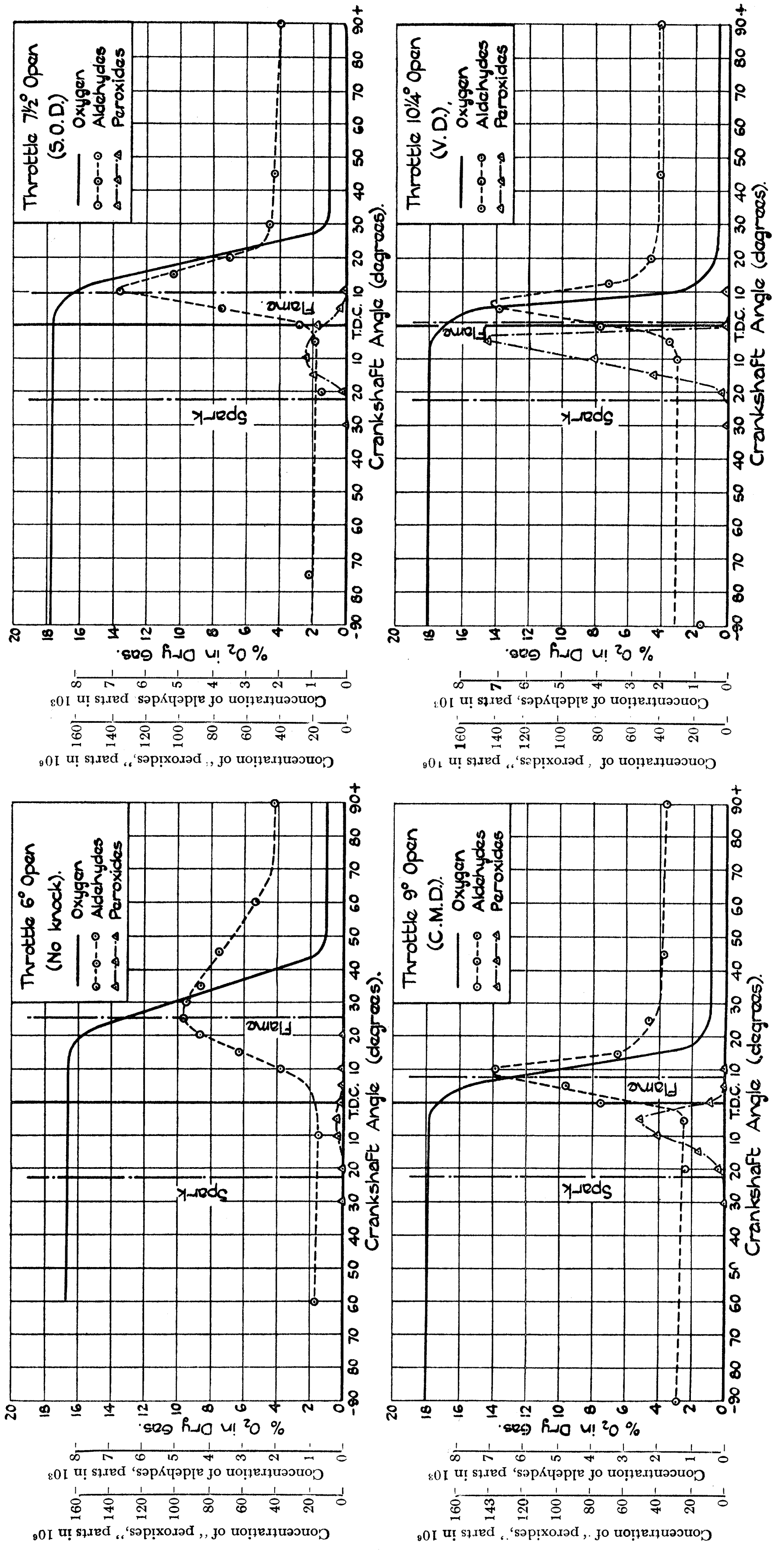

Fig. 10—Formation of aldehydes and "peroxides"—Shell No. 1

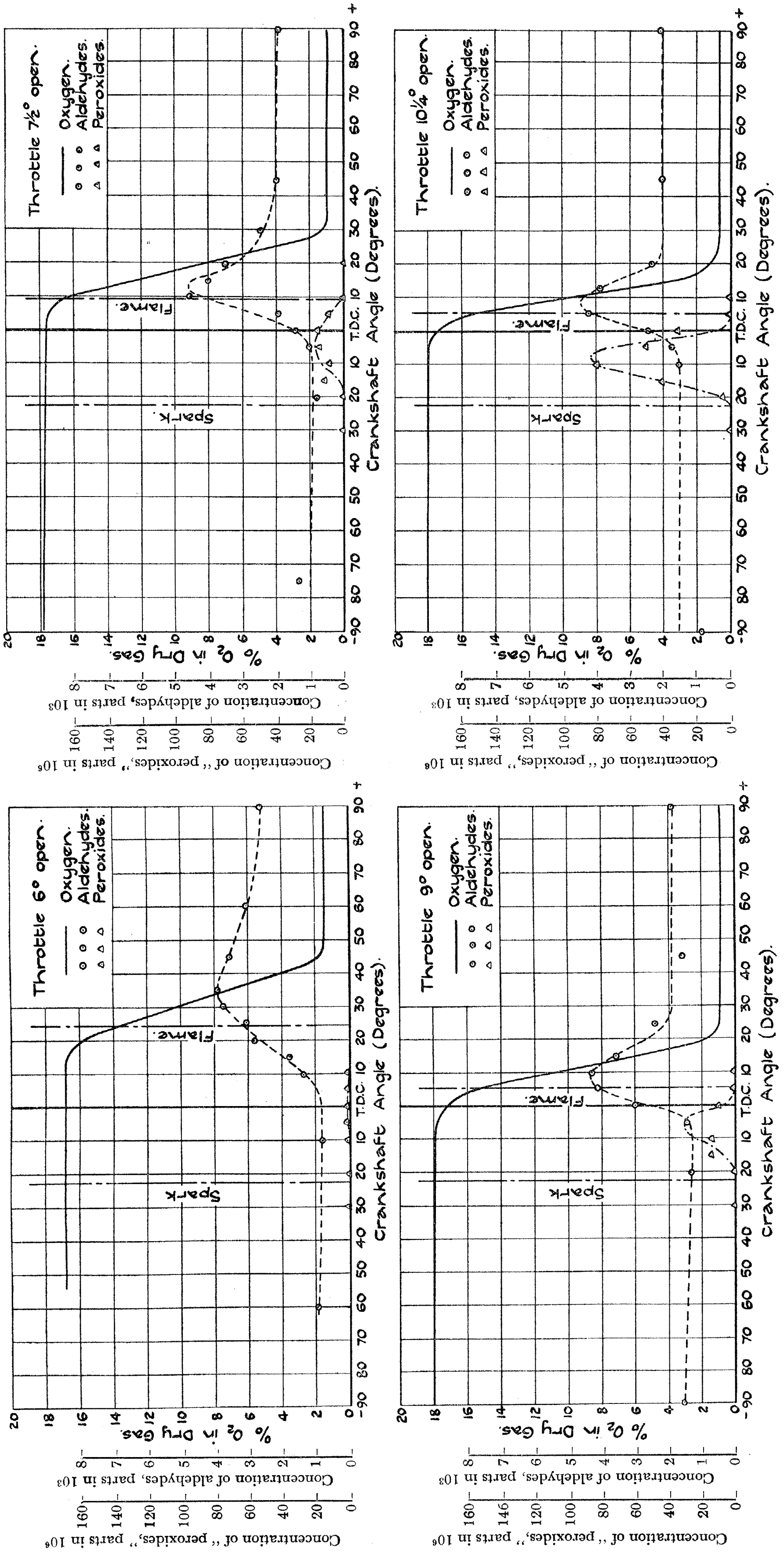

Fig. 11—Formation of aldehydes and "peroxides"—Shell + 8 cc. ethyl fluid per gallon

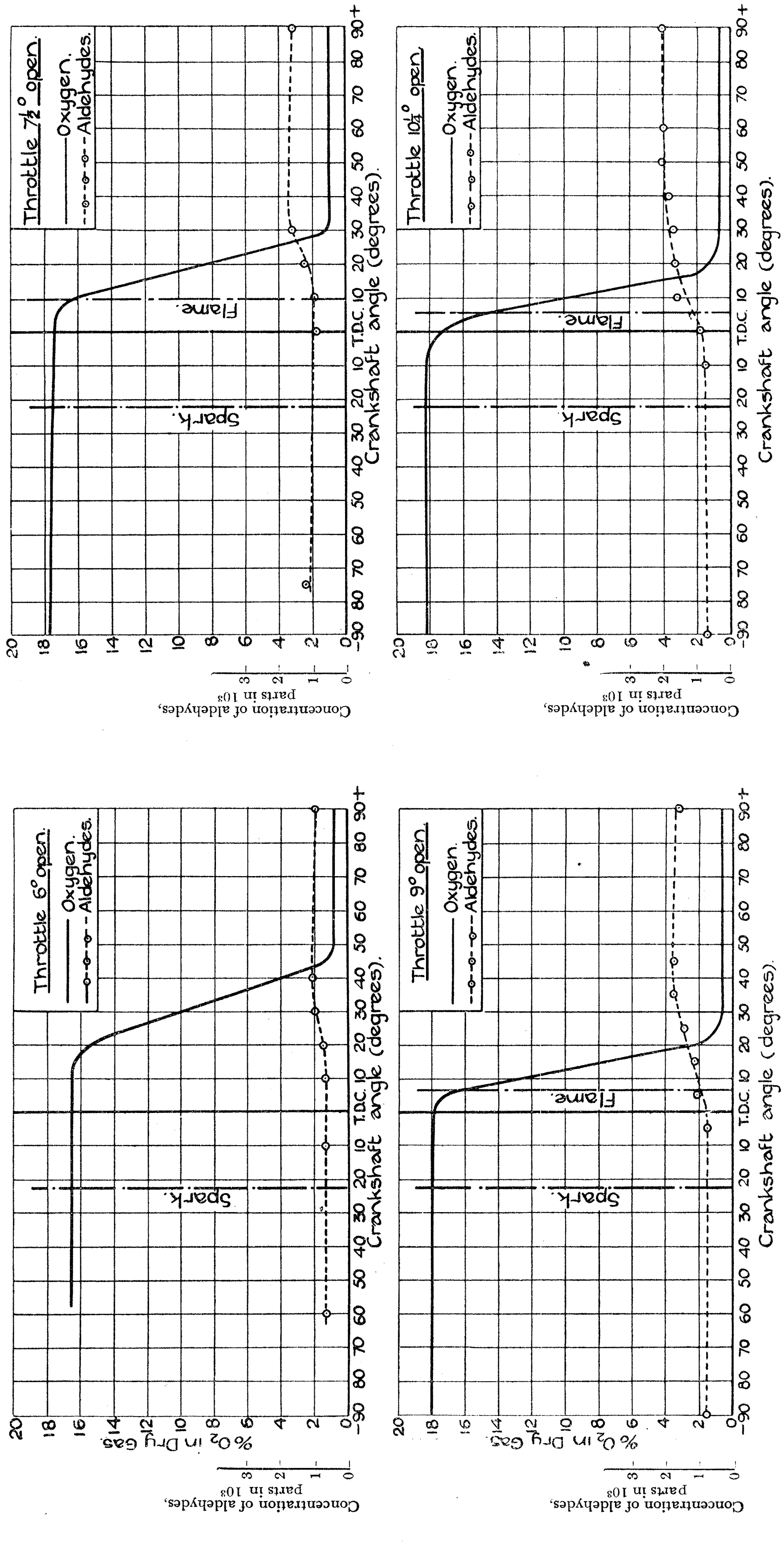

FIG. 12—Formation of aldehydes. No "peroxide" detected—Benzole

the maximum aldehyde formation is some 1/10th by weight of the fuel in the original charge.

" *Peroxides* "—No " peroxides " at all were measured with the benzole used, but with Shell petrol, both doped and undoped, the formation of substances behaving as such were definitely indicated. The term " peroxides " is used for convenience to denote oxidizing substances which react with KI ; nothing more at this stage is implied.

With Shell petrol alone no " peroxides " were detected until the last 20° or 30° of the compression stroke. The concentration rose rapidly to a maximum at some 5° before t.d.c., after which it just as rapidly fell to zero again, reaching this point some 5° before the aldehyde concentration attained its peak. The maximum concentration of " peroxides," unlike that of aldehydes, rose rapidly as the throttle opening was increased and the knocking became more severe. The greatest measured concentration was about 1·5 parts in 10,000.

The absence of " peroxides " with benzole has been explained by subsequent work.

For the aldehydes there was very little falling off of concentration as the length of the tube connecting the " droplet " chamber with the valve increased, whereas with the " peroxides " a marked decrease was noticed, so that the actual " peroxide " content in the cylinder was probably considerably higher than that measured.

In his experiments on the supercharged petrol engine, MUCKLOW* found nitric acid to collect in the pipe which connected the non-return valve of the maximum cylinder pressure indicator to the pressure gauge. This gave evidence of the formation of oxides of nitrogen in the engine at the moment of maximum pressure. The occurrence of a similar effect in the Delco engine was suggested by the fact that the steel stem of the sampling valve showed distinct signs of acid corrosion after being in use for a short time.

Griess's reagent (1 cc 0·1% solution of naphthylamine in N/100 acetic acid and 1 cc 0·5% solution of sulphanilic acid in N/100 acetic acid + 0·1 cc glacial acetic acid) is a sensitive test for nitrous acid, and well suited to the " droplet " method of analysis. On applying this test to the gas sampled from the engine, it was found that the " droplets " coloured a bright pink in 2 minutes at the point of maximum " peroxides," and also in the same time both at the position of maximum aldehydes (no " peroxides ") and at a position 10° later than this. The " droplet " coloured in 4 minutes at a point 10° prior to that for maximum " peroxides," at which setting the KI reagent showed hardly any coloration.

As the Griess reagent is considerably more sensitive than KI to nitrous acid, and as the coloration of the KI " droplet " did not accord with the behaviour of the Griess " droplet," it seemed to follow that nitrogen peroxide was not responsible for the peaks on the " peroxide " curves with KI. As a result of a series of engine experiments using different fuels, this conclusion was shown later to be incorrect. Nitrogen

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* ' Rep. Aero. Res. Comm.,' Lond., No. 1460 (Nov. 1931).

peroxide is the main " peroxide " present. But the proof of this, and the explanation of the peaks in the " peroxide " curves which occur prior to the maxima in the aldehyde curves was a problem of some complexity, the elucidation of which will be described in Part II.

(*d*)—*Addition of Aldehydes to Fuel*

Some experiments were made at this stage of the investigation to find out whether the " peroxides " could be aldehyde peroxides.

There was a sufficient quantity of aldehyde present during the compression stroke to give rise to the relatively small amount of " peroxide " formation without the process being evident on the analysis curves. This possibility was investigated by adding large amounts of aldehyde to the fuel and examining the effect on the " peroxide " formation. If the maximum concentration of " peroxides " did not undergo any appreciable increase they could confidently be regarded as not being formed from the aldehyde.

A mixture was made up of 90% Shell and 10% acetaldehyde. Of all the aldehydes, this latter was most likely to peroxidize during the early stages of combustion. On analysing the samples for aldehydes and " peroxides," the results shown in Table IV were obtained. The engine throttle was 9° open.

TABLE IV—ADDITION OF ACETALDEHYDE TO FUEL

Position from t.d.c.	Fuels	Concentration	
		Aldehydes $\times 10^3$	" Peroxides " $\times 10^6$
− 90°	Shell + aldehyde	About 8	—
	Shell	1·2	—
− 40°	Shell + aldehyde	—	None
	Shell	—	None
− 25°	Shell + aldehyde	About 8	None
	Shell	1·2	None
− 15°	Shell + aldehyde	—	6
	Shell	—	8
− 10°	Shell + aldehyde	About 8	—
	Shell	1·2	—
− 7½°	Shell + aldehyde	—	6
	Shell	—	8
t.d.c.	Shell + aldehyde	About 8	—
	Shell	2·5	—
+ 5°	Shell + aldehyde	About 8	None
	Shell	5·2	None
+ 12°	Shell + aldehyde	4·8	—
	Shell	4·2	—

Thus, contrary to there being an increase in the " peroxide " formation when acetaldehyde was added to the petrol, there was actually evidence of a decrease, proving that the " peroxides " detected were not oxidation products of the aldehydes.

Assuming that the maximum power mixture strength of the engine charge was 13 to 1 air/petrol by weight, the presence of 10% of acetaldehyde in the fuel would result in a concentration of 5 parts in 1000 of aldehyde in the gaseous mixture. Adding to this the 0·1% which is found in the compression stroke when no aldehyde is added to the fuel, we should expect a concentration of some 6 parts in 1000 of aldehyde during the compression stroke with the mixed fuel. In view of the insensitiveness of the " droplets " at high concentrations, this is in fair agreement with the results of the analyses, which gives a concentration of 8 parts in 1000 for this part of the cycle.

The effect on the " peroxide " formation of the addition of valeric aldehyde to the fuel was also examined and with similar results. There was no appreciable difference in the " peroxide " formation between the tests when pure petrol and the petrol-aldehyde mixture were used, though for the latter the observed concentration with the mixture was, if anything, the larger of the two. Again, with the valeric aldehyde mixture, the calculated aldehyde content during the compression stroke agreed closely with that measured.

With a view to testing whether hydrogen peroxide had anything to do with the production of the " peroxides," a similar test was run in which hydrogen was added to the intake gases through an extension attached to the induction pipe. The addition of hydrogen to the order of 1% of the total charge, whilst not appreciably affecting the engine output for the same throttle opening, had a distinct anti-knock effect ; whereas the addition of 2% was sufficient to suppress entirely a slight continuous " knock." This effect had been recorded by RICARDO. On testing the samples with the " droplets " of KI reagent, the mixture of hydrogen with the charge in the above proportions had, if anything, a slight inhibitory effect on the formation of the " peroxide " substances.

Several tests were run to investigate the effect which the addition of aldehydes to the fuel had on the tendency of the engine to " knock." In these experiments a mixture of Shell petrol and aldehyde was matched against Shell petrol plus lead tetraethyl. The addition of 10% of either acetaldehyde or butyric aldehyde to the fuel had no noticeable effect on the knocking characteristics of Shell, though additions of 20% and more of the former had a " pro-knock " effect. The addition of propionic or valeric aldehyde had a very slight " anti-knock " effect, the former to a greater extent than the latter. Thus :—

Shell + 10% propionic aldehyde = Shell 0·4 cc $PbEt_4$ per gall.
Shell + 10% valeric aldehyde = Shell 0·3 cc $PbEt_4$ per gall.

Paraldehyde was observed to have a slight " pro-knock " effect, the addition of 5% to Shell being equivalent to the subtraction of some 0·3 cc of lead tetraethyl per gallon in this respect. The effects of these last three substances were so small as to be negligible, and it is obvious that, apart from the usual effect of diluting the petrol with a second fuel of slightly different " knock " value, their presence has no radical influence on the chemical processes which determine the liability to detonate.

5—SUMMARY

The preliminary experiments with Shell petrol, ethyl petrol, and benzole, here described, showed that :—

(1) Some combustion occurred in the knocking zone prior to the passage of flame, as shown by the analyses of gases drawn from the sample valve at various stages of the stroke.
(2) This combustion was attended by formation of aldehydes ; the maximum concentration (1 in 150 approximately) was attained at the moment when the flame reached the sampling valve.
(3) Substances behaving as " peroxides " (towards potassium iodide) were also formed (concentration about 1 in 10,000), but seemed to disappear before the flame reached the valve.
(4) The amount of such " peroxides " increased as " knock " increased.
(5) " Benzole " apparently gave no such " peroxides."
(6) Ethyl lead decreased both the quantity of aldehydes and " peroxides " formed, confirming that it slows down the reaction occurring prior to inflammation.
(7) Aldehydes did not increase the quantity of " peroxides " obtained, nor the tendency to " knock " ; neither did hydrogen.

PART II — ESTIMATION OF NITROGEN PEROXIDE

By A. EGERTON, *F.R.S.*, F. LL. SMITH, *and* A. R. UBBELOHDE

1—INTRODUCTION

The estimation of the aldehyde and " peroxide " content of the sample gas described in Part I indicated that the " peroxides " were formed before inflammation, and that the occurrence of " knock " was in some way related to them ; for the amount of such " peroxides " was greater under knocking conditions. Hardly any " peroxides " were found using benzole ; in fact, benzole appeared to destroy them. Since nitrogen peroxide could be detected by the Griess reagent in that part of the stroke where no " peroxides " affecting potassium iodide were obtained, the pronounced maximum in the " peroxide " curve did not seem to be connected with the formation of NO_2. The effect of the addition of aldehydes, however, seemed to prove that the " peroxides " were not formed as a result of the oxidation of aldehydes. It was also observed that the quantity of " peroxide " appeared to decrease as the distance from the sampling valve increased. Further experiments with fuels whose chemical nature was precisely known were necessary in order to find out the cause of this behaviour.

The outcome has been to show that the oxidizing substances or " peroxides " which affect the potassium iodide reagent are mainly nitrogen peroxide, while other processes are at work which cause its disappearance and so produce the sudden maximum.

2—ENGINE EXPERIMENTS WITH VARIOUS FUELS

Experiments were made using various fuels ; the results are summarized in this section. The same arrangements were used as described in Part I. An improvement was made in the sampling valve. It was found that the stem of the former valve became slightly pitted and rusted by corrosive condensate. The whole valve and stem were therefore chromium plated inside and out. The exit tube for the gases was removed and replaced by a glass tube ($\frac{1}{8}$-in bore), to which the disc holder was connected.

For various reasons, such as scarcity of certain fuels, it was not possible to make such complete experiments as quoted in Part I ; only the general type of curve obtained with different fuels was determined.

Aldehydes—It was shown in Part I that additions of acetaldehyde, butyraldehyde, and valeraldehyde up to 10% had no deleterious effect on knocking, neither was the " peroxide " maximum appreciably changed. Additions of paraldehyde slightly increased the knocking, but not to a marked extent, and as with ether, aldehyde was shown to destroy the efficacy of lead tetraethyl. Pure acetaldehyde (B. Pt. 21°) was found to knock so violently that the engine could not be run on this fuel. It became of interest to find out at what concentration, when added to Shell petrol, the aldehyde would increase the knock. An increase of " knock " was observed for an addition of 20% and over.

Peroxides—The following peroxides had been prepared :—diethyl peroxide (B. Pt. 64° at 740 mm), mono-ethylhydrogen peroxide (B. Pt. 95° Baeyer), and hydroxymethyl ethyl peroxide (B. Pt. 47° at 13 mm Rieche). These had been used for investigation of their chemical behaviour towards certain reagents. The remains left over from those tests were used up in the engine with the following results :—

Petrol (Shell) + 1% ethyl hydrogen peroxide knocked more than petrol + 1% ether.
Petrol + 1% diethyl peroxide knocked more than petrol + 1% ether.
Petrol + 1% oxymethyl ethyl peroxide knocked more than petrol + 1% ether.
Petrol + 0·02% diethyl peroxide knocked slightly more than the same petrol alone.
Petrol + 2·5% diethyl peroxide knocked very violently and sharply.

It was unfortunate that insufficient material was available to make a knock-rating test of the standard kind on these mixtures, but these trials show that the organic peroxides are lively " pro-knocks."

Although the hydroxymethylethyl peroxide caused a "knock," it probably contained ethylhydrogen peroxide and therefore no conclusions could be drawn as to the knocking of the pure compound.

Alcohols—Since alcohols do not give rise to a knocking type of explosion under normal conditions, some tests were done to find out whether the KI "droplet" was affected by its combustion products. A smaller choke tube and larger jet were fitted in the carburettor, so that the engine conditions should remain much the same as for the hydrocarbon fuels. The "droplet" times before t.d.c. were probably delayed by the unburnt fuel ejected and condensed on the "droplet," but the results showed that alcohols can give rise to "peroxide."

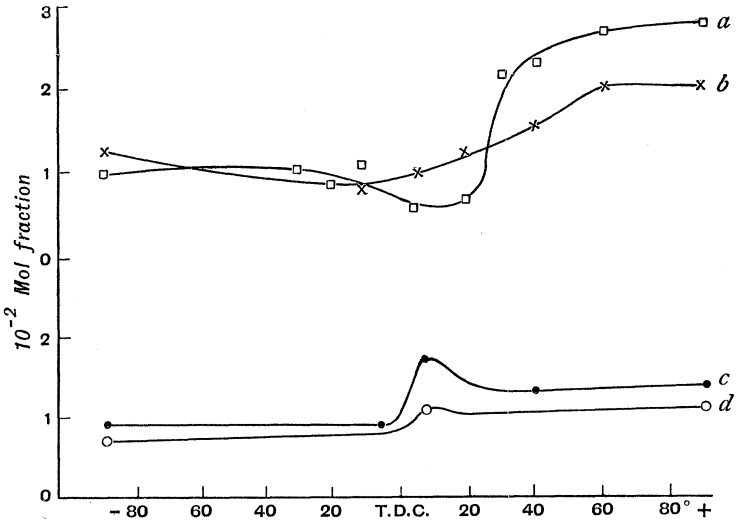


FIG. 13—Concentration of aldehydes. (*a*) Ethyl alcohol ; (*b*) butyl alcohol ; (*c*) butane ; (*d*) methane

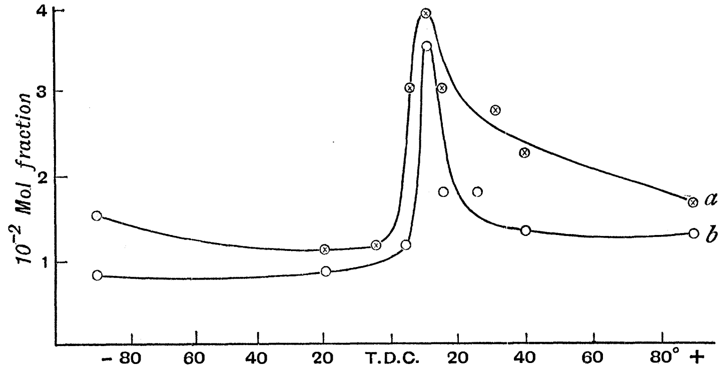


FIG. 14—Concentration of aldehydes. (*a*) Hexane ; (*b*) cyclohexane

The quantity of aldehydes formed was also determined, fig. 13. These curves should be compared with the results for a fuel such as hexane, fig. 14 ; they show a striking difference, for the amount of aldehyde appears to decrease rather than increase towards the end of the compression stroke.

Cyclohexane (B. Pt. 81·5° C)—A quantity of pure cyclohexane was kindly provided by the Anglo-American Oil Co. Unexpected results were obtained with this fuel. The quantity of " peroxides " formed was particularly large, although no knocking occurred.

The cyclohexane was tested with KI and other reagents, and no impurities likely to give rise to substances liberating iodine were found, though a trace of sulphur was present.

Hydrogen—Previous tests had shown that addition of hydrogen reduced the amount of knocking when running on petrol, and the KI " droplet " coloured up at much the same rate.

The engine could be run on hydrogen alone by connecting the carburettor with the mixing chamber previously mentioned, and regulating the flow of hydrogen from the cylinder as the petrol supply was gradually cut off. With the throttle at 9° the hydrogen flow was adjusted to give continuous slight detonation, and the speed reduced to 600 revolutions. The load was about 60% of that given by Shell petrol at the same throttle opening. (Violent knocking was possible with a larger flow and greater load.)

Hydrogen appeared to give " peroxides " in all parts of the stroke, gradually increasing to t.d.c. — 7°, and then more quickly and continuing to increase throughout the working stroke (*see* fig. 15). The addition of " benzole," as in former tests, prevented the coloration of the " droplet," and appeared to destroy the " peroxides."

Another observation made with hydrogen is noteworthy ; lead tetraethyl did not stop the " knock " ; whereas, when running on petrol alone and knocking with the same intensity, this substance immediately stopped the knocking in similar conditions.

Hexane—*n*-Hexane cannot readily be obtained in quantity. Supplies from petroleum distillates contain methyl cyclo-pentane and cyclohexane, etc.

The purest available hexane, kindly supplied by the Anglo-Persian Oil Co., and also that obtained from Messrs. British Drug Houses, Ltd., was rewashed and shaken with fuming sulphuric acid until the acid was only slightly discoloured, then washed with NaOH (20%), with water, and then distilled. Another sample was treated with benzene, cooled and the frozen mixture of cyclohexane and benzene removed by filtration at low temperature ; the remaining product was distilled. The resulting distillate contained about 1% of benzene, but probably less naphthenes than the other sample as a result of this treatment. B. Pt. 68° to 70°.

Hexane gave a curve with a peak for the " peroxides " characteristic of petrol, but there remained an appreciably higher concentration in the expansion stroke. The " knock " was considerably greater under the same engine conditions. No significant difference in behaviour was observed between the two samples.

Heptane—As the hexane was not a pure paraffinic fuel, though it probably did not contain any large proportion of naphthenes, a test on pure heptane was carried out. A small quantity of pure *n*-heptane (B. Pt. 98·5°) was kindly supplied by the Anglo-American Oil Company.

This test definitely showed that the pure paraffins provided " peroxides," and that it was not peculiar to naphthenes, such as cyclohexane. A peak occurs as with petrol, but the " peroxide " does not disappear in the expansion stroke.

Butane.—A supply of butane was kindly sent by the Asiatic Petroleum Company, and introduced in much the same way as the hydrogen. It knocked very much less than Shell petrol. Butane gave very little " peroxides " or aldehydes. A slight peak occurred in the " peroxide " curve and the " peroxides " did not disappear in the expansion stroke.

Methane—A cylinder of methane was obtained from the Insole Colliery Company. The methane, introduced in the same manner as for butane, was found not to " knock." Very little aldehyde was obtained. The " peroxides " gradually increased during the expansion stroke, in the same way as they do in the test with hydrogen, though they were produced in much less quantity.

Amylene (B. Pt. 39°)—As an example of an " unsaturated " hydrocarbon amylene was tested.

A little " peroxide " was obtained, but no peak was observed ; the amount was never large. The amylene did not " knock."

Benzene (A.R.)—A curve for pure benzene has been included ; it was found that the Pratt's pure benzole used in the previous tests gave entirely different results from thiophene-free benzene. The " peroxide " concentration increased throughout the stroke in the latter case.

The time of coloration of the aldehyde and " peroxide droplets " (Schiff and KI reagent respectively) for all these fuels has been converted to mol fraction concentration by calibration curves similar to figs. 9 and 16, and these have then been plotted on a single diagram, fig. 15. (The calibration curve used for KI is one based on NO_2 concentrations, but the character of the curves would have been little altered if it had been based on the H_2O_2 calibration curve used in Part I.) The " peroxide " curves show certain curious features ; the peak noticed for Shell petrol is very marked for the paraffin-like knocking fuels, but still more so for cyclohexane. Hydrogen and pure benzene, on the other hand, gave an increase throughout the expansion stroke. There is a tendency for a slight peak to show itself with butane, and perhaps methane. The rise in " peroxide " concentration begins considerably before the flame was observed to arrive at the valve, whether as

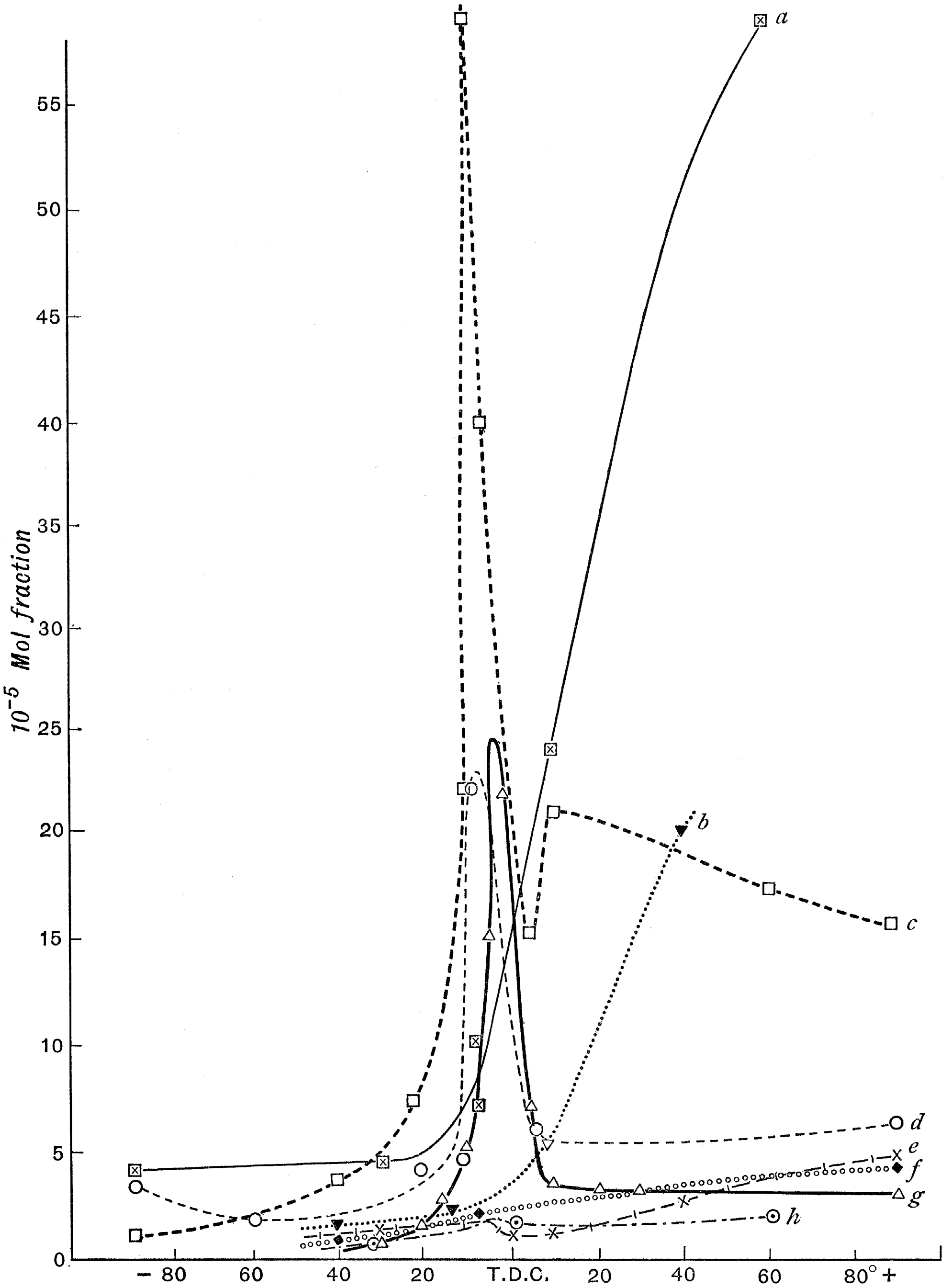


FIG. 15—NO_2 concentration estimated by KI "droplet" at various engine settings on different fuels. (*a*) Hydrogen; (*b*) benzene; (*c*) cyclohexane; (*d*) heptane; (*e*) methane; (*f*) amylene; (*g*) hexane; (*h*) butane

found by means of the stroboscope, or as measured by the analysis of the sample gases, or as indicated by the position of maximum aldehyde concentration.

Table V briefly summarizes the above observations.

TABLE V

Fuel	Notes.
Aldehydes + Petrol	Mixtures $>$ 20% by volume " knock ".
" Peroxides " + Petrol	Strongly " pro-knock ".
Butyl alcohol	Aldehydes decrease before t.d.c.
Ethyl alcohol	
Hydrogen	" Peroxide " formed, increasing throughout stroke.
Cyclohexane	" Peroxides " formed, peak.
Hexane	" " "
Heptane	" " "
Butane	" " in smaller quantity
Methane	" " " "
Amylene	Only small quantity of " peroxide " detected.
Benzene (pure)	" Peroxide " formed increasing throughout stroke.

The difference in behaviour of these various fuels, and particularly the complete absence of "peroxide" in the expansion stroke with Shell petrol, in distinction to the pure paraffin hydrocarbons, needed further investigation.

3—INTERPRETATION OF THE BEHAVIOUR OF THE " PEROXIDE " AS SHOWN BY THE " DROPLETS "

(*a*)—*Engine Experiments with Lead Reagent*

In the course of an investigation on methods of testing for various peroxides (see Part III), a reagent containing colloidal lead hydroxide was found which gives a brown colour with peroxides. The test was intensified by adding solutions of tetrabase and acidifying. After passing the sample gases for 10 mins. through water, the latter was tested with this reagent. Using petrol and cyclohexane, it was found that the blue colour was developed when sampling within the " peak " region of the peroxide curve only. With cyclohexane at t.d.c. $-$ 7° throttle 9, the aquamarine colour appeared almost immediately.

Nitrogen peroxide gives rise to a green colour with the reagent which only slowly develops, and when very dilute is almost the same aquamarine blue-green colour as obtained in the above tests. The blue given by hydrogen peroxide develops at once, and then fades, and the test is considerably more sensitive towards hydrogen peroxide than towards nitrogen peroxide.

Tests were carried out at various settings of the valve; with Shell petrol, coloration was only obtained round about t.d.c. Although the stability of the green colour appeared to indicate that it was definitely due to NO_2, the presence of other " peroxides " was not entirely ruled out by this test.

(*b*)—*Engine Experiments with Titanous Reagent*

Using cyclohexane (throttle 9) and sampling at t.d.c. — 8°, the gases were bubbled through 3 cc of titanous reagent for 23 mins, but no trace of yellow was observed. A visible colour would have been given by about 5×10^{-7} moles H_2O_2, so that the concentration of H_2O_2 in the sample gas must have been less than about 10^{-7} mol fraction ; but 50×10^{-5} was indicated by the KI " droplet " time. Similarly no coloration was obtained with titanous reagent used as a " droplet," the limit for which was found by a direct determination to be about 10^{-5} mol fraction H_2O_2. Other negative tests were obtained by allowing spray from the valve to collect in a tube, and then adding a drop of titanous reagent.

A test was carried out using hydrogen as fuel at t.d.c. + 60°, and it appeared that not more than 1/100th of the coloration of the KI " droplet " was due to H_2O_2.

The time of coloration of a titanous chloride " droplet " was directly ascertained in the same manner as for the KI " droplet " in different H_2O_2 vapour concentrations. NO_2 in weak concentration (10^{-3} mol fraction) does not affect the rate of coloration of $TiCl_2$ by H_2O_2 vapour; in strong concentration (about 10^{-1}) it prevents the coloration.

Although these tests again indicated that no " peroxide " other than nitrogen peroxide was present, it has to be remembered that the titanous reagent is very much less sensitive to organic peroxides than to hydrogen peroxide (see p. 491).

(*c*)—*Standardization of " Droplet " Times in Relation to* NO_2 *Concentration*

The failure of the titanous chloride test when the engine was run on hydrogen, made it important to test to what extent the time of colouring of the KI " droplet " could be accounted for by the concentration of NO_2 in the sample gas. The KI and Griess " droplets " were therefore standardized against NO_2 vapour in much the same way as the KI " droplet " had been standardized against H_2O_2 vapour.

The vapourizer containing N_2O_4 was maintained at temperatures in the neighbourhood of — 70° to — 100° C. Dry nitrogen was passed through the vapourizer, then over the " droplet," and then through acid potassium iodide or through a train of vessels containing iced water (air having been previously replaced by nitrogen). The quantity of HNO_2 could be determined colorimetrically using the Griess reagent. The reaction $2NO_2 + H_2O = HNO_3 + HNO_2$ was assumed. The colour was matched against solutions of Rhodamine previously standardized against $NaNO_2$ solution, whose content of HNO_2 was determined with permanganate. Estimates of NO_2 concentration are liable to error owing to incomplete dissolution, and to loss of HNO_2 by decomposition, but various tests showed that under the conditions used not more than one-sixth escaped undetected.

When *acid* KI is used as absorbent a further difficulty is that the equation for the reaction might be written

$$NO_2 + 2HI = NO + I_2 + H_2O \quad \text{2 equivalents I per mol } NO_2 \text{ or}$$

$$\left.\begin{array}{l} 2NO_2 + H_2O = HNO_3 + HNO_2 \\ HNO_2 + HI = H_2O + NO + I \end{array}\right\} \tfrac{1}{2} \text{ equivalent I per mol } NO_2.$$

It was found that aniline sulphate prevents the attack of HI by HNO_2, but not by NO_2, which is evidence for assuming that most of the NO_2 is directly reduced by HI without the intermediary of water. HNO_3 at these dilutions does not attack HI. Further evidence was found for this conclusion. NO_2 contained in a small bulb and crushed under water, and allowed to stand, provides a solution of HNO_2 which agrees excellently with the reaction $2NO_2 + H_2O = HNO_3 + HNO_2$, but a weighed amount of the vapour of NO_2 passed into acid KI solution behaved nearer in accordance with the reaction $NO_2 + 2HI = NO + I_2 + H_2O$.

Assuming, therefore, this reaction for the acid KI absorptions of NO_2 vapour, the results obtained by both methods led to the graph, fig. 16. (It is unnecessary to include the graph obtained for the droplet with Griess reagent.)

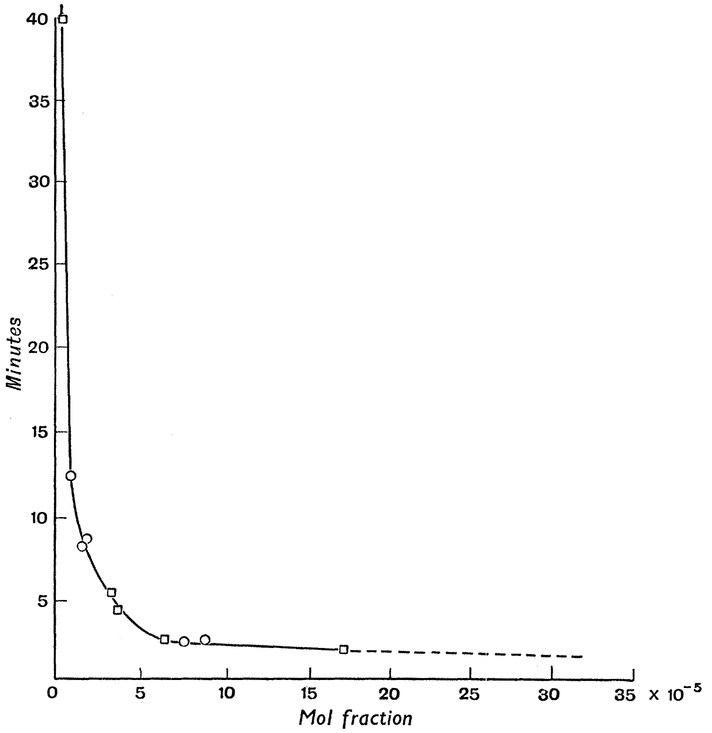


FIG. 16—Standardization KI " droplet " by NO_2 vapour. □ Griess estimations, ○ KI (acid) titrations

(*d*)—*Engine Tests using Direct Absorption and Comparison with " Droplet " Times*

Previous experiments on the direct collection of " peroxides " from the engine gases in acid KI had given results which checked fairly well on the " droplet " calibration curve obtained with H_2O_2 (*see* Part I). On account of the great similarity between the curves for H_2O_2 and NO_2 with a KI " droplet," the results might equally well have been used for checking the NO_2 curve. Further experiments have been made in this way. With hydrogen practically the whole of the NO_2, collected at a certain point in the expansion stroke, could be accounted for as NO_2 acting on the " droplet." It was necessary to find out to what extent this was so with other fuels.

A number of experiments was made and the results are plotted on two curves, *see* figs. 17 and 18, the one gives Griess "droplet" times as determined on the sample gases, against mol fractions as determined by the two methods already described, the other gives KI "droplet" times against concentration, determined similarly.

The points lie fairly well on the standard curve determined as described in the preceding section and drawn in as a full line. However, some of the points are completely off the curve. For instance, with Nos. 10 and 11, fig. 17, the "droplet" times are definitely too long for the amount collected. Both the Griess and the KI "droplets" are inhibited by some product from the engine in the expansion stroke. In other cases only the KI "droplet" appears to be inhibited, and then the first bubbler in which the sample gases are collected yields very little, the second absorbing vessel taking up most of the NO_2. The discrepancies are partly accounted for by lack of oxygen to oxidize the NO in the gases after the passage of flame, partly by the presence of SO_2 which prevents the liberation of iodine till it is washed out, partly by the presence of other inhibitors such as unsaturated compounds, and also perhaps at times by the formation of nitroso compounds which slowly hydrolyse. These matters are referred to in the next section. The points which lie to the right of the curve are explained by such inhibition, those to the left are probably mainly accounted for by the NO_2 being incompletely collected. They might also be accounted for if other "peroxides" were present in small amounts, giving too fast a coloration of KI; but there was no convicing evidence of this at this stage of the investigation (*cf.* Part III).

The concentrations of NO_2 in the gases directly determined by absorption have also been plotted for various engine settings and fuels (*see* fig. 19). There is no evidence of the maxima which are given by the "droplets." The concentrations as determined by the "droplet" in the expansion stroke—and also apparently in the compression stroke—are clearly affected by inhibition.

These experiments have shown that nitrogen peroxide is mainly responsible for the estimates of "peroxide" obtained by the "droplet" method. Nevertheless there remain certain peculiar features, such as the sudden peak in the curves, which have to be explained by various inhibiting influences.

(*e*)—*Influence of Various Substances on Time of Coloration of "Droplets"*

Three possible ways in which NO_2 and "peroxides" might fail to act on KI and Griess "droplets" have been investigated. These are :—

(i) Presence of substances which dissolve from the gaseous phase and then react faster with HNO_2 than either HI or the Griess reagent; or of substances which react with iodine as fast as it is liberated (*e.g.* SO_2).

(ii) Presence of substances in the gas samples which combine with NO_2 and so prevent the liberation of iodine from KI, or the action of the HNO_2 on the Griess reagent.

(iii) Lack of sufficient oxygen to combine with NO from the flame before reaching the droplets or solutions.

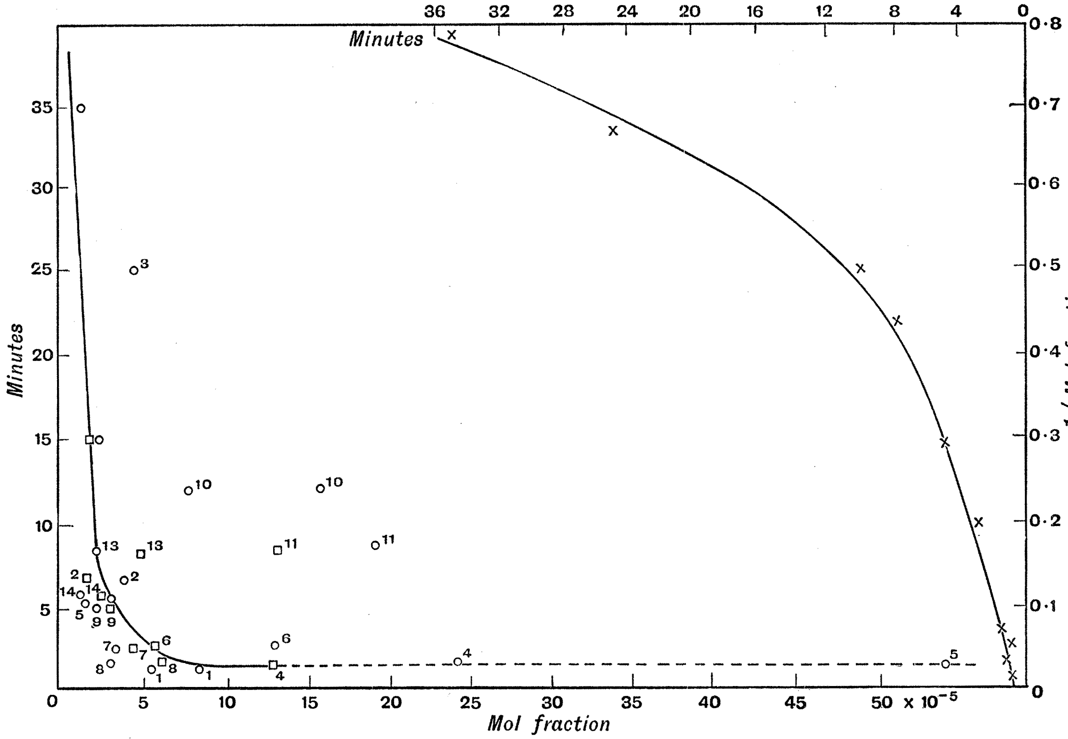


FIG. 17—Engine experiments (Griess "droplet"). □ Griess "droplet," KI titration; ○ Griess "droplet," Griess estimation

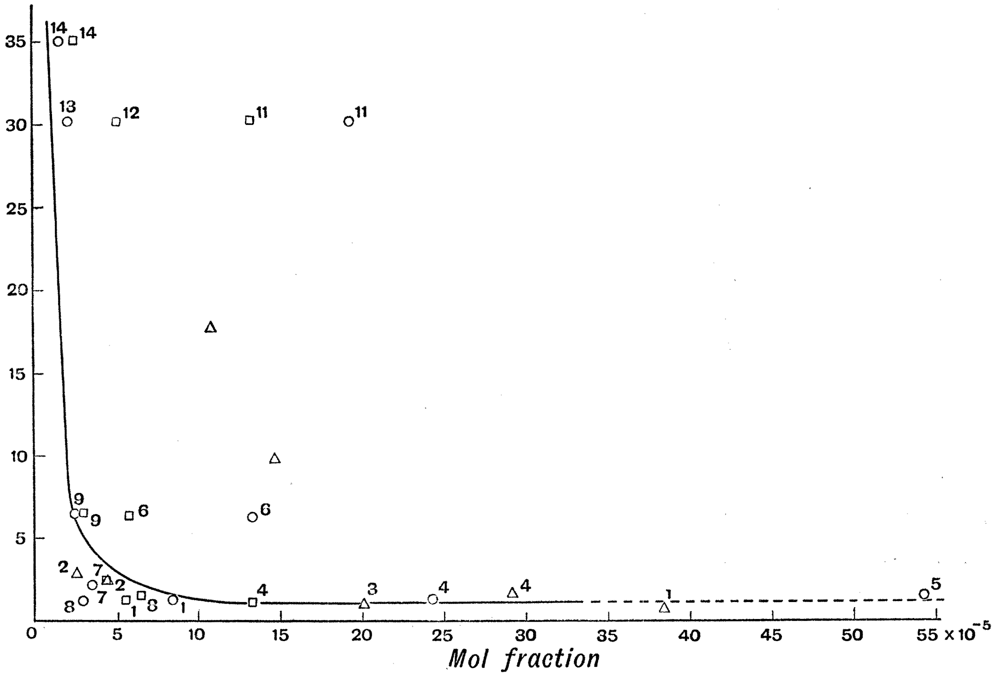


FIG. 18—Engine experiments (KI "droplet"). □ KI "droplets," Griess estimations; ○ KI "droplets," KI titrations; △ KI "droplets," Griess estimations (H_2, etc., as fuel)

(i) *Inhibition of KI and Griess Reagent in Solution*—(*a*) The tests summarized in Table VI were made on substances which might react in solution with nitrous acid, and therefore might compete with the test reagent.

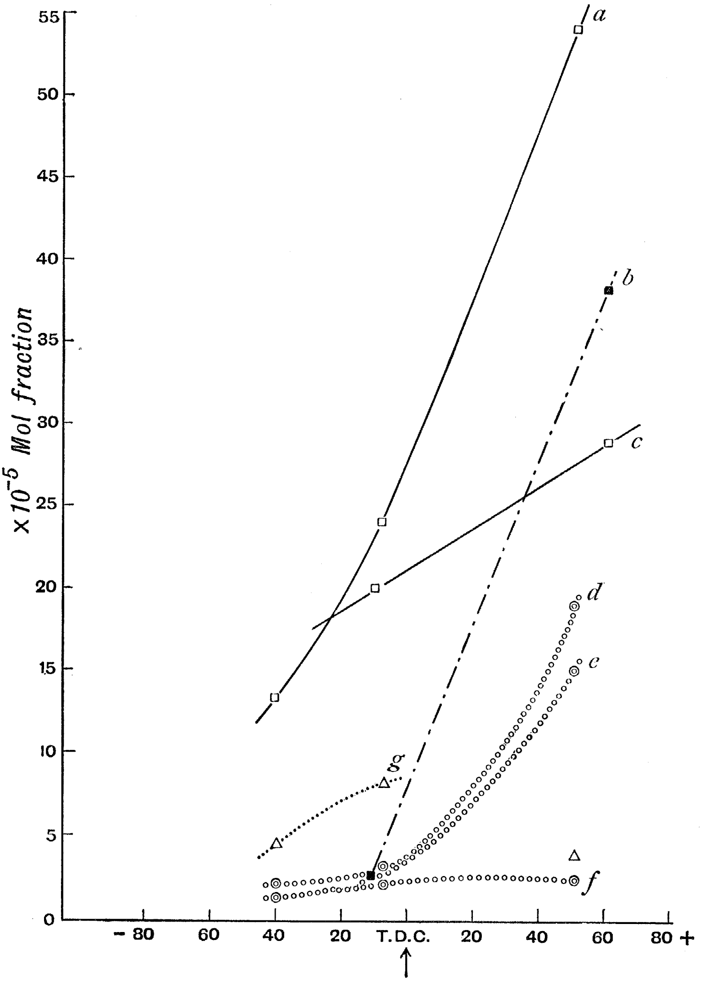


FIG. 19—NO_2 concentration in engine gases at various settings. Estimated by Griess reagent. (*a*) Cyclohexane Th. 10¼ ; (*b*) hydrogen, Th. 9 ; (*c*) cyclohexane, Th. 9 ; (*d*) Shell petrol, Th. 10¼ ; (*e*) Shell petrol, Th. 9 ; (*f*) Shell petrol, Th. 6½ ; (*g*) ethyl petrol, Th. 10¼

TABLE VI

Substances	Concn. %	Effect on [HNO_2 + KI]
Hydroquinone	2	1 cc N/10^4 $NaNO_2$ only 1/5 coloration. 1 cc N/10^5 ,, complete suppression.
Phenol	About ½	No inhibition
Dimethylaniline	1	About same as hydroquinone.
Aniline	1	Inhibition complete with 1 cc N/10^4 $NaNO_2$.
,, ...	0·1	,, ,, ,, 90% N/10^4 $NaNO_2$.
Xylidine	1	,, ,, ,, N/10^4 $NaNO_2$.
,, ...	0·1	,, ,, ,, 90% N/10^4 $NaNO_2$.
α-Naphthylamine	0·1	Slightly more inhibition than with aniline.

Certain other tests were made (*see* Table VII) :—

TABLE VII

Substance	Effect on [H_2O_2 and KI] or [HNO_2 + Griess]
Hydroquinone	Inhibits rate of coloration of Griess reagent partially (about 1/3).
Aniline	No inhibition of Griess reagent.
,, ...	Slows the reaction with H_2O_2, but reaches same final colour.

It is possible, therefore, by addition of aniline to prevent the action of the nitrite ion on HI, without appreciably delaying that of H_2O_2.

The next experiments were carried out with H_2O_2 and NO_2 vapours, since it seemed possible that a KI " droplet " with aniline solution might respond to H_2O_2 only, and not to NO_2, and incidentally afford a direct test for hydroperoxides even in presence of NO_2. This was found impracticable, as the next paragraph shows.

(*b*) Droplets of the following solution:— 8 cc 0·1% of α-naphthylamine, 10 cc H_2O, 4 cc H_2SO_4, 2 cc KI, 1 cc starch, coloured with H_2O_2 in the same time as those made with the normal reagent. The above solution increased the time of colouring with NO_2 from 5 minutes 42 seconds to 8 minutes 21 seconds in a characteristic case, but it was found impossible to prevent the formation of colour in the " droplet " completely, however much α-naphthylamine was added. Similar results were obtained with aniline sulphate, while with hydroquinone the rate of coloration was if anything quicker than in its absence. At first this was ascribed to absence of mixing in the " droplet," since this would lead to local concentration of NO_2 much higher than in the tests already described, and thus make complete inhibition impossible. Experiments were therefore tried in which the stream of nitrogen containing NO_2 was bubbled through a solution containing 10cc 5% KI, 10 cc 6% aniline sulphate, 10 cc water, 10 cc 2N . H_2SO_4 ; " droplets " containing this solution coloured only a little slower than pure KI reagent, and when NO_2 was bubbled through the solution, the apparent concentration only changed from $7 \cdot 2 \times 10^{-5}$ to $6 \cdot 6 \times 10^{-5}$ (mol fraction) in one case, and from $1 \cdot 9$ to $1 \cdot 0 \times 10^{-5}$ in another. The incomplete inhibition under these conditions, when the liquid was kept stirred and the concentration of dissolved NO_2 at any moment was far less than concentrations of HNO_2 for which complete inhibition had been observed in the former test tube experiments, showed that nitrous acid could not be the main product acting on the HI. This is one piece of evidence for considering the reaction $NO_2 + 2HI = NO + H_2O + I_2$ may under certain circumstances take place directly without previous hydrolysis to HNO_2. This hydrolysis is known to be slow, and the degree of inhibition of NO_2 with the solution used, shows that it does not account for more than 10% of the NO_2 at concentrations of 7×10^{-5} or 45% at 2×10^{-5} ; at higher concentrations, such as are found in the gas samples from the engine, the hydrolysis is probably quite negligible. It does not therefore seem to be practicable to use such inhibitors to distinguish between NO_2 and H_2O_2 in the vapour state.

(ii) *Effect of Gaseous Inhibitors on* KI " *Droplet*"—Table VIII records the inhibiting effect of various vapours on the rate of coloration of the " droplets " ; they were mixed in with the stream of nitrogen containing NO_2. A sketch of the apparatus will make clear the method used, *see* fig. 20. The nitrogen flow was adjusted so that on changing from inhibitor to pure nitrogen the same dilution of NO_2 vapour was obtained.

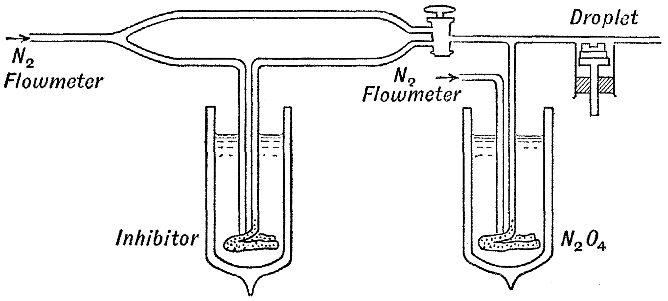


FIG 20

TABLE VIII

Substance	Concentration	Increase in " droplet " times	
		KI	Griess
Petrol	2%	No effect	About 30%
Acetaldehyde	0·64	Complete inhibition	—
,, ...	10^{-2}	About 25%	—
Formaldehyde	10^{-2}	No effect	—
Furfuraldehyde	—	,,	—
Benzene	$5 \cdot 10^{-2}$	,,	—
Ethylene	30%	,,	—
Amylene*	Approx. 5%	About 400%	—

* The inhibition shown with amylene was apparently not due to removal of iodine from aqueous solution, which only takes place slowly.

The conclusion from this work is that unsaturated hydrocarbons are the only likely inhibitors of this list affecting KI "droplets" in the engine experiments, at any probable concentration.

The results summarized in Table VIII made the problem of the absence of NO_2, noted with Pratt's " pure benzole " as fuel, more insistent. Trials with A.R. thiophene-free benzene were made (as mentioned on p. 467) and gave entirely different results from those previously obtained with Pratt's " pure benzole."

Tests for traces of sulphur compounds were therefore made on Shell petrol, and " Pratt's benzole," and showed that the latter contained comparatively large amounts ; samples of gas collected in water in the expansion stroke gave definite tests for SO_2 with acid $BaCl_2$ after oxidation with iodine. The concentration of SO_2 was of the order 5×10^{-3} (mol fraction), which is sufficient to account for inhibition of the droplet. For Shell petrol similar tests showed that although SO_2 was present in the expansion gases, it did not exceed 5×10^{-4}, and probably could only account for part of the observed inhibition, and the same seemed to apply to cyclohexane.

The unsaturated hydrocarbons (homologues of ethylene, and cyclohexane) may account for inhibition of the "droplets" at settings before the arrival of flame at the valve. The slight fall in concentration which sometimes was noted to occur at — 7° was quite possibly due to the formation of phenols before the arrival of flame, which then combine with some of the NO_2, since this fall was observed even for pure A.R. benzene.

The result of these tests is that the inhibition of the coloration of the KI "droplet" can be mainly accounted for by the presence of SO_2, though unsaturated substances may play a minor role.

(iii) *Other Influences*—In the earlier work mention was made of the apparent loss of "peroxides" as the distance of the "droplet" chamber from the valve was increased. The repetition of the experiments with the careful cleaning of the chromium-plated valve at frequent intervals, gave results which are given in Table IX.

TABLE IX

	Distance from valve							
Conditions	5·5 cm		12·5 cm		20 cm		35 cm	
	KI	Griess	KI	Griess	KI	Griess	KI	Griess
Shell petrol — 9° throttle 9	2′ 53″	2′ 58″	5′ 7″	3′ 25″	6′ 17″	3′ 6″	6′ 32″ 6′ 52″*	—
Ditto — 50° throttle 9	Nil	2′ 35″	—	—	—	—	Nil	3′ 24″
— 50° (5 cc water in bubbler before "droplet" chamber)	6′ 0″	6′ 5″	—	—	—	—	—	—
Cyclohexane — 7° throttle 10¼	1′ 34″	—	—	—	—	—	2′ 0″	—
Shell petrol (similar conditions)	1′ 44″	—	—	—	—	—	2′ 31″	—
Cyclohexane—50° throttle 10¼	1′ 4″	—	—	—	—	—	1′ 35″	—
Ditto after bubbler (similar conditions)	1′ 46″	—	—	—	—	—	—	—

* With glass wool plug.

The conclusions drawn from these experiments were as follows:—

(1) The increase in time of coloration of the KI "droplet" as the length of the tube was increased was partly due to the removal of spray of liquid, but the experiments with glass wool show that this removal was nearly complete at 35 cm distance.

The Griess "droplet," however, showed much less decrease than the KI "droplet". The apparent concentration after the spray had condensed was about four times that determined by the KI "droplet." This was due to the presence of SO_2 which would have affected the KI and not the Griess tests. (The fact that the spray affected the KI more than the Griess, seemed to suggest that other oxidizing agents were present besides NO_2.)

(2) The effect of washing the gases at t.d.c. + 50° was to give the same apparent concentration for both types of " droplet," so that this process removed the inhibitors.

(3) The results with cyclohexane (which appeared to be fairly free from sulphur) showed that a certain amount of oxidizing spray was present at $-7°$, and that washing at $+50°$ merely removed NO_2.

(4) From certain other experiments the use of petrol to which aldehydes had been added appeared to contaminate the valve and delay future tests. This effect on subsequent tests was also particularly marked when using Pratt's benzole, and is probably to be ascribed to the accumulation of products containing SO_2, etc., which may have been condensed in small traces in the valve.

The gas samples from the expansion stroke after passage of flame do not contain more than a small quantity (1 or 2%) of residual oxygen and therefore NO formed in the flame, or NO_2 dissociated by the flame, might not have formed NO_2 when it reached the reagents. The effect of the addition of small amounts of oxygen to the sample gas at the valve was therefore tested, and the results are recorded in Table X.

Table X

Conditions	Composition of gases	" Droplet " times and concentration	
		KI	Griess
Shell petrol— + 50° throttle 9	100% residuals	20′ (6.10^{-6})	4′ 57″ (49.10^{-6})
	15% O_2 85% residuals	2′ 25″ (150.10^{-6})	3′ 28″ (96.10^{-6})
	43% O_2 57% residuals	11′ 22″ (12.10^{-6})	—

The main effect here, as shown by the Griess " droplet," was roughly to double the apparent concentration of NO_2 : the effect on the KI " droplet " was more complex owing either to autoxidation by NO, or to some other oxidizing agent.

This deficit of oxygen partly accounts for the low results obtained in the expansion stroke, and the " peak " in the curve of NO_2 concentration in the engine gases as determined by the " droplet." But that it was not the only effect, or even the major effect, was shown by the experiments in which the engine gases were directly absorbed and determined by Griess reagent. The presence of the SO_2 (which in the latter experiments was washed out) was no doubt mainly responsible for the sharpness of the peak.

The experiments which have been described in this section have therefore cleared up most of the difficulties in interpreting the results obtained by the method adopted for finding the " peroxide " concentration.

4—SOURCE OF THE NITROGEN PEROXIDE

Addition of NO_2 *to Fuels*

It is well known that nitro compounds, organic nitrites and nitrates act as " proknocks." It was therefore of interest to determine the quantity of NO_2 produced in the cylinder when such compounds are added to the fuel. (*See* Table XI.)

TABLE XI

Fuel (composition by weight)	Effect on speed revs	Effect on " knock "	Effective NO_2 by weight	Effective mol fraction in cylinder
Amyl nitrite in petrol 0·5% . .	— 20	C.M.D. to V.C.D. . .	0·2	8.10^{-5}
Liquid NO_2 in petrol 0·44% . .	— 10	Very slight increase in " knock " only . . .	0·72	29.10^{-5}
Amyl nitrite in cyclohexane 0·2%	(— 5)	No audible " knock " .	0·09	$3{\cdot}6.10^{-5}$
Amyl nitrite in ethyl petrol 0·5% .	— 5	No " knock "	0·2	8.10^{-5}
Amyl nitrite in benzene 0·25% .	0	No " knock "	0·1	4.10^{-5}
Aniline in petrol 1·7%	— 5	" Knock " decreased .	—	—

The engine was run on these fuels with the throttle set at 9, and speed 600 revs. : tests were made at various positions for quantity of NO_2 using the KI " droplet " and the Griess " droplet." The valve was washed out with alcohol between each series of tests and between the tests carried out before and after t.d.c., and checked back on the " droplet " time for Shell at t.d.c. — 7°. The results are presented in a series of curves, fig. 21. In all tests there was a pronounced drop in apparent concentration at t.d.c. due mainly to lack of oxygen.

It was surprising to find that the quantity of NO_2 in the gases at the maximum in the curve was larger than the amount with which the fuel was charged. The concentrations of NO_2 estimated to be present in the cylinder at the commencement of the stroke are given in column 5 of Table XI, and are in good agreement with the initial points on the curves (*see* arrows, fig. 21). The maximum is usually about 60×10^{-5}, which is about ten times the amount added, and the shape of the curve shows that a considerable increase is already taking place before the spark. Since the estimate of concentration had to be made from a steep portion of the standardization curve, the effects may be somewhat enhanced thereby, but the results are comparative, and give the order of the effect.

This unusually large concentration was probably either due to production of NO_2 during the compression stroke by catalysis, or to the escape of the fuel as fine spray towards the end of the stroke, but the latter possibility was unlikely, for the difference was too large to be accounted for by a recondensation of part of the fuel : furthermore accumulation beyond the valve entry was excluded because successive experiments at — 7° and + 10° showed no trace of residues. On the other hand, tests repeated on petrol at the same setting (t.d.c. — 7°), after washing the sample valve with alcohol, showed that the inside of the cylinder retained its activity in promoting the formation of NO_2.

Amyl nitrite at the concentration used, showed a marked increase in audible " knock " as compared with the ordinary petrol, whereas the fuel charged with three and a half times as much NO_2 (by weight of effective NO_2) showed much less increase. The quantity of NO_2 in the gas sampled in the two cases, however, did not show any marked difference. The knock was not therefore mainly influenced by the NO_2 present in the gases. This was further borne out by the addition of amyl nitrite to the other fuels—(*a*) petrol + ethyl fluid, and (*b*) cyclohexane. In these mixtures, the " knock " was practically non-existent, but the NO_2 production was considerable. The effect of aniline on the petrol reduces the " knock," but had little influence on the NO_2 concentration. This is significant, because the " anti-knock "

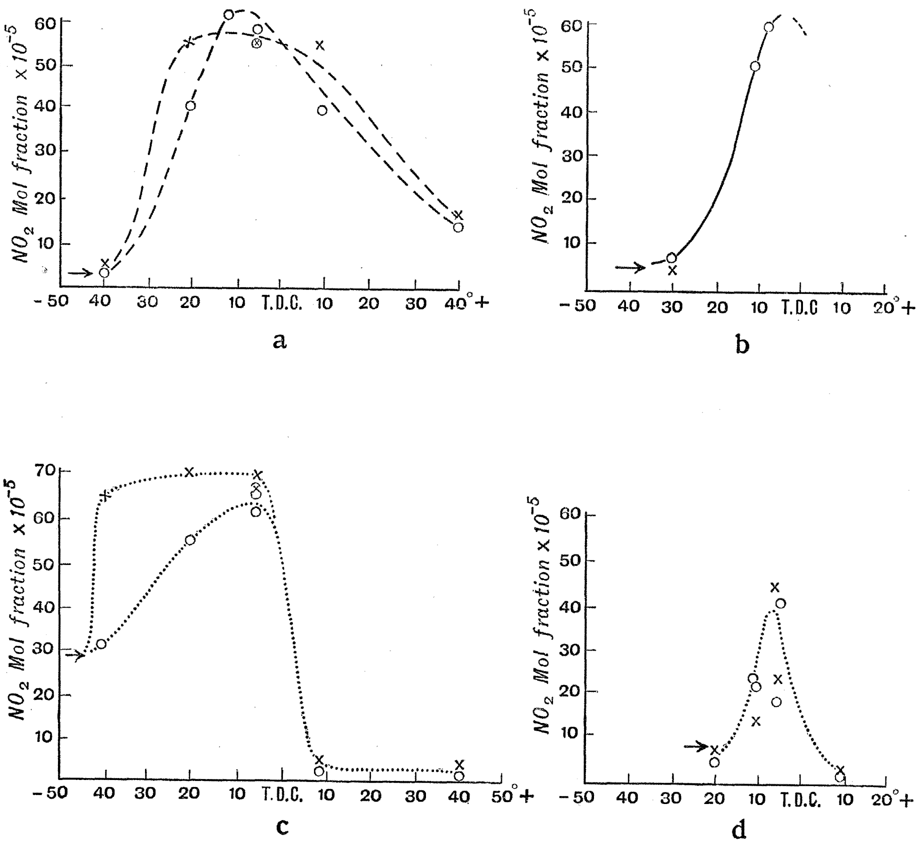


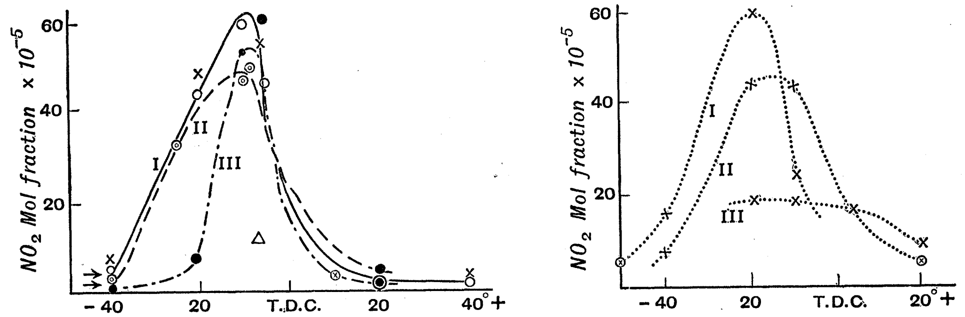
FIG. 21—(*a*) Cyclohexane and amyl nitrite ; (*b*) benzene and amyl nitrate ($\frac{1}{4}$%) ; (*c*) petrol and NO_2 ($\frac{1}{2}$%) ; (*d*) ethyl petrol and amyl nitrite ($\frac{1}{2}$%) ; O KI, × Griess

effect of such organic substances cannot depend on their removal of NO_2, as might have been suggested.

Pure NO_2 was next allowed to enter with the inlet gases by vaporization, and in small quantities it had little effect, larger quantities actually reduced the " knock," and increased the speed.

All these observations tend to show that the " pro-knock " effect of organic nitrites is not directly due to the NO_2 formed from them.

In order to probe matters further, a series of experiments was carried out to test whether catalytic formation of NO_2 or reformation of fuel drops rich in NO_2 would account for the early increase observed. By varying the amount of nitrite from $\frac{1}{2}$% to $\frac{1}{8}$%, as shown on the curves in fig. 22 (*a*), it became clear that the height of the maximum was independent of the amount of nitrite added, and therefore was not likely to be due to condensation. In view of this, the main cause of formation of NO_2 seemed to be catalysis at the hot exhaust valve. The temperature corresponding with the peak concentration of NO_2 would be about 1000° C, using the equilibria data of Nernst and Jellinek, and of others.* The temperature corresponding with a concentration of 5×10^{-5} would be 730° C. These NO_2 concentrations were in accord with *possible* surface temperatures of the exhaust valve, though perhaps they were somewhat high at the maximum concentration, particularly as the engine was not run at high speed under full load.



a b

Fig. 22—(*a*) I, petrol and amyl nitrite ($\frac{1}{2}$%) ; II, petrol and amyl nitrite ($\frac{1}{4}$%) ; III, petrol and amyl nitrite ($\frac{1}{8}$%). (*b*) I, petrol and acetyl peroxide ; II, petrol alone (after I) ; III, petrol and amyl nitrite (0·05%)—after fast running ; ○ KI; × Griess

There is some further evidence that NO_2 formation is, at least in part, dependent on the state of the surface of the exhaust valve. For instance, if the engine had been knocking for some time using (say) amyl nitrite, and tests of NO_2 were then made for ordinary petrol, the results showed an increase, whereas if " benzole " (which contains sulphur) was used before making a test on the petrol, the results were definitely lower than the average, as if the valve surface had been poisoned. By

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* *Cf.* Mellor, " Inorganic Chemistry," vol. 8, p. 369.

alternate use of amyl nitrite and benzole the amount of NO_2 given by petrol varied, as the "droplet" times given in Table XII, column 2, show.

TABLE XII

− 7° throttle 9	
Amyl nitrite + Petrol 2′	Moderate knocking
Petrol	1′ 58″
"Benzole," 5′	—
Petrol	2′ 34″
Amyl nitrite + Petrol	Violent knocking
Petrol	1′ 55″
"Benzole," 3½′	—
Petrol	3′ 0″

The tests were made shortly after the respective treatments, keeping the sample valve setting unchanged at − 7°, and taking precautions to wash out any trace of the previous fuel from the valve and carburettor before making tests.

By using fuel containing acetyl peroxide in petrol ($6 \cdot 2 \times 10^{-6}$ mol per cc) the results were similar to those obtained with amyl nitrite, but an increase in NO_2 concentration at a remarkably early stage was noticed, well before the spark.

Table XIII gives the "droplet" times.

TABLE XIII—ACETYL PEROXIDE + SHELL

t.d.c.	Griess—"droplet" time	Concentration
− 60°	—	Nil
− 50°	3′ 39″	42.10^{-6}
− 40°	1′ 36″	15.10^{-5}
− 20°	1′ 0″	60.10^{-5}
− 10°	1′ 24″	25.10^{-5}

This effect was confirmed in a later test and appeared to depend on the amount of "peroxide" present in the aldehydic petrol solution.

The use of this fuel seems to have left the surface in a highly activated condition, as results on ordinary petrol, determined immediately afterwards, demonstrated (*see* curve, fig. 22 (*b*)). On the other hand, by running the engine fast for some time, the consumption of lubricating oil increased, and the surface of the exhaust valve was apparently poisoned, as much lower NO_2 concentrations were subsequently obtained.

The experiments recorded above, suggest that the NO_2 formation occurs mainly at hot surfaces in the cylinder by heterogeneous catalysis.

With the engine running on hydrogen as fuel, and under such load that it was just not knocking, it was found that nitrogen peroxide introduced with the intake air produced a definite and sharp "knock." This was particularly interesting as with hydrocarbon fuels (butane, petrol and heptane) NO_2 introduced in identically the same way had a definite " anti-knock " effect and the speed increased. Furthermore, amyl nitrite had little effect and diethyl peroxide (30% solution) no effect in producing increase in detonation when running on hydrogen as fuel ; though with butane, under similar circumstances, amyl nitrite had a pronounced effect in causing " knock " to occur. It thus seems probable that knocking with hydrogen is induced by the nitrogen peroxide formed in its combustion in the cylinder, but this is not so for hydrocarbon fuels. (Tests were made which showed that the NO_2 had not been removed by combination with the fuel.)

When air was passed over shavings from the " Silchrome " exhaust valves, heated in a small silica tube to temperatures up to 950° C, no appreciable formation of NO_2 was noted (Griess test), not even in presence of acetyl peroxide. In these circumstances the oxidized metal does not seem to act as an efficient catalyst, for the equilibrium concentration of NO_2 should have given a very definite test at a temperature of 700° C. If a small proportion of coal gas is added to the air there is slight production of NO; while inspection of the metal shows that in the absence of the coal gas, the shavings are rapidly oxidized and become quite inactive. To follow the point further, investigation would be necessary at higher pressures ; from the work of other investigators (*e.g.* HÄUSSER,* BONE†) the amount of NO_2 formed at higher pressures is known to be influenced by the other oxidation reactions which are taking place.

5—DISCUSSION of §§ 3 and 4.

The " peroxides " in the engine gases determined by the " droplet " method, and recorded on the curves in this and the former paper, are shown to be mainly nitrogen peroxide. The pronounced maxima which characterize those curves are found to be due to two effects, (*a*) the presence of small quantities of sulphur compounds which give SO_2 and prevent the liberation of iodine in the " droplet," and (*b*) the lack of oxygen in the burnt gases to combine with NO formed or NO_2 dissociated by the flame. A third reason for obtaining lower concentrations of NO_2 than are actually present is its removal by unsaturated vapours, but this effect is less pronounced.

The nitrogen peroxide commences to increase in concentration quite early in the stroke before t.d.c., and therefore apparently when the mean temperature is quite low. Surface reaction at the hot exhaust valves is a possible source of this "peroxide," but other reactants influence its formation and it is not purely a matter of the catalysis of the $N_2 + O_2 = 2NO$ reaction at the surface of the valve. If the NO_2 is formed in the flame, and comes from regions already burnt and mixed up by turbulence, then it is not easy to explain the fact that some fuels behave so differently from others. Furthermore, if the NO_2 is formed in the small flamelets seen through

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* 'J. Soc. Chem. Ind.,' vol. 41, p. 253 R (1922).

† 'Proc. Roy. Soc.,' A, vol. 105, p. 426 (1924 *et seq.*), *see also* 'Proc. Roy. Soc.,' A, vol. 139, p. 74 (1933).

the quartz window as flashes during the dark period, prior to passage of the flame, the increase in NO_2 concentration should bear some relation to the ratio of the CO_2 concentration at the same stage to final CO_2 concentration, but the CO_2 concentration at the earlier stage seems too small. In some experiments the increase in the nitrogen peroxide concentration actually occurred before the spark had passed, so that it could hardly have been caused by flame. Further investigations will be needed to settle definitely the source of the nitrogen peroxide ; for it is possible that the proportion of NO in the exhaust gas is considerable, and that during the compression stroke the residual NO becomes converted to NO_2, the detection of which, if SO_2 is also present, may sometimes be interfered with. The quantity of NO_2 should then be dependent mainly on the temperature of the flame during the explosion.

Whatever the source of the NO_2, there is very little evidence that it has more than a secondary effect on the phenomenon of " knock " except with hydrogen. Although organic nitrites, etc., are "pro-knocks," NO_2 itself is not an active "pro-knock" of hydrocarbon fuels in the engine. Furthermore, some substances, such as cyclohexane, which give rise to large amounts of NO_2, do not readily knock. The fact that the amount of nitrogen peroxide formed increases with the intensity of " knock," however, indicates that the same causes which produce the nitrogen peroxide also produce the conditions necessary for "knock" to occur. There is, in fact, evidence that the two processes are very closely interconnected, for the addition of acetyl peroxide induces NO_2 formation at a very early stage in the stroke. If the NO_2 is formed by catalysis at the surface of the valves, the experiments suggest that the amount also depends on active products from other reactions which are taking place there, and particularly those reactions connected with formation and decomposition of those substances present when " knock " occurs.

6—ESTIMATION OF ALDEHYDES

During the tests described in § 1, the concentrations of aldehydes were also determined in most cases. The results are expressed in figs. 13 and 14. The figures for the concentration of aldehyde were taken from the previous calibration curves.

It will be noted that cyclohexane and hexane give similar results to the former ones with Shell petrol cited in Part I, and that butane also gives a similar type of curve, though with a smaller maximum. The formaldehyde from methane shows still less of a peak. These facts may possibly indicate that, at the peak, higher aldehydes are present which are rapidly burnt, and only the formaldehyde survives. Experiments to test this hypothesis are quoted below, but it has been difficult to reach a final decision.

There is the evidence from absorption spectra that in the combustion of a hydrocarbon* the higher aldehydes, whether they are formed immediately or not, are not

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* EGERTON and PIDGEON, ' Proc. Roy. Soc.,' A, vol. 142, p. 26 (1933).

present in the products to any considerable extent ; and where there is formaldehyde, it is generally present in much larger amount than any other aldehyde. Two methods have been employed to distinguish between formaldehyde and total aldehyde :

(1) Direct volumetric estimate of total aldehyde by the bisulphite method, and of formaldehyde by the potassium cyanide and silver nitrate method.

(2) Comparison of coloration given by a standard amount of the liquor with ordinary Schiff reagent and with Schiff reagent diluted with an equal volume of 10% H_2SO.* The sulphuric acid slows down the reaction of formaldehyde, but suppresses that of the higher aldehydes almost completely. The results obtained are given in Table XIV.

TABLE XIV

	Aldehyde equivalents	
Conditions	Bisulphite method	KCN method
Shell petrol (throttle 9)		
+ 7½°	$4\cdot3.10^{-5}$	$3\cdot7.10^{-5}$
+ 8°	$3\cdot9.10^{-5}$	$3\cdot2.10^{-5}$
t.d.c.	$2\cdot6.10^{-5}$	Small
t.d.c.	$4\cdot6.10^{-5}$	$0\cdot9.10^{-5}$
+ 8°	$1\cdot9.10^{-5}$	Small
+ 8°	$2\cdot0.10^{-5}$	$1\cdot8.10^{-5}$
+ 40°	$0\cdot6.10^{-5}$	$0\cdot8.10^{-5}$

Tests by the second method carried out in the last two cases showed that nearly all the aldehyde was formaldehyde. Comparison of the titres with the " droplet " times showed that the whole of the aldehyde was not collected ; since formaldehyde is more volatile than the higher aldehydes the proportion of the former in the vapour would be greater than the figures in Table XIV suggest.

At the Research Laboratory of General Motors, Ltd.† it has recently been shown by an absorption spectra method that combustion is occurring ahead of the flame in the region of " knock " in the engine cylinder and that formaldehyde is one of the main products formed. The work here described leads to a similar conclusion and provides a measure of the quantity of aldehyde formed. The conclusion that formaldehyde is only formed in knocking explosions, however, is not in agreement with the conclusions of this work, though the quantity is certainly greater under those conditions. Indeed, some of the experiments quoted (p. 1365) appear to show that formaldehyde is detectable when no appreciable " knock " occurs. EGERTON and PIDGEON (*loc. cit.*) have shown that the spectroscopic method would fail to detect

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* *Cf.* BONE, ' Proc. Roy. Soc.,' A, vol. 143, p. 16 (1933).

† RASSWEILER and WITHROW, ' J. Ind. Eng. Chem.,' vol. 25, pp. 923, 1359 (1933).

quantities of formaldehyde formed by the combustion of hydrocarbons below a certain minimum concentration. The conclusion that the presence of the formaldehyde does not give rise to " knock " is in agreement with the present work, as is also the statement that " the greater concentration of materials which absorb light below 2900 A is present before the arrival of the flames and that they disappear very rapidly in the flame fronts."

The remark that with alcohol fuel the " bands do not appear even at the time of inflammation, although in their slow oxidation alcohols pass through an aldehyde stage," is also in agreement with the quantitative measurements quoted earlier in this paper. Organic peroxides give rise to a continuous absorption in the ultra-violet, but the quantity formed would probably be too small to detect readily by the spectroscopic method. It is probable, however, that the band near 2600 found by EGERTON and PIDGEON to be present in the spectra of burning hydrocarbons* would be detectable as well as the bands of nitrogen peroxide. The precise origin of the former is at present under investigation.

7—ESTIMATION OF ACIDS

Tests have been made to find out how much acid is obtained in the gases sampled from the engine cylinder. There are difficulties, mainly because of the small quantity in comparison with the large quantity of carbonic acid. The procedure adopted was to boil a small quantity of the solution through which the gases had been bubbled for 1 to 2 minutes and to titrate into the hot liquor from a microburette using phenolphthalein ; the CO_2 could be rapidly removed by this method and the loss of volatile organic acid was found by blank tests to be about 15%. The quantity of acid obtained was very small ; for instance, using Shell petrol at throttle 9 and t.d.c. $+ 7°$ . . . mol fraction 2×10^{-4} and 5×10^{-5}, while at $+ 90°$ 3×10^{-5}. Bromphenol blue (p_H 3·0 to 3·6) and bromcresol green (p_H 3·8 to 5·4) gave similar results. A droplet of bromphenol blue gradually changed to a pale watery blue and since it was not affected by carbonic acid, stronger acids were evidently present —*e.g.* nitric, sulphurous, and formic acids.

Although the pitting of the valve stem before it was plated must be due to these acids, the amounts found were always of the same order as the " peroxide " concentration and never equal to the aldehyde concentration which was about 100 times greater.

The main conclusion is that, in the engine, aldehydes formed in the combustion of hydrocarbons do not appear to oxidize in such a way that organic acids remain as stable end products. It might be of interest to carry out tests on other fuels such as alcohols, as these experiments and those on the NO_2 production have a bearing on the question of cylinder wear.

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* This band is visible only when the hydrocarbon has four or more carbon atoms.

PART III—ORGANIC PEROXIDES

By A. R. UBBELOHDE *and* A. EGERTON, *F.R.S.*

1—INTRODUCTION

Apart from general theories of hydrocarbon combustion and in spite of the main conclusion of Part II as to the nature of the " peroxides," certain experimental facts indicated that organic peroxides might still have an important connection with the phenomenon of " knock."

These indications were that :—(1) organic peroxides were found to be pronounced " pro-knock " substances ; (2) metallic anti-knocks markedly inhibited their effect ; (3) the detonation of hydrogen was not prevented by metallic anti-knocks ; (4) the effect on the KI " droplet " was not always accounted for entirely by the NO_2, particularly in the neighbourhood of the top dead centre ; (5) metallic anti-knocks inhibit the ignition of hydrocarbon mixtures, and particularly seem to counteract the effect of pressure, which should favour the formation of peroxides ; (6) the use of fuels with more than 15 times the maximum aldehyde formed in the cylinder did not enhance the " knock " and alcohols do not knock, so that no main product formed during the course of the reactions postulated by the hydroxylation theory seems to explain it ; (7) cyclohexane and other fuels can be made to knock if the cylinder temperature is raised. The large amount of NO_2 formed with this substance under normal conditions, and other effects, indicate that NO_2 itself has only a secondary influence on " knock " with hydrocarbons.

It seemed worth while, therefore, to pursue the matter further. No progress was possible until fresh knowledge had been gained of the behaviour of various kinds of peroxides towards reagents used to detect them: so the next section deals with the means of detecting hydrogen peroxide and various organic peroxides.

2—TESTS FOR PEROXIDES

Although potassium iodide and starch is a very sensitive reagent for the detection of oxidizing agents, circumspection has to be exercised before a positive or negative test can be taken as indicating the presence or absence of peroxides, for not only can certain oxidizable organic substances act as autoxidants in the presence of starch iodide and air, but also some classes of peroxides do not liberate iodine. A study of the behaviour of potassium iodide towards various peroxides, and the investigation and development of other tests for them, was all the more necessary, as there appears to be some misapprehension regarding the behaviour of the various reagents which have been used for the detection of peroxides.*

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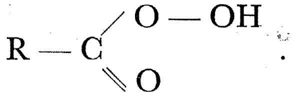
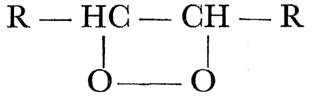
* *E.g.*, BONE and HILL (' Proc. Roy. Soc.,' A, vol. 129, p. 440, 1930) state that they can detect 1 part of " peroxide " in 5×10^5 parts of water, and use a 5% titanic sulphate in 5% sulphuric acid. This reagent would detect H_2O_2 at such concentration, but not $R.O_2R$ or $R.OOH$.

a.—Preparation of Peroxides

The following represent the main *types* of peroxides which might be met with as peroxidized products of hydrocarbons :—

$R-O-O-H$	alkyl hydrogen peroxide.
$R-O-O-R$	dialkyl peroxide.
$CH_2OH-O-O-CH_2OH$	dihydroxy-alkyl peroxide.
$R-O-O-CH_2OH$	monohydroxy-alkyl peroxide.
$R-O-O-CHOH-R$	dialkylmonohydroxy peroxide.
$R-CHOH-O-O-CHOH-R$	dialkyldihydroxy peroxide.
 $R-\overset{\diagup O-OH}{\underset{\diagdown O}{C}}$	acyl peroxide.
 $\begin{array}{l} R-HC-CH-R \\ \quad\ \ \vert \qquad\ \ \vert \\ \quad\ \ O-\!\!-O \end{array}$	alkylidene peroxide.

Of these " peroxides " the following were prepared :—

(*a'*) *Diethyl peroxide* was prepared by Baeyer's method from diethyl sulphate and hydrogen peroxide. It is a fairly stable colourless liquid, boils at 63° at 740 mm, and inflames at a low temperature.

(*b'*) *Monoethyl hydrogen peroxide,* also prepared from diethyl sulphate and hydrogen peroxide, is a liquid with a sharp tang to its ethereal odour. It boils about 92° C (Baeyer 94° C). It is less stable than the diethyl compound, but inflames at a somewhat higher temperature. (The final fraction contained a high percentage of the compound.)

(*c'*) *Hydroxy-methyl-ethyl peroxide* was prepared from ethereal solutions of formaldehyde and ethyl hydrogen peroxide. The fraction boiling between 40° and 70° C at 100 mm pressure contained the hydroxymethylethyl peroxide, but it has not been obtained in the pure state.

(*d'*) *Acetyl peroxide* was prepared by passing oxygen through acetaldehyde in sunlight, and stabilized by the addition of hexane. The resulting solutions contained up to 1% of acetyl peroxide, together with unchanged aldehyde.

(*e'*) *Amylene peroxide* and other peroxides mentioned later were prepared similarly.

Table XV records the results of tests made on solutions of *hydrogen peroxide* freshly made from Merck's perhydrol, with equal volumes (usually 2 cc) of the following reagents :—

1. Potassium iodide (5% KI 2 cc, water 18 cc, 2N . H_2SO 4 cc, 1% starch 1 cc).
2. Titanous chloride—
   (*a*) 1 cc of (1 cc 15% $TiCl_2$, water 8 cc, concd. HCl 2 cc) in 100 cc water.
   (*b*) 1 cc of (*a*) adding 10^{-3} M . H_2O_2 till just not coloured.

3. Potassium ferricyanide solution—
   1 gm iron alum in 50 cc water, and 1 gm $K_3Fe(CN)_6$ in 50 cc water.
4. Lead acetate solution—
   (*a*) Solution of 5 cc lead acetate, water 20 cc, 20% ammonia 5 cc (mixed in this order).
   (*b*) The same with a few drops of " tetrabase " and clarified with glacial acetic acid,*
   (*c*) or of fluorescein + KBr clarified with glacial acetic acid.
5. Thiocyanate solution†—
   5 gm $FeSO_4\ 7H_2O$, 5 gm NH_4CNS, 0·5 cc H_2SO_4 conc. 50 cc acetone, 50 cc water (reduced in presence of iron wire till colourless).

TABLE XV—HYDROGEN PEROXIDE

Mols/cc	1 KI	2 Titanous	3 Ferricyanide	4 Lead Reagent	5 Thiocyanate
10^{-4}	Immediate blue-black	Yellow	Deep green	(*a*) Brown red (*b*) Deep blue (*c*) Deep pink	Deep red
10^{-6}	Blue colour appears in 1 minute	Yellow	Green	(*a*) Yellow brown (*b*) Blue (strong) (*c*) Pink (strong)	Red
10^{-7}	Pale blue in 5 minutes Full blue in 2 hours	(*a*) Just perceptible (*b*) Definitely perceptible	Pale green	(*a*) Just detectable (*b*) Strong blue (*c*) Pale pink	Definite red in 5 minutes
10^{-8}	Very pale blue in 12 minutes Blue in 2 hours	Nil	Green tint just detectable	(*a*) Nil (*b*) Pale blue but evanescent (*c*) Nil	Just detectable in 5 minutes
Blank	Very faint in 2 hours	Nil	Yellowish	Nil	Nil

Only potassium iodide, thiocyanate, ferricyanide, and the lead reagent with tetrabase, detected H_2O_2 at a concentration of 10^{-8} mols per cc ; of these the first two were the more sensitive, but time has to be given for the colour to appear. The lead reagent depends on the production of lead peroxide in colloidal solution, which reacts with the leuco base, giving the sky-blue dye. The ferricyanide test is uncertain, for other substances act similarly, and the colour change, yellow to green, is indefinite.

A similar set of tests has been made for diethyl peroxide.

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* *Cf.* TRILLAT, 'Ann. Chim. Anal.,' vol. 80, p. 408 (1903) (for use of tetrabase for detection of lead).

† *Cf.* YULE and WILSON, 'J. Ind. Eng. Chem.,' vol. 23, p. 1254 (1931).

It was confirmed that potassium iodide seemed not to react, or only reacted very slowly with diethyl peroxide, but on adding a drop of ferrous sulphate (N/3) the iron acted as catalyst, and the iodine was rapidly liberated. (*See* column 1 (*b*), Table XVI.) Column 6 shows that alkaline methylene blue is not decolorized. The limit of detection of diethyl peroxide with potassium iodide appears to be about 10^{-6} mols per cc, even when ferrous sulphate is present along with the potassium iodide. Apart from this, only the thiocyanate test will detect its presence. If peroxides of this class are formed in small quantities in any process they would be very difficult to detect by the iodide test.

TABLE XVI—DIETHYL PEROXIDE

Mols per cc	1 KI	2 Titanous	3 Ferri-cyanide	4 Lead reagent	5 Thiocyanate	6 Methylene blue
7×10^{-5}	(*a*) Nil . . . (*b*) Blue	Nil . .	Nil . .	(*a*) Yellow on warming (*b*) No blue	Deep red . .	Not bleached
7×10^{-6}	(*a*) Nil . . . (*b*) Blue perceptible in 5 minutes	Nil . .	—	Nil	Red	—
7×10^{-7}	(*a*) Nil . . . (*b*) Nil	Nil . .	—	—	Definite red . .	—
10^{-8}	(*a*) Nil . . .	—	—	—	Just detectable .	—

The results of tests on ethyl hydrogen peroxide are given in Table XVII. Reaction with KI is much slower than H_2O_2,* and below about 10^{-7} mol per cc, even with the addition of ferrous sulphate, the peroxide is not detectable. The titanous reagent only appears to detect high concentrations of peroxide, whereas the tetrabase lead reagent can detect concentrations to 10^{-6} mol per cc. Ammonium molybdate acts more efficiently than ferrous sulphate as a catalyst for the action of this peroxide on potassium iodide, the limit being 10^{-8} (*see* (*c*), Table XVII).

With the hydroxymethylethyl peroxide the titanous reagent gave no coloration. The distinguishing test for hydroxy peroxides—the bleaching of alkaline methylene blue—was successful, showing that the liquid contained a considerable percentage of the substance, for neither formaldehyde, hydrogen peroxide, nor the higher aldehydes alone, were found to bleach the reagent on warming. However, formalin (0·4%), in presence of the ethyl hydrogen peroxide solution, bleached it on warming.

The aldehyde (acyl) peroxides and the ethylidene peroxides also were found to react rapidly with potassium iodide and the lead reagent. It is interesting to note

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* It has been stated that higher alkyl hydrogen peroxides react more rapidly.

that acyl peroxides seem to attack HI even more rapidly than H_2O_2. The results of these tests are summarized in Table XVIII.

Most of the tests require time for the oxidation to occur. The titanous reagent does not appear to be suitable for the detection of small quantities of the organic peroxides. The lead reagent giving the blue tetrabase dye appears to be fairly sensitive and distinctive, while the thiocyanate test and the acid potassium iodide are still more sensitive. The latter reagent can be activated by various catalysts, which

TABLE XVII—ETHYL HYDROGEN PEROXIDE

Mols per cc	1 KI	2 Titanous	3 Ferri-cyanide	4 Lead reagent	6 Methylene blue
5×10^{-5}	(*a*) Begins in 10 minutes, dark blue on standing	(*b*) Slowly colours yellow		(*a*) Pale brown in 3 minutes	Not bleached
	(*b*) Begins immediately, ultimate colour same as (*a*)	(*b′*) Activated by $FeSO_4$ faint yellow	Green .	deep brown in 10 minutes	
	(*c*) Same as (*b*)				
5×10^{-6}	(*a*) As above . . .	Nil	Nil . .	(*a*) Standing 10 minutes, just visible	—
	(*b*) As above				
	(*c*) As above			(*c*) Pale blue, with tetrabase standing 10 minutes	
5×10^{-8}	(*a*) Nil	—	—	(*a*) Nil . . .	—
	(*b*) Nil (even after 20 minutes)				
$1{\cdot}5 \times 10^{-8}$	(*c*) With Mo, 6 minutes	—	—	(*c*) Nil . .	—

TABLE XVIII

Reagent	Mols per cc		
	H_2O_2	$(C_2H_5)_2O_2$	(C_2H_5) OOH
KI (on standing 2 hours)	10^{-8}	Nil (10^{-7} Fe)	10^{-7} (10^{-8} Mo)
Titanous (special sensitive)	10^{-7}	Nil	10^{-5}
$K_3Fe(CN)_6$	10^{-8}	Nil	10^{-5} (?)
Lead reagent alone	10^{-7}	Nil	(5×10^{-7})
Lead reagent + tetrabase	10^{-8}	Nil	10^{-7}
Thiocyanate	10^{-8}	10^{-8}	—

renders it more convenient for distinguishing between the different types of peroxide than the thiocyanate test. The figures in the table give the approximate limits only.

Tests showed that (1) nitrous acid acts immediately on acid KI solutions liberating iodine, whereas hydrogen peroxide reacts fairly slowly. The limit of detection of nitrous acid by KI (acid) is also about 10^{-8}. (The limit with the Griess reagent is between 10^{-10} and 10^{-11}.)

(2) Nitrous acid in weak concentration does not influence the detection of H_2O_2 by the titanous reagent, neither does dilute nitric acid have an appreciable effect. Fairly strong concentrations (10^{-5}) of NO_2 vapour will prevent the coloration of the titanous reagent for quite large concentrations of H_2O_2, but smaller quantities of NO_2 (10^{-7}) do not so prevent the coloration.

(3) The lead reagent and tetrabase slowly change through greenish-blue to a green colour on addition of sodium nitrite (concn. 10^{-5}); but this change is very slow in weak concentration (concn. 10^{-7}). H_2O_2 gives a distinct and immediate blue colour for 10^{-8} mol per cc. The lead test thus provides a means of distinguishing NO_2 from H_2O_2, for the blue colour due to H_2O_2 appears at once, fades, and leaves a faint residuum of blue-green, whereas with nitrogen peroxide the colour only appears slowly, becoming green on standing, and retaining its colour.

(4) The thiocyanate reagent also gives a test with HNO_2, and the limit of sensitiveness and the speed of reaction is about the same as for other peroxides. This test is thus very useful *except* in the presence of oxides of nitrogen such as arise in combustion in air under pressure.

3—ORGANIC PEROXIDES AND " KNOCK "

(i) It has been mentioned in Part II that organic peroxides are effective " pro-knocks."* Precise measurement of this " pro-knock " effect in various fuels with the bouncing pin would have involved making inconvenient quantities of the peroxides, and it has been necessary to be content to confirm previous observations by spraying part of the peroxide products in solution in petrol into the air drawn into the throttle, while the engine was running on Shell petrol. These spraying experiments only give a rough indication of the " pro-knock " effect of these peroxides, and it is obvious that difference in vapourization, etc., would affect the results to some extent. Nevertheless, without large quantities of the materials, no other method was available.

The results given in Table XIX were obtained.

Diethyl peroxide appears to be even more violent as a " pro-knock " than amyl nitrite, and about 2% is necessary to give a similar effect to 30% of ether. Acetaldehyde, on the other hand, was again found to be quite ineffective.

When similar experiments were made with the engine running on " ethyl petrol " (*see* Part I), 1·5% $(C_2H_5)_2O_2$ was found to have no audible effect, though the speed dropped by 10 revolutions. Clearly, then, the lead tetraethyl has a very marked influence on the " pro-knock " effect produced by diethyl peroxide.

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* EGERTON and UBBELOHDE, 'Nature,' vol. 133, p. 179 (1934).

Ethyl hydrogen peroxide sprayed with petrol into the engine gave a similar effect to diethyl peroxide.

Some experiments were made in a similar manner using strong "perhydrol" (30% H_2O_2 = 100 vols.). The tests showed that this strong solution of hydrogen peroxide, when sprayed, had a definite tendency to increase slightly the knocking and to lower the power. From the rate and area of delivery of the spray, it was possible to estimate the approximate amount of peroxide entering the throttle, and so the maximum mol fraction in the engine gases, viz.: 6×10^{-4}; how much of this survives to the end of the compression stroke has not been determined, but the small extra quantity of molecular oxygen (0·15%) which would be derived, supposing decomposition of the H_2O_2 to be complete, could not alone account for the slight increase in "knock." These experiments indicate, therefore, that some H_2O_2 probably survives, and has a slight effect on the combustion reactions.

TABLE XIX

Fuel volume % in petrol	Effect on speed in revs.	Effect on "knock"
Petrol alone	– 10	Allays "knock."
30 C_2H_5 OOC_2H_5 in petrol . .	—	Intense "knock." Stopped engine.
6 ,, ,, .	– 25	Violent "knock."
3 ,, ,, . .	– 25	Heavy "knock."
1·5 ,, ,, . .	– 15	Considerable increase in "knock."
30 ethyl ether in petrol	– 20	Same as about 2% $C_2H_5OOC_2H_5$.
3·4 amyl nitrite in petrol . . .	– 20	Same as 30% ethyl ether.
0·5 ,, ,, . . .	—	Produced no change.
30 CH_3CHO in petrol	– 10	Allays "knock."

It is interesting to compare this concentration with that required to give a *pronounced* "knock" in the case of diethyl peroxide by spraying a 1% solution; the concentration in this case would be about $1 \cdot 6 \times 10^{-5}$, allowing for the measured difference in the delivery of the spray. This estimate of concentration agrees with that obtained, $1 \cdot 5 \times 10^{-5}$, if the engine is run on a fuel composed of 0·1% diethyl peroxide in petrol (Shell), which also gives rise to a pronounced increase of "knock." One-fortieth of the concentration estimated for H_2O_2 is thus sufficient for the organic peroxide to give a much greater degree of knocking; but it is probable that a much larger fraction of the latter survives the compression stroke. Another important point becomes evident; it is no use looking for the organic peroxides with a reagent such as titanous sulphate where the limiting mol fraction detectable is about 2×10^{-5} even with H_2O_2.

Some other tests with the spray are cited in Table XX.

These tests confirmed that the diethyl peroxide caused a fuel like cyclohexane to "knock," but that the lead tetraethyl in ethyl petrol (8 cc ethyl fluid per gallon Shell petrol) had a marked effect in destroying its "pro-knock" action. Similar results were obtained using amyl nitrite as the "pro-knock"; the lead tetraethyl had slightly less effect on it, while it caused cyclohexane to knock slightly less than the same amount of diethyl peroxide ; but these differences in behaviour were not marked.

TABLE XX

Fuel	Spray	Throttle	Effect on speed	Effect on "knock"
Cyclohexane	—	—	—	No "knock."
,,	3% d.e.p.	—	− 20	Loud "knock."
,,	3% amyl nitrite	—	− 15 to 20	Loud "knock" (slightly less).
Ethyl petrol	—	9	—	No "knock."
,,	3% d.e.p.	9	− 15 to 20	Occasional very slight "knock."
,,	3% amyl nitrite	9	− 15 to 20	Occasional slight "knock."
,,	—	$10\frac{1}{4}$	− 10	No knock, or very slight.
,,	3% d.e.p.	$10\frac{1}{4}$	− 10	Continuous moderate detonation.
,,	3% amyl nitrite	$10\frac{1}{4}$	− 10	Continuous moderate detonation (slightly greater).

d.e.p. = diethyl peroxide.

Although acetaldehyde has no "pro-knock" effect, if it contains acetyl peroxide the effect is pronounced. A solution of acetyl peroxide in hexane is comparatively stable, and on spraying into the engine running on petrol at throttle 9, the speed dropped by 25 revolutions, the "knock" was very violent, and the engine came to a standstill. At one-third the concentration at throttle 8 the "knock" is still considerable, but at one-fifteenth the concentration the "knock" is no longer noticeable. By titration in a CO_2 atmosphere after removing the peroxide from the hexane, the strength of the solution could be determined (0·3%), and the estimate of the concentration in the cylinder comes to about 2×10^{-6} when "knock" is *just* detectable—about the same order as for diethyl peroxide. Acetaldehyde peroxide is therefore also a strong "pro-knock," and much of it appears to survive the compression stroke.

Butyraldehyde peroxide was also tested. Although a difference in speed (− 10 revolutions) occurred, there was no noticeable effect on the "knock" with the engine running on petrol at throttle 8.

A similar experiment with *amylene peroxide* gave no indication of "pro-knock" effect at throttle 8, 9, or $10\frac{1}{4}$.

These peroxides were made by bubbling oxygen through the liquid until a strong test was given with the lead reagent or potassium iodide, and the solution contained as much peroxide as a solution of diethyl peroxide, which gave a definite "pro-knock" effect, so that they either do not survive, or do not act as strong "pro-knocks."

Summarizing these results it was found that :—(1) diethyl and ethyl hydrogen peroxide are very potent "pro-knocks," even more so than amyl nitrite, with petrol as fuel ; (2) acetyl peroxide acts also as a strong "pro-knock" ; (3) hydrogen peroxide either does not survive the compression stroke, or is only a very mild "pro-knock" ; (4) butyraldehyde peroxide and amylene peroxides appear not to act as potent "pro-knocks" ; (5) the concentration of diethyl peroxide or ethyl hydrogen peroxide necessary to give pronounced "knock" is only of the order 10^{-5}.

By their behaviour, therefore, certain of these organic peroxides appear to be connected with the phenomena of "knock," but as the quantity necessary to give pronounced "knock" is less than one-tenth of the quantity of nitrogen peroxide present, and the only known reagents approaching the sensitivity necessary to detect them are potassium iodide and thiocyanate, with which nitrogen peroxide reacts, the chance of discovering their presence in the products of reaction from the sampling valve seemed very remote. Nevertheless, attempts were made as described below.

4—Tests for Peroxides in Presence of Nitrogen Peroxide

Attempts to distinguish other peroxides in the presence of nitrogen peroxide by using inhibitors such as aniline, or by means of complex metal ions (*e.g.* HgI_4, CdI_4, etc.) had already been made. These methods were not sufficiently successful to be of any use for the present purpose. Eventually the following procedure was employed, depending on the comparative rate of reaction of NO_2 and other peroxides with HI.

The solution containing the mixed peroxides was treated with acid potassium iodide; the nitrogen peroxide acts immediately, and provided the NO was removed by a rapid stream of CO_2, the iodine liberated could be titrated with a weak thiosulphate solution, and the HNO_2 completely removed. On standing, the iodine liberated by the action of the other peroxides, which act much more slowly, developed and could eventually be titrated. This method worked quite well, using known mixtures of $NaNO_2$ and H_2O_2. It is also quite satisfactory when using NO_2 solution and H_2O_2. With diethyl peroxide, the action of KI is so slow that no colour appeared in any reasonable time, and it is necessary, after removing the NO_2 by titration as above, to add a drop of ferrous sulphate to act as a catalyst; the blue colour then rapidly appears and remains. With other peroxides, ferrous sulphate causes a rapid appearance of colour which quickly fades; when dealing with very small quantities, this catalyst is not very satisfactory, except for diethyl peroxide, for the first appearance of colour might easily be missed. Fortunately it was found that a drop of ammonium molybdate (20%)* acted as a catalyst to ethyl hydrogen peroxide, but hardly at all to diethyl peroxide, so that this provided a useful means of distinguishing between these organic peroxides. These catalysts enable the KI to be used for organic peroxides with a sensitivity about equal to that which it provides for the detection of H_2O_2, and render possible the detection and identification of minute amounts of organic peroxides in the presence of NO_2.

The following describes the behaviour of various substances towards the KI reagent, when the tests are carried out in the above way.

Hydrogen peroxide—The initial appearance of the blue colour of starch iodide is accelerated by the molybdate and the ferrous reagent, but the latter rapidly fades. Calling the blank B, the solution to which a drop of ferrous sulphate is added, F, and

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* Used with H_2O_2 by Kolthoff, 'Pharm. Weekbl.,' vol. 56, p. 949 (1919).

the other to which molybdate is added, M, the result of this test may be expressed $M \geq B > F$.

The colour is fairly rapidly developed even in the blank, and very rapidly with the molybdate.

With very weak solutions, 10^{-9} to 10^{-8} mols cc, the appearance of the blue colour is accelerated by the molybdate, but the sensitivity is not increased appreciably.

Ethyl hydrogen peroxide—The blank develops its colour very slowly; with the molybdate the colour comes up quicker, but not so rapidly as with H_2O_2, with ferrous sulphate the colour develops immediately but quickly fades; in weak solution there is no colour developed with the latter.

Thus . . . $M > B > F$.

Diethyl peroxide—The blank gives no colour, the molybdate only very slowly and the ferrous sulphate rapidly colours, and does not fade. $F > M > B$.

Acetyl peroxide—Weak solutions in water gradually decompose. The reaction with iodine is so rapid that the molybdate does not catalyse it, the ferrous sulphate solution remained colourless. So that $M = B$ and $F = 0$.

Butyraldehyde peroxide behaved similarly.

Benzoyl peroxide—The molybdate catalysed the liberation of iodine, and $M > B$ and $F = 0$; the reaction with HI is very slow.

Amylene peroxide—This behaved like ethyl hydrogen peroxide, but the blank became the same intensity as the solution to which molybdate was added, very much sooner. The ferrous solution initially catalysed the reaction, but rapid fading occurred. So that $F > M > B$ at first, then $M > B > F$, and in fifteen minutes $M = B > F$.

TABLE XXI

Type of peroxide	Behaviour	Rate of action
Hydrogen peroxide	$M \geq B > F$ . . .	Fairly rapid.
Ethyl hydrogen peroxide	$M > B > F$ . . .	Slow.
Diethyl peroxide	$F > M > B$ . . .	M and B very slow.
Acteyl peroxide and butyraldehyde peroxide	$M = B, F = 0$ . .	Rapid.
Amylene peroxide	$M = B > F$ . . .	Fairly rapid.

The results are summarized in Table XXI (*see also* control tests, p. 503). The behaviour of the various kinds of peroxides in the presence of these catalysts* appears to make possible their differentiation.

Alkoxy peroxides can be differentiated from hydrogen peroxides by their decolorizing action on methylene blue, otherwise these behave similarly to ethyl hydrogen peroxide.

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* Titanium salts were also tried, but were not so useful.

5—Engine Experiments Demonstrating Presence of Organic Peroxides

Using the technique described, tests have been made on the solutions obtained by bubbling the gases sampled from the engine through 8 cc of ice-cold water. If organic peroxides are present in those gases at concentrations not much less than 10^{-5}, it ought to be possible to detect them, provided that their rate of decomposition in the valve and in the bubbler is not too rapid.

Searching for such small quantities, it was essential to work with great care against any contamination and special precautions were taken. The quantities were determined colorimetrically. The quantity of iodine was usually checked by titration from a microburette. The detail of the method was as follows.

The contents of the bubbler were quickly transferred to a tube through which CO_2 was rapidly passed while titrating with 0·006 N thiosulphate solution, after addition of 1 cc KI solution. About 1 to 2 cc of the original solution (before the addition of KI) were kept in another tube, and 1 cc of Griess solution was added, the results obtained for NO_2 concentration (in mols per cc) are given in Table XXIV under G_1. The result of the titration for the removal of the iodine liberated by the NO_2 is also given (in mols per cc) in the column headed θ. The resulting solution was divided between four tubes, to one of which a drop of ferrous sulphate was added and marked F, to another 1 drop of ammonium molybdate solution and marked M, to another 1 cc of Griess reagent and marked G_2, and the remaining one was marked B (blank). The volume in each tube was approximately 2 cc, and the tubes were filled with CO_2 and set aside, tightly corked. The quantity of iodine, which may be liberated quickly or slowly, was noted from the blue colour at definite intervals, and was determined after a given time by titration with 0·002 N . thiosulphate, or estimated when it was only at the limit of detectability. The coloration of the solution in G_2 after 30′ was compared with a set of standard pink-tinted solutions of different strength, and the resulting concentration in mols per cc was multiplied by 2. (*See* p. 504.)

A preliminary series of experiments were performed using petrol as fuel, the results are given in Table XXII.

Table XXII

Engine conditions and fuel	Setting in degrees	Results
Petrol. Throttle 10¼ . .	− 6	B slight coloration, F colourless, M not used, G_2 pale.
	− 10	No coloration, G_2 pale.
	− 2	M > B pale, G_2 nil.
Petrol. Throttle 9	− 3	No coloration, G_2 pale (10^{-8} approx.).
	+ 7	No coloration, G_2 pale (10^{-8} approx.).
	− 7	M > B, F no coloration, G_2 pale (10^{-8} approx.).
Petrol. Throttle 10¼ . . .	− 7	No coloration, G_2 pale.
	− 10	M > B, F faint, G_2 pale (M = B later).
,, ,, 9 . . .	− 7	M = B, F faint, G_2 pale.
,, ,, 10¼ . . .	− 7	M > B, G_2 pale.

These preliminary runs indicated that there were substances present in the engine gas other than nitrogen peroxide which acted on HI and liberated iodine, for, as will be shown, the starch iodide coloration could not be accounted for by the NO_2 remaining after titration. Nevertheless, the behaviour of the products appeared not to be very consistent ; this was not surprising, for petrol has already been shown to give rise to small quantities of inhibiting substances such as SO_2, and to contain olefines which may give rise to peroxides at an early stage of the cycle.

It was, therefore, decided to use hexane as fuel ; unfortunately, insufficient *n*-heptane was available. The hexane was " aromatic free " but contained a small proportion of cyclohexane.

TABLE XXIII—SERIES II. HEXANE. V.C.D.

Throttle	Setting in degrees	Result	Mols per cc of solution × 10^8				
			G_1	θ	G_2	B	M
9	− 4	M > B	—	—	1·2	2	4
		M pale, B very pale					
9	− 7	Nil	—	—	0·2	—	—
9	− 3	M > F > B	—	4·5	1·6	—	4
		Later F fades, M strong, B pale .					
9	+ 6	Nil	—	—	—	—	—

The results in Table XXIII indicated definitely that a substance behaving like ethyl hydrogen peroxide was formed near t.d.c., but that at − 7° the chance of finding it was small, and at + 6° in the region of flame there was no trace.

At the end of this trial, the engine was run at throttle 9 on a solution of ethyl hydrogen peroxide in petrol, and the gases collected from the sample valve at — 30° ; B gave a pale blue, but M > B ; thus the ethyl hydrogen peroxide survived, and was detected in the cylinder gases behaving exactly in the same manner as the " peroxide " from the engine run on hexane, and sampled at — 3°. The mol fraction of ethyl hydrogen peroxide in the sample gas, as found by titration, was about 7×10^{-6} ; the concentration estimated to be present in the cylinder gas from the strength of the petrol solution (about 0·3%) was between 5×10^{-5} and 10×10^{-5}.

The results of this series and the previous one gave *no* indication of the presence of any detectable quantity of a peroxide similar to diethyl peroxide. The limit of sensitivity of potassium iodide to this type of peroxide appears to be low even when catalysts such as iron are used, so it is doubtful whether any such peroxide could be found even if present in amount sufficient to give rise to pronounced knocking.

Both the tests at throttle 8½ and 9 were in definite agreement with the previous results (*see* Series III and V, Table XXIV).

At throttle 6°, — 3°, owing to the later arrival of flame, not so much would be expected as at the other positions of the throttle. There is some indication that the best yields, however, may not be obtained at the highest throttle opening, although the "knock" is greater; perhaps because the temperature is higher and the rate of decomposition faster.

Another series (VI) gave at − 4° to − 3° definite but very feeble results.

The intensity of the effects seem to vary with the state of the engine. It is hardly to be wondered at that the rate of decomposition of such minute amounts will vary greatly, as the amounts which can be caught will depend so much on the exact setting of the valve, on the exposure to active surfaces, and other conditions.

Table XXIV gives a summary of these engine experiments.

Table XXIV—Summary of Engine Results

1	2	3	4	5	6	7	8	9	10	11	12
Fuel and throttle	Setting in degrees	θ $\times 10^8$	$\frac{\theta}{G_1}$	G_2 $\times 10^8$	B $\times 10^8$	M $\times 10^8$	$\frac{M}{G_2}$	Mol fraction RO_2H $\times 10^6$	Mol fraction NO_2 $\times 10^6$	$\frac{RO_2H}{NO_2}$	Result
Hexane—											
Series II :											
9	− 4	—	—	1·2	2	4	3·3	7·0	—	—	M > B*
8	− 7	—	—	0·2	—	—	—	—	—	—	—
9	− 3	4·5	—	1·6	—	4	2·5	9·5	10·7	0·9	M > B*
9	+ 6	—	—	—	—	—	—	—	—	—	—
Series III :											
8½	− 3	2	(0·3)	0·6	—	(1·3)	2·1	3·9	6·0	0·7	M > B*
Series V :											
8½	− 4	5	0·7	0·9	—	4·7	5·2	12·7	13·5	0·9	M > B*
9½	− 4	6	0·7	1·6	—	1·3	0·8	3·3	15·5	0·2	M > B*
6	− 3	2	0·7	0·8	—	1	1·2	2·3	4·6	0·5	(M > B)
Series VI :											
8½	− 4	3	0·4	0·4	—	2	5	3·1	4·4	0·7	M > B*
8⅜	− 3	1·5	0·4	0·6	1	2	3·3	4·1	3·1	1·3	M > B
8⅜	− 1	5	0·2	0·3	—	—	(1·5)	—	—	—	(M > B)
8½	− 2	1·75	0·5	0·4	—	1	2·4	2·2	3·9	0·6	M > B
8½	− 4	1	0·5	0·4	(0·5)	(0·5)	1·2	1·1	2·2	0·5	(M = B)
Cyclo hexane—											
Series III :											
10¼	− 7	22	1·4	0·4	1	—	(2)	—	63	—	(B > M)
10¼	− 3	22	1·4	1·3	(0·5)?	< 1	(0·8)	2·7	60	0·05	(M > B)
10¼	+ 3	0·9	—	—	(0·5)?	—	—	—	—	—	—
10¼	+ 1	8	0·9	0·2	—	—	—	—	3·4	—	—
Benzene —											
Series III :											
10¼	− 7	1	0·4	0·2	—	< 1	—	1·5	3·0	0·5	(B > M)
10¼	− 3	1	0·5	0·1	—	—	—	—	—	—	—
10¼	t.d.c.	1	0·5	1·0	—	< 1	(1)	3·2	3·2	1·0	(M > B)

Column 3 (θ) gives the mols per cc NO_2 in the water through which the sample gas is bubbled as determined from the titration with thiosulphate (0·006 N). Column 4, the ratio of the mols determined thus to the value obtained colorimetrically by the Griess reagent. This ratio varies between about 1 and 0·25. Columns 5, 6, and 7, the mols per cc of solution corresponding to the G_2, B and M tests. Column 8, the ratio of the mols per cc of peroxide as determined by titration of the iodine liberated in presence of molybdate, to the mols per cc of NO_2 in the final liquid as determined by the Griess reagent (which probably gives an over-estimation of the concentration of NO_2). Column 9, the mol fraction of organic peroxide in the sample gas from the engine, determined from $(KM)/(tf)$ where t is the time, f the rate of flow of sample gas, M is the peroxide concentration, and K is a constant $1 \cdot 9 \times 10^{-5}$. Column 10 gives the mol fraction of NO_2 determined from $(K\theta)/(tf)$, and column 11 the ratio of these two mol fractions in the sample gas ; column 12 gives the results of the experiment as regards the behaviour of the peroxide. In those cases marked * the result was quite definite ; in those bracketted, the amounts were at the limit of detectability.

It may be gathered from this table that :—

(1) The hexane gave rise to " peroxides " whose reaction with iodine was slowly catalysed by molybdate ; they seemed to be of the type of ethyl hydrogen peroxide or hydroxymethylethyl peroxide.

(2) The ratio M/G_2 shows that this " peroxide " cannot be ascribed to residual NO_2 not removed by titration. A still stronger argument is that $M > B$, for with NO_2 $B > M$. For several reasons, it is probable that throughout there is an over-estimation of the residual NO_2 as given by G_2, column 5.

(3) The concentration of organic peroxide in the sample gas varies between 0·1 and $1 \cdot 3 \times 10^{-5}$. 1×10^{-6} is a practically indetectable concentration. Even if the full amount of peroxide which is likely to give rise to strong " knock" were collected (*see* p. 493), a concentration of not more than about 5×10^{-5} could be expected. It is very unlikely that the whole amount would be obtained without some decomposition, and the observed mol fractions are consistent with the amount to be expected.

(4) The concentration of nitrogen peroxide in the sample gas varies from about 0·2 to $1 \cdot 5 \times 10^{-5}$; actually it was probably considerably greater, as previous experiments (Part II) showed, where precautions were taken to collect the NO_2 more thoroughly. The amount of organic peroxide obtained seems to increase with the total amount of NO_2 ; the temperature and activity of the hot surfaces of the valve have been shown to influence the amount of NO_2 present, and the temperature of the gas in the neighbourhood of these hot surfaces probably also influences the rate of formation of the peroxides, as well as their rate of decomposition.

(5) The results with cyclohexane give some indication at t.d.c. — 3° of a trace of organic peroxide (possibly an olefine peroxide). The NO_2 concentration in the sample gas was very much higher, and the results with cyclohexane (and those with hexane at settings other than — 4° to 2°) confirm that nitrogen peroxide has nothing

to do with the reappearance of the blue colour in the liquor after the thiosulphate titration, in those cases where $M > B$. Where $B > M$, and B very faint, it may possibly be due to a trace of NO_2.

(6) The benzene results are similar to those with cyclohexane and give very little indication of any organic peroxide (except a trace at t.d.c.).

Two further experiments may be quoted which serve to confirm the results obtained. In one series the engine was run on *hydrogen under knocking conditions* with the results given in Table XXV.

TABLE XXV—HYDROGEN

Throttle setting	θ $\times 10^8$	θ/G_1	G_2 $\times 10^8$	B $\times 10^8$	M $\times 10^8$	M/G_2	Mol fraction per-oxide	Mol fraction NO_2 $\times 10^6$	Result
– 5°	15	(2)?	2·0	2·0	2·0	1	—	About 70	$M = B$
– 4°	13	1·5	0·2	—	—	—	—	About 30	Nil

In the first case a little residual NO_2 remained after the titration, and the coloration of M and B was precisely the same, and M corresponded to the G_2 test. In the second test, no residual NO_2 remained, the titration was carried as nearly as possible exactly to the end point and absolutely no coloration in either M or B resulted.

These experiments acted as a good blank test for the method.

In the second series, *with pure normal heptane* (B. Pt. 98°), however, the following result, Table XXVI, was obtained.

TABLE XXVI—HEPTANE (KNOCKING)

Setting	θ $\times 10^8$	θ/G_1	G_2 $\times 10^8$	B $\times 10^8$	M $\times 10^8$	M/G_2	Mol fraction per-oxide $\times 10^6$	Mol fraction NO_2 $\times 10^6$	Ratio	Result
– 3° to 4°	5	0·3	0·1	—	1·5	15	3	10	0·3	$M > B$

Thus the pure hydrocarbon heptane behaves like the less pure hexane, and gives evidence of the presence of a hydroperoxide.

Caution was needed before even these results could be accepted. Their validity rested on (1) the catalysis by molybdate of the action of the residual organic peroxides upon hydrogen iodide ; (2) the nitrogen peroxide being removed, and the residual nitrogen peroxide being shown less than the residual organic peroxides ; and (3) showing that organic peroxides added to the fuel could be collected from the engine, and estimated by the same methods.

In connection with (1) and (2), many control tests have been made, and a few of the more important will be mentioned. (1) The fact that the molybdate solution rapidly catalyses the decomposition of the organic peroxides after removal of NO_2 would be conclusive evidence of their presence, provided it could be shown that no other type of substances gives similar effects. Solutions of NO_2 in water, and of petrol + NO_2 shaken in water, have been tested, using the same procedure as used in the test, with the results that either there is no residual NO_2, and both M and B remain colourless, or that if an appreciable residue remains due to incomplete titration, M and B colour immediately to the same faint tint. (Molybdate indeed appears to slow down, rather than hasten, autoxidation of residual NO purposely left in the solution in presence of air, for the B was then greater than M.) Amyl nitrite solution in petrol, diluted to suitable concentration, when tested in the same way gave no immediate coloration in B or M, and on standing $M < B$. Fresh acetaldehyde solution, neither in presence of NO_2 nor alone, showed any coloration in B or M. It is true that the molybdate will hasten autoxidation by air in presence of starch iodide, but many tests have been made showing that the procedure adopted—rapid bubbling of CO_2 and corking of the tubes—satisfactorily prevented this. No other substance likely to be present has been found to behave so as to interfere with the test.

It was noted that the blue colour of starch iodide did not appear in G_2, when organic peroxides were known to be present, until their concentration was somewhat greater than that at which they would be expected to produce a coloration. This matter was investigated, and shown to be due to a direct reaction of amines with the organic peroxides,* and may indeed account for the " anti-knock " action of the former. In spite of this, in some cases the blue colour made its appearance in G_2 when the pink due to nitrogen peroxide was quite faint, showing definitely that other " peroxides " were present in considerable amounts.

(2) Residual nitrogen peroxide might affect the validity of the test by (*a*) influencing the rate of the reaction of organic peroxides on the hydrogen iodide and starch in presence or absence of catalyst, or (*b*) by its effect on the Griess reagent being masked, so that the true measure of the amount of the residual nitrogen peroxide is not obtained.

(*a*) As mentioned under heading (1), tests have been made on mixtures of NO_2 in water, or in aqueous suspensions of hexane or petrol, etc., to which NO_2 had been added, in presence of various peroxides to ascertain (*a*) whether the NO_2 can be satisfactorily removed by the titration, and (*b*) whether slow hydrolysis of any nitrites or nitroso compounds might be hastened by a catalyst (like molybdate), which might result in misleading conclusions.

Two check tests, Table XXVII, may be cited : dilute ethyl hydrogen peroxide with an aqueous solution of NO_2 vapour, A; another solution of ethyl hydrogen peroxide and a somewhat stronger NO_2 solution, B.

These tests illustrate that the NO_2 can be effectively removed, and the test for the organic peroxide is not affected.

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* *Cf.* BAEYER and VILLIGER, ' Ber. deuts. chem. Ges.,' vol. 34, p. 738 (1901).

It is probable, nevertheless, that slow hydrolysis of nitroso compounds, etc., might occur to some extent, and so tests have been done using NO_2 dissolved in petrol and shaken with water, the fine emulsion being diluted and used for the test. The estimates of NO_2 given by G_2 show evidence of slight hydrolysis, but after 20 minutes, when the concentration of NO_2 has become about 2×10^{-8}, the blue colour of B was only just visible, and $M < B$ showing that no difficulties arise on this account.

TABLE XXVII

A

G_1 5×10^{-8} mols per cc	Interval after titration				
	1 minute	2 minutes	5 minutes	8 minutes	30 minutes
B	Nil	Very pale	—	—	—
F	Very pale	Fades	—	—	—
G_2	Nil	Nil	—	—	Very pale
M	Nil	Very pale	$M > B > F$	—	Strong blue.

B

G_1 10×10^{-8} mols per cc	Interval after titration			
	1 minute	2 minutes	5 minutes	15 minutes
B	Nil	Very pale	—	1×10^{-8} mol fracn.
F	Rapid blue	$F < M$	—	$F \leqslant B$
G_2	Nil	2×10^{-9}	4×10^{-9}	—
M	Very pale	$M > F$	$M > F > B$	4×10^{-8} mol fracn.

(*b*) A number of tests on the effect of various substances on the rate and intensity of coloration of the Griess reagent in presence of NO_2 has been made. These have shown that in presence of potassium iodide and tetrathionate ions (and starch) both the rate and intensity are diminished, but only to the extent that under the conditions of the test, if the concentration observed is doubled, the true concentration will *not be greater* than the figure so obtained. In all tests, therefore, in order to be on the safe side, the values under G_2 have been given at double the concentration estimated from the tint observed.

It is important to arrive at an estimate of the limiting concentration at which the starch iodide blue can be observed under the conditions of the tests. It has been found that NO_2 can be detected with certainty at a concentration 1×10^{-8} mols per cc, the colour developing almost immediately, similarly in 6 minutes (in presence of molybdate) a concentration of 5×10^{-9} H_2O_2 can just be detected, and a concentration of $1 \cdot 5 \times 10^{-8}$ ethyl hydrogen peroxide could be detected in 10 minutes quite definitely, but not of course without the addition of molybdate. When, therefore, the concentration given by G_2 is less than 1×10^{-8}, and by M greater than $1 \cdot 5 \times 10^{-8}$, as in several tests, there can be no question that NO_2 is then not responsible for the iodide blue.*

Agreement between the concentrations of NO_2 determined by the colorimetric test with that by titration with thiosulphate is not always obtained at these great dilutions. If NO_2 is allowed to dissolve in water, and to stand, then the reaction with acid KI solution is the usual one

$$2NO_2 + H_2O = HNO_3 + HNO_2,$$

and

$$HNO_2 + HI = H_2O + NO + I\ ;$$

so that 1 mol of $NO_2 = \frac{1}{2}$ equivalent of iodine, but under certain circumstances direct reaction appears to take place, and

$$NO_2 + 2HI = H_2O + NO + I_2$$

so that 1 mol $NO_2 = 2$ equivalents of iodine ; this appears to occur when NO_2 vapour is dissolved in acid KI solution, as already pointed out (Part II). A special series of experiments was made to investigate this question. In very dilute solutions the latter reaction seems to take place under certain circumstances, which probably accounts for the variation of the ratio θ/G_1 in Table XXIV. At all events, if the first equation were correct in all circumstances, it would only have the effect of making all the G_2 values lower, and so the ratio M/G_2 greater ; purposely the less favourable basis, viz. : 1 mol $NO_2 = 1$ mol I_2, has been assumed, instead of that suggested by the θ/G_1 ratio.

It seems quite definite that the figures given in Table XXIV, in columns 7 and 8, in the majority of tests cannot be accounted for as the effects of residual NO_2, even allowing for those where the effects are so near the limit of the detectable as to be of less weight.

(3) The result of adding ethyl hydrogen peroxide to the hexane, and sampling from the engine at t.d.c. − 30° has already been mentioned (following Series II, p. 498). Although, as the figures show (*see* Table XXVIII), the quantity was somewhere near the limit of detection, the behaviour with molybdate was quite definite, and confirms the efficacy of this method of detecting the organic peroxides. Quite 10% of the total ethyl hydrogen peroxide added to the fuel was recovered in the gas sampled at − 30°.

Acetyl peroxide has likewise been added to hexane, and sampled from the engine in an early part of the compression stroke. This test was done immediately following Series V. From the titration of the original petrol solution the strength was estimated to be not less than $6 \cdot 2 \times 10^{-6}$ mols acetyl peroxide per cc, which gives a mol fraction in the cylinder of about $1 \cdot 6 \times 10^{-5}$. The increase in "knock" was just detectable at this concentration. After removal of the NO_2 by titration, the

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* The hydroperoxide formed in the engine is not necessarily ethyl hydrogen peroxide, so that the esnsitivity of the reagents to the actual " peroxide " may be somewhat different.

residuals M and B solution both coloured up rapidly at practically equal rate. After 5 minutes, M was titrated with weak thiosulphate, but a shade of blue colour reappeared, and was titrated again after 20 minutes, and the same total iodine was obtained for B and for M. This test showed that the acetyl peroxide (unlike nitrogen peroxide) had a certain survival and reacted very quickly with HI, but not too rapidly for the reaction to be completed during the NO_2 titration. This peroxide could have been detected in the sample gases at concentrations about 1×10^{-5}; it appeared to survive in the compression stroke better than the ethyl hydrogen peroxide.

TABLE XXVIII

Conditions	Setting	$G_2 \times 10^8$	$B \times 10^8$	$M \times 10^8$	M/G_2	Mol fraction $(C_2H_5)O_2H$ $\times 10^6$	Result
Petrol + 0·3% (?) ethyl hydrogen peroxide. Throttle 9. V.C.D.	− 30°	< 1	Very pale	1·5	1·5	7	M > B after 10 minutes, M slightly > B after 15 minutes.
						Mol fraction CH_3CO_3H	
Petrol + 0·05%(?) acetyl peroxide. Throttle 9. $G_1 = 17 \times 10^{-8}$ $\theta = 3 \cdot 7 \times 10^{-7}$ C.M.D.	− 30°	$2 \cdot 6 \times 10^{-8}$	Immediate blue 9	9	3·4	23	M = B immediately

By determining the quantity of acetyl peroxide remaining *after* titration at various strengths of initial aqueous suspension of an acetyl peroxide hexane mixture, the survival ratio, Table XXIX, shows that for the dilutions obtained in the engine samples the blue colour would appear at once in both M and B, provided it had not all been removed in the NO_2 titration (θ). Since no such behaviour is observed to occur in the solution of the gases collected from the engine, when run under knocking

TABLE XXIX

Initial concentration, mols per cc $\times 10^6$	Results after 5 minutes	Survival
3·6	$M \gg B > F$	$\frac{1}{17}$
1·5	$M = B$	$\frac{1}{25}$
0·3	Nil	Nil

conditions, it does not seem likely that aldehyde peroxides are present in any considerable amount at the moment when " knock " takes place.

Another argument against acetyl peroxide, or indeed other aldehyde peroxides, being those specially connected with the phenomenon of " knock," is that the addition of aldehydes does not occasion an increase of " knock." Although acetyl peroxide has been shown to survive part of the compression stroke, and occasions " knock " to much the same extent as diethyl and ethyl hydrogen peroxide, the evidence obtained in this work is against its being present in any appreciable quantity at the moment when " knock " takes place.

The outcome of these experiments is to demonstrate that close to t.d.c. (— 3°) there appears to be formed quite definitely a hydroperoxide (or possibly a hydroxy-peroxide) in an amount which is sufficient to account for the " knock " which occurs. The region over which this is obtainable seems very narrow, and from the experiments made in Part I, it is probable that the amount of the peroxide diminishes just before the aldehyde maximum is reached (*i.e.* with the arrival of flame).

Since (*a*) hydroperoxides give rise to knock ; (*b*) they are present in the neighbourhood of the exhaust valve just prior to arrival of flame ; (*c*) they are apparently not formed when knock does not occur or with fuels which do not knock ; and (*d*) no other substances have been detected during the combustion of hydrocarbons which give rise to knock (except NO_2, which has been shown to have only a secondary effect), it seems legitimate to conclude that these " peroxides " which have been found are connected with the phenomenon of " knock " and possibly occasion it.

Experiments have been made on the "peroxide" obtained from hexane by MONDAIN MONVAL's* method ; this behaved like a hydroxy peroxide. It was interesting to find it was only a weak " pro-knock," or possibly it did not survive the compression stroke.

6—CONCLUSION

One outcome of this part of the investigation is to make clear how it is that organic peroxides have not been observed in much of the work that has been done on the combustion of hydrocarbons : even spectroscopic technique has failed to show them.† They might indeed be formed as a first step in the combustion of a paraffin hydrocarbon; but unless the conditions are suitable, they are only a transient product, and are never present in sufficient quantity to be detected. Even when the conditions are an optimum, so that a small number of the molecules remain in existence for an appreciable time, it needs special technique to detect them.

It may be concluded that the presence of organic peroxides behaving like ethyl hydrogen peroxide, or perhaps of the hydroxy type, has been demonstrated in the gases in a petrol engine taken from the region where " knock " occurs just prior to passage of the flame, and that the amount is of the same order as that required to give " knock " if the hydroperoxide were added to the cylinder gases.

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* MONDAIN MONVAL and QUANQUIN, ' Ann. Chim. Phys.,' vol. 15, p. 309 (1931).

† EGERTON and PIDGEON, ' Proc. Roy. Soc.,' A, vol. 142, p. 26 (1933).

PART IV—EXPERIMENTS ON THE BEHAVIOUR OF "ANTI-KNOCKS"

By A. EGERTON, *F.R.S.*, and F. LL. SMITH

EGERTON and GATES* found that, amongst other metals, the vapours of potassium and thallium were very effective in raising the temperature of ignition of petrol. The metals were volatilized from an electric arc, and the vapour and condensed particles carried into the ignition pot in a stream of nitrogen or argon. During the former investigation RICARDO and THORNYCROFT had checked the "anti-knock" property of thallium by arranging for the vapour from a thallium arc to be drawn into an engine. They had also observed that with lead introduced in this same manner, it mattered little whether the lead was drawn in along with nitrogen or with air.

It was decided to extend such investigations by determining the effect of introducing vapours of various metals into the cylinder of the petrol engine. It was desirable that the vapour should not be exposed to oxygen until the last possible moment, so that the effect of introducing the vapour to oxygen previously to passing it into the engine could be investigated separately. With potassium it was essential that the vapour should be excluded from oxygen and moisture, until actually in the engine.

An auxiliary inlet valve was screwed into the boss provided for the bouncing pin and actuated by a cam and rocker mechanism. The cam was so designed that the auxiliary valve opened simultaneously with the main inlet valve, but was completely closed when the piston reached bottom dead centre, so as to avoid all danger of blowback of air into the vaporizing system.

The vaporizing pot is shown in fig. 23. The substance under investigation was contained in a cup screwed into the bottom of a cylindrical iron vessel, 10 cm high by 6 cm diameter. The gas which was to be saturated with the vapour was led through a pipe welded into the top of the pot, and leading down to the cup. The gas outlet pipe was connected to the auxiliary inlet valve of the engine. The gas inlet pipe was cooled at its extremity by means of a small water-jacket, so that a rubber connection might be made to a flow meter, thence to phosphorus pentoxide drying tubes, which in turn were connected to a cylinder containing the gas. The

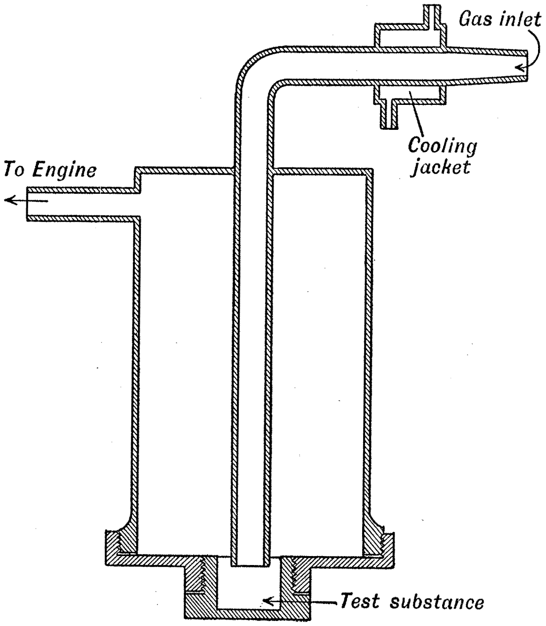

FIG. 23—Vaporizing pot

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* 'Rep. Aero. Res. Comm.,' Lond., No. 1079 (Dec. 1926).

vaporizing pot was mounted side by side with a second one identical save that no provision was made for containing the test substance. The two pots were electrically heated to the same temperature, and placed in a well-lagged container. The gas might be passed through either the vaporizing pot or the dummy pot at will. The temperature of the pots was recorded by means of a thermocouple. The pipe work connecting the pot to the valve was heated electrically. The reason for the large size of the pots was that with this arrangement, despite the necessarily intermittent delivery into the engine, the flow into the pot was substantially constant, and the outflowing gas was evenly saturated with the vapour (complete saturation was not attained).

In the event of the substance in the pot proving an anti-knock, the following procedure was adopted to arrive at some measure of its efficacy. The pot was heated until a temperature was reached at which the corresponding vapour pressure of the " anti-knock " was of the order of 1 mm of mercury. One fuel container of the engine was filled with Shell petrol and the other with a mixture of Shell and benzole (for instance, in the proportions of 0·4 to 1), so as to give a definite difference in " knock " between the two fuels. The engine was switched over to the benzole mixture and about 3 litres per minute of gas was allowed to flow through the dummy pot and into the cylinder by means of the auxiliary valve. The engine speed and throttle were adjusted until knocking was just audible. The engine was then switched over to Shell petrol alone, the gas diverted into the vaporizing pot, and the gas flow adjusted until knocking was again just audible. Once more the engine was switched back to the benzole mixture without the " anti-knock," and so on until the benzole mixture without the anti-knock matched against the Shell petrol with the anti-knock, the engine conditions and gas flow through the pots being constant. If necessary the temperature of the pots was raised or lowered according to the anti-knock value of the substance, so as to get a sufficient " anti-knock" effect with a convenient gas flow. The quantity of " anti-knock " being used was calculated from the pot temperature and the gas flow assuming that the gas delivered to the engine was saturated with the vapour. The petrol consumption was measured and hence the ratio of " anti-knock " to petrol was known.

In this manner it was found that both potassium and thallium were extraordinarily effective in suppressing detonation, the latter more so than the former. The potassium was passed into the engine in a stream of nitrogen alone. With thallium a nitrogen stream was first used and only a slight " anti-knock " effect resulted. As soon, however, as 15% of air was mixed with the nitrogen, the " anti-knock " effect was enormously increased. When the thallium was passed in with nitrogen alone, no measurement of " anti-knock " value was made, since it was too small for accurate assessment; but when air was added to the nitrogen the thallium became 11 times as effective as lead, weight for weight, assuming that the gas was saturated with the vapour. On the basis of the number of molecules of combustible mixture to one of " anti-knock," the thallium was again some 11 times as effective as lead tetraethyl. Unfortunately, it was not possible to introduce lead vapour in the same manner, as the volatility of metallic lead is insufficient at the temperatures at which the pots could be maintained.

Potassium was some four times as effective as lead on a weight for weight basis. In this case the vapour must certainly be rapidly oxidized on contact with the air in the engine cylinder. The evidence provided by these two metals gives conclusive support to the observations of EGERTON and GATES, that, for an " anti-knock " to be effective, it must be in an incipient state of oxidation.*

The method was then applied to find the " anti-knock " properties of other substances. Selenium and tellurium were each found to be fairly effective suppressors, the former slightly more so, the higher the oxygen content of the gas. Tellurium was equally effective in air or nitrogen. Sodium, cadmium, zinc, iodine, and sulphur were ineffective. In view of the success with potassium, the inactivity of sodium was particularly interesting, and definitely confirmed.

Phenol and aniline were also introduced by this method, the former was not found effective and the latter, although effective, was apparently much less so than it is known to be when added directly to the petrol. For investigation of volatile liquids it was, therefore, decided to modify the apparatus with a view to increasing the degree of saturation of the air and other gas passing over. The two iron pots were replaced by U-tubes, one of which was filled with glass wool soaked with the liquid. The tubes were placed side by side in a bath of water heated electrically to any desired temperature. Provision was also made whereby the gas and vapour could be passed through a second heated tube before entering the engine.

Lead tetraethyl was tried by this method, but although it suppressed detonation it was only one-eighth as effective as when added to the petrol. This is, no doubt, mainly due to the fact that the gas passing through the tube was not nearly saturated with the vapour, but a secondary cause may be that, when mixed with the petrol, the anti-knock is more intimately associated with the fuel during vaporization and the first stages of combustion, and is thus rendered more effective.

When the gas and lead tetraethyl vapour were passed through the heated tube before entering the engine, the anti-knock value was found to fall off slightly as the temperature was raised to 375° C, the value at any temperature being the same whether the vapour was in the presence of nitrogen, air, or 50% nitrogen and oxygen. The apparent diminishing effect, with little doubt, was due to the increasing pro-knock effect of the hot gas. Above this temperature the " anti-knock " effect continued to fall in much the same way as before when nitrogen was used, but in the presence of oxygen, yellow PbO formed on the walls of the heater tube, and the " anti-knock " effect fell off rapidly.

When iron carbonyl was tested by this method, a deposit of Fe_2O_3 commenced to form in the heater tube when the temperature of the latter was raised to 185° C, with air passing through the U-tube. Above this temperature the " anti-knock " effect was greatly reduced. It was found that iron carbonyl was only effective when introduced

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* *Cf.* LORENTZEN, ' Z. angew. Chem.,' vol. 44, p. 131 (1931).

as such ; if it was previously decomposed so as to give a fine russet fog of iron oxide, by allowing the iron carbonyl to smoulder at a wick, it was no longer effective.

Aniline was introduced by means of the U-tube and was found to be about one-thirtieth as effective as lead tetraethyl, weight for weight. Ethyl iodide was found to be about two-thirds as effective as aniline for equal weights of each. The effect of ethyl iodide is interesting in view of the fact that iodine vapour was found to be ineffective. This is, however, contrary to the experience of MIDGLEY,* who found that iodine vapour suppressed detonation, but is in accordance with the work of EGERTON and GATES,† who state that iodine had little or no effect in raising the igniting temperature of petrol.

The results of these experiments are summarized in Table XXX. The figures are calculated on the assumption that the gas passing over the test substance became

TABLE XXX

Substance	Apparatus	Relative efficacy on weight basis	No. of mols of combustible mixture to 1 of " anti-knock " to give same effect as 1 cc $PbEt_4$/gal.	Remarks
Lead or leadethyl	Introduced as $PbEt_4$ with petrol	—	365,000	—
Thallium (680°)	Pot	11 × as lead	3,950,000	Introduced with air.
Potassium (200° – 400°)	Pot	4 × as lead	275,000	Introduced with N_2.
Selenium	Pot	0·067 × as lead	74,300	Slightly greater effect in presence of O_2 than not.
Tellurium (580°)	Pot	0·014 × as lead	6,300	White deposit (TeO_2).
Lead ethyl	U-tube	1/8th as when introduced with petrol	45,600	Formed PbO at 375° C.
Aniline	U-tube	0·019 × as lead 0·031 × as $PbEt_4$	3,170	—
Ethyl iodide	U-tube	0·012 × as lead 0·017 × as $PbEt_4$	3,150	—

The following elements were found to be ineffective : sodium, cadmium, zinc, iodine, and sulphur.

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* 'J. Ind. Eng. Chem.,' vol. 14, p. 894 (1922).

† 'J. Inst. Pet. Tech.,' vol. 13, p. 244 (1927).

saturated with its vapour. The minimum effectiveness is therefore recorded. It has been assumed that the average selenium and tellurium molecules are triatomic under the conditions prevailing in the vaporizing pot.

As regards the accuracy of the figures in Table XXX, the " anti-knock " values of aniline and ethyl iodide, when vaporized in the U-tube, are of the same order as is found when the compounds are mixed with the petrol. In these cases the gas flowing through the U-tubes must have become fairly saturated with the " anti-knock " vapours, but with lead tetraethyl this may not have been so. Assuming that the atoms of selenium and tellurium are as effective in the form of diethyl compounds as when existing as vapours of the elements, the relative " anti-knock " values of selenium and tellurium from the values in Table XXX would be as follows :—

	Number of molecules of charge to 1 of " anti-knock " to give same effect as 1 cc $PbEt_4$ per gallon.
Selenium diethyl	9,300
Tellurium diethyl	3,130

The corresponding quantities from knock ratings of solutions of petrol and the above compounds* are :—

Selenium diethyl	20,000
Tellurium diethyl	91,800

This would indicate that the concentration of anti-knock vapour in the gas was of the order of one-half and one-thirtieth respectively of the saturation limit. The discrepancy between the relative merits of selenium and tellurium when added to the petrol as diethyl compounds, and when introduced to the engine as elemental vapours, may be due to the differing decomposition and oxidation rates of the compounds in the former case, but these comparisons suggest that there was considerable lack of saturation and that the actual " anti-knock " effect of the thallium and potassium was greater than the estimate.

By passing the air through a flow meter, a filter tube, a small vaporizing pot, and either into the engine induction system or into a glass wool filter so that the flow was not disturbed, it was possible to weigh the actual quantity of thallium passing into the engine, and in this way figures of 20 and 30 times the effectiveness of lead (introduced as $PbEt_4$) were obtained.

Thallium oxide (Tl_2O) is one of the few metallic oxides with appreciable volatility at 500° C, and the engine was run for a quarter of an hour by drawing the air over the substance heated at 500° to 600° C before volatility and therefore effectiveness as an " anti-knock " was destroyed. DUNCAN† has measured the dissociation of Tl_2O_3. At 400° C the equilibrium would be well in favour of the higher oxide. The dissociation pressure of the " peroxide " Tl_2O_4 is only 52 mm at 454° C as shown by CENTNERSZWER and TREBACZKIEWICZ,‡ so that this oxide would probably

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* *Cf.* MIDGLEY, 'J. Ind. Eng. Chem.,' vol. 14, p. 894 (1922).

† 'J. Amer. Chem. Soc.,' vol. 51, p. 2697 (1929).

‡ 'Z. phys. Chem.,' A, vol. 165, p. 367 (1933).

also be present. These facts, together with the volatility of Tl_2O, probably account for the potency of thallium as an "anti-knock." BLUMENTHAL* has measured the dissociation pressure of K_2O_4 and K_2O_3 which at 450° C are about 300 and 20 mm, respectively, so that both oxides would be present under engine conditions. There is no evidence of the existence of Na_2O_3 above 290° as a product of Na_2O_2. KRUSTINSONS† states that in the range 350° to 308° C, the dissociation pressure of pure lead peroxide changes from 914 mm to 90 mm, so that the peroxide would not be present, except in solid solution, at high temperatures ; the product of dissociation is not pure PbO, and as Pb_3O_4 has only a small dissociation pressure at 400° C, it is probable that several oxides of lead are capable of existing at the temperatures in the engine.‡

These facts and all the experiments described are in line with former conclusions§ :—

(1) that the "anti-knock" has to be oxidized ; (2) that it should be dispersed so as to be almost as a vapour ; and (3) that it should be capable of being oxidized to a higher oxide.

While a certain amount is known about the dissociation of metal alkyls, the information as to their oxidation is limited. Lead tetraethyl vapour along with air passed through a heated tube commenced to oxidize rapidly at 280° C, and gave white, yellow, buff and brown deposits. The brown deposits were partly PbO_2, but after washing with pentane to remove any excess $PbEt_4$, part of the reddish-brown deposit still gave off volatile compounds explosively and corresponded to the possible composition Et_2PbO . OPb, when analysed for lead. Insufficient of this deposit was obtained pure enough to make a complete analysis ; and it is not therefore certain that it is not a mixture of lead oxides in which $PbEt_4$ had been absorbed. The substance, however, possessed oxidizing properties and may have been formed as an intermediate product in the oxidation of $PbEt_4$, somewhat in the same manner as zinc ethyl has been shown probably to provide $ZnEt_2O_2$||. The white deposits were proved to be chiefly $PbCO_3$ and PbO and the yellow and buff deposits PbO in a very finely divided state.

An attempt was made to study the kinetics of the decomposition by introducing small measured quantities of lead tetraethyl from a graduated capillary tube into a glass bulb maintained at a constant temperature and containing air at various pressures. At 218° C (naphthalene) no oxidation occurred at 20 cm total pressure (4 cm $PbEt_4$ pressure), but on suddenly letting in a further quantity at a higher total pressure decomposition set in with a red flash, black and brown vapours filled the bulb, and the heavy cloud slowly deposited at the base of the bulb.

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[*] ROCZN, 'Chem.,' vol. 12, p. 119 (1932).

[†] 'Z. Elektrochem,' vol. 40, p. 246 (1934).

[‡] The "anti-knock" mainly acts in the vapour state, and some caution is needed in using equilibrium data determined for the solid lattice.

[§] EGERTON and GATES, 'J. Inst. Pet. Tech.,' vol. 13, p. 286 (1927).

[||] THOMPSON and KELLAND, 'J. Chem. Soc.,' p. 756 (1933).

At 306° C (benzophenone) and 280° C (bromo-naphthalene) decomposition followed by partial oxidation occurred at every injection. The deposits were found to be similar to those obtained in previous experiments by the flow method. It is interesting to note that GARRATT and THOMPSON* found a similar behaviour with $Ni(CO)_4$, rendering the kinetics of the oxidation difficult to ascertain. So far as they have gone, these experiments show that lead tetraethyl tends to decompose explosively into lead and ethyl radicals, the residues being subsequently oxidized. It would be more to the point to study the oxidation in the presence of hydrocarbon vapours, for the course of the oxidation might be modified and the formation of intermediate oxides favoured.

Nickel and iron carbonyls decompose somewhat similarly at a lower temperature than $PbEt_4$, various intermediate compounds may also be formed ; but it seems probable that nickel and iron oxides are the actual inhibitors, the reason for the lack of effect (*see* p. 510) of a disperse cloud of iron oxide (or even of lead oxide) being that the dispersion is insufficient unless formed by a decomposition of the vapour along with the fuel, the oxidation of which is inhibited.

If the "anti-knock" acts in an oxidized state, as seems to have been proved by (1) the above experiments on thallium and potassium, (2) those of PIDGEON and EGERTON† on the effect of lead tetraethyl on the induction period, and (3) the fact that many oxidizable metals are ineffective, it must break reaction chains either (1) by being peroxidized so that it removes oxygen from or adds on to the oxygen of the active chain carrier ; or (2) by mutual destruction of two peroxides to form oxygen and two lower oxygenated products ; or (3) by removing energy from the active molecules which take part in the chain. Until more is known about the actual chain carriers, the exact nature of the process will remain doubtful‡ ; but taking all facts into consideration, the first process is the most plausible. Besides stopping chains, these inhibitors also prevent the start of chains, and this is mainly a surface effect.

PART V—DISCUSSION

By A. EGERTON, *F.R.S.*

The phenomenon of "knock" is definitely a chemical one. Whether or not a combustible mixture will give rise to a knocking type of explosion, depends on the character of the chemical reactions which are taking place, not on the physical

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* 'J. Chem. Soc.,' p. 1822 (1934).

† 'J. Chem. Soc.,' p. 684 (1932) ; *cf.* LORENTZEN 'Z. angew Chem.,' vol. 44, p. 131 (1931).

‡ The fact that the concentration of inhibitor necessary to prevent "knock" is of about the same order as the concentration of "peroxide" necessary to cause "knock" points to the collision of two active molecules of the chain carrier as being needed for the chain branching, for then the chance of breaking the chain by the inhibitors becomes similar to the chance of the explosion. This possibility is being further examined.

conditions in which the explosive mixture finds itself except so far as those affect the rate of those reactions.

During the compression stroke, the gas mixture, in a more or less turbulent state, is exposed to the hot carbonized piston head, to the still hotter face of the exhaust valves, and it is also rising in temperature owing to compression; some reaction must be going on catalysed by the surfaces (*see* p. 481). Towards the end of the stroke the temperature generally is high enough for slow combustion in the body of the gas to be occurring at a considerable rate, though the time is insufficient for the reaction to proceed very far. It is indeed fortunate that there is this delay, for ignition of the mixture would occur, if it were exposed to the temperature for a second or so, but the time of exposure in the last 20° of the stroke is only about 0·005 second before the flame has consumed the mixture. It is the last part of the charge to burn that suffers the longest exposure and therefore is "presensitized" to the greatest extent.* But these gases are exposed to the flame (*ca.* 2800° C) radiating heat and supplying a number of activated molecules projected forward, which act as the promoters of combustion in those layers of gas yet unburnt. The rise in pressure in and behind the flame front as a result of the start of combustion is communicated to the rest of the gas as a wave of high pressure which precedes the combustion front and must be succeeded by other waves as the advance of the flame meets obstruction of any kind. The flame itself (particularly for strong mixtures) is a fairly narrow band of combustion proceeding when once started with fairly uniform velocity across the cylinder head from the spark through the turbulent gases, the rate of travel being dependent on the mixture, the charge density, etc., and the pressure rising rapidly and fairly uniformly. Towards the end of the travel conditions may arise such that the flame meets with a pressure wave, whereby enhanced combustion might ensue and consequently a knocking type of explosion. This view has indeed been advanced as an explanation of "knock." Although such conditions may assist "knock" to occur, evidence is available to show that it is an insufficient cause of "knock"; a very small quantity of lead tetraethyl added to the fuel will not change the behaviour of the engine at all except for just removing the "knock" in the last part of the charge to burn, the rate of flame travel and the power obtained may be the same, and it is only in the last stages that the effect of the lead makes itself apparent.† So small a difference to the physical conditions could hardly be the cause for the disappearance of the "knock," which is due to the difference in the chemical reactivity of the last part of the charge to burn occasioned by the presence of the lead.

The last portion of the gas to burn is that exposed longest to "presensitization,"

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* In an ordinary ignition there is a delay during which the reactions are accelerating, but at a certain stage either the energy cannot be dissipated with sufficient rapidity, or the concentration of certain reactants become sufficiently great; the reactions suddenly become enormously rapid and ignition ensues—it is these processes preliminary to ignition that are referred to as "presensitization."

† *Cf.* PONTREMOLI and SERRUYS, 'C.R. Acad. Sci., Paris,' vol. 199, p. 25 (1934).

both on account of the hot surfaces of the valves and of the flame and on account of the rapid pressure rise. It is not merely a question of the temperature to which the gases are exposed, otherwise many fuels which do not knock, should knock, or even of their ignitibility under normal conditions, otherwise mixtures to which acetaldehyde, etc., had been added should knock more readily, but it is a question both of the temperature and of the ignitibility as influenced by the " presensitization " and the pressure. On these views, auto-ignition ahead of the flame in the last part of the charge to burn is possible and indeed has been observed, but it more frequently happens that the seat of the "knock" is the touch off of a "presensitized" region of the gas as soon as the flame reaches it. Other portions may be set off almost simultaneously, and more than one compression wave as a result may be propagated through the burnt gases.* SERRUYS† has shown that the "knock" endures for less than 1/10,000 second, the very great pressure rise corresponds to an exceptionally high local temperature occasioned by a sudden release of energy in a small portion of the gas. The reason why the region of gas which is touched off burns differently from the rest of the mixture and indeed provides a mode of combustion very akin in character to a gaseous detonation, in spite of the mixture being far removed from one which can give rise to true detonation‡, will be dealt with further on. To sum up this discussion to this point, " knock " is due to a peculiar type of combustion in a small portion of the gas.

Intricacies of the kinetics of combustion of hydrogen and oxygen have proved difficult enough partly to understand, but with complicated hydrocarbon molecules satisfactory knowledge of the kinetics of the combustion process must prove still more troublesome to achieve. It is not intended to discuss in this paper the nature of hydrocarbon combustion but only to consider some of those facts which bear on the particular mode of combustion that gives rise to " knock."

Since " knock " has been identified with a special process of ignition, it might be expected that "knock" and ignition should exhibit close relationship. This in general is so, but there are many points of difference.

The type of ignition that occurs in knocking is similar to that which is produced by the adiabatic compression method *except* that in the former the gas is " presensitized"; this fact explains why anti-knocks have very little effect on the ignition point determined by the latter method but a great effect on " knock."

Comparisons of behaviour on ignition with "knock" behaviour are often made, using an ignition apparatus in which the fuel is dropped into a heated vessel through which a stream of air is passed. Such a method enhances the effects of surface on some of the reactions while the pressure conditions are quite different. Qualitatively the method indicates what occurs in the presensitizing period of the knocking explosion, and the influence of " anti-knocks " and " pro-knocks " is shown by a rising

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* *See* RASSWEILER and WITHROW, 'J. Ind. Eng. Chem.,' vol. 25, p. 1359 (1933).

† 'C.R. Acad. Sci., Paris,' vol. 194, p. 1894 (1932).

‡ EGERTON and GATES, 'Proc. Roy. Soc.,' A, vol. 114, p. 152 (1927).

and lowering of the ignition temperature. But important differences in behaviour are found, for instance :—

(*a*) diethylperoxide raises the ignition point of hexane instead of lowering it, as its pro-knock effect would suggest ;

(*b*) nitrogen peroxide lowers the ignition point of hydrocarbons, whereas it does not give rise to pronounced "knock" with fuels such as butane, hexane or petrol ;

(*c*) aldehydes lower the ignition point of hydrocarbons, whereas they have little influence on "knock" ;[*]

(*d*) selenium has a more pronounced effect in raising the ignition point of petrol than lead tetraethyl, whereas it has a comparatively small effect on "knock."

These and other such points of difference can be explained when the different conditions are taken into account, particularly the time during which events can happen.

Diethylperoxide has a low ignition point but, like carbon disulphide, it raises the ignition point of a hydrocarbon like hexane ; this is probably due to the assistance afforded to the normal chain reactions of the hydrocarbon during its own combustion (probably by starting more chains at the surface of the vessel), for it is noted that the flameless combustion appears to be enhanced. But in the engine, the peroxide is exposed to conditions wherein the rate of its disruption is greater than the rate of its combustion : the molecule disrupts and can give rise to the explosion characteristic of a branched chain type of combustion.[†] On the other hand, nitrogen peroxide, though it undoubtedly has an effect on ignition, probably does so by forming compounds with other radicals which are formed in the course of the reactions ; unless the conditions are such or the time sufficient for those small quantities to be formed, the NO_2 has little effect. The experiments which have

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[*]	Ignition point °C		Ignition point °C
Petrol	380	Petrol + 2 cc $PbEt_4$/gal.	484
,, + 5% acetaldehyde	366	,, ,, + 5% acetaldehyde	448
,, + 5% propionaldehyde . . .	364	,, ,, + 5% propionaldehyde	412
,, + 5% butyraldehyde	378	,, ,, + 5% butyraldehyde	442
,, + 5% valeraldehyde	380	,, ,, + 5% valeraldehyde	446
,, + 5% paraldehyde	340	,, ,, + 5% paraldehyde	438

The propionic aldehyde had a slight anti-knock effect, 10% valeric aldehyde was equivalent to 0·3 cc $PbEt_4$/gallon, 10% acetaldehyde and butyraldehyde did not influence the "knock" rating even in the presence of lead tetraethyl. But paraldehyde (and valeraldehyde) had a pronounced poisoning effect on the dope. Thus

Petrol + 10% paraldehyde + 2 cc $PbEt_4$/gall. = petrol + 0·4 cc $PbEt_4$ per gall.

Petrol + 1% paraldehyde + 2 cc $PbEt_4$/gall. = petrol + 1·5 cc $PbEt_4$ per gall.

As the content of paraldehyde increased, the relative "poisoning" effect on the lead tetraethyl decreased.

[†] Ubbelohde and Egerton, 'Nature,' vol. 135, p. 67 (1935).

been made on the effect of NO_2 on the ignition of hydrogen and oxygen mixtures (and of NH_3 and C_2N_2) and on methane and oxygen mixtures seem also to indicate that the behaviour of NO_2 cannot simply be the result of the production of more O atoms. Further investigation is here necessary; it is quite possible, for instance, that NO_2 might increase " knock " with methane as fuel, for the conditions could be made more drastic and more primitive radicals (OH, etc.) would then be in control. Nevertheless the fact that NO_2 by itself does not cause " knock," while OR radicals from organic nitrites and nitrates (*e.g.* ethyl nitrite and ethyl nitrate) do, is of interest, for it shows that the production of chain carriers as oxygen atoms is not the cause of the ignition phenomenon involved in " knock."

With hydrogen, however, nitrogen peroxide acts as a strong " pro-knock " ; in fact " knock " with this fuel is almost certainly due to NO_2 formed from the nitrogen of the air, for such inhibitors as lead tetraethyl had no effect in stopping it. Diethylperoxide also did not give rise to " knock " and amyl nitrite only in a very minor degree. Although the temperature conditions for ignition are somewhat different, these observations indicate that it is the intrinsic nature of the chain reactions in the " presensitization " period, which is the important point and not only the disruptibility of the sensitizer.

An important step in the study of ignition has been made by TOWNEND and his collaborators.* Instead of allowing the compressed fuel and air, separately introduced, to interdiffuse and ignite after an arbitrarily fixed period of delay, as did DIXON, they introduce the compressed gas already mixed into a heated vessel and determine the influence of pressure and composition of the mixture on the temperature of ignition. This is certainly more akin to engine conditions, but the time factor is very different. It takes a certain time for the gas to enter and to heat up, and ignition only occurs after a delay which may vary from 1 to 20 seconds or more. There is time for substances to be burnt and for substances to be formed which, under engine conditions, might disrupt or not be formed in sufficient amount to affect ignition. It is possibly for such reason that diethyl peroxide (0·5%) did not seem to change the ignition temperature of a pentane mixture in our experiments on ignition under pressure, whereas acetaldehyde, according to TOWNEND's observations, lowers the ignition point very markedly ; the diethyl peroxide undergoes combustion at the surface of the pressure vessel and is not exposed to the extreme conditions necessary for its disruption. Acetaldehyde undoubtedly forms acetyl peroxide during its photochemical oxidation† and also probably during its thermal oxidation.‡ In the engine, conditions are either such that it is burnt as fast as formed without disruption, or that the rate of formation is too low for an appreciable amount of aldehyde peroxide to be formed and stabilized in the time available, except at concentrations of aldehyde above 20%. In the ignition apparatus, however, the aldehyde peroxide may be formed and may influence the ignition ; in fact, it seems

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* ' Proc. Roy. Soc.,' A, vol. 141, p. 484 (1933) ; vol. 143, p. 168 (1934).

† BOWEN and TIETZ, ' J. Chem. Soc.,' p. 234 (1930).

‡ BODENSTEIN, ' Z. phys. Chem.,' B, vol. 12, p. 151 (1931).

probable that the lower range of ignition is mainly due to the formation of a small quantity of these peroxides, though the quantity may be very small.* It is necessary to point out at this stage that the quantity of disruptible peroxide to give rise to ignition may be exceedingly small and even indetectable ; for once a branched chain reaction is started explosion at once ensues. It is perhaps for this reason that the writer has not been able to detect a trace of " peroxide " in ignition experiments with pentane mixtures under pressure, although at ordinary pressures quite appreciable quantities were formed. However, the " peroxides " then appear to be mainly hydroxyalkyl peroxides and probably fairly stable products which are of minor importance to ignition.

In Part III it has been shown that peroxides are present in the gases sampled from the engine just prior to " knock " and reasons are given to show that they are not aldehyde peroxides and that aldehyde peroxides are not present in amount sufficient to detect. Reasons are also given for the contention that " knock " is associated with the presence of peroxides of the alkyl hydrogen type. But it is possible that the peroxides observed are similar to those obtained by MONDAIN MONVAL and QUANQUAIN, and by ourselves in the low-pressure ignition which in our experiments does not seem to be specially " knock " inducing. The actual peroxides or substances which give rise to ignition might be present in too small quantities to observe. The reasons against this interpretation are that only knocking fuels give rise to the peroxides, and only just prior to " knock," while the quantities were in accordance with the observation of the effect of knock-inducing peroxides. Further work is in hand to attempt to decide this difficult point.

It appears that the general characteristics of reaction of a straight chain paraffin are fairly similar.†‡ First a wall reaction sets in, measureable at quite low temperatures, 100° to 150° C, but apparently not extending into the gas appreciably, till suddenly between 200° and 300° C, at a certain " reacting temperature," reaction becomes rapid, extends by chains into the gas, and gives rise mainly to condensable products such as aldehydes which provide CO in their subsequent combustion and also gives rise to emission of light—in fact, cool flames become visible at this stage. As the temperature rises, this stage is succeeded by *slower* reactions, and less luminosity, until at considerably higher temperatures ignition finally takes place.

The reaction temperature stage is without doubt the same stage as leads to the low-temperature ignition range of TOWNEND, and to the cool flame region noted by many investigators. At the higher pressures of TOWNEND's experiments the chains are either protected from the chain-breaking influence of the walls so that reaction heat cannot be dissipated and ignition occurs, or products are formed which eventually disrupt and lead to a branched chain type of explosion.

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* The influence of lead tetraethyl on the ignition of aldehydes and the effect on the destruction of the knock effect of acetyl peroxide are in support of the view that the lower ignition range is connected with the formation of aldehydes and of their peroxides.

† PEASE, 'J. Amer. Chem. Soc.,' vol. 51, p. 1839 (1929).

‡ BEATTY and EDGAR, 'J. Amer. Chem. Soc.,' vol. 51, p. 1875 (1929) ; vol. 56, p. 102 (1934).

The former interpretation might be held to fit the character of the combustion process best, for, as required by SEMENOV's criterion for this type of combustion, $\log p/T = A/T + B$, where T is the temperature of ignition, and p the pressure ;* but the latter interpretation is more in accord with the influence on ignition of small quantities of substances, such as aldehydes, NO_2, etc. Most likely the phenomena are due to both causes, the final act of ignition being the disruption of certain molecules, probably " peroxides," which are formed during the course of the chain reactions and only a small amount of which exist for an appreciable time. Unless some such effect takes place, it would be difficult to explain on the purely thermal basis the negative temperature coefficient of the reaction at higher temperatures ; but if there is a temperature range over which certain products of the reaction are comparatively stable, while their life decreases again as the temperature rises, an explanation is possible. The higher ignition points then correspond to the normal ignition points which the hydrocarbons would have, if such products did not exist other than as links in the reaction chain.

In the " reaction temperature " stage, primary reacting molecules must be formed, either as the unsaturated residues of dehydrogenation†, or more likely as molecules nearly dissociated which at that moment are attacked by oxygen giving a complex (temporary peroxide) which immediately provides an aldehyde and water. The aldehyde is presumably active and goes through a series of reactions‡ propagating the chain, and presumably one of the chain carriers, $R - C \leqq O$, or whatever it may be, activates a further hydrocarbon molecule. As pointed out before, the process is autocatalytic.§

Owing to the marked effect of inhibitors on the aldehyde oxidation, one would expect firstly that this would be the stage at which the chain would be broken, and secondly that the knock would be due to a product (such as peroxide) of this part of the combustion process. But this has yet to be reconciled with the facts which have been set out in this discussion and with the further facts, that hydrocarbons such as heptene (or even alcohols), although they give rise to aldehydes, do not readily knock, and that the concentration of aldehydes at t.d.c. for hexane which knocks and cyclohexane which does not knock were found to be very much the same. Perhaps this may be due to a difference in the activity of the aldehyde molecules which have to propagate the chain, but it is possible that the " knock " may be due to disruption of a peroxide of the ethyl hydrogen type stabilized from the earliest stage of combustion and which can, like the aldehyde products, be destroyed by " anti-knocks," and in that case it is likely enough to be that which has been found.

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* SAGULIN, 'Z. phys. Chem.,' B, vol. 1, p. 275 (1928) and BURKE, FRYLING, and SCHUMANN, 'J. Ind. Eng. chem.,' vol. 24, p. 804 (1932).

† No absorption bands corresponding to those unsaturated residues were noticed in previous work (EGERTON and PIDGEON, *loc. cit.*), nor do those substances which give hydrogen easily (cyclohexane, etc.) ignite most easily.

‡ *Cf.* BODENSTEIN *loc. cit.* and BACKSTRÖM, ' Z. phys.-Chem.,' B, vol. 25, p. 99 (1934).

§ EGERTON and GATES, ' Rep. Aero. Res. Comm.,' London, 1079 (Dec. 1926).

From this brief discussion of the interesting phenonema connected with knocking explosions, it is evident that there still remains a number of difficulties associated particularly with the details of the combustion of hydrocarbons.

To Professor R. V. Southwell, F.R.S., we are greatly indebted for the facilities provided in the Engineering Department, Oxford University, and to the Anglo-American Company, whose gift of the engine enabled this work to be carried out. We wish also to acknowledge gratefully receipt of grants from the Air Ministry and the Department of Scientific and Industrial Research. Mr. G. L. Barrett's assistance, particularly in the construction of the valve mechanism, was invaluable.

VI—GENERAL SUMMARY

In the first part a method of sampling the gases from the cylinder of a petrol engine at any stage during the compression and working strokes is described. The sampling valve could be opened and closed over a small angle (about 2°). Analyses of the gases for CO_2, CO, O_2 and H_2 were made and the results given in a series of curves for the fuels Shell petrol, with and without ethyl fluid, and commercial benzole. From these results, it was deduced that " knock " is associated with an accelerated flame velocity, but only in the last portion of the gases to burn, confirming the conclusions of various other investigators (*see* Introduction). It was also shown that some combustion of the charge occurs in the neighbourhood of the hot valves prior to the arrival of flame. Aldehydes reach their maximum concentration (about 1 in 150) at the moment when the flame reaches the valve, but " peroxides " (substances oxidizing potassium iodide) appeared to reach a maximum (about 1 in 7000) prior to this (about t.d.c. $-$ 7°) and thereafter decrease, giving a peak in the curve of concentration against crank angle. This peroxide maximum was greater for knocking explosions, and with benzole practically no " peroxide " was detected. Aldehydes were not responsible for the production of these " peroxides " nor for the " knock." Addition of hydrogen reduced the amount of " knock."

In the second part, it has been shown by experimenting with various pure fuels that the " peroxides " were mainly nitrogen peroxide and that the peak in the curve was due partly to the simultaneous production of sulphur dioxide and partly to the lack of oxygen to oxidize the nitric oxide produced. Pure benzene was found to give rise to " peroxides." The effect of nitrogen peroxide on knocking was examined; the quantity formed increases when " knock " occurs, but with a hydrocarbon fuel it did not induce knocking. It was also shown that the organic radical and not nitrogen peroxide obtained from the decomposition of amyl nitrite is the effective pro-knock. With hydrogen, " knock " was induced by nitrogen peroxide. The source of the nitrogen peroxide formed in the combustion process in the engine prior to arrival of flame is discussed, further investigation being needed to settle the various possibilities. The quantity of aldehyde and acids formed was also determined, and

it was shown that except at the maximum, the aldehydes were mainly formaldehyde. Very little organic acid is present, such acids as are formed being mainly strong acids.

In the third part of the investigation, a study of the tests for organic peroxides of various kinds was made and a method worked out for their detection in presence of excess of nitrogen peroxide. It was shown that a small quantity of organic peroxide behaving as a hydro (or hydroxy) alkyl peroxide was detectable near t.d.c. using pure paraffinic fuels. The quantity was sufficient to account for the amount of " knock," which a similar organic peroxide would produce. Experiments were made which showed that the aldehyde peroxides which also give rise to " knock," do not account for the organic peroxide detected.

In the fourth part it is shown that the vapours of thallium and potassium are more effective as " anti-knocks " than even lead tetraethyl, and that they act as oxides ; experiments on the behaviour of " anti-knocks " are described which support the former conclusions of EGERTON and GATES, that the oxides have to be capable of being oxidized to a higher state of oxidation.

A general discussion of the points raised in this investigation with their bearing on ignition and combustion is given in Part V, so as to bring together the pertinent experimental observations made during the course of this work, and that of other investigations.

It is pointed out that the phenomenon called " knocking " is due to a special type of combustion occurring in a small portion of the charge in an engine cylinder which has undergone "presensitization"; in other words substances have been formed by preliminary and partial combustion in certain regions ; these substances subsequently disrupt and give rise to sudden explosion probably owing to a branch chain type of reaction. Organic peroxides, organic nitrites, and nitrogen peroxide, etc., do not have similiar action in inducing ignition and in causing " knock" in various mixtures. It is suggested, therefore, that their effect is not simply due to oxygen atoms formed by their decomposition, but to the production of other radicals, which are essential to the propagation of chains and which may give rise to branching of the chains, and so to explosive ignition. The general character of hydrocarbon combustion is very briefly reviewed and is held to be consistent with the view that certain products such as aldehyde peroxides are formed, disruption of which may give rise to the lower ignition range. But it is also possible that alkyl hydrogen peroxides may be stabilized from the first step in the combustion process and become detectable as the experiments described in Part III indicated. It remains to prove, however, that the "peroxides" there detected were not merely certain hydroxyperoxides which when isolated as products in the combustion of hydrocarbons at ordinary pressure are substances which do not give rise to intense knocking.