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SPONTANEOUS IGNITION OF LIQUID FUELS

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AGARDograph No. 4

SPONTANEOUS IGNITION
OF LIQUID FUELS

TO
MY WIFE

SPONTANEOUS IGNITION OF LIQUID FUELS

By

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PREFACE

THIS AGARDograph was written at the request of the Combustion Panel, Advisory Group for Aeronautical Research and Development within the North Atlantic Treaty Organization and was sponsored by them with funds made available by the United States Air Force under Contract No. AF 18(600)-972. It is essentially a review and assessment of the state of knowledge in one area of the combustion field, but it should serve in addition as a sourcebook of the great amount of experimental information on spontaneous ignition published in the scientific literature during the present century.

The spontaneous ignition temperature of a combustible is not an absolute property and all spontaneous ignition data need to be interpreted carefully in the light of the conditions of the test methods by which they were obtained. Hence the various test methods were classified under eight main headings and have been described in some detail, frequently with the aid of a line diagram. These descriptions, together with accounts of the work undertaken with the various apparatuses, form the substance of eight chapters.

Spontaneous ignition temperature data is presented in Chapter 11 (pages 61 to 72) for 433 substances arranged in alphabetical order and comprises more than 900 entries. Other chapters deal with general theoretical considerations, fuel additives and applications of spontaneous ignition data.

I wish to record my deep indebtedness to Mr. P. Lloyd, M.A., F.R.I.C., Deputy Director, N.G.T.E., British Ministry of Supply, for many stimulating discussions on combustion in general and spontaneous ignition in particular during the ten years that I have been associated with him and out of which has grown my general approach to combustion science as well as many of the views expressed in this AGARDograph. I wish also to thank Mrs. M. F. Mullins, M.A., for assistance in preparing the line diagrams. Acknowledgement is made to the Chief Scientist, British Ministry of Supply, for permission to publish this book.

B. P. M.

Farnborough, Hants,
England

November, 1954

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LIST OF MATHEMATICAL SYMBOLS

- a, A, A'' = constants
 A' = a constant called the 'frequency factor'
 \bar{A} = cross-sectional area of duct
 b' = number of oxygen bubbles per minute
 b, B = constants
 C = heat of reaction per unit weight of fuel
 C_N = cetane number
 C_p = specific heat at constant pressure
 γ = ratio of specific heats of gas at constant pressure and constant volume
 d = sphere diameter
 D = internal diameter of parallel-sided duct leading to the diffuser
 D' = rod diameter
 e = exponential number
 \exp = exponential function
 E = activation energy
 \bar{E} = average energy of all molecules in the system with energy greater than E
 G = a constant for a given fuel, which includes the heat of reaction
 h = heat transfer coefficient from the solid sphere to the gas
I.V.F. = Jentzsch's ignition value factor
 K = reaction velocity constant
 K' = a constant
 \ln = natural logarithm
 n = number of energy terms representable by 'square terms'
 O_N = octane number
 p_E = ether partial pressure
 p_N = nitrogen partial pressure
 p_O = oxygen partial pressure
 P = pressure
 P_s = standard atmospheric pressure
 P' = probability or steric factor
 π = 3.1416
 q = fuel/air ratio (by wt.)
 q' = fuel/air ratio (by wt.) initially present
 Q = air weight flow rate before the slave combustion chamber
 r = sphere radius
 R = molar gas constant
 t = time
 T = temperature or ignition temperature
 T_θ = temperature of gases at a distance remote from the spherical surface or rod
 T_1 = temperature of gases initially

LIST OF MATHEMATICAL SYMBOLS

- T_h = higher ignition temperature
 T_s = temperature of gases in immediate proximity of the spherical surface or rod
 τ = ignition delay
 τ_x = time taken for the moving gas stream to traverse a distance x along the diffuser
 θ = slant angle of diffuser
 \bar{u} = root mean square velocity
 \bar{U} = average energy of all molecules in the system
 V_{\max} = maximum velocity at which combustion is stable close to the rod
 x = distance of flame front from the face of the diffuser entry flange, measured axially downstream
 Z = collision number
 Z' = Jentzsch's ignition value
 ∞ = infinity

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- 18 N.G.T.E. 3° rig mathematical notation

LIST OF ABBREVIATIONS

- A.G.A.R.D. = Advisory Group for Aeronautical Research and Development
A.I.T. = Auto-ignition temperature
A.S.T.M. = American Society for Testing Materials
C.I.T. = Critical inflexion temperature
I.D. = Internal diameter
M.I.T. = Massachusetts Institute of Technology, U.S.A.
O.N.E.R.A. = l'Office National d'Etudes et de Recherches A ronautiques, France
N.G.T.E. = National Gas Turbine Establishment, United Kingdom
R.A.E. = Royal Aircraft Establishment, United Kingdom
S.I.P. = Self-ignition point
S.I.T. = Spontaneous ignition temperature
U.O.P. = Universal Oil Products Co., U.S.A.

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Figures have been taken from the following sources and the author wishes to thank the authors and publishers of the papers concerned for granting permission to reproduce.

- Fig. 1(a) D. T. A. Townend and M. Maccormac. Institute of Petroleum
- Fig. 1(b) M. Maccormac and D. T. A. Townend. The Chemical Society
- Fig. 5 H. Moore. 'Liquid Fuels—their manufacture, properties, utilisation and analysis.' Technical Press, London (1935)
- Fig. 6 A. W. Nash and D. A. Howes. 'The principles of motor fuel preparation and application.' Vol. II, Chapman and Hall, London (1935)
- Fig. 7 J. L. Chaloner. Institute of Petroleum
- Fig. 8 J. L. Jackson. National Advisory Committee for Aeronautics
- Fig. 9 C. E. Frank and A. U. Blackham. National Advisory Committee for Aeronautics
- Fig. 10 J. L. Chaloner. Institute of Petroleum
- Fig. 11 N. J. Thompson. Industrial and Engineering Chemistry
- Fig. 12 N. J. Thompson. Industrial and Engineering Chemistry
- Fig. 14 W. A. Leary, *et al.* National Advisory Committee for Aeronautics
- Fig. 15 H. F. Coward. The Chemical Society

INTRODUCTION

THIS AGARDOGRAPH is a survey and review of the present status of knowledge in that area of the combustion field concerned with spontaneous ignition. It deals with the spontaneous ignition of combustibles that are liquid at normal temperature and pressure; the title should not be interpreted absolutely literally, therefore, but in this sense, for so far as is known fuels that ignite in an atmosphere containing some oxygen, first vaporize and then burn in the gaseous phase. Liquid phase reactions are believed to take place during the ignition of bipropellant mixtures as used in rockets, but this represents only a minor region of the subject under review.

In the first instance, some of the characteristic phenomena that are observed experimentally when combustibles are heated in the presence of an oxidizing atmosphere (generally, air or oxygen) under various conditions, will be described. This is necessary before any theoretical discussion can be made as the field of combustion, involving as it does many novel and totally unpredictable* phenomena, is one in which theory normally follows in the wake of experiment. In other words, the chemical steps involved in ignition reactions are so complex that, at best, a theoretical treatment can aim at co-ordinating a number of existing experimental data into a coherent scheme. Very rarely is theory able to predict very far into the experimental sphere and when it does it is always necessary to perform the confirmatory experiments to consolidate the position.

The earliest determinations of the spontaneous ignition temperature of a fuel were undertaken in 1906 by FALK⁷⁹ at the suggestion of Nernst; a rapid adiabatic compression apparatus was used with cylinder diameters ranging from 1 to 2 in. Cylinder pressures were not measured directly and this apparatus gave no evidence of the phenomenon of ignition delay which was first clearly recognized by Dixon and co-workers some eight years later. In 1914 DIXON, BRADSHAW and CAMPBELL⁵⁵ carried out adiabatic compression experiments with stout glass tubes so arranged that the flame was photographed on a rapidly moving film. They recognized the existence of a 'pre-flame period' which is nowadays referred to as a 'delay period' or 'delay'.

* Unpredictable not merely because of lack of development of the theory, but from the very nature of the complexities involved. For example, by the time there is amassed sufficient theoretical knowledge to 'predict' cool-flame phenomena, the phenomena of current interest will be entirely new and different—and unpredictable.

INTRODUCTION

Another method, the so-called 'heated crucible method' of measuring ignition temperatures was used in an elementary form by HOLM¹²³ in 1913 and is especially suitable for liquid fuels. By allowing drops of the fuel to fall upon a heated porcelain surface, the temperature of which was measured by a thermocouple, the ignition temperatures in air at atmospheric pressure were determined for a number of common fuels.

During the past forty years developments of these two methods and many others have been employed in many countries to measure ignition temperatures of liquid fuels. Countries which have published extensively in this area of investigation include France, Germany, Japan, Russia, United Kingdom and United States.

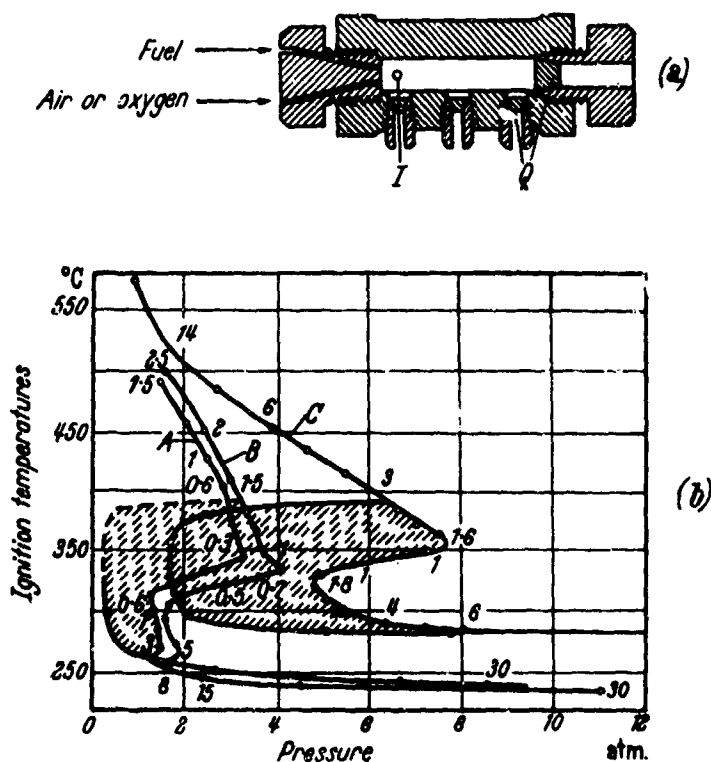
A description of these various methods will be given in the following chapters together with a summary of the test results obtained and a discussion of their relevance and application in aircraft combustion engineering. It is remarkable how little changed are the early methods of test that are in use today; it is thus relevant to describe in some detail such methods as those associated with the name of H. Moore and the name of H. Jentzsch notwithstanding the fact that these methods originated some thirty years ago.

The aeronautical applications of spontaneous ignition data include the spark-ignition engine, the aero-gas turbine, the rocket and the pulse jet. Although the compression-ignition engine is not employed in aircraft applications (other than model aircraft) it is desirable to include this in the present survey on account of the correlations that are found to exist between ignition delay, octane numbers and cetane numbers, and the analogies or contrasts that occur between the combustion mechanisms of these different prime movers.

It is now known that the ignition of most hydrocarbons, and indeed of many other combustibles in air or oxygen, is a two-stage process. In 1919, White discovered that with ether-air mixtures in a 2.5 cm diameter horizontal glass tube there were two independent ranges of inflammability, one for normal flames (1.88–9.45 per cent) and another for cool flames (19.0–34 per cent) separated by a range of mixtures which were incapable of flame propagation³²⁴. The normal flame range could be determined by spark ignition but the cool flames were only initiated at atmospheric pressure by means of a heated wire and using rich mixtures. Later White explored these two ranges at reduced pressures in a 4.5 cm tube and discovered that there were two separate systems for each type of flame propagation which were linked together at about 600 mm pressure³²⁵. TOWNEND and CHAMBERLAIN³²⁶ recognized a close analogy between White's observations in regard to the cool-flame ranges at room temperature and their own observations in spontaneous ignition experiments under pressure and examined the cool-flame propagation in cold media more closely, particularly to find out whether at higher pressures the cool flames would give rise to

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normal ignition. This anticipation was fulfilled and they reported in collaboration with HsIEH¹²⁵ furthermore, that at an adequate pressure which was very critical, ignition occurred as a second-stage event in the combustion products behind the cool-flame front. Further work proved that the establishment of such a two-stage process in this way is the same phenomenon whether the cool flames were ignited spontaneously in a heated vessel or artificially by a hot wire in a cold vessel, the crucial



I = ignition plug. Q = quartz windows.

Fig. 1 (a). Townend and Maccormac's explosion vessel fitted with windows for determining inflammable ranges under pressure

Curve A = *n*-octane-air mixtures. Curve B = *n*-heptane-air mixtures. Curve C = *iso*-octane-air mixtures. Figures along curves denote time lags in seconds. Shaded areas represent cool-flame regions.

Fig. 1 (b). Ignition temperature v. pressure diagrams for *n*-octane, *n*-heptane and *iso*-octane (after Maccormac and Townend)

difference being that in a given case a much higher pressure was necessary to cause ignition in the cold than in the heated media.

Much of the now classic work of Townend and his collaborators made in this field between 1930 and 1940 was carried out upon hydrocarbons and is reported and summarized in references^{179, 320 and 315}. A diagram of the explosion vessel used in this work and a typical set of results for *n*-octane, *n*-heptane and *iso*-octane (2,2,4-trimethylpentane) mixtures with air is shown in Fig. 1. The shaded areas represent cool-flame regions and the numerals on the curves are ignition delay times in seconds.

INTRODUCTION

The cool flame, so-called because it is not accompanied by a large heat release, has a spectrum containing bands identical with those due to activated formaldehyde, first discovered by Emeleus in the cool flame of ether ⁷⁷. Reproductions of this spectrum are to be found in references ⁹⁵ and ²⁰⁵, together with the spectra of the hotter flames formed at higher mixture temperatures. By 1946 the only two hydrocarbons which had not exhibited any cool-flame phenomena were methane and benzene. Since then cool flames of benzene have been noted by SOKOLIK, GEN and YANTOVSKII ²⁸¹ and by MULLINS ²¹².

Many combustionists have confirmed the two-stage ^{92, 251, 284} or even three-stage ²⁰⁵ nature of ignition processes and some have reported the formation of various special types of flame such as blue flames ^{180, 310, 205} and green flames.

In view of these complications, and, furthermore, the existence of temperature zones of non-ignition at temperatures above that at which ignition is known to occur ^{283, 47, 137}, it is not surprising that it is very difficult to define an 'ignition temperature' of a fuel-oxidant mixture even under fixed experimental conditions. The criterion that is usually taken to indicate ignition is quite subjective as is exemplified by the recent work of CARHART, CRELLIN and JOHNSON ³³ who, writing in 1952, defined ignition as a visible and/or audible combustion observed under ordinary laboratory conditions. Last December, FRIEDMAN ⁹³ pointed out the difficulty of defining an ignition point ahead of a laminar flame front as that point at which the measured temperature exceeds a theoretical temperature based on the assumption of no heat release. Fundamentally such an objective definition is straightforward, but in practice the definition is not precise enough, as not only are present temperature traverse determinations insufficiently accurate, but also much more accurate knowledge of thermal conductivities of the reacting media at elevated temperatures is required.

Other factors have also emerged that have complicated the task of defining an absolute ignition temperature. These are that in addition to fuel composition and mixture strength, ignition temperatures depend always upon the delay time employed and frequently also upon the static pressure, the shape and volume of the measuring apparatus, the oxygen concentration in the 'atmosphere' used, and the presence or absence of solid surfaces, additives in the fuel or atmosphere and light.

These matters will be surveyed, reviewed and summarized in the following chapters, but first let us review the general theoretical approaches that have been made to the subject of spontaneous ignition.

GENERAL THEORETICAL CONSIDERATIONS

1. ACTIVATION ENERGY AND THE ARRHENIUS EQUATION

THE most satisfactory method for expressing the influence of temperature on chemical reaction velocity is that used by ARRHENIUS ², viz.:

$$\frac{d \ln K}{dT} = \frac{E}{RT^2} \quad \dots (1)$$

or its integrated form

$$\ln K = -\frac{E}{RT} + \text{const.} \quad \dots (2)$$

which may be re-written as:

$$K = A'e^{-\frac{E}{RT}} \quad \dots (3)$$

This equation requires the plot of $\ln K$ or $\log K$ against $(1/T)$ to be a straight line, a relationship which has been found to hold for many homogeneous and heterogeneous chemical reactions. The quantity E , the activation energy, may be determined from measurements of the specific rate, K , at two or more temperatures; E is then obtained from the slope of the straight line which is $(-E/R)$.

Arrhenius suggested that a chemical explanation of these equations was that as the temperature of the reactants increased heat is absorbed by normal molecules converting them into active molecules. Only the latter, he supposed, were capable of taking part in chemical reaction. This explains the large influence of temperature on reaction velocity, for although the number of molecular collisions is only slightly altered, the concentration of active molecules may be doubled by a 10° rise of temperature. In fact, the kinetic theory of gases suggests that the probability that a molecule will possess energy in excess of an amount E per mole, at the temperature T , is proportional to $e^{-E/(RT)}$, where R is the molar gas constant. If the energy is restricted to two 'square terms' (for example, in two translational components for one molecule, or in one component for each of two molecules taking part in reaction) the fraction of molecules having energy in excess of E is actually $e^{-E/(RT)}$.

If time t is required for a definite fraction of the reaction to be completed, e.g. as assessed by the fraction of initial reactants disappearing, then $t \propto 1/K$ and equation 3 may be written:

$$t = A''e^{\frac{E}{RT}} \quad \dots (4)$$

If now we assume that during the induction period for a fuel-oxidant reaction the ignition delay, τ , may be taken to represent a given

GENERAL THEORETICAL CONSIDERATIONS

fractional completion of the reaction for the given mixture at a given pressure, then equation 4 may be written as:

$$\tau = Ae^{\frac{E}{RT}} \quad \dots (5)$$

Owing to the subjective and indefinite nature of the criterion by which τ is estimated (see Chapter 1) it is unlikely that this assumption is very accurate. However, for many homogeneous fuel-oxidant induction reactions the relation expressed by equation 5 holds. We shall refer to equation 5 in this monograph as the Arrhenius Equation.

There are other possible complications. Four will be mentioned briefly, the first three having been discussed fully by HINSHELWOOD¹²⁰.

(i) Activation of Molecules with Many Degrees of Freedom

The probability factor $e^{-E/(RT)}$ previously referred to is only applicable to the case of energy E restricted to two 'square terms'. As an approximation it may be used for any small number of terms. Rigorously, however, for a bimolecular colliding system the fraction of such systems which possess energy greater than E in n 'square terms' is:

$$\frac{1}{(\frac{1}{2}n - 1)!(RT)^{\frac{1}{2}n}} \int_E^\infty e^{-\frac{E}{RT}} E^{\frac{1}{2}n - 1} dE \quad \dots (6)$$

Using this it may be shown that the really correct form of equation 1 is:

$$\frac{d \ln K}{dT} = \frac{\bar{E} - \bar{U}}{RT^2} \quad \dots (7)$$

When n is small \bar{E} and $\bar{E} - \bar{U}$ are very nearly equal³⁰⁹.

(ii) Reactions Depending on Molecular Collisions at High Temperature

For a collisional reaction the following equation applies:

$$K = \text{const.} \bar{u} e^{-\frac{E}{RT}} \quad \dots (8)$$

The term \bar{u} varies as \sqrt{T} and though this temperature dependence is much less than that of the exponential term, it should strictly be allowed for. With this refinement equation 1 becomes:

$$\frac{d \ln K}{dT} = \frac{E + \frac{1}{2}RT}{RT^2} \quad \dots (9)$$

MULLINS³⁰⁸ has shown that, in the case of the kerosine-air induction reactions, ignoring this $\frac{1}{2}RT$ term causes no noticeable departure from linearity when $\log \tau$ is plotted versus reciprocal absolute temperature instead of the formally correct $\log (\tau \cdot \sqrt{T})$ versus reciprocal absolute temperature.

FREQUENCY FACTOR

(iii) *Variation of Activation Energy with Temperature*

Since heat of reaction is the difference of the activation energies of the direct and reverse reactions, it follows that, in principle, \bar{E} is temperature-variable also. In practice, however, the variation for a given reaction amounts to only a few per cent.

(iv) *Variation of Activation Energy During an Induction Period for Chemical Reasons*

The chemical reactions that occur during the induction period when a hydrocarbon such as *iso*-octane is mixed with air or oxygen are very complex and far from completely known. It may well be that during this slow but critical self-heating period the nature of the bond-breaking reactions that occur at, say, 300° C differ entirely from those occurring at 500° C and 800° C (assuming that ignition occurs at a higher temperature than 800° C for the purposes of this illustration). If this is so, then clearly the implicit assumption that E is fixed which is implied by the very use of the Arrhenius equation, is incorrect. The magnitude of the change in E during the induction period cannot be calculated in any given case because of the aforementioned complexities. This uncertainty serves however to underline the fact that we must not place any simple chemical interpretation upon the E values calculated from the slopes of Arrhenius curves but must merely regard them as overall or global values which take into account many separate chemical reaction steps. Interpreted thus they may be of great value in chemical engineering calculations involving combustion processes. These considerations also serve to show how futile would be any attempts to calculate E values for other than the simplest of reactions for which the chemistry and kinetics were reasonably well established.

2. FREQUENCY FACTOR

The term A' in equation 3 has been called the 'frequency factor'^{101, 102}. It may be regarded as the product $P'Z$ where Z is the appropriate collision number and P' is a 'probability' or 'steric' factor which is a measure of the deviation of an actual reaction from the idealized behaviour based on simple collision theory.* With a few exceptions P' usually is of magnitude 0.1 to 1.0. The term A in our Arrhenius equation (eq. 5) is of course nominally the reciprocal of A' .

In a critical survey⁴⁸ of 28 unimolecular gas-phase reactions reported in the literature between 1936 and 1941 Daniels found that the value of A' was between 10^{12} and 10^{14} in 60 per cent of the reactions. It should also be pointed out that A' (and therefore A in the Arrhenius equation) is slightly temperature dependent²⁸⁰.

* Or, as HINCHELWOOD¹⁸¹ puts it, the probability that other conditions beyond mere propinquity must be fulfilled.

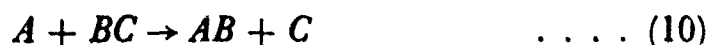
GENERAL THEORETICAL CONSIDERATIONS

3. CALCULATION OF ACTIVATION ENERGIES

This is not the place to describe at length the theory of rate processes which has been well described in many text-books. It is sufficient to mention one or two results only that have a bearing upon the present subject; this connection mainly arises through the fact that some spontaneous ignition processes consist of simple thermal decomposition reactions (e.g. organic nitrates).

POLANYI, EYRING and their collaborators¹⁰² have done much work on the *a priori* estimation of reaction rates and activation energies on a quantum mechanical basis. Although this research has been of very great value and importance in providing a consistent fundamental basis for chemical kinetics, the method is semi-empirical in its application to specific reactions. Because of the drastic approximations that have to be made, especially when polyatomic reactants are involved, the results are highly approximate and do not yield useful values of activation energies.

From the practical viewpoint therefore, an approximate working rule such as that stated by HIRSCHFELDER and BOYD¹²² may be of more value. These writers point out that the activation energy may be closely related to the electronic structure of the reacting molecules. For example, if the reaction



is written in the endothermic direction, the activation energy is approximately 5.5 per cent of the strength of the bond between *B* and *C*.

If the reaction



is written in the exothermic direction the activation energy is approximately 28 per cent of the energy of the bond *AB* plus 28 per cent of the energy of the bond *CD*. These bond strengths are known accurately from thermochemical data²³⁴.

4. THERMAL THEORY

The thermal theory of spontaneous ignition reactions is based upon the classical views of Arrhenius concerning chemical reaction rates which have been described above. According to this idea the rate of slow combustion is controlled by the number of molecules whose energy exceeds the required activation energy, *E*, this number being proportional to $e^{-E/(RT)}$. The ignition temperature is thus regarded as that temperature to which the mixture must be raised so that the heat lost from the system is more than counterbalanced by the rate at which it is evolved by chemical reaction, the temperature rising until ignition occurs and a flame appears.

SEMENOV gave an exact formulation of the thermal theory of ignition²⁷². He assumed that heat conduction was the only significant mode

THERMAL THEORY

of loss of heat from a homogeneous reaction system, and gave numerical solutions for plane, cylindrical and spherical vessels. He devised a relationship between ignition delay and temperature at constant pressure which is identical with the integrated form of equation 5 viz.:

$$\ln \tau = \frac{E}{RT} + \text{const.} \quad \dots (12)$$

and showed that the relation connecting delay time and pressure, P , at constant temperature, is:

$$\ln \tau = \text{const.} - n \ln P \quad \dots (13)$$

where n is a positive constant.

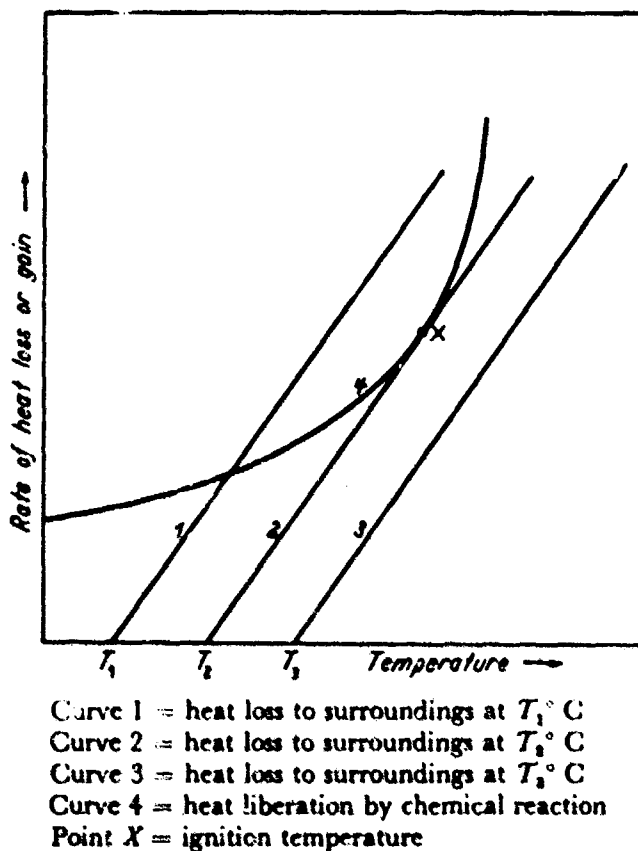


Fig. 2. Thermal theory of ignition temperatures

This thermal theory may be simply illustrated as in Fig. 2 which is based on one originally presented by Semenov. Point X represents conditions at the ignition temperature.

A more rigorous theory of thermal explosion, based on Semenov's work, was developed by TODES³⁰⁸ and by FRANK-KAMENETSKII⁹⁰ and this indicated the possibility of computing spontaneous ignition temperatures at various pressures under very precisely defined thermal conditions for very simple types of chemical reaction.

Successful though this theory has been, many phenomena are known which have invalidated the universal acceptance of this simple view. Examples are: the critical influences of diluents, inhibitors and promoters on ignition (e.g. NO_2 , H_2O); the observation of abrupt

GENERAL THEORETICAL CONSIDERATIONS

transitions from slow reaction to explosion with variation in temperature or pressure; the observed decrease in reaction rate of certain fuels with air with increasing temperature. For these reasons the chain theory of ignition arose.

5. CHAIN THEORY

Chemical changes in flames and in the induction zones leading to flames are believed to take place by what are known as chain reactions. The essential idea is that one of the products of a series or chain of reactions is capable of attacking one of the initial reactants to start the chain again. Such a product is termed a chain carrier. At first these

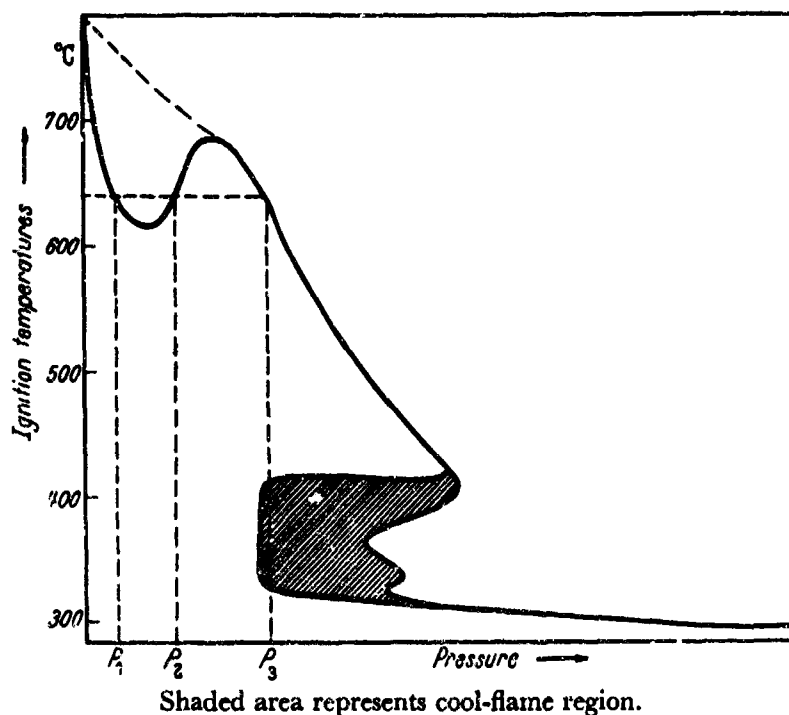


Fig. 3. Comprehensive ignition temperature v. pressure diagram

chain carriers were thought to be energized molecules but the discovery of 'photo-sensitization' of combustion reactions led to the view that they were probably atoms or free radicals²²⁵ and subsequent work has fully confirmed this. The reaction rate is thus controlled by the rate of increase of chain carriers (or active centres). The latter is not simply a temperature function but depends very much upon diffusion and collision processes. Typical phenomena are summarized in Fig. 3, which is a Pressure v. Ignition Temperature diagram of a type which has been well substantiated for CO, H₂, CS₂, PH₃, C₂H₆, C₃H₈ mixtures with air and probably occurs with most higher paraffins, olefines and other hydrocarbons, alcohols, aldehydes etc.

In Fig. 3, the upper explosion peninsula indicated in the temperature region 600–700° C indicates that a hypothetical explosive mixture may be ignited if admitted to an evacuated vessel maintained at 650° C provided the pressure exceeds P_1 mm mercury. This is the *lower ignition*

limit I. If the experimental pressure be raised, however, ignition will occur until P_2 , the *upper ignition limit II* is reached above which it will not occur. At some still higher pressure P_3 located in the super-atmospheric region, a *third ignition limit III* may be found, above which ignition will once again be possible. Outside certain ranges of mixture composition, the low-pressure ignition limits no longer exist and the ignition curve may then be smooth (see dotted line). In the high-pressure region the shape of the curve depends upon the composition of the fuel. The graph indicated in *Fig. 3* is representative of paraffin hydrocarbons with three or more carbon atoms, the shaded area depicting cool-flame formation. Corresponding naphthenes and olefines behave in a similar way but higher pressures are usually required for ignition.

In general terms, ignition limit I may be attributed to the critical diffusion of chain carriers to the walls of the reaction vessel with consequent chain breaking; ignition limit II may be ascribed to gas phase chain breaking reactions (due to collisions) whilst ignition limit III may be due to the intervention of a new type of collision process (e.g. three body) which continues the chain reaction and reduces diffusion of chain carriers to the walls.

In hydrogen, moist carbon monoxide, and hydrocarbon oxidation reactions the important chain carriers are known to be H atoms, O atoms, OH and HO_2 radicals. If one chain carrier reacts with another substance (atom, molecule or radical) to produce more than one chain carrier this process is known as Chain Branching and has been shown to lead to a rapid increase in the reaction rate (explosion).

The present status of this branch of the subject is that it is believed that the low-temperature ignition processes occur by the chain mechanism, whereas in the high-temperature region, both the thermal and the chain theories of ignition are capable of explaining, qualitatively, the experimental data.

Between 1930 and 1935, HINSHELWOOD¹²⁰, PRETTRE²⁵⁰, SEMENOV²⁷² and others laid the foundation of and developed the theory of chain reactions. In particular, Semenov calculated that the condition for explosion could be represented in the form

$$\tau P^n = A e^{\frac{E}{RT}} \quad \dots \dots (14)$$

or

$$\tau \left(\frac{P}{T} \right)^n = A e^{\frac{E}{RT}} \quad \dots \dots (15)$$

The former if it is assumed that the length of the chain and the reaction rate is determined by the pressure, and the latter if they are determined by the density of the reacting gases. Equation 14 is often referred to as Semenov's equation, and represents the relationship between all three quantities—ignition delay, pressure and temperature. In these calculations it is assumed that the reaction accelerates isothermally to the

GENERAL THEORETICAL CONSIDERATIONS

moment of ignition; this is not correct as in practice any increase in reaction rate is accompanied by some rise of temperature. A precise theory should take account of this.

Two objections to the free-radical theory of chemical reactions were elegantly overcome by Rice and Herzfeld. Not only must the theory account for the products of organic decompositions, but also for the kinetics of such processes. Experimentally it has been established that the majority of organic decomposition reactions follow a first-order rate law and the theory must therefore answer two questions: (a) If the measured process is really the summation of a complex series of reaction steps, how is it that the overall reaction follows a first-order rate law? (b) If, as is postulated, most reactions occur by the breaking of a C—C bond, how is it that experimental activation energies for decomposition reactions are usually much smaller than the strength of this bond? RICE and HERZFELD²⁵⁵ answered these questions by devising free-radical mechanisms that led to a first-order rate; further, by a suitable choice of the activation energies of the various reaction steps, the global activation energy of the overall reaction could be made to agree with the experimental value. STEACIE²⁸⁸ concludes that free radicals play some part in the decomposition of many organic substances, but the importance of their role is still uncertain.

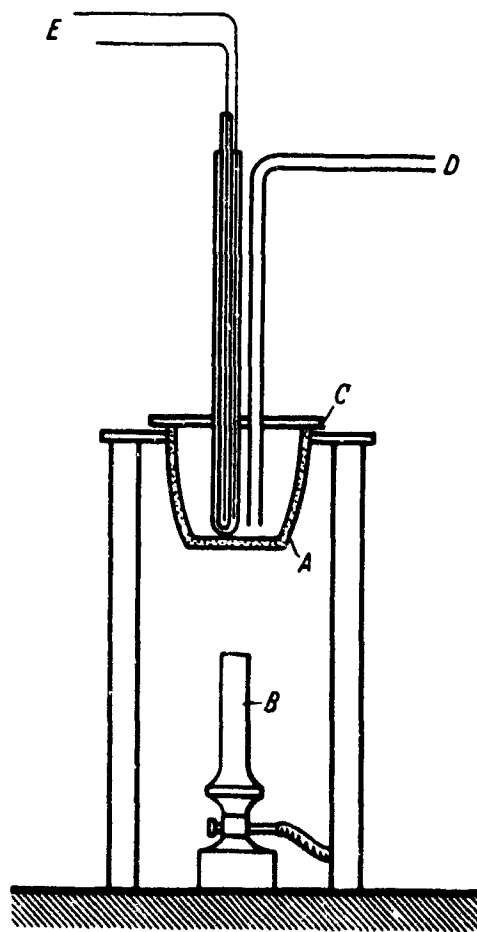
RICE, ALLEN and CAMPBELL²⁵⁴ have studied the decomposition of azomethane and ethyl azide and attempted to derive the ignition delay time by means of a simple thermal theory during which they set up an equation giving the amount by which the temperature of the reacting gas exceeds that of its container as a function of time. The differential equation which they obtained could not be integrated analytically but was solved numerically by the use of the Runge-Kutta formula. The method is described by the authors themselves as only an approximation.

MOORE'S HEATED CRUCIBLE METHOD

MOORE²⁰¹ defined the spontaneous ignition temperature (S.I.T.) of a fuel as that temperature at which it would ignite without the assistance of a flame or spark; although he did not say so, he implied that the S.I.T. is the minimum temperature at which this ignition occurs. He

A = platinum crucible packed round with ignited sand. *B* = gas burner. *C* = asbestos lid. *D* = oxygen feed tube. *E* = platinum-rhodium thermocouple wires connected to a galvanometer.

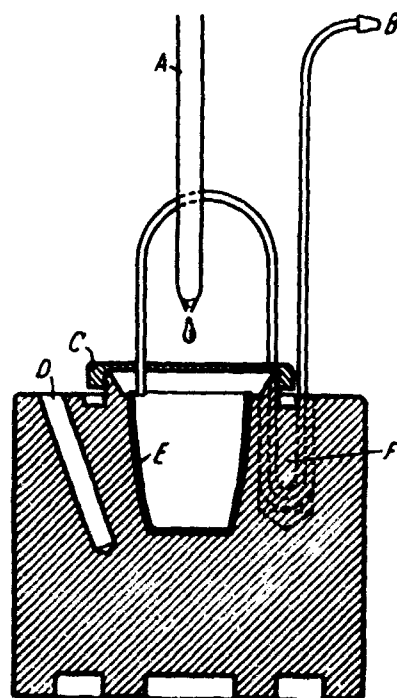
Fig. 4. Constam and Schl  pfer's ignition temperature apparatus



devised a simple heated crucible apparatus for determining this temperature for liquid fuels which, though similar in principle to the then existing methods of HOLM¹²³ and of CONSTAM and SCHL  PFER^{39, 40}, was more sensitive in that it could differentiate more clearly between fuel samples. Holm allowed drops of liquids to fall upon a heated porcelain surface, the temperature of which was measured, whereas Constam and Schl  pfer used a platinum crucible in a gas heated sand bath (see *Fig. 4*). The last-named authors investigated the effect of crucible material by using sometimes a nickel or a porcelain crucible and also fed pure oxygen into the crucible via a delivery tube projecting into the crucible in some of their experiments with the platinum

MOORE'S HEATED CRUCIBLE METHOD

crucible. In developing his ignition tester in 1917 while engaged in a study of diesel fuels, MOORE¹⁹⁴ reduced the size of the crucible employed by his predecessors from 160 ml. to 24 ml. and, furthermore, embedded his platinum crucible in a steel block (see *Fig. 5*). The first of these modifications reduced the magnitude of the explosion produced upon ignition and the second improved the uniformity of the temperature of the crucible and the control of this temperature to within fine limits for appreciable periods of time. A stream of air or oxygen of the same temperature could be passed into the crucible at a definite rate, say, three bubbles per second. When the temperature of the steel diffusion block was constant at a given value one drop of the test fuel



A = oil dropper. *B* = oxygen feed tube. *C* = cap.
D = hole for pyrometer. *E* = platinum crucible.
F = thermal plug.

Fig. 5. Moore's ignition tester

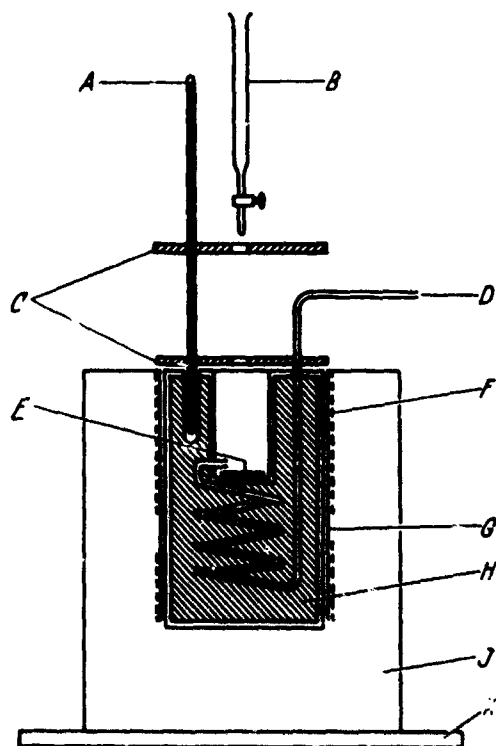
was allowed to fall through the hole in the centre of the cover of the instrument. If the temperature greatly exceeded the S.I.T. a sharp explosion occurred almost immediately; if the temperature were slightly above the S.I.T. the explosion followed some 10 sec after the introduction of the oil. By repeating the tests at slightly lower temperatures the lowest temperature at which ignition occurred (the S.I.T.) was determined. Using air instead of oxygen the violence of the ignitions was much less and the delay time was always finite, being never less than 1 sec. Presumably this is the time required for the vaporization of the minimum amount of the liquid fuel necessary to give ignition in the vapour phase.

Moore subsequently modified his instrument slightly by reducing the size of the crucible to 9 ml. and deepening the thermometer pocket by drilling through the block obliquely past the side of the crucible. This apparatus is depicted in *Fig. 6* and is described in references 112, 194-201. The preheating of the air or oxygen stream is accomplished

MOORE'S HEATED CRUCIBLE METHOD

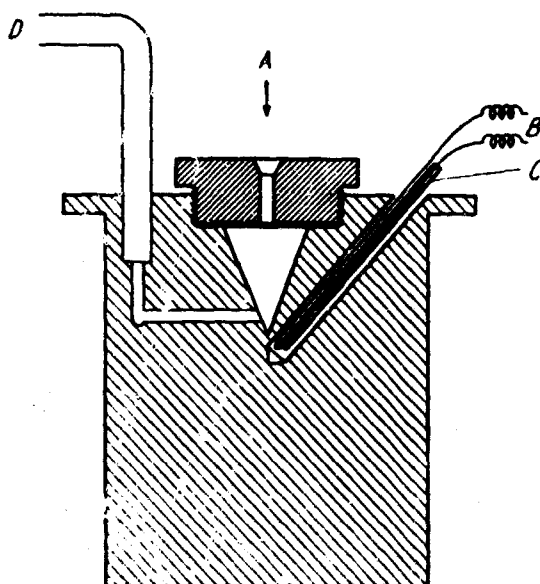
by a small coil in the steel block. Moore himself recommended that it was advisable to use oxygen for standard measurements as the determinations were clearer and more convenient.

There has been some controversy³⁵ concerning the usefulness of the S.I.T. values obtainable with the Moore ignition tester. Moore believed that the S.I.T. of the fuel determined the limit of compression pressure which may be employed without the onset of pre-ignition and knocking phenomena in internal combustion engines¹⁹⁵. LE MESURIER^{166, 167}, on



A = thermometer. B = oil feed. C = asbestos discs. D = air feed tube. E = highly polished steel disc. F = electrical winding. G = mica insulation. H = solder. J = asbestos packing. K = asbestos plate.

Fig. 6. Improved Moore type apparatus



A = fuel supply. B = thermocouple leads. C = quartz tube. D = oxygen supply.

Fig. 7. Krupp ignition block

the other hand, went so far as to say that in his opinion the figures quoted for S.I.T. obtained in the Moore apparatus were practically useless. The fact remains however that this method of measuring ignition temperatures has been widely used and is still in vogue, although in many cases with some modifications aimed at improving accuracy or ease of operation. Reference to these investigations will now be made, although the work between 1924 and 1927 will be treated only very briefly in view of the excellent review published by BRIDGMAN and MARVIN³³ in 1928.

SINNATT and B. MOORE³⁷⁷ (1918) were among the earliest users of an H. Moore type apparatus, but in 1921 WOLLERS and EHMCKE³³⁴ described an ignition tester known as the Krupp ignition block, a diagram of which is given in Fig. 7. This block could be fitted into an electric

furnace with either chromium nickel heating for temperatures up to 800° C or 'silit' bar heating for temperatures between 800° C and 1300° C. The block is of Krupp's rustless steel provided with a conical shaped cavity which acts as the 'crucible'. With continuous oxygen supply, fuel is added dropwise until it ignites with a definite report. The ignition temperature is determined with the aid of a calibration curve, from the instantaneous temperatures in the ignition zone and ignition block as indicated by thermocouples.

ORMANDY and CRAVEN²²⁹ in 1924 devised a 38 ml. heated steel crucible fed with an oxygen stream, and with this measured the effect of anti-knock additives on the ignition temperatures of hydrocarbon fuels, especially *n*-heptane. It was realized that some exothermic reactions took place during the induction or delay period, and the authors postulated that this initiates the ignition and explosion. Two years later ORMANDY and CRAVEN²³⁰ reported further work upon a 16 ml. steel crucible with which they had measured the influence of various factors upon the ignition temperature of *n*-heptane. They observed that the S.I.T. of *n*-heptane was raised from 245° to 278° C by the use of the smaller crucible; strong infra-red radiation produced no change in the S.I.T.; raising the block to a potential of 200 V was without effect, and extreme drying of the fuel produced a negligible effect in the S.I.T. Ormandy and Craven found that some of their S.I.T. values, e.g. for aromatic hydrocarbons, were much higher than Moore's corresponding values; they attribute this to the greater purity of their liquids. They found little difference between the S.I.T. of a liquid or its vapour and refute the suggestion that the ignition points measured are those of the hydrocarbon decomposition products.

TAUSZ and SCHULTE²³⁶ measured ignition temperatures of combustibles in an iron crucible of 25 ml. capacity in the presence of either an air stream or an oxygen stream. All but four of the substances tested by them had lower ignition temperatures in oxygen than in air; butyric anhydride, trinitrophenol and valeric anhydride had higher ignition temperatures in oxygen, whilst nitrobenzene gave the same S.I.T. in both atmospheres.

TANAKA and NAGAI^{234, 235} investigated the ignition temperatures of various combustible liquids in an oxygen current using an improved Moore type apparatus and then measured the effect of the additives diethyl selenide, tetraethyl lead and water vapour. The ignition temperatures of pure ethyl alcohol determined after tests in which lead tetraethyl had been employed were very high, due, it appeared, to the effects of the latter material on the surface of the platinum crucible used.

EGERTON and GATES⁷²⁻⁷⁶ presented a very large number of experimental results of 'igniting temperature' measurements in an iron crucible of 51 ml. capacity fed by an air stream. They found that many anti-knock type additives such as lead tetraethyl raised the igniting

temperature of certain combustible vapours; a similar effect was obtained when lead was volatilized and dispersed by means of an electric arc in nitrogen or argon. Other metals were tested in this way and it was concluded that the metal atom itself was responsible for suppressing the incipient oxidation reactions of the combustible, though the magnitude of this effect varied with the composition of the fuel, alcohols for example being less affected. They also studied the effect of varying the quantity of fuel dropped into the crucible, the effect of the surface (e.g. presence or absence of a layer of iron oxide) and the material of the walls of the crucible. All of these factors had some effect upon the ignition temperature and the results obtained are tabulated in reference ⁷⁴. One especially interesting result was that the igniting temperature of a liquid drop was generally found to be lower than that of the corresponding vapour.

WEERMAN ³²¹ also used an iron crucible fed with air though its capacity was 116 ml. which was more than twice that of Egerton and Gates' crucible. He studied especially the effect of anti-knock type additives upon the spontaneous ignition temperature of petrol. The crucible was heated electrically and single drops of combustible allowed to fall into the centre of it when the air flow was 330 c.c./min. Qualitatively, compounds which produced an increase in the S.I.T. in the crucible had an anti-knock effect in the engine and vice versa. Two substances producing the same S.I.T. at a certain concentration did not necessarily produce the same highest useful compression ratio (H.U.C.) in a spark-ignition engine. Only those elements were active which could produce oxides that were easily reduced under engine conditions during the compression stroke or could appear in various degrees of oxidation.

The influence of oxygen concentration upon the S.I.T. of a fuel was measured by PAHL ²³¹ using an electrically heated ignition block containing an 11 ml. cavity into which the fuel was added through a small orifice. Benzene, benzine, allyl alcohol and a gas oil were tested. It was found that using known mixtures of oxygen and air the S.I.T. increased and the ignition delay (estimated from the time that the fuel dropped into the combustion space) increased as the oxygen concentration decreased. The intensities of the explosions were measured approximately by observing the heights of the flames produced; they diminished with decreasing oxygen partial pressure.

SUWA ^{291, 292} measured the auto-ignition temperatures of a number of diesel fuels, mainly tar oils, in a modified Moore type apparatus containing a 14.8 ml. platinum crucible into which flowed 15 c.c. oxygen/min. The cylindrical diffusion block of semi-steel was 110 mm in diameter and 105 mm in height, and was heated at the rate of 1°-2°/min. Suwa concluded that the auto-ignition temperature was the most important property for distinguishing between various fuels,

especially oils of non-petroleum origin, in regard to their suitability for compression-ignition engines.

GREBEL^{104, 105} determined the S.I.T. of several petroleum products with the addition of various proportions of a number of organic or metallo-organic substances. He used the Krupp modification of the Moore type apparatus and noted that small quantities of anti-knock additives raised the S.I.T., whereas high concentration lowered it; also iron pentacarbonyl proved to be more effective under these conditions than 'ethyl' fluid (mainly lead tetraethyl).

In 1930 the American Society for Testing Materials (A.S.T.M.) published²²⁶ a tentative standard method (D-286-28T) for measuring the autogenous ignition properties of petroleum products. This was modified two years later and became known³⁴² as standard method, designation D-286-30. The apparatus consisted of a Pyrex glass conical flask heated in a gas heated molten solder or lead bath and into which oxygen flowed and the drop of test fuel was allowed to fall.

NASH and HOWES²¹⁷ pointed out in 1935 that the accuracy of the Moore type ignition point determination could be increased by modifying the test procedure slightly so that the time interval elapsing between the moment of falling of a fuel drop into the heated crucible and the moment of ignition as indicated by a flash could be measured by a stop-watch or similar device.

An interesting study was made by TAWADA²⁹⁹ of the effect of 0.1-0.2 per cent ozone on the S.I.T. of a motor gasoline as determined by the Moore type apparatus. The S.I.T. and ignition delay were measured for an oxygen concentration range 26-50 per cent and a gas flow of 0-50 c.c./min. Generally the ozone had little effect on the S.I.T., but it did shorten the delay period very much. The effect was greater the lower the temperature and the greater the gas flow, and Tawada stated that this might explain the known pro-knock effect of ozone in spark-ignition engines.

Using the Krupp modification of the Moore type apparatus BAYAN¹⁶ measured the S.I.T.s in oxygen of various gasolines and expressed his conclusion that there was no exact correlation between these data and the anti-knock quality (octane number) of the fuels. He noted that alcohol-containing fuels had the highest S.I.T.s

JONES, YANT, MILLER and KENNEDY¹⁴¹ described the drop-method apparatus used at the U.S. Bureau of Mines for the measurement of the minimum ignition temperatures of liquid combustibles. They employed a Pyrex tube fed at the bottom with air or oxygen via a Pyrex spiral tube, or alternatively a simple Pyrex tube, quartz tube or porcelain crucible.

In 1937 the Universal Oil Products Co. of U.S.A. published³⁴⁷ details of their U.O.P. Method J-89 for determining 'the spontaneous ignition temperature of liquid fuel (Moore bomb)'. They employed a

nickel or platinum crucible in a cylindrical Moore type steel or cast-iron diffusion block 100 mm in diameter and 75 mm in depth, the base of which was turned on a lathe in grooves to present a greater heating surface to the gas flame below. The test procedure was the same as that of Moore but the use of a stop-watch to determine the delay time is advocated and at least five duplicate results must be obtained. Although reproducibility is within 3 F°, the method states that the test results are to be regarded as only capable of distinguishing high from low ignition temperatures. This special care in making measurements and interpreting and using the results of the determinations is entirely praiseworthy.

SORTMAN, BEATTY and HERON²⁸³ employed a steel crucible fed with an air stream. They found that the S.I.T. varied appreciably with the size of the drop used and the rate of air flow and clearly demonstrated the existence of two temperature zones of non-ignition above the minimum ignition temperature in the case of both *n*-heptane and cetane. Furthermore, addition of lead tetraethyl to a combustible inhibited ignition up to 450° to 540° C.

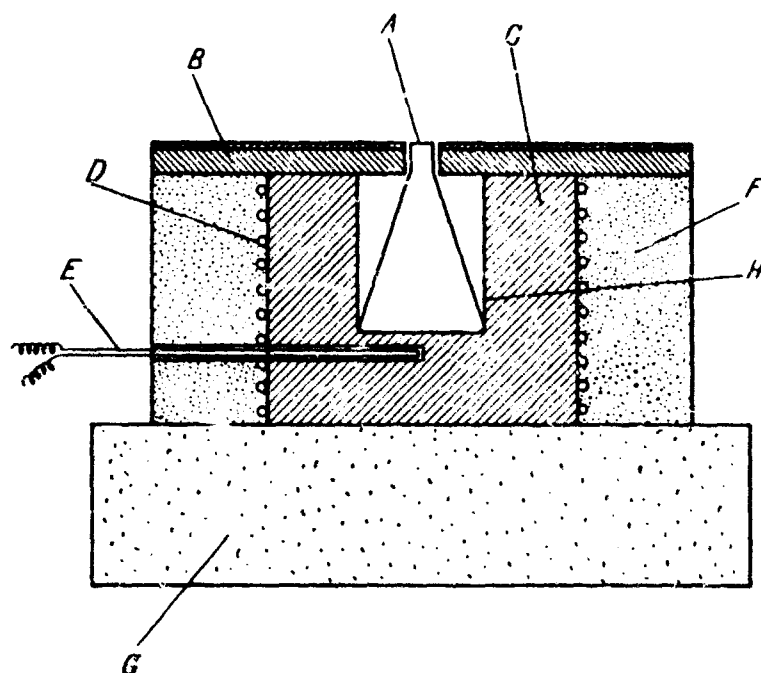
An extensive series of ignition temperature determinations have been made by YAMAKITA³³⁵⁻³³⁷ using a Moore type apparatus. The reliability of the apparatus was investigated by varying the test conditions. Iron, nickel, platinum and porcelain crucibles were used in succession and the latter was chosen as most satisfactory since the delay time observed at a given crucible temperature for a given fuel was most nearly reproducible in this type of crucible. In fact, Yamakita very rightly, in the opinion of the present writer, paid special attention to the measurement of the actual delay times and plotted his results in the form of ignition temperature versus delay time curves. The crucible was heated from 500° to 750° C by electrically heated Nichrome wire, and a drop of the test fuel was introduced into it from a pipette. The gases were blown out after each test which was repeated several times to obtain a mean result. Yamakita tested various pure hydrocarbons, alcohols, ether, ketones, petroleum products with and without additives of either a pro-knock or an anti-knock type. He suggested that since both an increase in pressure and an increase in oxygen concentration of the atmosphere was known to decrease the ignition temperature of a given fuel, in general, perhaps the influence of pressure could be inferred from measurements in oxygen or oxygen-enriched air. A year later, in 1946, ONO²²⁸ published some results of a study of the influence of wall material and oxygen concentration upon the spontaneous ignition time lag curves of seven combustibles, using Yamakita's experimental method. He used crucibles made of alumina, porcelain, quartz, terex glass, aluminium, stainless steel, platinum, copper and nickel, and found that only the last three gave greatly different results which he ascribed to catalytic or catalyst poisoning effects. The absolute influence

of wall material was found to vary not only with different fuels but also with different oxygen concentrations. Ono also discovered that whereas some compounds (for example graphite, lampblack, lead oxides) accelerated the ignition of one fuel, they tended to retard the ignition of another.

SCOTT, JONES and SCOTT²⁷⁰ in 1948 described a modified A.S.T.M. (D-286-30) procedure for determining the minimum ignition temperature by the drop method. They substituted an electrically heated stainless steel block for the gas heated molten solder or lead bath. The block weighed about 50 lb. and was wound with 27 ft. of 18-gauge Nichrome wire encased in a sheath of asbestos tubing. The block rested on a disc of 85 per cent magnesia insulation supported on an iron disc. A quartz test flask was fitted into the block which was designed for a temperature of 750° C. The ignition temperatures of the compounds tested were from 28° to 41 C° lower than with the molten liquid (nitrate) bath when air was used, and from 6° to 62 C° lower when oxygen was used. The A.S.T.M. apparatus was again slightly modified in 1951 by BOODBERG and CORNET²¹ to permit better observation of the ignition. These workers investigated the effect of various concentrations of isoamyl nitrate in a diesel fuel and found that concentrations between 0.25 and 2 per cent produced the highest values of ignition temperature. At about this period JACKSON^{129, 130} also made much use of the Scott, Jones and Scott modification of the A.S.T.M. apparatus; he actually embedded the 125 ml. quartz Erlenmeyer flask in an electrically heated Inconel block. Great care was taken to avoid being misled by the existence of zones of non-ignition (cf. ref. ²⁸³) when determining the minimum ignition temperatures. Nevertheless, differences of up to 41 F° were obtained between corresponding S.I.T.s by Jackson and by Scott, Jones and Scott; the reasons for such deviations are unknown. This serves to emphasize the undesirability of comparing ignition temperature data from different sources even when the methods of test are ostensibly similar. Jackson presented data for a large number of pure hydrocarbons and commercial fluids, and a diagram of his apparatus is shown in *Fig. 8*.

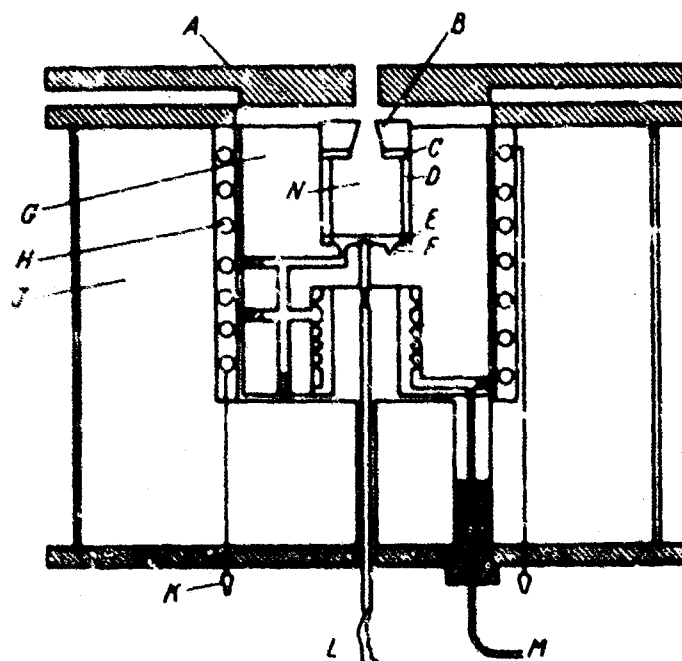
The most recent Moore type apparatus with which many measurements of ignition temperature have been made and reported is that due to FRANK and BLACKHAM^{86, 87}. The apparatus used by them is an adaptation of that described by SORTMAN, BEATTY and HERON²⁸³ and employed by ZISMAN and co-workers^{23, 290} in their inflammability studies. The apparatus used by Frank and Blackham is shown in *Fig. 9*. Blocks were prepared from both copper and stainless steel; the two gave completely parallel results, although the copper block was not as satisfactory at the higher temperatures because of the rapid formation of a heavy oxide layer under those conditions. The effect of various metal surfaces could be determined by the use of metal inserts comprising a

MOORE'S HEATED CRUCIBLE METHOD



A = 125 c.c. Pyrex Erlenmeyer flask. *B* = Transite cover plate. *C* = Inconel block 8 in. dia. and 5½ in. deep. *D* = 14-gauge chromel heating wire. *E* = 20-gauge chromel-alumel thermocouple. *F* = Fuller's earth. *G* = 85 per cent magnesia block. *H* = hole 2½ in. dia. and 3½ in. deep.

Fig. 8. Jackson's heated flask apparatus



A = asbestos cover. *B* = stainless steel cap. *C* = lid. *D* = sleeve. *E* = disc. *F* = circular groove for passage of air. *G* = metal block 4½ in. dia. and 5 in. high. *H* = heating coils. *J* = insulation. *K* = heater terminal. *L* = thermocouple wires. *M* = copper tube carrying the air feed flow. *N* = ignition chamber 1½ in. dia. and 1½ in. high.

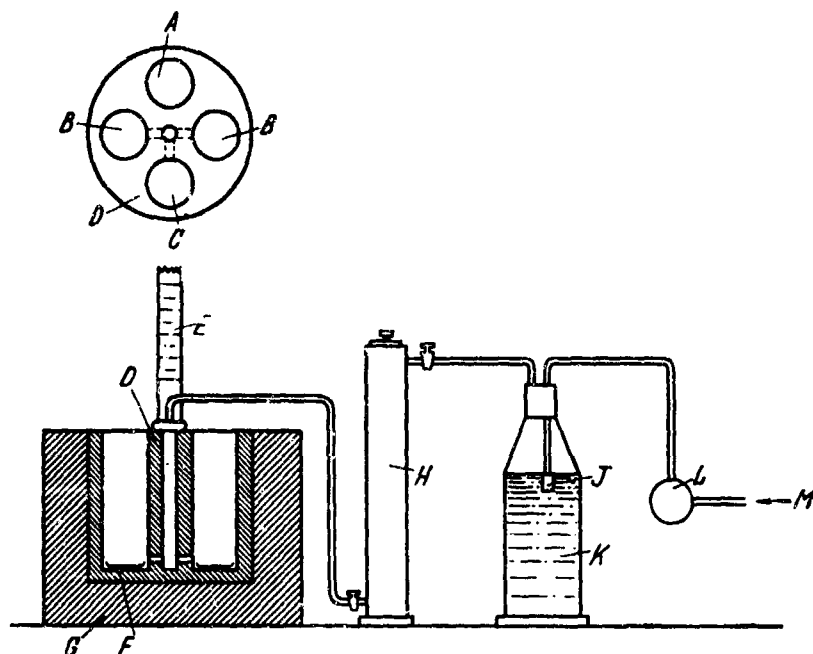
Fig. 9. Frank and Blackham's ignition apparatus

MOORE'S HEATED CRUCIBLE METHOD

base plate, cylinder and lid which accurately line the walls of the ignition chamber. Preheated air at a flow rate of 125 c.c./min. (or sometimes 25 c.c./min.) enters the ignition chamber through four small openings in the base of the $2\frac{1}{8}$ in. \times $1\frac{3}{4}$ in. dia. cylinder. A large number of organic liquids were tested and the effects of numerous additives were measured with *n*-dodecane as parent combustible. Three different types of phenomena were observed and classed as ignitions, namely, (i) a visible flame or flash, blue or yellow in colour, (ii) a visible glow (cool flame) within the chamber, usually green or blue, which may or may not be followed by a puff of smoke, and (iii) a definite puff of smoke after a lengthy induction period. The last two types were observed usually only at the S.I.T. or at temperatures slightly above. In this range the optimum fuel/air ratio to produce a flame is quite sensitive; if it is slightly exceeded a glow or puff of smoke results instead of the flame. Frank and his co-workers devised a method of spraying the test fuel into the ignition chamber when working with lubricating oils^{88, 89} in an endeavour to overcome the effect of reduced vapour pressure which tends to increase the 'physical' portion of the induction period when large single drops are used.

JENTZSCH'S HEATED CRUCIBLE METHOD

JENTZSCH¹³² in 1924 described a new type of ignition meter which, though basically of the Moore type, possessed a special feature in the presence of four equal and symmetrically disposed pockets in a rustless steel block that was situated in an electric furnace. A diagram of the



A = thermometer pocket. *B* = auxiliary chambers. *C* = admission chamber. *D* = ignition crucible. *E* = thermometer. *F* = vaporization dish. *G* = furnace. *H* = drier. *J* = jet. *K* = bubble counter. *L* = adjusting valve. *M* = oxygen supply.

Fig. 10. Jentzsch's ignition tester

Jentzsch ignition tester is shown in Fig. 10. One of the four chambers acts as a thermometer pocket and the other three are ignition chambers each of which is fed with oxygen from a common central pipe. There is an easily removable evaporating dish at the bottom of each ignition chamber. The spontaneous ignition temperature is taken to be the minimum temperature at which an oil drop will self-ignite in the presence of a rich oxygen stream. Jentzsch defined an ignition value, Z' by the formula

$$Z' = \frac{T}{b' + 1} \quad \dots (16)$$

where T is the ignition temperature and b' is the number of oxygen bubbles per minute. He realized that the amount of oxygen flowing greatly affected the value of the ignition temperature determined; thus

from a large number of tests he found that several substances have the same S.I.T., whereas the amount of oxygen required for ignition is in the ratio 10 to 1.

SWIETOSLAWSKI *et al.*²⁹³ used Jentzsch's apparatus with benzine, alcohol and a number of liquid fuels and drew curves relating the ignition temperature and rate of supplying oxygen for given fuels. They found that using mixtures of liquids the ignition temperature increased with increasing proportion of benzine and water and decreased with increasing proportion of ether. Two years later, in 1932, ZERBE and ECKERT³⁴⁰ published similar curves of ignition temperature versus rate of oxygen supply for many organic combustibles, and like Jentzsch, but unlike Swietoslowski *et al.*, noted a low and a high ignition temperature, the lower one being called the true S.I.T. Thus they concluded that, in general, ignition temperatures decrease to a minimum with increasing rate of oxygen supply, but for aliphatic and naphthenic hydrocarbons not containing conjugated double bonds (which increase resistance to ignition), there exists a region defined by upper and lower ignition temperatures between which no ignition occurs. Furthermore, they found that changes in the structure of compounds produced certain types of effect. For example, presence of oxygen in aliphatic molecules increase the ignition temperature whereas the presence of oxygen in aromatic compounds lowers the ignition temperature. The influence of the proportion of hydrogen in a compound upon ignition temperature is only understandable when regarded in conjunction with the structure of the compound.

SCHAEFFER²⁵⁹ analysed a large number of results obtained with a Jentzsch ignition tester. Results with this apparatus show clearly that the ignition temperatures of vapours of liquid fuels tested are the same as those of the liquid fuels themselves, which is evidence that it is not a liquid but its vapour which burns. Under the conditions of the ignition chamber, operated at 600° C, a 4 mm diameter coal tar diesel oil drop requires approximately 8 sec for total vaporization and there is evidence of some fractionation of the components.

In passing, it is of interest to note that the Jentzsch ignition tester has been used for determining the ignition temperatures of solid substances. Thus SCHAFER²⁶⁰ used it for testing insulating materials employed in building and on ships, HACK¹⁰⁹ tested coal dusts and VERSEPUY³¹⁷ tested semi-cokes.

In 1933 SCHAFER²⁶¹ discussed the significance of ignition temperature data obtained with Jentzsch's apparatus as an assessment or indication of the performance of fuels in spark-ignition engines. He considered the results that had been obtained with various classes of organic combustible liquids such as paraffins, naphthenes and aromatic hydrocarbons and concluded that the Jentzsch method gave the best and most promising results of any ignition tester in existence from this

viewpoint. Nevertheless, as CHALONER³⁵ had stated one year previously, there were other German research workers who attached no importance to the ignition curve as obtained with the Jentzsch apparatus. Although there was and still is doubt about the practical interpretation that can be put upon data obtained from this crucible test method, academic interest certainly is attached to these results. Consequently, as in the case of Moore's method, it is valuable to summarize and refer to the studies that have since been undertaken with the Jentzsch apparatus.

ZERBE, ECKERT and JENTZSCH³⁴¹ investigated the catalytic influence of a large number of metals and metal compounds upon the spontaneous ignition of pentane-oxygen and benzene-oxygen mixtures and discussed the contact mechanism involved. Generally they found that such additives exert only a secondary effect, temperature, oxygen concentration and chemical structure of the parent liquid being the main factors as before.

KRUBER and SCHADE¹⁵⁹ made measurements with various aromatic hydrocarbons, particularly ortho compounds, and found that generally the ortho compounds were more ignitable than the corresponding sym. meta compounds, whilst the asym. ortho compounds were intermediate.

WINTER and MONNIG³³⁰ and WINTER³²⁹ have reported some spontaneous ignition temperature measurements upon various liquids ranging from gasoline to lubricants. Winter stated that the interval between the upper ignition temperature and the S.I.T. is a magnitude that gives useful information in comparative studies of other fuel properties. ZERBE and ECKERT³⁴⁰ had tabulated values of this interval in their work and Jentzsch himself had defined an Ignition Value Factor (I.V.F.) by the expression:

$$\text{I.V.F.} = \frac{T - T_h}{b'} \quad (17)$$

where T = S.I.T., T_h = higher ignition temperature and b' = number of oxygen bubbles per minute.

MOHR¹⁹² measured the effect of various anti-knock type additives upon ignition temperatures. The S.I.T.s of pure lead tetraethyl and of 'Ethyl fluid' were both found to be 150° C. Longer delay times were noted with alcohol-containing motor fuels and the oxygen demand at the lower ignition point (S.I.T.) was smaller than expected, this being attributed to the incomplete oxidation of the alcohols.

HERSTAD^{116, 117} placed special value upon the ignition lag as determined by the Jentzsch ignition tester and considered its relation to the knock characteristics of motor fuels. The data of Zerbe and Eckert were referred to and certain correlations were attempted. No very certain conclusions could be stated. He also correlated crucible test results with cetane numbers in the case of diesel fuels¹¹⁸.

JENTZSCH'S HEATED CRUCIBLE METHOD

Since the Second World War, Jentzsch has continued using his tester and the same apparatus has found further favour in U.S.A. JENTZSCH¹³³ determined the effect of the diluents nitrogen and carbon dioxide upon the S.I.T.s of benzine, cyclohexane, diesel fuel and a mixture of benzene and benzine. The results showed that with the predominantly aromatic hydrocarbons, nitrogen raises the S.I.T. less than does carbon dioxide, but these differences only showed up when the oxygen partial pressure was less than 21 per cent by volume, i.e. the air was vitiated. Once again Jentzsch drew a parallel between increase in oxygen concentration in the crucible and increase of compression pressure in engines. He also employed his tester to determine the ignitability of a mixture of $H_2 + 2O_2$ ¹³⁴.

GILMER and CALCOTE¹⁰⁰ tested a number of pure fuels, mixed fuels and fuels with additives in the Jentzsch apparatus and believe that the results give an approximate indication of knock tendency in spark engines.

JOHNSON, BLIZZARD and CARHART¹³⁶ made an evaluation of the Jentzsch ignition apparatus and used it extensively in studying diesel fuels and pure hydrocarbons¹³⁷⁻¹³⁹ though certain modifications were made from time to time for specific investigations, one of these being the conversion from a three-cell to a one-cell ignition unit. In this work the oxygen partial pressure was used over the whole range 0 to 100 per cent and careful observations were made of the cool-flame phenomena as well as the normal ignitions. They defined the self-ignition point (S.I.P.) as the lowest temperature at which a drop of fuel ignites when oxygen is supplied at the rate of 300 bubbles (approx. 25 ml.)/min., and it was determined as follows: A clean crucible was placed in each of the three cells of the Jentzsch ignition chamber, the oxygen flow was set at 300 bubbles/min. and the block was heated rapidly to about 230° C. Then the block heater was adjusted to give a temperature rise of 2° to 3°/min. and a drop of fuel was added to the front cell. If no ignition occurred within 30 sec, the chamber was purged with air, the crucible replaced by a clean one and the procedure repeated at about 5 C° intervals until ignition did take place. After this approximate determination, the tests were repeated at slowly falling temperatures until the S.I.P. was established to the nearest degree. Reproducibility was to within ± 2 C°. The S.I.P. in the single-cell chamber was about 10° to 15 C° lower than that found with the standard three-cell Jentzsch chamber. Cool flames were obtained using both types of chamber, when nitrogen was supplied, showing that there was sufficient back diffusion of air to supply the low concentrations of oxygen required for this type of ignition. The authors concluded that the S.I.P. is inversely related to the cetane number and this holds even for fuels containing additives. Ignition delay measured at a fixed temperature was also found to be related to cetane number, but was more closely related to the S.I.P.

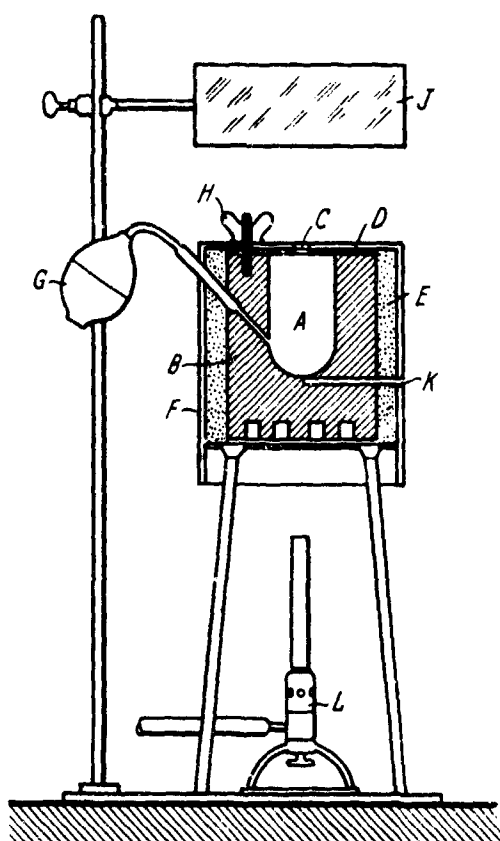
STATIC HEATED CRUCIBLE AND FURNACE METHODS

MANY research workers have devised a heated crucible method for the determination of the ignition temperatures of fuels, and some have not fed a stream of air or oxygen into the crucible. This latter method might be termed a static crucible method to contrast it from the dynamic crucible methods such as those of Moore and of Jentzsch. In addition to this, various forms of furnace techniques have been employed.

1. STATIC HEATED CRUCIBLE METHODS

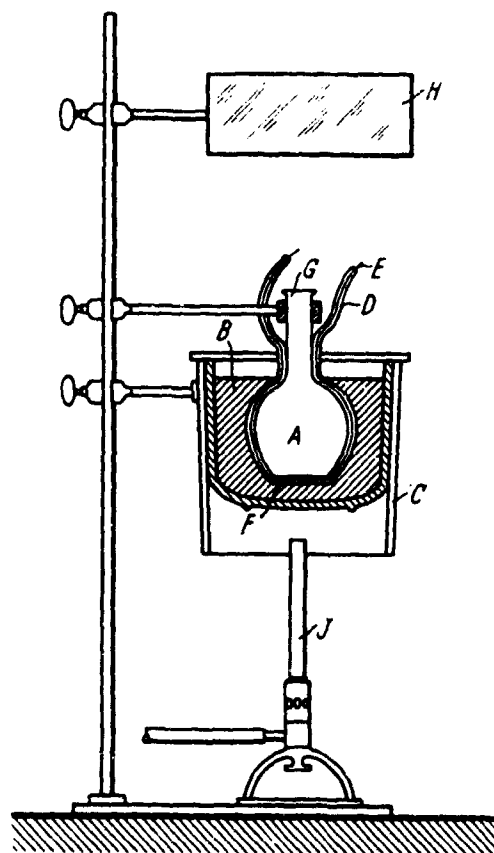
BRIDGMAN²² has summarized the various types of metal or glass crucible employed by the Factory Mutual Laboratories and the Underwriters Laboratories in U.S.A.^{343, 346} in 1927. The capacity of the crucibles used ranged from 1270 ml. to 160 ml. and in every case the ignition temperature corresponded to some unknown and arbitrary delay time. Two years later THOMPSON³⁰³ described in some detail fundamental researches on ignitability that he had undertaken with static crucible types of apparatus. His apparatus comprised a copper block (see *Fig. 11*) containing a cylindrical cavity with a rounded bottom in communication with the outside via a small hole; the atmosphere in the ignition chamber could thus be scavenged when desired between tests. The top of this cavity was closed by a metal disc, held down tightly by wing nuts and provided with a hole for introduction of the fuel sample. The capacity of the ignition chamber was 106 ml. Later the cavity was machined out without increasing the depth so as to make the lower portion of the cavity spherical with a diameter of 6.4 cm, the top or neck being left unaltered at 4.4 cm diameter. The purpose of this was to note the effect of the increased capacity (140 ml.) and altered shape. A second apparatus used by Thompson is shown in *Fig. 12*. This is similar in principle to that of the Underwriters Laboratory³⁴⁶ and consists of a 125 ml. or 150 ml. Pyrex glass flask resting in a solder bath. The testing procedure was similar in both these cases. The temperature of the crucible or flask was raised to a value giving ready ignition and the character of the ignition was noted, using different quantities of fuel. The fuel was expelled from a specially drawn out dropper that delivered approx. 0.01 ml. drops of liquid. Varying the temperature and the fuel quantity as required the lowest ignition was obtained with the most favourable fuel proportions. In some tests the liquid was expelled rapidly

as a fine spray. Delay times of 30 sec or more were noted with some petroleum products. Ignition was judged from the appearance of flame in all cases; a tilted mirror and darkening of the room was used to help the observations. Thompson reported many results for more than thirty organic compounds with his various apparatuses. The copper apparatus was unsatisfactory because of the variable influence of an



A = ignition chamber, 3 in. deep and $1\frac{1}{2}$ in. dia. *B* = copper block. *C* = $\frac{1}{8}$ in. dia. hole. *D* = $\frac{1}{8}$ in. thick metal plate. *E* = $\frac{1}{2}$ in. Min-wool insulation. *F* = $\frac{1}{2}$ in. asbestos board. *G* = rubber bulb. *H* = three $\frac{1}{2}$ in. studs spaced 120° . *J* = tilted mirror. *K* = $\frac{3}{8}$ in. dia. thermocouple hole. *L* = gas burner.

Fig. 11. Factory Mutual Laboratory copper block ignition apparatus



A = 125 c.c. Pyrex flask. *B* = solder. *C* = $\frac{1}{8}$ in. asbestos board. *D* = $\frac{1}{8}$ in. dia. braided asbestos tubing. *E* = thermocouple wires. *F* = thermocouple hot junction. *G* = $\frac{1}{8}$ in. dia. hole. *H* = tilted mirror. *J* = gas burner.

Fig. 12. Factory Mutual Laboratory Pyrex flask ignition apparatus

oxide layer; chromium plating of the copper reduced this variation. However, glass proved to be the most reliable material and the easiest to use. For practical application, Thompson favoured the use of a steel crucible as the ignition temperatures determined in such a vessel ought to be relatable to the ignitability in the steel combustion chambers of engines, although a steel vessel is not cleaned so readily as a glass vessel. Generally the best mixtures, i.e. those giving the minimum ignition temperatures, were richer than stoichiometric according to simple calculations upon the quantity of air and fuel in the ignition chamber during testing conditions.

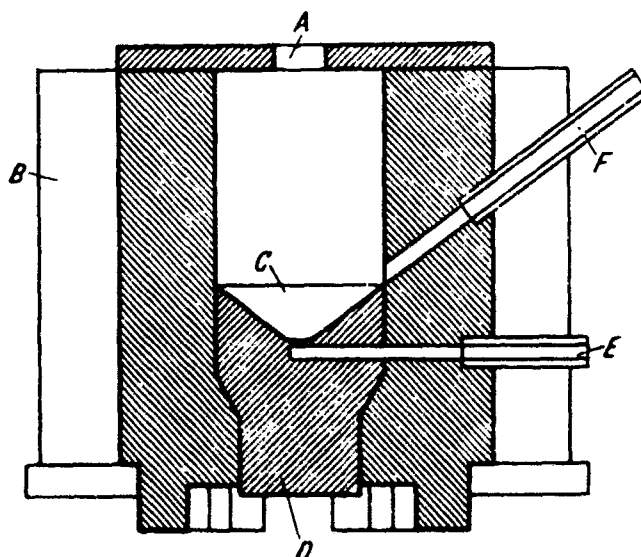
MASSON and HAMILTON¹⁸⁶ in 1927 devised a static crucible method for the determination of auto-ignition temperatures (A.I.T.) consisting of an electrically heated 160 ml. platinum crucible into which a drop of the test fuel could be introduced through a hypodermic needle. They claimed that the apparatus was accurate and simple to operate and could be modified to determine the auto-ignition temperatures of solids and gases in any medium at ordinary or increased pressures. A.I.T.s of a number of pure compounds were evaluated and a separate study was made of the catalytic effect of various surfaces¹⁸⁷. In a third paper¹⁸⁸ they reported measurements of the A.I.T.s of some petroleum products for which the knock ratings were known and correlated these data. The work also included a study of mixed fuels and gasoline containing various amounts of lead tetraethyl; gold, platinum, glass and lead-platinum surfaces were used in the latter tests. Masson and Hamilton pointed out that though the mixture ratio in the heated crucible was not easy to specify, it was probable that there always existed a zone around the drop where the mixture conditions were optimum, that is, suitable for causing ignition at the lowest possible temperature. Since these optimum conditions could not be regarded as invariant but dependent upon a number of factors which varied from experiment to experiment, they suggested that the term 'auto-ignition temperature' ought to be revised and the term 'relative ignition temperature' substituted.

LEWIS¹⁷² used a heated 125 ml. glass bulb with a long narrow neck for measuring ignition temperatures. The liquid fuel was introduced into the glass bulb in a small wide-mouthed tube of thin glass which was of such a length that the amount of liquid that gave the minimum delay (determined by trial and error) at a particular temperature just filled it to the brim. He found that to get reproducible results with a given bulb it had to be very carefully cleaned and dried between successive tests; it also had to be seasoned, somewhat, as a new bulb gave unduly long delays at low temperatures. The effect of catalysts (powdered glass, charcoal, metals) and additives was investigated with *n*-octane or hexane as the parent fuel. Lewis concluded that the delay in the ignition of hydrocarbons was preferable to the ignition temperature as a measure of the ignitability of paraffins and petrols since it is a function of the molecular weight or boiling range. As the temperature is raised the ignition delay, as observed in the drop method, diminishes until eventually a temperature is reached above which the mixture fails to ignite spontaneously (temperature zone of non-ignition—cf. refs. 47, 137, 139 and 283). Finally, Lewis predicted (accurately as we now know) that the rate of change of delay with temperature might provide further useful information; he did not himself obtain such data, though.

Another static crucible method was devised by WIEZEVICH, WHITELEY and TURNER²⁸⁷. The essential feature of their apparatus, which is

shown diagrammatically in *Fig. 13*, is the ignition block with its cup-shaped surface; the thermocouple is inserted in a well below the cup which is covered by a plate with a central hole for admitting the fuel drop. A sloping side tube is built into the apparatus for blowing compressed air into the cup for scavenging purposes between tests. The authors studied various petroleum products including kerosines and lubricating oils and correlated the spontaneous ignition temperatures and average boiling points of the liquids tested.

In 1948 FRIEDLANDER and GRUNBERG⁹² reported upon their work with an electrically heated 60 ml. silica crucible into which drops of fuel were introduced. The crucible was immersed in a molten lead bath



A = fuel inlet. *B* = insulation material. *C* = cup-shaped surface. *D* = ignition block. *E* = thermocouple pocket. *F* = cleansing tube for compressed air.

Fig. 13. Wiezerich, Whiteley and Turner's ignition apparatus

and the combustion gases were bubbled through water and the aqueous solution subsequently analysed for aldehydes using Schiff's reagent, for oxides of nitrogen using Griess's reagent, and for peroxides using acidified potassium iodide solution. With normal heptane, between 316° and 400° C a pre-ignition pulse preceded ignition, above 400° C normal ignition occurred, and below 316° a strong pressure pulse was noticed but no ignition. Mixtures of *n*-heptane and benzene were tested with rather similar results, a two-stage type of ignition occurring within a certain temperature interval. The influence of lead tetraethyl added to *n*-heptane was then studied and an attempt was made to explain the results in terms of a reaction mechanism in which the free radical OH played a crucial role.

It is evident that the static crucible method has not been used so widely for the determination of ignition temperatures as the dynamic crucible methods of the Moore type and Jentsch type. The reason for this appears to be that S.I.T.s are more reproducible by the dynamic

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method and generally are slightly lower than in the static method. Also, the use of different air or oxygen flow rates enables additional information to be obtained, though the validity of interpreting oxygen-rich atmospheres as a 'substitute' for increased pressure has not been proved.

2. FURNACE METHODS

The furnace method of measuring ignition temperatures is analogous to the static heated crucible method, the chief differences being that a tube (usually vertical) instead of a crucible is employed and the fuel is usually vaporized and mixed with air and then fed into the furnace.

ALILAIRE¹ in 1919 fed mixtures of ether vapour and air into a U-tube one limb of which contained a thermometer and the other a number of points as in Vigreux tubes. The U-tube was immersed in an oil bath. He noted that the ether began to burn at 190° C, a temperature which is very close to that determined much later in far more elaborate apparatus by other workers. He also studied the effect of iron, nickel and copper oxides on the reaction and found no catalytic influence.

MASON and WHEELER¹⁸⁴ three years later used an 81 ml. capacity quartz tube, and though they studied mainly methane-air mixtures, the apparatus could also be used with vaporized fuel-air mixtures. Ignition delays which were called 'pre flame periods' were measured and were of the order of 10 sec duration. It was recognized that the nature and extent of the solid igniting surface had some influence upon the resultant ignition temperatures. Nine years later DUNKERLEY⁷⁰ described a much more elaborate electrically heated silica-tube furnace for determining the spontaneous ignition temperature of oils, and in the same year, 1931, FREITAG⁹¹ reported ignition temperatures in furnaces for a number of common solvents quoting two values for each substance, the first for a glass and the second for a steel tube. There seemed to be no regular trend in the differences between ignition temperatures for given combustibles in tubes of different materials.

More recently BLINOV¹⁹ described measurements of the ignition temperature of a liquid in a narrow vertical tube with the surface of the liquid at different distances from the upper end of the tube. The tube was 3 mm in diameter and though not actually in a furnace, was heated from outside by means of a resistance wire wound round it. Benzene, toluene, ethyl alcohol and amyl alcohol were investigated and it was found that the ignition temperature increased with the depth of liquid used.

BOMB METHODS

THE bomb methods of measuring ignition temperatures differ from the heated crucible method in several respects. The ignition space is sealed, the mixture is usually homogeneous, though some investigators sprayed liquid fuel into their bombs. The criterion of ignition is frequently based upon the measurement of pressure versus time, ignition being inferred as having occurred when the static pressure in the bomb rose sharply. Ignition temperatures may be determined over a range of starting pressures by this method.

In 1917 McDAVID¹⁸⁹ and in 1919 WHITE and PRICE³²⁴ devised a bomb method in which the fuel-air mixture to be tested was confined inside a soap bubble. McDavid's bubble was 3.7 cm in diameter and the ignition temperature was recorded as that occurring with the minimum delay time; it is not surprising therefore, that his ignition temperatures were relatively high, e.g. benzene 1062° C. White and Price used bubbles of 2.5 cm, 3.7 cm or 5.0 cm diameter and ignition was promoted by means of an electrically heated platinum spiral inside the bubble. The delay times corresponding to their ignition temperature data were of various magnitudes.

A more robust bomb which could be operated at elevated pressures was used by BROOKS²⁸ for testing oils which were spread out upon paper or asbestos and placed in the bomb which was sealed and then heated. Oxygen was admitted to the bomb at the desired pressure in these experiments, and the temperature was recorded at 1 min intervals to determine the ignition point. The effect of the charging pressure upon ignition temperature was negligible in this case, although of course the explosive pressure depended upon it.

In 1924 three different groups of workers devised bomb techniques. MASON and WHEELER¹⁸⁵ used an 85 ml. quartz tube and studied several paraffin-air mixtures; in these tests no special control of delay time was possible, although some special measurements were made with methane and with ethane of the variation of delay time before ignition with initial temperature and mixture composition. Mason and Wheeler stated clearly that the ignition temperature depends upon the material and texture of the walls of the bomb and whether the mixture is quiescent or turbulent as this governs the duration of the contact time with the walls. CRAY and GARNER⁴³ using glass bulbs or steel containers, found that the slower the explosion the more complete it was, which showed that the ignition temperature of hot gases projected into

cold air depends on the rapidity of the mixing process. TAUSZ and SCHULTE^{297, 298} used iron or steel bombs of 25 ml. or 10 ml. capacity and injected the test fuels either with or without spraying into heated air under pressures ranging from 1 to 40 atm. They found that pressure had a different effect upon different fuels and concluded that the order of ignitability of a series of fuels at high pressure could not be inferred from the measured order at atmospheric pressure.

In 1926 BIRD¹⁸ and NEUMANN^{222, 223} devised steel bombs into which liquid fuel could be injected and the ignition temperatures recorded. Both of these workers were interested in studying the ignition of diesel fuels, and Neumann, like Tausz and Schulte, used a 10 ml. capacity bomb and starting pressures up to 40 atm. These bomb techniques were to receive many refinements in later years which increased the accuracy of observation and enabled the delay time before ignition to be measured.

Between 1927 and 1930 LEWIS¹⁶⁹⁻¹⁷¹ published the results of a very extensive series of measurements of the ignition temperatures of paraffin-air and paraffin-oxygen mixtures, using a large cylindrical glass bulb (125 or 225 ml. capacity) connected to a mercury manometer by glass capillary and rubber pressure tubing. A known quantity of the test liquid was placed in the glass bulb and was slowly heated. Pressure readings were taken at small intervals of temperature and a pressure-temperature diagram was drawn. In the absence of chemical reaction the curve followed approximately the gas laws, but a sudden rise or inflexion indicates chemical reaction. These 'critical inflexion temperatures' (C.I.T.) were determined for a number of paraffin hydrocarbons and are kind of ignition temperatures. The effects of the rate of heating of the bulb, the quantity of fuel used, metallic catalysts and organic additives were studied. The pressure-temperature curves for hydrocarbon-oxygen mixtures were similar to those for hydrocarbon-air mixtures, differing only in that the critical inflexion temperatures were more abrupt and completed within a narrower range of temperature (1° - 2°); the actual temperatures were only slightly lower with oxygen, the difference being no more than would be expected from the change in mixture strength when oxygen was used in place of air. Amylene-oxygen mixtures were studied by Lewis in considerable detail and the effects of static pressure and catalysts were measured. He finally concluded that the relative ignitabilities of hydrocarbons could be measured better in terms of the delay for equimolecular concentrations at some point above the ignition temperature.

Auto-ignition tests bearing some relationship to ignition in engines were conducted by BRIDGMAN and MARVIN²² who employed a heated steel bomb with a combustion chamber similar in volume and shape to that of the Liberty engine used for routine fuel testing at the U.S.

Bureau of Standards. Three thermocouples measured the temperature of the air in the bomb and a Bourdon type gauge recorded the initial pressure. A plunger pump in which the stroke was set and measured by a micrometer was used to meter the fuel and to inject it into the bomb through a capillary tube. The onset of ignition was recorded automatically by an electrical synchronous timer whose circuit was broken when the pressure in the bomb rose appreciably. Delay times could be measured to within ± 30 to 50 msec with this apparatus—times long compared with engine combustion chamber residence times. Bridgman and Marvin stressed the care needed in interpreting ignition temperatures obtained in bomb and crucible types of apparatus, pointing out that the ignition temperatures differed with different apparatus and thus the conditions of measurement—apparatus design, method of operation and especially the ignition delay applicable—needed to be specified. They discussed the possibility of defining an absolute ignition temperature with delay time zero, i.e. the minimum temperature which must be reached by instantaneous heating of an element of volume within a homogeneous combustible mixture to initiate inflammation or explosion *instantly*. This concept has never been, and in the writer's opinion never will be, a practicable one since ignition delays can only tend towards zero: thus it is always essential to quote temperatures and delay times in the form of (T, τ) pairs of values if spontaneous ignition is to be specified precisely. Since it is also necessary to state the method of determination, ignition data even in this form have no fundamental and absolute significance, though they may be of great practical value and relative significance.

In 1932 HELMORE and CODE HOLLAND^{112, 113} developed an ignition tester known as the Royal Aircraft Establishment (R.A.E.) apparatus. It embodied many novel features and was specially developed for the testing of diesel fuels. The apparatus simulates actual engine conditions as far as possible with two important exceptions: (i) it is only operated at atmospheric pressure, and (ii) only relatively long ignition delays (greater than 200 msec) can be employed and measured. The wrought iron cylindrical explosion vessel (18 in. \times 6 in. diameter) is electrically heated and fitted into it or connected with it there are a fuel injection system (fixed charge), an electrical timing mechanism, an explosion-timing mechanism, an electrical recording mechanism for measuring the ignition delay, and a thermocouple pocket for indicating the air temperature. A series of determinations of ignition temperature and delay time are made, the ignition chamber being scavenged and recharged between each test. Temperature intervals are taken at 20 to 30 C° intervals until finally, at the lowest temperature, no explosion occurs after an indefinitely long delay. The results obtained with various fuels, with and without additives, agree fairly well with the known corresponding engine behaviour, though the apparatus is not capable

of differentiating between fuels of closely similar cetane ratings. A detailed description of the R.A.E. apparatus has been given by FOORD⁸⁴, and LE MESURIER¹⁶⁶ has shown that the results obtained with it are of value in indicating the ease of engine starting with various fuels, but cannot be correlated with the delay angle under all running conditions. HELMORE¹²¹ patented the apparatus in 1933; the test method is sometimes referred to as the Farnborough procedure.

Rich mixtures of hexane or gasoline and air were heated under an initial pressure of 5 Kg/cm² in a bomb by MONDAIN-MONVAL and WELLARD¹⁹³. With hexane spontaneous ignition occurred at 232°. Most of the experiments by these research workers were, however, conducted with electrical ignition of the fuel-air mixture in the bomb and hence it is not necessary to elaborate them here.

WIEZEVICH, WHITELEY and TURNER³²⁷ constructed a heated closed bomb that could be used with oxygen at super-atmospheric pressures. They studied the effect of hydrocarbon structure upon the ignition characteristics of fuels injected into this bomb.

In an attempt to eliminate the need for engine tests to rate diesel fuels KLAULIN, NEIMAN and SERBINOV^{152, 153} devised a cetane scale based on bomb tests. Their bomb could be operated at pressures over 30 atm. and they studied mixtures of cetane and mesitylene. For example, they found that at 525° C and 21 atm. pressure, the ignition delay increased from 4 to 6 msec when the cetane content of the mixture was increased from 30 to 80 per cent.

Ignition temperature data in the form of limiting pressure/temperature curves was obtained by BARON⁸ with a 12 cm × 2 cm diameter Pyrex glass furnace. Very reproducible results were obtained provided the glass tube was activated by some preliminary ignitions of rich fuel-air mixtures, whereas treatment of the tube with hydrogen fluoride lowered the ignition temperatures determined afterwards. Diethyl ether, dipropyl ether and acetaldehyde mixtures with nitrogen and oxygen were studied. The rather complex results obtained were interpreted in terms of the chain theory of combustion; a little additional information was obtained using additives in the combustible mixtures.

LAURE¹⁶⁰⁻¹⁶² has published numerous ignition delay versus temperature and ignition delay versus pressure curves for petroleum products, for pure hydrocarbons (cetane, cetene, α -methylnaphthalene, tetrahydronaphthalene, etc.) and for binary mixtures of these hydrocarbons. His apparatus consisted of a cylindrical bomb 50 cm high and 12 cm in diameter which was electrically heated by an alloy ribbon wound around the outside. Pressures up to 21 Kg/cm² were employed, the air being fed through a pipe fitted to the top of the vessel. Fuel was sprayed vertically downwards from a centrally mounted pressure injector operated by a known displacement of a small piston. As in the case of the R.A.E. apparatus care was taken to ensure that the fuel spray did not

strike the side walls of the bomb. Photographic records were obtained of the start of injection and ignition through windows situated along the side of the bomb. Laure concluded that whilst his results were not representative of engine conditions, he had shown definitely that increase in pressure facilitated ignition. For gas oil he determined the relationship

$$\tau P^{0.6} = \text{const.} \quad (18)$$

at a given temperature.

WOLFER³³³ working in Bird's laboratory carried out measurements of ignition delay at various temperatures and pressures using two types of closed ignition vessel. The first chamber was a hollow steel cylinder of length 48.3 cm and diameter 7.94 cm whose shape could be changed by the insertion of variously shaped blocks. The ignition chamber was enclosed in an air jacket and the whole unit was mounted horizontally and heated with gas jets. 70 to 700 mg of fuel could be injected from a Blackstone injection valve through the cover plate of the cylinder. The second chamber was designed so that the effect of air turbulence could be studied, and comprised a spherical cast-steel vessel with two shells with inserted hot plates which formed a characteristic combustion chamber which corresponded to that of an engine with opposed pistons. It had a diameter of 20 cm and a height of 5 cm (maximum) that could be varied. The shells were fixed on two axles which were rotated by a wedge belt drive off an electric motor. The hot wire was introduced through the axle, the plug at the end of the axle being taken out during the rotation of the shells. The vessel was cooled in an oil bath. The rotating shells transmitted corresponding air rotation in the ignition chamber. Fuel injection was effected by a needle valve which was connected to an accumulation pump. The smallest delay time recorded was 45 msec. Using a diesel fuel it was found that the effects of pressure and temperature upon delay time were large and the effects of all other factors were only secondary in magnitude. The relation found was

$$\tau P^{1.19} = 0.44 \exp. \left(\frac{4560}{T} \right) \quad (19)$$

which was quite accurate for fuels with a cetane number greater than 50. SMALL²⁷⁸, working with the second of Wolfer's bombs, confirmed that air turbulence had only a minor influence upon the ignition delays observed.

SELDON²⁷¹, working with a constant volume bomb, found that ignition characteristics of diesel fuels could be correlated with the engine ratings obtained in an engine, but that the order of merit obtained in a bomb depended somewhat upon the initial air temperature or density used for the tests.

SOKOLIK and YANTOVSKII²⁸² admitted combustible mixtures into a heated steel reaction vessel, the filling time being approximately 50 msec,

and followed the pressure difference between the reaction vessel and the admission vessel by means of an optical gauge consisting of a thin steel membrane between two thicker perforated membranes. With this equipment the small pressure pulses from cool flames were recorded as well as the large pulses from explosions. *n*-Heptane, *iso*-octane, benzene and diisopropyl ether were all studied at the same relative mixture strength. A temperature range 200° to 600° C and a range of initial pressures 0 to 8 atm. were fully explored. Two ignition delays, τ_1 and τ_2 were noted at two different pressure levels. It was found that τ_1 varied inversely as (pressure)^{*n*} where $n < 1$ for paraffin hydrocarbons and $n \approx 4$ applied to the case of the τ_2 pressure dependence. The influence of lead tetraethyl and other additives was also studied. It was concluded that engine knocking is caused by inflammation of a portion of the unburned charge in a time less than 10^{-5} sec which generates a shock wave. Knocking thus takes place as a result of two-stage auto-ignition if $\tau_2 \sim 10^{-5}$ sec and τ_1 is less than the duration of the engine combustion process (2 to 3 msec). High temperatures promote knocking by reducing τ_1 , high pressures by reducing τ_2 . Increasing turbulence reduces knocking by decreasing the duration of the combustion process and prolonging τ_1 because of better homogeneity. Anti-knock additives act by prolonging τ_2 , according to Sokolik and Yantovskii, and pre-ignition rating of fuels has no connection with knock rating. Diisopropyl ether has a good knock rating because τ_2 is long, even though it readily forms cool flames.

In 1941 STALLECHNER²⁸⁶ measured the ignition delays of diesel fuels in a bomb developed by Wentzel. Fuel was injected into the heated bomb and observation of ignition was recorded with a photo-electric cell the radiations being filtered through colour filters passing different wavelength bands. The shortest delays, that is, the intervals between the beginning of fuel injection and the first flash recorded, in the visible range were observed at approximately 5700 Å. Tests with a red sensitive photo-electric cell without filter and without diaphragm, however, gave even shorter ignition delays. These results showed that combustion of the fuel commenced with long-wave radiation. Considerably longer delays were recorded with a piezo-electric indicator, probably because the latter was insensitive to the first local ignition due to the smaller and more quickly evaporated droplets in the injected fuel spray. Delay times as small as 17 msec were recorded by Stallechner. Two years later LONN¹⁷⁸ reported experimental work of the same kind in which fuel was sprayed into a heated cylindrical bomb 75 cm long and 19 cm in diameter, ignition being observed by means of a photocell.

A return to the simpler pressure method of recording events leading to ignition was made in 1943 by PESCHARD^{237, 238} who introduced homogeneous combustible mixtures at pressures not exceeding 2 atm. into an unoxidizable steel cylinder previously empty. This bomb was situated in an electric furnace and a thermocouple-potentiometer

BOMB METHODS

indicated the temperature of the gas mixture. An optical manometer recorded the instantaneous pressure from the moment the gas was introduced and during the whole period of slow combustion. The time taken to introduce the combustible mixture into the apparatus was of the order of 100 msec. Peschard studied *n*-heptane, *iso*-octane and their mixtures; also benzene, ethyl alcohol and several petroleum oils. He found qualitative agreement between the ignition behaviour at various pressures in the bomb and the known octane numbers of the fuels examined, and suggested that a better correspondence might be obtained if much higher pressures and oxygen instead of air were used.

GAYLOR⁹⁶ measured the spontaneous ignition temperatures of a number of pure hydrocarbons, which included *n*-heptane and *iso*-octane, in a heated bomb and discussed the relationship of these data, flame speeds and combustion pressures with knock resistance in spark-ignition engines. Qualitative conclusions only were presented, but these included a discussion of the measured behaviour of several fuel additives. More recently HUM and SMITH¹²⁷ have studied ignition delays in a constant volume bomb and attempted to correlate the results with the corresponding cetane numbers of the paraffin and olefine hydrocarbons examined. Their method involved the taking of pressure-time records at given bomb temperatures. No universal correlation was obtained that applied to all types of fuels tested. The work included measurements of the ignition delays of some gas oils.

ADIABATIC COMPRESSION METHODS

HISTORICALLY, the first method employed for the determination of spontaneous ignition temperatures was that involving the rapid compression and therefore heating of a homogeneous combustible mixture. Although this method is almost fifty years old it is still used today, but the modern form of apparatus is considerably superior to the earlier forms; for this reason the earliest apparatus will not be described in detail but merely referred to together with an indication of their limitations and the use to which they were put.

The first determinations of the spontaneous ignition temperature of a fuel appear to have been undertaken in 1906 by FALK⁷⁹ as was mentioned in the Introduction. This work was carried out with hydrogen-oxygen mixtures, but Falk soon extended it to carbon monoxide and mixtures of hydrogen plus carbon monoxide in oxygen and oxygen plus nitrogen atmospheres⁸⁰⁻⁸². The gases were saturated with water vapour at laboratory temperature and pressure and the temperature after compression was calculated from the adiabatic law

$$\left(\frac{P_1}{P_2}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma} \quad \dots \quad (20)$$

since the deviations from this law under the conditions of the experiments were believed to be small.

As mentioned in the Introduction, DIXON, BRADSHAW and CAMPBELL⁵⁵ compressed fuel-air mixtures in glass tubes. Later, however, DIXON and CROFTS^{44, 45, 53, 58} used a cylindrical steel compression vessel (compression time approximately 60 msec) and though they attempted to (i) reduce errors due to wall cooling, (ii) create a quite finite and accurately measurable final volume, and (iii) produce a piston that was rapid in operation and gas-tight without the lubricating oil interfering with the gas mixture, they were not entirely successful. The main source of error was due to the piston bouncing at the end of each stroke with consequent cooling of the gas mixture. This defect was overcome in 1916 by CASSEL³⁴ who built an improved compression machine with a compression time of 43 msec.

The next piece of rapid compression equipment for ignition temperature determinations was built by Ricardo and used by TIZARD and PYE^{305, 306}. The piston stroke was 8 in. and the compression time was approximately 140 msec. The engine-like experimental cylinder had an internal diameter of $4\frac{1}{2}$ in. and the piston, which was moved by a

crank connected to a heavy flywheel, could be stopped at the point of maximum compression. The machine was the first to provide direct measurements of cylinder pressures, and Tizard and Pye were able to demonstrate very clearly the existence of ignition delays under experimental conditions akin to those occurring in a compression-ignition or a spark-ignition engine. The gas temperatures were calculated from readings of the pressure indicator and timing device measuring the time interval between compression and explosion. Heptane, ether and carbon disulphide were included in the studies. In 1926, TIZARD and PYE³⁰⁷ described an improved form of apparatus, but even with this, there was a grave danger of fracturing moving parts with compression times smaller than about 140 msec. Tizard and Pye's apparatus was subsequently taken over by FENNING and COTTON⁸³ who studied hydrogen, acetylene, benzene and hexane mixtures with air and attempted to overcome the difficulties in obtaining consistent results by modifying the apparatus; the chief modification was the use of a well-lubricated cylinder so as to eliminate friction effects. It was found that the initial stages of combustion were confined to a very small portion of the total gas charge and that this chemically active 'nucleus' appeared to survive despite very adverse conditions.

Pignot built a compression machine similar to Dixon's improved apparatus that had a compression time of only 25 msec but suffered from piston bounce; the apparatus has been described by AUBERT³. Compression was achieved by dropping a large weight on the piston of the vertical test cylinder. PIGNOT²⁴¹⁻²⁴³ presented curves of air/fuel ratio versus the initial mixture temperature (i.e. before compression) necessary to produce ignition, and later²⁴⁴ employed a three-dimensional type of graphical representation the third variable being the volumetric compression ratio which is necessary and sufficient to produce ignition at the end of compression. Several alcohols, paraffin hydrocarbons and aromatic hydrocarbons were investigated and it was found that the temperature required for auto-ignition showed a minimum as mixture strength was varied for the alcohols and aromatic hydrocarbons, but showed a steady rise as the mixture strength was increased in the case of the paraffin hydrocarbons. For air/fuel ratios (by wt.) of 10:1 and with a compression ratio of 9:1, the required initial mixture temperatures were in the range 40° to 90° C. AUBERT and PIGNOT and their collaborators also investigated the effect of adding anti-knock compounds in the vapour phase upon the auto-ignition of hexane- and heptane-air mixtures and found only a small influence^{6, 245} in the case of lead tetraethyl although the duration of the combustion period, as measured by the duration of the rise of pressure, was appreciably increased in the cases of lead tetraethyl, toluidine and methyl alcohol⁴. PIGNOT²⁴⁶ later reported further that at higher compression ratios both the ignition delay decreases and also the ratio of

the maximum pressure to the initial pressure decreases. A fluctuating pressure-time curve was obtained with hexane containing lead tetraethyl.

Some novel experiments were described by DAVID⁴⁹ who effected the adiabatic compression of inflammable gas mixtures by the flow of compressed air in a tube containing the mixture. The spontaneous ignition temperature decreased with increase of pressure in mixtures of methane and oxygen.

In 1930 SMITH²⁷⁹, using compressed air as the driving force for the piston instead of a falling weight or heavy flywheel as hitherto, attempted to shorten the compression time, but, due to the difficulty of bringing the piston to a dead stop at the end of the stroke without rebound or mechanical fracture, found that 50 msec was the practical limit.

WHEELER³²² in 1935 investigated the ignition of methane-air mixtures over a wide range of concentrations by compression methods. His apparatus comprised a pressure cylinder connected with a low-pressure chamber by a small aperture. Ignition occurred in the pressure cylinder only when this aperture connecting the low-pressure chamber, containing a similar mixture, was less than 2.25 mm in diameter. The hole was covered by a thin copper diaphragm which ruptured suddenly at a sufficiently high pressure. Wheeler also reported that mixtures could not be ignited by the passage of a compression wave which heats them only momentarily. DIXON and HARWOOD⁵⁹ working also with methane found that mixtures containing 7.0 to 7.5 per cent of the fuel had the lowest ignition temperatures and the ignition temperatures fell regularly as the pressure was raised. They found that with sufficiently rapid compression, ignition could be obtained even though there was continuous release of pressure through a hole in the vessel. WÖHLBIER³³² reviewed the data on the ignition of methane-air mixtures by compression two years later.

SCHMIDT^{264, 265} built special apparatus to simulate the adiabatic compression of fuel-air mixtures in spark-ignition and compression-ignition engines. He recorded pressures piezo-electrically, temperatures were calculated from initial temperatures and pressures, and a high piston speed was found to be necessary and was used. He analysed his experimental results and the results of previous workers and concluded that the ignition characteristics could be summarized with the aid of not less than three constants, the first being a proportionality factor, the second an exponential temperature factor and the third a pressure exponent.

Jost and his collaborators Teichmann and Rögner devised and used a compression-ignition apparatus in which the movement of the piston was effected by a falling weight. Gas mixtures were compressed in a steel cylinder 56 mm in diameter with the piston connected to a reaction vessel; the piston was held at the point of maximum compression

and the time of compression occupied 50 to 100 msec. JOST and TEICHMANN^{145, 149, 301} tested heptane, *iso*-octane and benzene, and plotted induction period *v.* temperature curves and calculated activation energies from the slopes of these curves. They attributed the higher auto-ignition temperatures found by WEBER and RASTETTER³²⁰, who used a 40 mm bore cast-iron vertical cylinder, to the fact that these workers did not cause the piston to be held at its lowest point. JOST and RÖGENER¹⁴⁸ made extensive measurements with the apparatus and in order to gain knowledge of the knocking process, investigated the behaviour of *n*-heptane containing additives such as lead tetraethyl, iron pentacarbonyl, aniline, acetone peroxide, ethyl nitrate and amyl nitrite. They found that whilst aniline and iron pentacarbonyl caused the induction times to be increased, lead tetraethyl had the opposite effect. RÖGENER²⁵⁸ subsequently investigated heptane, pentane and butane mixtures with air and found evidence that the spontaneous ignitions followed by a two-stage mechanism. The pressure range studied was 5 to 40 atm. and the compression temperatures were in the region of 400° to 500° C. JOST^{146, 147} recently explained the testing technique, summarized many of the results obtained, and discussed the significance of the two induction periods the first of which decreases and the second of which increases with temperature though both decrease with pressure.

SCHEUERMEYER and STEIGERWALD²⁶² made use of compressed air to drive the piston of their adiabatic compression apparatus which was afterwards held in the end position. In such experiments it is necessary, if accurate measurements of delay times are to be obtained, to ensure that the compression time is small compared with the delay time so that the reactions occurring during the compressing (when conditions are varying) are negligible. Thus the compression rate must be high and the heat transfer small. The apparatus employed had a cylinder diameter of 80 mm and piston velocities of up to 60 m/sec were obtained with very small loss of heat. Ignition could be inferred either from the readings of photo-electric cells or from the increase in pressure. Generally the delay times obtained by the use of these two criteria of ignition were approximately equal, but under low-pressure conditions with long induction periods the times indicated by the photo-electric cells were shorter than those obtained from the pressure readings. Mathematical investigations by PFRIEM²⁴⁰ on the loss of heat from apparatus of this kind with a cylinder diameter of 80 mm and about 40 m/sec piston velocity showed that the quantity of heat lost during the compression would be about 3 per cent, compared with 11 per cent for a cylinder of diameter 40 mm and a piston velocity of 10 m/sec. Pfriem concluded also that the ignition delays measured might easily be increased by 100 per cent due to heat transfer from the ignition vessel.

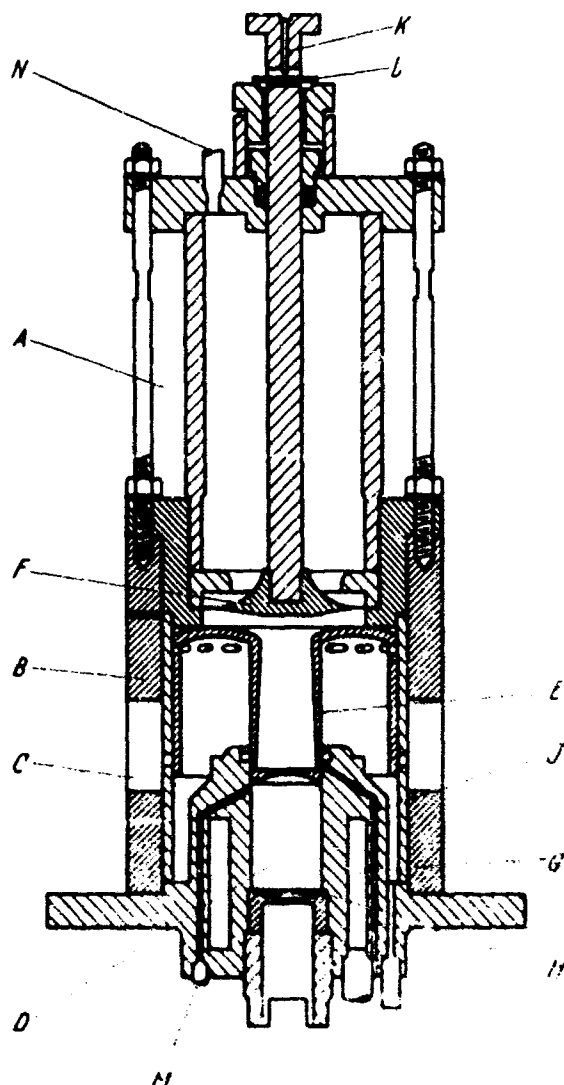
SPENCER²⁸⁵ studied the ignition characteristics under somewhat specialized conditions of a number of fuels which included *iso*-octane, toluene, benzene, gasoline and methyl alcohol with the addition, in some cases, of lead tetraethyl. He suddenly compressed the fuel-air mixture in a cylinder in contact with an electrically heated hot spot and followed the course of the burning by indicator cards and schlieren photography. He concluded that a combination of ignition temperature, heat of combustion and specific heat of the combustion products might enable the maximum permissible performance of an internal combustion engine to be predicted.

The most recent compression-ignition apparatus to be developed is very remarkable. This was described in 1948 by LEARY *et al.*^{164, 300} and possesses the following features: the compression is completed in approximately 6 msec, provision is made for obtaining simultaneous records of piston motion and cylinder pressure and the combustion chamber is unlubricated. The piston is operated by the release of a high nitrogen pressure, and a nitrogen cushion chamber prevents the piston from damage. Ports in the piston then come into register with ports in the lower cylinder sleeve and the cushion pressure is released, allowing the driving pressure to hold the piston to its seat with no rebound. A sectional diagram of this compression apparatus which is known as the M.I.T. (Massachusetts Institute of Technology) apparatus is given in *Fig. 14*. In practice the driving nitrogen pressure is 500 lb./in.² and the initial cushion chamber nitrogen pressure is approximately 110 lb./in.² which rises to approximately 800 lb./in.² at the end of the piston stroke. LEARY, LIVENGOD and their collaborators^{165, 300} used this apparatus to determine the variations in ignition delay and rate of pressure rise after compression of *iso*-octane, gasoline, triptane, benzene and butane-air mixtures with mixture strength and compression ratio as the only independent variables. Generally it was found that a minimum value of ignition delay occurred at approximately stoichiometric mixture conditions and that delay time increased with decrease in compression ratio. It was suggested, from the test results, that the high knock rating value of triptane was mainly due to a long ignition delay, whereas the high knock rating value of benzene was mainly due to a relatively slow rate of pressure rise after ignition commenced. JOVELLANOS *et al.*¹⁸¹ reported an investigation of the effects of lead tetraethyl and of ethyl nitrate additives upon the ignition delay of fuel-air mixtures in a modified version of the M.I.T. apparatus. It was found that lead tetraethyl had an insignificant effect on the ignition delay, although ethyl nitrate caused an appreciable reduction in the delay. LIVENGOD and LEARY¹⁷⁴ recently examined the non-uniform nature of gas heating by rapid compression and concluded that bright spots first appear locally and these spread through the mixture. Schlieren photographs proved the existence

ADIABATIC COMPRESSION METHODS

of temperature gradients in the compressed gas even when it consisted of dry air.

Very recently the ignition of gas mixtures by impulsive pressures has been investigated experimentally and discussed theoretically by two groups of workers. GERSHANIK *et al.*⁹⁷ used a vertical glass tube of length 150 cm and internal diameter 2.1 cm, sealed at the bottom and



A = upper cylinder. *B* = lower cylinder. *C* = cushion chamber. *D* = combustion chamber. *E* = piston. *F* = poppet valve. *G* = water jacket. *H* = impact rings. *J* = nitrogen duct. *K* = locking pin. *L* = shear pin. *M* = conduit to mixing chamber. *N* = conduit to nitrogen bottle.

Fig. 14. M.I.T. rapid compression machine

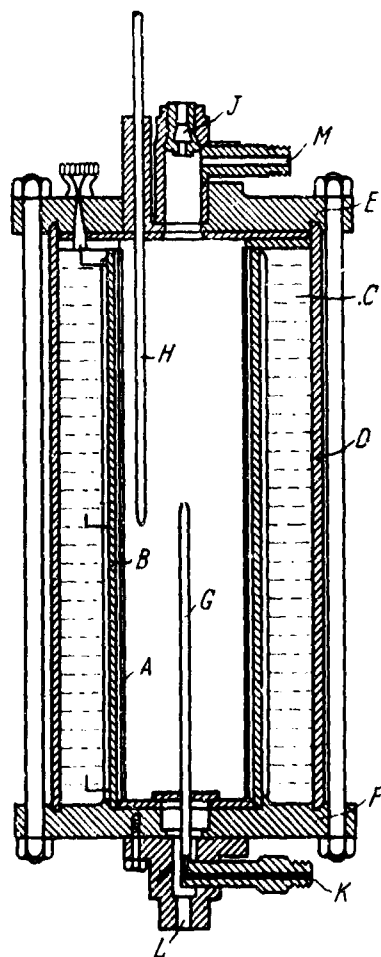
stoppered at the top, which was filled with the test combustible mixture at low pressure and heated to a given temperature. Upon withdrawing the stopper the inflowing air compressed the mixture to atmospheric pressure and adiabatically raised its temperature, whereupon the occurrence or non-occurrence of ignition was observed photographically. This air moved at a velocity of 80 to 300 m/sec and $\text{H}_2\text{—O}_2$; $\text{H}_2\text{—O}_2\text{—CS}_2$; $\text{CS}_2\text{—O}_2$ and $\text{C}_2\text{H}_2\text{—O}_2$ mixtures were studied; ignition delay times as small as 10 msec were recorded in some instances. SHEPHERD²⁷⁴, on the other hand, promoted the ignition of gas mixtures by permitting a shock wave to travel through them.

FLOW METHODS

FOR some forty years there has been a succession of combustion research workers who favoured a method of measuring ignition temperatures and delay times in which the combustible mixture flows along a tube at a controlled temperature. The forms of apparatus and conditions of operation have differed widely though generally speaking they have all possessed the advantage that mixing of the fuel and oxidant was more rapid than in the static methods of test with consequent reduction of the 'physical' portion of the observed delay time.

DIXON and his collaborators⁵⁷ were the earliest to use the flow technique and their 'concentric tube' apparatus was used by them for more than twenty years. Air or oxygen was fed along a wide porcelain tube the temperature of which was slowly increased by an external electrically heated platinum wire spiral. The combustible gas was fed up a narrow tube, co-axial with the main tube, terminating in an orifice. In this manner the fuel and oxidant were separately heated and continuously renewed. As the temperature rose, a point was reached at which ignition occurred; this ignition temperature was recorded by a quartz tube covered thermocouple. DIXON and COWARD⁵⁸ reported in 1909 that several gases had ignition points that were relatively insensitive to variation in the rates of flow of the two gas streams and changes in the dimensions and materials of the two tubes, although this did not apply in the case of the paraffin hydrocarbons. During the years 1922-1930, Dixon employed a modified procedure; instead of passing continuous streams of the two gases, he made the stream of fuel intermittent and recorded for a succession of temperatures, the intervals of time between the sudden turning-on of fuel and the appearance of flame. In this way ignition delay times of 0.5 to 10 sec were observed at different temperatures, but he regarded those measurements at 0.5 sec delay as the most fundamental as in his opinion they approximated to the instantaneous inflammation condition that he had earlier defined. A diagram of Dixon's later concentric tube apparatus is shown in *Fig. 15*, this being used over a pressure range extending from 50 mm mercury up to 11 atm. The larger tube consisted of a glazed silica cylinder of 12 cm I.D. and 65 cm length and was closed at both ends by heavy steel plates. The central tube was of quartz, 4 mm external diameter and with an orifice of 2 mm diameter, the rim of which was ground and lightly fused. A resistance thermometer was suspended in a silica cover inside the main tube. Ignition was observed through a small plate-glass

window situated at the top of the furnace. Times between the admission of the fuel and the occurrence of ignition were estimated to 0.1 or 0.2 sec either by a stop-watch or by pendulums set to beat 0.5 and 0.6 sec. The fuel was turned off immediately after ignition to avoid overheating the rim of the orifice. Hydrogen, carbon monoxide and their mixtures, methane, *n*-pentane, ethane, ethylene, propylene, acetylene, carbon disulphide and ether were all tested in air and/or oxygen and special attention was paid to differentiating between dry and moist



A = glazed silica cylinder 65 cm long and 12 cm I.D. *B* = clay tube. *C* = kieselguhr insulation. *D* = steel case. *E* = heavy steel end-plate. *F* = heavy steel end-plate. *G* = quartz tube 4 mm external dia. with an orifice 2 mm dia. *H* = resistance thermometer in silica cover. *J* = plate-glass window. *K* = conduit for the fuel vapour. *L* = conduit for the atmosphere. *M* = conduit for exhaust gases.

Fig. 15. Dixon's concentric tube apparatus for experiments under various pressures

air when carbon monoxide was the test fuel⁵⁴. For some tests additives were introduced into the air stream, for example, iodine, ethylene dibromide, *iso*amyl bromide, bromobenzene, phosphoryl chloride, lead tetraethyl and nitrogen peroxide. In the special case of the last-named additive it was found to be desirable to employ a narrower main tube of 5 cm diameter made of smooth silica to avoid slow diffusion of the peroxide into the furnace lagging and back again which occurred with the standard apparatus with the consequent upsetting of subsequent tests. Many test results with the concentric tube apparatus are to be found in papers by DIXON and HIGGINS⁶⁰⁻⁶⁵ and the summarizing paper by COWARD⁴¹. Generally it was found that ignition temperatures (with delay equal to 0.5 sec) were lower in oxygen than in air for a given fuel. The effect of static pressure upon the ignition temperature

was different with different fuels. The presence of small amounts of nitrogen peroxide lowered the ignition temperatures of the fuels studied.

In 1919, WHITE and PRICE ³²⁴ employed a dynamic tube method of measuring ignition temperatures. They fed combustible mixtures into glass tubes of various diameters and found that with increasing diameter the ignition temperature decreased at first and then increased. This effect was in some measure due to the changes in the flow velocities and residence times as White and Price themselves demonstrated with a 14 per cent ether-air mixture for which ignition temperature increased with flow velocity in a given tube.

WARTENBERG and KANNENBERG ³¹⁹ studied hydrogen-oxygen and carbon disulphide-oxygen mixtures in an apparatus similar in principle to that of Dixon. Though their ignition temperature for carbon disulphide was the same as that observed by Dixon, their value for detonating gas mixture was rather higher.

CALLENDAR ³⁰⁻³² in 1927 reported measurements of the temperature of initial combustion of a number of organic compounds in air. His technique consisted in passing the combustible mixture through a heated glass tube of 1.2 cm I.D. and 50 cm length at the rate of 1 l./hr. The criterion of initial combustion was taken to be the formation of carbon dioxide, aldehydes and other products of reaction which included organic peroxides.

GOLDMANN ¹⁰³ investigated the ignition temperatures of hydrogen-oxygen and carbon monoxide-oxygen mixtures by means of a technique based on that of Dixon. Two heated gas streams 2 mm in diameter were caused to meet at right angles under a large bell jar and the temperature at the junction was measured by pyrometers. 80 l./hr. of oxygen and 40 to 70 l./hr. of hydrogen were fed into the system and ignition temperatures were reported as pairs of values, one for each stream. Nitrogen dilution had little effect, but addition of carbon dioxide raised the ignition temperatures. Goldmann compared and contrasted his results with those of DIXON ⁵⁶ and those of WARTENBERG and KANNENBERG ³¹⁹.

A very careful study of the reactions occurring between propane and oxygen in a dynamic system was made by BURKE and SCHUMANN ²², who passed the gaseous mixture at a given pressure and mixture strength through a long narrow tube coiled in a molten bath at a given temperature. The criterion of ignition and further reaction was determined by analysis of the issuing gases. The rate of flow of the combustible mixture, and the length and diameter of the reaction tube were varied. This investigation gave information over and above the temperature and pressure at which chemical reaction commenced for a given mixture, and the authors attempted to place a kinetic interpretation upon their results.

In 1934 DYKSTRA and EDGAR²⁷ adopted an ignition apparatus of the Dixon type to study the vapour phase ignition temperatures of hydrocarbons in mixtures of nitrogen and oxygen. The outer Pyrex glass tube was 75 cm long and 3.4 cm I.D. and the inner tube was of the same material, 0.65 cm I.D. drawn out to a 2 mm orifice. The two tubes were mounted concentrically with the orifice of the inner tube 18 cm from the exit of the outer tube. A little nitrogen was added to the vaporized fuel stream as a carrier gas and an aid to vaporization. Heating was achieved by means of an electrical resistance winding around the outer tube. The temperature of the mixed gases at the time when explosion occurred was taken as the spontaneous ignition temperature. Gasoline, *n*-octane and *iso*-octane were reported upon in the paper by Dykstra and Edgar. A striking phenomenon was observed; for a given percentage of fuel vapour in the mixture the ignition temperatures decreased steadily as the oxygen/fuel ratio was increased, until suddenly an abrupt fall of 200 C° occurred with only a small change in this ratio. Similar abrupt changes were noted corresponding to small changes in the fuel concentration at constant oxygen/fuel ratio. These experimental results were shown to be a manifestation of the existence of 'zones of non-ignition' in a temperature oxygen/fuel ratio diagram, which in turn arose on account of the chain character of the reactions preceding ignition.

Yet another apparatus of the Dixon concentric tube variety was described in 1935 by BUNTE and BLOCH²⁸ who tested hydrogen, carbon monoxide, methane, ethylene and Karlsruhe manufactured gas. Their apparatus comprised two separately heated streams of combustible and air which mix at the entrance to a capillary tube 3 cm long and 2 mm I.D. that widens out into a larger tube. All tubes were situated in an electric furnace and the wider tube beyond the capillary was slightly hotter so that ignition took place there where a thermocouple was situated to record the temperature. As was typical with this method, no special attention was paid to the residence time and the test results were plotted on the basis ignition temperature *v.* percentage combustible in the mixture. It was found that the ignition temperatures of hydrogen and the manufactured gas depended only slightly upon mixture strength.

A novel variation upon the flow method of ignition temperature measurement was introduced by SACHSSE²⁵⁷, who, in an endeavour to study short ignition delays, fed a combustible mixture through a tube along which there was established an increasing temperature from 100° to 850° C. Sachsse regarded the time spent by the gas mixture in warming up to, say, 820° C as contributing little towards the ultimate ignition, so that the true delay time was the time spent at 820° to 850° C. This viewpoint cannot be true for hydrocarbons (possible exception methane) which will undergo considerable chemical changes during

the long time spent at the lower temperatures and has been rightly criticized by SOKOLIK ²⁰⁰.

KONDRATJEV ¹⁵⁸ determined the pressure ignition limits of combustible mixtures by passing them through a heated reaction vessel at given pressures and gradually raising the temperature of the vessel. The occurrence of ignition is indicated by a sudden rise in pressure. The accuracy of the method was not very great.

Three entirely different flow methods have been described in the recent post-war years. MULLEN, FENN and IRBY ²⁰³ passed a high velocity stream of combustible gases over heated cylindrical rods. The surface temperature of the rod was increased electrically until just sufficient to cause ignition at various flow velocities. This method will be referred to more fully in the next chapter.

Between 1945 and 1946 an entirely different flow technique of measuring spontaneous ignition delay times at various temperatures and pressures was developed by MULLINS at the National Gas Turbine Establishment, Farnborough, England and this is known as the N.G.T.E. Method ²⁰⁷. The possibility of measuring ignition delays in a simple duct through which are passed a hot combustion chamber exhaust stream and the test fuel had been noted during a series of spectroscopic studies with a 4 in. diameter parallel duct ²⁰⁵ and this basic method was developed and adopted as a standard testing technique. Although the hot air stream produced in this manner is vitiated, i.e., is deficient in oxygen and contains some carbon dioxide and water vapour, from the point of view of similarity to gas turbine conditions and, indeed, similarity to many technical combustion processes, this is an advantage. Furthermore, ignition delays of different fuels or ignition delays of the same fuel measured under different physical conditions are directly comparable (at a given temperature) notwithstanding the presence of air vitiation since, broadly speaking, the actual degree of vitiation is a simple function of the air temperature. Thus the oxygen index, defined ¹¹ as the fractional partial pressure of the oxygen in the air, depends on the air temperature at the entry to the ignition delay measurement section approximately as indicated in the Duplex scale in Fig. 16.

A full description of the N.G.T.E. apparatus and the standard technique of operating it has been given in ref. ²⁰⁸. Briefly, the apparatus consists of a lagged nimonic 3° diffusing test section 36 in. long and 6 in. I.D. at entry fitted with a row of fused silica observation windows (see Fig. 17). Through this duct passes a high velocity (150-250 ft./sec at entry to the diffuser) hot vitiated air stream and the test fuel which is injected into the duct either as a finely atomized spray or a vapour.

Assuming that the pressure in the diffuser remains sensibly constant and that the injected fuel molecules rapidly acquire the velocity of the

FLOW METHODS

flowing air stream, the delay time from the diffuser entry to a plane x ft. along the axis of the diffuser (see notational diagram in *Fig. 18*) may be shown to be

$$\tau_x = \frac{\pi P}{4QRT} \int_0^x (D + 2x \tan \theta)^2 dx \quad \dots (21)$$

which for a 3° diffuser and under the standard test conditions reduces to

$$\tau_x = \frac{69 \cdot 2}{QT} \left(\frac{P}{P_s} \right) (0 \cdot 0625x + 0 \cdot 0131x^2 + 0 \cdot 000915x^3) \quad \dots (22)$$

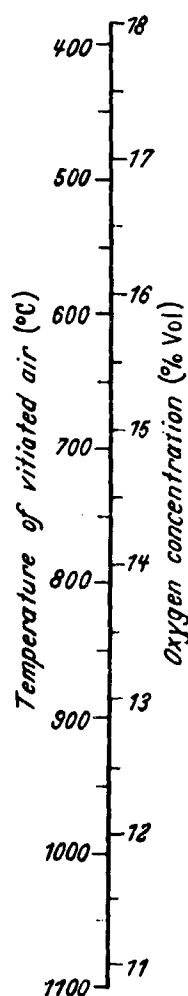
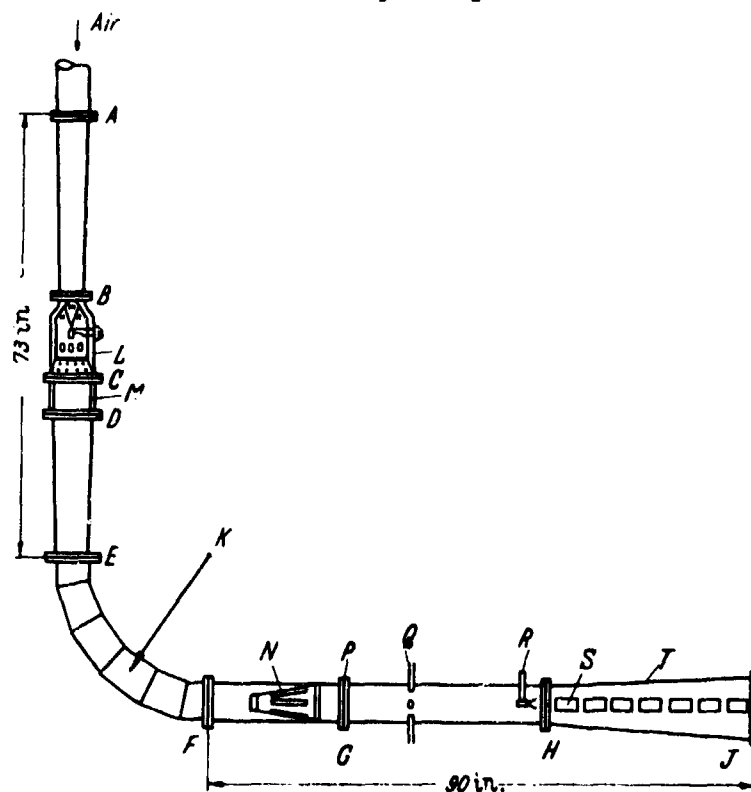


Fig. 16. Hot vitiated air stream oxygen content (duplex scale)

Small corrections are applied, an 'end correction' (due to the fuel injection plane not coinciding with the diffuser entry plane) and a 'dilatation correction' (due to the change in the number of moles of the slave combustion chamber gas stream at inlet and outlet). Flame front positions are estimated visually, care being taken to ignore any intermittent flashes of flame ahead of the steady flame front position, as these are due to local pockets of mixture richer than the average for the whole stream²⁰⁹. A method of calculating the 'global' activation energy was worked out; the slope of the log (ignition delay) versus reciprocal (absolute temperature) curve is approximately proportional

to this activation energy. The equation which corrects for vitiation effects and the temperature dependence of r.m.s. velocities is:

$$E = \frac{R \log_e \left[\frac{\tau_1'}{\tau_2'} \left(\frac{T_1}{T_2} \right)^{\frac{1}{2}} \right]}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \quad \dots \dots (23)$$



Internal diameters of flanges: $A = 6$ in., $B = 4\frac{1}{2}$ in., $C = 7$ in., $D = 7$ in., $E = 6$ in., $F = 6$ in., $G = 6$ in., $H = 6$ in., $J = 9\frac{1}{2}$ in., $K =$ segmented bend of 24 in. radius. $L =$ T-scheme combustion chamber. $M =$ nimonic liner. $N =$ nimonic mixer. $P =$ perforated nimonic plate. $Q =$ four chromel-alumel shielded thermocouples. $R =$ fuel injector. $S =$ fused silica observation windows. $T =$ diffuser with 3° slant angle. *Note:* All ducts downstream of flange C are made of 16-gauge nimonic alloy and are heavily lagged.

Fig. 17. N.G.T.E. standard 3° spontaneous ignition rig

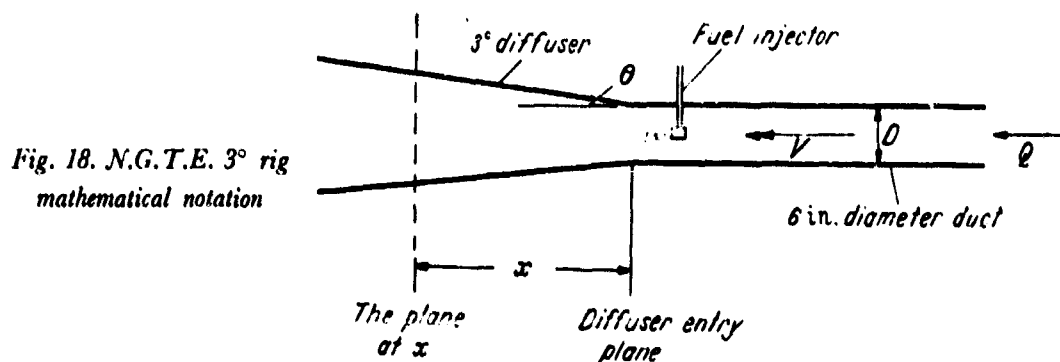


Fig. 18. N.G.T.E. 3° rig
mathematical notation

Over a period of seven years MULLINS studied the influence of physical²⁰⁹ and chemical factors²¹⁰ on the ignition delay of kerosine-air mixtures, tested seven gaseous fuels²¹¹ over a range of static pressures and more

than 130 liquid combustibles at atmospheric pressure^{212 215}. The physical factors included air temperature, spray particle size, fuel temperature, air turbulence, air/fuel ratio, gas velocity and static pressure. The chemical factors included fuel additives, fuel structure and oxygen partial pressure of the air stream. The gaseous fuels examined included methane, acetylene, hydrogen, carbon monoxide and vaporized kerosine. The liquid fuels tested included hydrocarbons, organic compounds containing nitrogen or halogen, alcohols, ethers, aldehydes, ketones, esters, *cyclo*-compounds, heterocyclic compounds and carbon disulphide. Delay times were measured within the range 0.5 to 50 msec.

In 1947 MULLINS²⁰⁴ calculated the relationships between T , x and t for a hot homogeneous fuel-air mixture flowing through a duct and undergoing preflame reactions. If the decrease in the fuel concentration due to reactions having already occurred is negligible he obtained the equations:

$$\frac{dT}{dx} = \frac{P \cdot \bar{A} \cdot B \cdot C \cdot q}{Q \cdot C_p \cdot R} \cdot \frac{e^{-\frac{E}{RT}}}{\sqrt{T}} \quad \dots (24)$$

and

$$t = \frac{C_p}{C \cdot B \cdot q} \int \frac{e^{\frac{E}{RT}}}{\sqrt{T}} dT \quad \dots (25)$$

which with an allowance for the amount of fuel consumed became

$$\frac{dT}{dx} = \frac{P \cdot \bar{A} \cdot B \cdot C \cdot q_1 \cdot e^{-\frac{E}{RT}}}{Q \cdot C_p \cdot R \cdot \sqrt{T}} \left[1 - \frac{C_p}{C \cdot q_1} (T - T_1) \right] \quad \dots (26)$$

and

$$t = \frac{C_p}{C \cdot B \cdot q_1} \int \frac{e^{\frac{E}{RT}} dT}{\sqrt{T} \left[1 - \frac{C_p}{C \cdot q_1} (T - T_1) \right]} \quad \dots (27)$$

Recently JACKSON and BROKAW¹³¹ reported a laboratory scale flow technique in which, after rapid mixing, the fuel and air were passed vertically along a Vycor tube 5 cm I.D. and 36 in. long. A constant temperature throughout the reaction volume was accomplished by wrapping resistance heaters in ascending sections on a metal tube surrounding the Vycor tube. Each section was individually controlled by a variable-voltage transformer. Ignition delays were recorded by a photocell relay and electric timer, or by a pressure recorder. Observation was at the top of the furnace when the photocell was employed. This method of observing introduces some uncertainty in the mixture strength giving rise to flame as there will be a gradient of fuel concentration at the interface region between the fully mixed gases and the leading stream of air or nitrogen. Delay times less than 200 msec could not be measured. Propane was the test fuel reported in these investigations, and all tests were made at atmospheric pressure.

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MANY workers have studied the ignition of combustible gas mixtures by heated surfaces. These surfaces are usually metal and take the form of wires, rods, particles, spheres or plane surfaces. The primary measurement is that of the limiting surface temperature above which ignition is achieved and this is termed the ignition temperature. Generally this temperature is higher, and often very much higher, than the corresponding ignition temperature for the fuel-air mixture as determined by, say, the heated crucible method. MORGAN²⁰² has suggested that this may be due to the fact that convection currents cause the time of contact between the mixture and the solid to be short, thereby necessitating the higher temperature always associated with a short delay. Alternatively some catalytic action may be responsible for the high ignition temperatures noted with the heated solids. The more important contributions to this branch of thermal ignition will now be reviewed, approximately in chronological order as usual, and the scope of the works and the status of knowledge will be discussed and summarized.

As early as 1907, CONROIT and MEUNIER³⁸ reported that whether or not an incandescent wire ignited an inflammable gas mixture depended upon the wire diameter. With soft iron wire the minimum diameter was 0.9 mm, whilst for platinum wire the critical diameter was 0.2 mm. Twelve years later THORNTON³⁰⁴ summarized the several investigations, including that of Conroit and Meunier, that had preceded his own comprehensive study of the ignition of gases by hot wires. He found from his own investigations that ignition by hot wires occurred at a definite rate of generation of heat in unit length which in a steady state at low temperatures is removed by convection and is nearly independent of diameter. He further discovered that ignition was independent of gas pressure, of the heat of combustion of the gas mixture and its composition, and for any given metal, independent of the nature of the fuel in so far as changing the wire diameter was concerned. This insensitivity of hot wire ignition towards many physical and chemical factors (contrast with spark ignition phenomena) led him to suppose that the critical events occurred either within the surface layer of the metal itself or very close to the surface and that oxygen was the chief substance concerned.

The phenomenon of flameless surface combustion was noted by SHEPHERD and WHEELER²⁷⁵ in 1926 whilst studying a matter of considerable importance in coal mines, namely, the ignition of methane-air mixtures by wires carrying a current (miners' electric lamp bulbs had

a 2 V glowing filament). Both platinum and tungsten wires could readily be made to give ignition, but for the former ignition only occurred within a narrow range of currents; below this range flameless surface combustion only takes place and above it the platinum wire fuses without causing ignition of the mixture. Shepherd and Wheeler concluded that ignition only takes place if the heated mixture remains in contact with the hot wire for a time greater than the ignition delay. In the case of tungsten it was shown that with a fuel-oxygen atmosphere the metal itself oxidized, its temperature rose and it burst into flame which, though of short duration, was very hot and promoted the ignition of the surrounding gas mixture. Morgan's second suggestion as to why hot wire ignition temperatures are greater than the corresponding homogeneous values, namely, that there is some catalytic action by the metal, is borne out by the test results of COWARD and GUEST⁴², who studied natural gas-air mixtures and heated metal bars. They showed that to cause ignition metals of greater catalytic effect must be hotter than metals or substances of smaller catalytic effect.

Until 1929 the work on hot wire ignition had been aimed at obtaining fundamental information that might be useful in assessing the explosion hazards as might occur in coal mines, battery rooms of submarines, or in manufacturing processes where combustible gas is set free. In 1929, however, SCHAAD and BOORD²⁵⁸ attempted to use a simple hot wire ignition tester to indicate the knock rating value of substances added to the fuel-air mixture. Using a platinum wire and toluene, *isoamyl* acetate or kerosine as parent fuel, they found that various known knock suppressors caused the current required to ignite the most easily ignitable fuel-air mixture to be increased and conversely known knock promoters decreased the required current. Similar spark tests failed to show up such effects and the authors attributed this to the fact that under hot wire ignition conditions many pre-ignition reactions occurred and, in fact, there occurred a finite induction period.

Between 1929 and 1935 a group of papers were published which dealt with the ignition of combustible mixtures by means of heated surfaces. JEUFROY¹³⁵ worked with electrically heated sheets of iron or nickel 4.5 cm by 14 cm by 0.5 mm or 1 mm thick. Temperatures were measured by an iron-constantan thermocouple soldered to the metal sheet and the temperature to which the metal had to be heated to ignite drops of various pure organic compounds and petroleum products were determined. Ignition temperatures recorded were in the range 445° to 765° C. The same ignition temperatures were obtained if, instead of the liquid, the corresponding vapour was passed over the heated metal surface. Also, it was reported in reference³⁴⁴ that ignition temperatures of liquid drops allowed to evaporate from an iron surface in a small-scale oven were much lower than the spontaneous ignition temperatures of the vapours.

GUEST¹⁰⁸ contributed a very comprehensive paper dealing with the ignition of natural gas-air mixtures by heated surfaces. He first of all confirmed the conclusions of previous workers that the ignition temperature, when the heat is supplied via a heated surface, is always higher than the true ignition temperature when the heating is applied directly to the gas mixture. He measured surface ignition temperatures with the gas mixtures flowing parallel to or perpendicular to the heated surface, and obtained results which could be satisfactorily explained in terms of the influence of gas convection from the surface. Large surfaces promoted ignition at lower temperatures than small surfaces of the same kind. Strongly catalytic surfaces or surfaces possessing an interstitial structure gave rise to higher ignition temperatures than surfaces of the same size not possessing these characteristics. The most easily ignited mixtures were those near the weak limit of inflammability, whilst the most difficult to ignite with a strong catalytic surface, such as platinum, were the stoichiometric mixtures. Surfaces consisting of high melting point substances ignited natural gas-air mixtures with similar ease except those forming a layer of scale or ash, e.g. iron or impure carbon; such a layer possesses a lower heat conductivity than the surface proper and serves to raise the ignition temperature. When several seconds are needed to heat the surface, the ignition temperature is not sensitive towards changes in heating rate. Vibration of the heated surface or the disturbance of the gas mixture by sound waves had no effect upon ignition temperature, although the presence of a powerful electrostatic field lowered the ignition temperatures appreciably, especially when the relative charge on the surface was positive rather than negative.

NAYLOR and WHEELER²¹⁸ studied the ignition of methane-oxygen mixtures with added nitrogen, argon or helium in heated vessels and concluded that thermal reactions occurred that were catalysed by the products of an initial slow and flameless combustion. Chemical analyses were made and it was found that iodine, halogen compounds and lead tetraethyl inhibited the chemical reactions. The temperature to which the surface had to be heated to cause ignition was found to depend upon the absorptive and conductive powers of the inert gas present, the oxygen/fuel ratio (especially when inert gases were present) and the ratio of gas volume to heated surface area. In extending their work²¹⁹ to higher paraffin- and olefine-air mixtures in 1933 they found some different effects. For example, the lowest ignition temperatures and longest ignition lags for methane-air mixtures occurred with excess oxygen, whereas for higher paraffins the opposite is true. Again, traces of iodine or organic halides accelerated the preflame reactions of ethane-air mixtures in contrast to the case of methane-air mixtures. Ignition temperatures decreased with increasing molecular weight of the hydrocarbon. Two years later they extended their methane-air measurements to reduced pressures²²⁰ and found effects which depended

critically upon the mixture strength; a 10.7 per cent methane-air mixture had two pressure limits of ignition, whereas richer mixtures had only one. At low pressures the ignition delay increased and at a given pressure the delay increased with fuel concentration. These curious effects are undoubtedly attributable to the influence of the surface in promoting the formation of active centres or breaking of already existing reaction chains. PRETTRE ²⁴⁹, for example, has given a detailed review of the ignition of hydrogen-oxygen mixtures by hot surfaces and has described original experiments with silica, porcelain glass and KCl coated glass surfaces, and other treatments of the effect of walls upon gaseous chain reactions will be found in modern text-books such as reference ¹²⁰.

AUBERT and PIGNOT ⁵ investigated the ignition of mixtures of various C₆-hydrocarbons and air in a 400 ml. cylinder (heated to 105° C) by means of a hot point which consisted of an electrically heated platinum wire. At some critical wire temperature a sudden increase in its temperature is noted which indicates the occurrence of ignition. In a later paper PIGNOT ²⁴⁷ described how this increase in wire temperature—the wire comprised a 10 cm spiral and was 0.1 mm in diameter—caused the displacement of a piston in the steel cylinder. Curves were given of piston displacement and wire voltage versus time for the four C₆-hydrocarbons tested; the wire temperature was a function of the voltage. In the following year, 1934, DAVIES ⁵⁰ reported upon the rate of heating of platinum, palladium, gold and silver wires in hydrogen-carbon monoxide-air mixtures using the electrical resistance of the wire itself as a measure of its temperature. No heating due to surface combustion was found in the cases of gold and silver wires. He also found that carbon monoxide suppresses the low-temperature reactions of hydrogen and explained this result using the Langmuir adsorption activation theory. Later DAVIES ⁵¹ did experiments with methane-air mixtures and gold or platinum wires and found that wires of 0.127 mm diameter failed to ignite these mixtures although ignition did ensue when the wires were fused. In this connection, the gold wires were the more effective as their lack of catalytic action more than compensated for their lower fusion temperature. A further influence is introduced by placing the wire in an electric field as MALINOVSKII and MALYAR ¹⁸² have shown using 1 mm nickel wires and methane-air or acetylene-air mixtures. When the wire acquires a negative charge the fuel burns more rapidly, whilst a positive charge increases the ignition delay or even prevents explosion altogether. This result is somewhat at variance with that found by Guest using heated surfaces and mentioned above.

During the years 1937-40 Silver, and then Paterson, using essentially the same form of apparatus in the same laboratory, made a very comprehensive study of the ignition of coal gas-, pentane- and hydrogen-air mixtures by hot moving spherical particles. These studies are of

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practical interest since friction sparks (e.g. from rock-cutting machines in mines) constitute an explosion hazard in many industrial undertakings, but they are also of scientific interest since they provide a method of studying the spontaneous ignition of gas mixtures under short delay conditions. SILVER²⁷⁶ heated 1 to 6 mm diameter quartz or platinum spheres in a silica tube to a given temperature, measured by an optical pyrometer, and using compressed air projected these spheres at a given velocity through a momentarily opened slot into a brass box filled with the test mixture. He measured at an approximately constant sphere velocity (2 to 5 m/sec) the limiting temperature at which ignition occurred and found that this temperature was lower the larger the diameter of the heated sphere. Methane mixtures were quite difficult to ignite, requiring spheres of at least 6.5 mm diameter and temperatures close to 1200° C. The limiting ignition condition was derived by Silver in terms of a thermal mechanism with the following result:

$$8\pi dh(T_s - T_0) dr = 4\pi d^2 dr G e^{-\frac{E}{RT_s}} \quad \dots (28)$$

where the term on the left represents the heat loss in unit time and the term on the right represents the heat release rate due to combustion reactions in the gas layer near the sphere. This equation may be rewritten in the form

$$\ln \frac{T_s - T_0}{d} = \ln \frac{G}{2h} - \frac{E}{RT_s} \quad \dots (29)$$

and upon plotting $\ln \frac{T_s - T_0}{d}$ against $\frac{1}{T_s}$ Silver found, surprisingly, that

the E value calculated from the slope of the straight line so obtained was the same for each of the three fuels investigated, i.e. 20.5 to 22.5 kcal/mole. This result suggests that heterogeneous reactions on the sphere surface govern the ignition, which is not consistent with the experimental fact that quartz and platinum spheres gave approximately the same results. PATERSON²³² extended Silver's experiments and used approximately the same apparatus with the addition of a means for measuring the sphere velocity and a device for preventing the compressed air from entering the explosion chamber together with the hot sphere. He found that for each temperature there was a limiting sphere velocity beyond which ignition did not occur and this velocity increased approximately linearly with temperature. Paterson modified Silver's equation by substituting a convective heat loss term in place of the heat loss by conduction. Fuel concentration greatly affected the limiting sphere velocity for ignition and, furthermore, platinum and quartz spheres had dissimilar behaviour at high velocities; in particular, platinum spheres improved their igniting ability with age. In a second paper PATERSON²³³ described experiments with spheres of many other materials which included alumina, alundum, porcelain and titania.

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Many interesting data were obtained and many of the apparent paradoxes could be removed by assuming that different thermal mechanisms operated in the cases of low and high velocity experiments. Ignition temperatures (of the sphere) as in Silver's experiments, were in the range 700° to 1200° C and were much higher than the corresponding known ignition temperatures for the gas mixtures alone; the ignition temperatures using fresh platinum spheres were the highest of all.

BELYAEV and SAMBURSKAYA¹⁷ devised a simple standardized procedure for measuring the relative inflammabilities of a number of secondary explosive liquids possessing boiling points in the range 65° to 300° C. Their procedure was to determine the minimum temperature to which the liquid needed to be heated to give total combustion when touched for 5 sec with a 0.4 mm diameter Nichrome wire heated until cherry red in colour. The values obtained lay in the temperature range below the liquids' boiling points and cannot be compared with other ignition temperature data as they really involve fuel volatility as a major factor contributing towards the subsequent ignition and combustion.

Recently MULLEN *et al.*²⁰³ have described experiments in which they determined the surface temperature of an electrically heated rod which was just sufficient to cause ignition of various homogeneous fuel-air mixtures flowing through a duct at different velocities. All surface temperature measurements were made with an optical pyrometer which was calibrated against a standard lamp. Stainless steel, platinum and sillimanite igniting materials were used and emissivity correction factors were applied. An attempt to use carbon rods at temperatures in the region of 2000° C was not successful owing to the rapid combustion of the rods themselves. Temperatures recorded were in the range 800° to 1300° C and Reynolds numbers based on rod diameter were in the range 5000 to 10,000. The authors argued that to a first approximation, the 'ignition delay' was proportional to (D'/V_{\max}) and the temperature to which the gases near the rod were heated was proportional to $D'(T_s - T_0)/V_{\max}$. Plots of $\log_{10} (D'/V_{\max})$ versus $V_{\max}/[D'(T_s - T_0)]$ yielded straight lines for each fuel. The slopes of curves obtained from data for rods of different diameters were not equal, however. Some tests were made at 1.7 atm., and the majority at 1 atm. pressure.

STOUT and JONES²⁸⁹ have published an account of their recent experiments upon the ignition of gaseous explosive media by hot wires which were heated electrically by the passage of a current for a predetermined time of between 1 and 60 msec. The fusion energies of the wires employed were measured and it was tentatively concluded that the fusion temperature of Nichrome wire is higher in inflammable mixtures than in air. Hydrogen-air and methane-air mixtures were studied, and the authors believe that the heat from the wire was communicated to these gases mainly by convection.

MISCELLANEOUS METHODS

1. MACKEY TEST

ONE of the earliest standard tests for determining the susceptibility of industrial materials towards spontaneous combustion was that devised by MACKEY¹⁸¹, in 1896, for textile oils. In this test the oil was spread on cotton-wool in the presence of a metal such as iron, and air was passed over it; the rise of temperature of the oil with time was measured. Tests lasted many minutes or even hours; the idea of an ignition delay period at a given temperature was not conceived at this time. The test was used initially for investigating vegetable oils and oleins and has been employed in various countries during the past half-century, in slightly modified form, for many other materials such as varnish and paint oils¹⁶⁸, and marine oils^{85, 267}. The method has been claimed to be very useful as it gives practical data that is superior to chemical data¹⁵⁵, and yet, on the other hand, it has been strongly criticized on the grounds that it is unrealistic¹¹⁴ or affected by irregular ventilation effects²⁶⁸. Using a modified Mackey apparatus²⁶⁶, SCHMIDT-NIELSEN and NAERLAND studied the heat development in various marine oils, and measured, as was normal, the maximum temperature achieved; in particular they made a comprehensive experimental study of the influences of acid value²⁶⁷, metal catalysts²⁶⁸ and peroxides²⁶⁹ upon this heat development. Recently KEHREN¹⁵⁴ found that mineral oils did not ignite under the conditions of the Mackey test even when iron or chromium soaps were present; he also showed that negative catalysts such as β -naphthol or hydroquinone retarded the heat development of oils. It would seem that, provided special care is taken, the Mackey test is useful as a means of determining the relative tendencies of different organic liquids toward auto-ignition upon storage.

2. DIESEL ENGINE METHODS

Since the ignition of fuel in Diesel engines takes place spontaneously after the fuel-air mixture has been compressed rapidly the possibility arises of being able to determine the ignition delay at various temperatures and pressures. From the nature of the process the pressure level will be high and atmospheric data will not be obtained. However, it should be possible to vary the pressure over a wide range and determine the pressure dependence of ignition delay for different fuels at given temperatures.

In 1932 BROEZE²⁵ developed suitable equipment for determining the spontaneous ignition delays in a Diesel engine at various operating conditions and correlated his results with the cetane numbers of the fuels.

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Seven years later HERELE¹¹⁵ made similar measurements while operating at full load conditions a 3-cylinder, 2-stroke Krupp Diesel engine that developed 75 h.p. at 500 r.p.m. Delay time was actually measured by the use of point electrodes placed inside one of the combustion chambers and noting the time at which ionization occurred. NEUMANN²²¹ introduced another engine method based upon the use of a bouncing-pin, and in the same paper discussed the earlier techniques for obtaining ignition delay data from Diesel engine tests. ERNST⁷⁸ has stated that in his opinion the best criterion of the onset of ignition in an engine is the radiation emitted by the flame, and he described a device for continuously and automatically indicating the ignition delay based on this principle. WIDMAIER³²⁵ pointed out that the cetane number can be calculated from the ignition delay data obtained from engine tests by this method described by Ernst. Other Diesel engine methods each of which differs in details of technique have been described by SCHMIDT and SCHMIDT²⁶³, STARKMAN²⁸⁷ and HULF *et al.*¹²⁶; Starkman asserted that the ignition delay in the Diesel engine is compounded of a physical portion (vaporization time) and a chemical portion (reaction time) and advocated the use of bomb methods for convenience in studying ignition phenomena at high pressures: limitations of the timing mechanisms involved did not permit delay times shorter than 5 msec to be resolved with accuracy.

3. OTHER METHODS

JONSSON¹⁴² has described measurements of ignition delay using a piezo-electric pressure indicator based on that of KLUGE and LINCKH¹⁵⁷ and a cathode ray oscilloscope. He obtained his results with a two-stroke motor and discussed their significance in his paper.

JOVIN¹⁵⁰ devised a special thermal balance which automatically made a photographic record of weight variations up to 100 mg. One of the uses to which he put the balance was the determination of the spontaneous combustion temperature of fuels.

VISHNEVSKY³¹⁸ has described an electronic indicator which measures an ionization current and can thus indicate the occurrence of pre-ignition. He used this instrument in an experimental engine and in spherical and cylindrical bombs and concluded that it was suitable for determining knock intensity and ignition delay.

Finally there should be mentioned the standard method recommended by the Institute of Petroleum Technology³⁴⁵ for determining the ignition point of a liquid fuel. The liquid fuel has to be heated in a crucible to such a temperature that it burns for at least 5 sec when a small naked flame is passed over the surface of the liquid. This method, which employs the same apparatus as is used for flash point determinations, does not give strictly a spontaneous ignition temperature but rather a criterion of volatility and ease of flame propagation.

SPONTANEOUS IGNITION TEMPERATURE DATA

IN THIS chapter the spontaneous ignition temperatures of liquid substances, determined by many of the methods described in previous chapters, are summarized in alphabetical order. For general comparison, data has also been included for some gaseous combustibles and a few solid compounds. All data refer to *atmospheric pressure* with the exception of the vitiated air data for acetylene and hydrogen which are marked with an asterisk; these values were determined at 0.9 atm. pressure.

Each entry consists of the name of the substance, the spontaneous ignition temperature in degrees *Centigrade*, the delay period in *milliseconds* where known (otherwise the letter N) and the literature reference letter which may be followed by a number.

References bearing the same letter usually refer to the same method of measurement, e.g. (y1), (y2) and (y3). A list of these literature references is given at the end of this chapter together with cross-references to the main list of references at the end of the AGARDOgraph whenever these exist.

Data for oxygen, air and vitiated air are given in this order of precedence following the key letters O, A and V. Some of the more important synonyms are included in the compilation with appropriate cross-references.

When the letter N is used, this signifies that the spontaneous ignition delay time was either not specifiable or not specified, but was probably in excess of 1000 msec.

An example follows illustrating the method of interpreting the data as set out.

The entry

'Methylcyclopentane O 329°, N (c); A 323°, 6000 (x); V 812°, 20 (z2); 1013°, 1 (z2).'

The interpretation

'Methylcyclopentane has a spontaneous ignition temperature (i) in oxygen, 329° C as measured by the method reported upon in reference (c) in which the delay time was not specified, but was probably in excess

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of 1000 msec; (ii) in air, 323° C as measured by the method reported upon in reference (x), the delay time being 6000 msec; and (iii) in vitiated air, 812° C with a delay time of 20 msec and 1013° C with a delay time of 1 msec, as measured by the method reported upon in reference (z2).'

Acetal O 174°, N (c1); A 230°, N (c1); V 768°, 20 (z4); 957°, 1 (z4); Acetaldehyde O 140°, N (a); 159°, N (c1); A 185°, N (a); 275°, N (c1); V 869°, 20 (z5); 1088°, 1 (z5); Acetanilide A 546°, N (i2); 547° N (c12); Acetic acid O 570°, N (b); 490°, N (c1); A 599°, N (l); 550°, N (c1); 566°, N (i2); Acetic anhydride O 361°, N (c1); A 392°, N (c1); 401°, N (i2); Acetone O 568°, N (a); 485°, N (c1); A 700°, N (a); 727°, N (l); 561°, N (c8); 538°, N (i2); 569°, N (c13); V 871°, 20 (z5); 1046°, 1 (z5); Acetone cyanhydrin A 688°, N (c12); Acetonitrile V 1000°, 20 (z3); 1059°, 10 (z3); Acetylacetone A 493°, N (i2); V 816°, 20 (z5); 996°, 1 (z5); Acetylene O 296°, N (c2); A 305°, N (c2); 335°, N (i2); V 623°, 20 (z1)*; 826°, 1 (z1)*; Acetyl oxide (see Acetic anhydride); Acrolein A 278°, N (m); 278°, N (c14); V 712°, 10 (z5); 859°, 1 (z5); Acrylaldehyde (see Acrolein); Acrylonitrile O 460°, N (c3); A 481°, N (c3); Aldol A 277°, N (i2); 248°, N (c12); Allyl alcohol O 348°, N (c1); A 389°, N (i3); V 767°, 20 (z4); 979°, 1 (z4); Allylamine A 374°, N (c12); Allyl bromide A 295°, N (c12); Allyl chloride O 404°, N (c1); A 487°, N (c1); 392°, N (i2); Allyl ether O 200°, N (b); V 749°, 10 (z4); 927°, 1 (z4); Aminobenzene (see Aniline); 2-Aminoethanol (see Monoethanolamine); Aminoethylethanolamine A 369°, N (i2); Ammonia A 651°, N (n1); *n*-Amyl acetate A 399°, N (n2); 378°, N (i2); 399°, N (c14); *iso*-Amyl acetate A 379°, N (i3); 378°, N (c14); *n*-Amyl alcohol O 390°, N (a); 332°, N (d); A 409°, N (a); 427°, N (c1); 327°, N (i2); V 806°, 20 (z4); 990°, 1 (z4); *iso*-Amyl alcohol A 518°, N (l); 343°, N (n2); 353°, N (i2); V 818°, 20 (z4); 1013°, 1 (z4); *sec*-Amyl alcohol 343-385°, N (i2); *tert*-Amyl alcohol A 437°, N (c12); V 814°, 20 (z4); 995°, 1 (z4); Amylbenzene O 255°, N (e); *n*-Amyl chloride A 259°, N (c14); *tert*-Amyl chloride A 343°, N (c12); *n*-Amylene A 273°, N (c14); *iso*-Amyl ether A 428°, N (l); Amylmethyl ketone A 311°, N (c14); Amyl nitrate V 524°, 20 (z3); 798°, 1 (z3); Amyl nitrite V 496°, 20 (z3); 910°, 1 (z3); *iso*-Amyl nitrite V 437°, 10 (z3); 918°, 1 (z3); Aniline O 530°, N (a); A 770°, N (a); 628°, N (l); 530°, N (p); 617°, N (c12); 593°, 6000 (x); V 907°, 20 (z3); 1065°, 2 (z3); *o*-Anisidine V 787°, 20 (z3); 1039°, 1 (z3); Anisole O 560°, N (b); V 744°, 20 (z4); 1025°, 1 (z4); Anthracene O 580°, N (b); A 472°, N (q); Antifebrin (see Acetanilide); Banana Oil (see *iso*-Amyl acetate); Benzaldehyde O 168°, N (a); A 180°, N (a); 192°, N (n2); V 744°, 20 (z5); 936°, 1 (z5); Benzene O 662°, N (a); 690°, N (b); 566°, N (f1); A 740°, N (a); 656°, N (l); 580°, N (i3); 645°, N (y1); 592°, 42000 (x); V 814°, 20 (z2); 1000°, 1 (z2); Benzene carbonal (see Benzaldehyde); Benzoic acid O 475°, N (b); 556°, N (c1); A 573°, N

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(c1); Benzyl acetate A 588°, N (l); 461°, N (i3); V 767°, 20 (z5); 1019°, 1 (z5); Benzyl alcohol O 373°, N (e); A 502°, N (l); 436°, N (i3); V 807°, 20 (z4); 1007°, 1 (z4); Benzyl cellosolve (see Ethyleneglycolmonobenzyl ether); Benzyl chloride A 627°, N (l); Benzyl ethanoate (see Benzyl acetate); Benzylethyl ether A 496°, N (l); Diphenyl A 577°, 36000 (x); Bromobenzene A 688°, N (l); V 858°, 20 (z3); 1046°, 1 (z3); 1-Bromobutane (see *n*-Butyl bromide); Bromoethane (see Ethyl bromide); 1,3-Butadiene O 335°, N (c1); A 418°, N (c1); *n*-Butaldehyde (see *n*-Butyraldehyde); *n*-Butane O 283°, N (c1); A 408°, N (c1); 430°, N (i2); 430°, 6000 (x); *iso*-Butane O 319°, N (c1); A 462°, N (c1); 543°, N (i2); 477°, 18000 (x); 2,3-Butanedione (see Diacetyl); 1-Butanol (see *n*-Butyl alcohol); 2-Butanol (see *sec*-Butyl alcohol); 2-Butanone (see Methyl ethyl ketone); 2-Butenal (see Crotonaldehyde); 1-Butene A 384°, N (c12); 2-Butene A 435°, N (c12); 2-Butanol (see *sec*-Butyl alcohol); 2-Butoxyethanol (see Ethyleneglycolmonobutyl ether); *n*-Butyl acetate A 423°, N (i3); V 793°, 20 (z5); 1040°, 1 (z5); *n*-Butyl alcohol O 385°, N (a); 328°, N (e); A 450°, N (a); 503°, N (l); 367°, N (i3); 359°, 18000 (x); V 809°, 20 (z4); 993°, 1 (z4); *iso*-Butyl alcohol O 364°, N (d); A 542°, N (l); 441°, N (n1); 414°, N (c13); V 794°, 20 (z4); 1010°, 1 (z4); *sec*-Butyl alcohol O 377°, N (c1); A 414°, N (c1); V 833°, 20 (z4); 990°, 1 (z4); *tert*-Butyl alcohol O 460°, N (c1); A 478°, N (c1); 483°, N (i2); *n*-Butylamine A 312°, N (c12); *iso*-Butylamine A 374°, N (c12); *n*-Butylbenzene A 412°, N (c12); 444°, 6000 (x); *iso*-Butylbenzene A 428°, N (c12); 456°, 12000 (x); *sec*-Butylbenzene A 443°, N (c12); 447°, 18000 (x); *tert*-Butylbenzene A 448°, N (c12); 477°, 72000 (x); V 779°, 20 (z2); 1000°, 1 (z2); 2-Butylbiphenyl A 433°, 12000 (x); *n*-Butyl bromide A 483°, N (l); 316°, N (i2); Butyl carbinol (see *iso*-Amyl alcohol); Butyl carbitol A 228°, N (i1); Butyl carbitol acetate A 299°, N (i2); Butyl cellosolve (see Ethyleneglycolmonobutyl ether); *n*-Butyl chloride A 460°, N (c1); α -Butylene (see 1-Butene); β -Butylene (see 2-Butene); γ -Butylene (see 2-Methyl-propene); *iso*-Butylene (see 2-Methyl-propene); β -Butylene glycol A 377°, N (i2); *n*-Butyl ether A 194°, N (i2); *n*-Butyl formate O 308°, N (c1); A 322°, N (c1); Butyl lactate A 382°, N (i2); *iso*-Butylmethyl ketone A 459°, N (c12); *n*-Butyl nitrite V 400°, 4 (z3); 490°, 1 (z3); Butylphthalate A 403°, N (i2); V 813°, 20 (z2); 1021°, 1 (z2); *n*-Butyl propionate A 426°, N (i3); *n*-Butyraldehyde O 206°, N (c1); A 408°, N (l); 230°, N (c1); *iso*-Butyraldehyde A 254°, N (i2); *n*-Butyric acid A 552°, N (l); Camphor A 466°, N (i2); Carbon disulphide O 107°, N (g1); A 149°, N (l); 120°, N (g1); 125°, N (i3); V 610°, 20 (z5); 842°, 1 (z5); Carbon monoxide O 588°, N (h); A 609°, N (h); 651°, N (i2); V 758°, 20 (z1); 848°, 1 (z1); Castor oil A 449°, N (i2); Cellosolve (see Ethyleneglycolmonoethyl ether); Cetane A 235°, N (r); 235°, N (y1); Cetene V 748°, 20 (z2); 1036°, 1 (z2); *o*-Chloroaniline V 885°, 20 (z3); 1084°, 2 (z3); *m*-Chloroaniline V 846°, 20 (z3); 1080°, 2 (z3); Chlorobenzene A 674°, N (i2);

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Chloroethane (see Ethyl chloride); 2-Chloro-2-methyl chloride O 318°, N (c1); A 343°, N (c1); 3-Chloro-(trifluoromethyl) benzene A 654°, N (y3); Creosote oil A 336°, N (i2); *o*-Cresol A 599°, N (l); 559°, N (i2); *m*-Cresol A 626°, N (l); V 836°, 20 (z4); 1100°, 2 (z4); Crotonaldehyde A 232°, N (c9); V 703°, 20 (z5); 924°, 1 (z5); Cumene A 467°, 6000 (x); V 802°, 20 (z2); 985°, 1 (z2); *pseudo*-Cumene V 770°, 20 (z2); 1025°, 2 (z2); Cyanogen A 850°, N (g2); *cyclo*Hexadiene O 360°, N (b); *cyclo*Hexane O 325°, N (b); 296°, N (e); A 259°, N (c12); 270°, 102000 (x); V 798°, 20 (z2); 980°, 1 (z2); *cyclo*Hexanol O 350°, N (b); V 814°, 20 (z4); 1030°, 1 (z4); *cyclo*Hexanone O 550°, N (b); A 557°, N (l); 453°, N (n4); V 816°, 20 (z5); 1046°, 1 (z5); *cyclo*Hexylamine A 293°, N (i2); *cyclo*Hexene O 325°, N (b); V 781°, 20 (z2); 972°, 1 (z2); *cyclo*Pentadiene O 510°, N (b); *cyclo*Pentane A 385°, 6000 (x); *cyclo*Pentanone O 540°, N (b); *cyclo*Propane O 454°, N (c1); A 498°, N (c1); *p*-Cymene A 466°, N (l); 494°, N (i2); 445°, N (n4); V 807°, 20 (z2); 1050°, 1 (z2); Decahydronaphthalene O 280°, N (b); A 262°, N (i1); 272°, 18000 (x); *trans*-Decahydronaphthalene V 814°, 20 (z2); 1002°, 1 (z2); Decalin (see Decahydronaphthalene); *n*-Decane O 202°, N (a); A 463°, N (a); 425°, N (l); 250°, N (s); 232°, 54000 (x); 236°, N (y1); 1-Decanol A 291°, N (y1); 1-Decene A 244°, 78000 (x); *n*-Decyl alcohol V 793°, 20 (z4); 960°, 1 (z4); Diacetone alcohol A 603°, N (i2); V 805°, 20 (z4); 1065°, 1 (z4); Diacetyl V 748°, 20 (z5); 930°, 1 (z5); 1,2-Diacetylene (see Acetonylacetone); Diallyl O 330°, N (b); Diallyl ether (see Allyl ether); Dibutyl ether (see *n*-Butyl ether); Dibutyl phthalate (see Butyl phthalate); Di-*n*-butyl tartrate A 284°, N (i2); *o*-Dichlorobenzene A 648°, N (c12); 1,2-Dichloro-*n*-butane O 250°, N (c1); A 276°, N (c1); Dichloro-1-(chlorotetrafluoroethyl)-4-(trifluoromethyl) benzene A 591°, N (y3); 1,2-Dichloroethane (see Ethylene dichloride); Dichloroethylene A 441°, N (c1); 458°, N (i2); V 738°, 20 (z3); 1079°, 1 (z3); 2,2'-Dichloroethyl ether A 369°, N (i1); V 766°, 20 (z4); 953°, 1 (z4); Dichloromethane (see Methylene chloride); 1,2-Dichloropropane (see Propylene dichloride); *Dicyclopentadiene* O 510°, N (b); Di-*n*-decyl ether A 217°, N (y1); Diethanolamine A 662°, N (i1); V 823°, 20 (z3); 1000°, 2 (z3); 1,1-Diethoxyethane (see Acetal); Diethylamine A 312°, N (c12); V 754°, 20 (z3); 977°, 1 (z3); Diethylaniline V 762°, 20 (z3); 965°, 1 (z3); 1,2-Diethylbenzene A 404°, 6000 (x); 1,3-Diethylbenzene A 455°, 12000 (x); 1,4-Diethylbenzene A 430°, N (c12); 451°, 12000 (x); Diethylcellosolve (see Ethyleneglycoldiethyl ether); 1,4-Diethylene dioxide (see Dioxane); Diethyl ether (see Ethylether); Diethylene glycol A 229°, N (i2); Diethyleneglycolbenzoate-2-ethylhexoate A 340°, N (y3); Diethylene oxide (see Dioxane); Diethylenetriamine A 399°, N (i2); Diethyl ketone A 608°, N (l); 3,3-Diethylpentane A 322°, N (c12); Diethyl peroxide A 189°, N (t); Diethyl sulphate A 436°, N (i2); Dihexyl (see Dodecane); Di-*n*-hexyl ether A 200°, N (y1); 2,2'-Dihydroxyethylamine (see Diethanolamine); Diisobutylenes A 470°, N (y2);

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V 799°, 20 (z2); 1064°, 1 (z2); Diisooctyladipate A 366°, N (y3); Diisopropyl (see 2,3-Dimethylbutane); Diisopropylbenzene A 449°, N (i2); Diisopropyl ether A 443°, N (i1); 416°, N (c12); 500°, N (y1); V 820°, 20 (z4); 1037°, 1 (z4); Dimethylamine O 346°, N (c1); A 402°, N (c1); Dimethylaniline A 371°, N (i1); V 780°, 20 (z3); 960°, 1 (z3); 2,2-Dimethylbutane A 425°, N (c12); 440°, 12000 (x); 2,3-Dimethylbutane O 298°, N (c1); A 420°, N (c1); 421°, 12000 (x); 2,3-Dimethyl-1-butene A 369°, 6000 (x); 2,3-Dimethyl-2-butene A 407°, 6000 (x); Dimethylchloroacetal A 232°, N (i2); 2,4-Dimethyl-3-ethylpentane A 390°, 12000 (x); 510°, N (y2); Dimethyl ether O 252°, N (c1); A 350°, N (c1); *uns*-Dimethylethylene (see 2-Methyl propene); Dimethyl formamide A 445°, N (i2); Dimethylglyoxal (see Diacetyl); 3,3-Dimethylheptane A 441°, 3600 (x); 2,3-Dimethylhexane A 438°, N (r); Dimethylketone (see Acetone); 2,3-Dimethyloctane A 231°, 72000 (x); 4,5-Dimethyloctane A 388°, N (y1); 2,3-Dimethylpentane A 337°, N (c12); 338°, 6000 (x); *o*-Dimethylphthalate A 556°, N (i2); 2,2-Dimethylpropane A 450°, N (i2); 456°, 3000 (x); Dimethyl sulphide A 206°, N (i2); 1,1-Dineopentylethane A 500°, N (y2); 1,1-Dineopentylethylene A 455°, N (y2); Dioctylbenzenephosphonate A 314°, N (y3); Di-*n*-octyl ether A 210°, N (y1); Dioctylisooctenephosphonate A 320°, N (y3); 1,4-Dioxane A 266°, N (c9); 179°, N (i2); V 775°, 20 (z4); 933°, 1 (z4); Diphenylamine A 452°, N (c12); 1,1-Diphenylbutane A 462°, 6000 (x); 1,1-Diphenylethane A 487°, 6000 (x); Diphenylmethane A 517°, 18000 (x); Diphenyloxide A 646°, 12000 (x); 1,1-Diphenylpropane A 466°, 6000 (x); Di-*n*-propyl ether A 189°, N (u1); Divinyl ether A 360°, N (c10); *n*-Dodecane A 232°, N (y1); *iso*-Dodecane A 534°, N (l); 500°, N (r); 500°, N (y2); V 827°, 20 (z2); 1010°, 1 (z2); 1-Dodecanol A 283°, N (y1); *n*-Eicosane A 240°, N (y1); Ethanal (see Acetaldehyde); Ethane A 472°, N (c11); 515°, N (c12); V 809°, 20 (z1); 991°, 1 (z1); Ethanol (see Ethylalcohol); Ethene (see Ethylene); Ether (see Ethylether); *p*-Ethoxyaniline (see *p*-Phenetidine); 2-Ethoxyethanol (see Ethyleneglycolmonoethyl ether); 2-Ethoxyethanol acetate (see Ethyleneglycolmonoethyl ether monoacetate); Ethyl acetate A 610°, N (l); 486°, N (i3); V 804°, 20 (z5); 1063°, 1 (z5); Ethyl alcohol O 425°, N (a); 375°, N (b); A 558°, N (a); 557°, N (l); 426°, N (i2); V 814°, 20 (z4); 1030°, 1 (z4); Ethylamine (70 per cent aqueous solution) A 384°, N (i2); Ethylaniline A 479°, N (l); Ethylbenzene O 468°, N (c1); A 460°, 18000 (x); A 553°, N (l); 477°, N (c1); V 785°, 20 (z2); 966°, 1 (z2); Ethylbenzoate A 644°, N (l); 2-Ethylbiphenyl A 449°, 18000 (x); Ethyl bromide A 588°, N (l); 511°, N (nl); V 883°, 20 (z3); 1055°, 2 (z3); 2-Ethylbutane O 273°, N (e); 2-Ethyl-1-butanol (see *iso*-Hexyl alcohol); 2-Ethyl-1-butene A 324°, 6000 (x); Ethyl-*n*-butyrate O 351°, N (c1); A 612°, N (l); 463°, N (c1); Ethyl caprate A 493°, N (l); Ethyl-*n*-caproate A 582°, N (l); Ethyl-*n*-caprylate A 571°, N (l); Ethyl carbonate V 782°, 20 (z5); 1013°, 1 (z5); Ethyl chloride O 468°, N (c1);

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A 516°, N (c1); 494°, N (c12); Ethylcyclobutane A 211°, N (c12); Ethylcyclohexane A 262°, N (c12); 264°, 114000 (x); Ethylcyclopentane A 262°, N (c12); Ethylene O 485°, N (c4); A 490°, N (c1); 543°, N (i2); Ethylene chlorhydrin O 400°, N (c1); A 425°, N (c1); Ethylene dichloride A 413°, N (i1); Ethyleneglycol O 500°, N (b); A 522°, N (l); 413°, N (i1); Ethyleneglycol diacetate A 635°, N (l); Ethyleneglycoldiethyl ether A 208°, N (i2); Ethyleneglycolmonobenzyl ether A 352°, N (i2); Ethyleneglycolmonobutyl ether A 244°, N (i1); V 792°, 20 (z4); 964°, 1 (z4); Ethyleneglycoimonoethyl ether A 238°, N (i1); V 790°, 20 (z4); 954°, 1 (z4); Ethyleneglycolmonoethyl ether acetate A 379°, N (i1); Ethyleneglycolmonoethyl ether monoacetate V 774°, 20 (z4); 960°, 1 (z4); Ethyleneglycolmonomethyl ether A 288°, N (i); 382°, N (c12); V 780°, 20 (z4); 933°, 1 (z4); Ethylene imine A 322°, N (c12); Ethylene oxide A 429°, N (i1); Ethyl ether O 178°, N (a); 182°, N (c4); A 343°, N (a); 491°, N (l); 186°, N (i3); 193°, N (y1); V 794°, 20 (z4); 947°, 1 (z4); Ethyl formate A 577°, N (l); V 768°, 20 (z5); 956°, 1 (z5); bis-(2-Ethylhexyl)-adipate A 262°, N (y2); Ethyl lactate A 400°, N (n5); Ethyl malonate A 541°, N (l); Ethyl mercaptan O 261°, N (c5); A 299°, N (c5); Ethylmethyl ether (see Methylethyl ether); Ethylmethyl ketone (see Methylethyl ketone); 1-Ethyl-naphthalene A 481°, 6000 (x); Ethyl nitrate V 426°, 20 (z3); 562°, 1 (z3); Ethyl nitrite A 90°, N (w); V 580°, 20 (z3); 833°, 1 (z3); 3-Ethyl-octane A 235°, N (y1); 4-Ethyl-octane A 237°, 54000 (x); Ethyl-oleate A 353°, N (l); Ethyl oxalate V 742°, 10 (z5); 880°, 1 (z5); Ethyl palmitate A 388°, N (l); Ethyl pelargonate A 524°, N (l); Ethyl propionate O 440°, N (c1); A 602°, N (l); 476°, N (c1); Ethylpropyl ketone A 575°, N (l); Ethyl-*n*-valerianate A 590°, N (l); Formaldehyde (37 per cent solution) A 430°, N (i2); Formamide V 969°, 20 (z3); 1032°, 10 (z3); Formic acid A 504°, N (l); Furan V 783°, 20 (z5); 982°, 1 (z5); 2-Furancarbal (see Furfuraldehyde); Furfuraldehyde A 391°, N (c1); V 696°, 20 (z5); 880°, 1 (z5); Furfuran (see Furan); Furfuryl alcohol O 364°, N (c1); A 391°, N (c1); 491°, N (i2); V 775°, 20 (z4); 944°, 1 (z4); Fusel oil (see *n*-Amyl alcohol); Gas oil O 270°, N (a); A 336°, N (a); Glycerol O 414°, N (a); 320°, N (i1); A 500°, N (a); 523°, N (l); 393°, N (i3); Glyceryl triacetate A 433°, N (i2); Glycol (see Ethylene glycol); *n*-Heptane O 300°, N (b); 214°, N (c1); A 451°, N (l); 230°, N (c1); 233°, N (i3); 250°, N (y1); 247°, 30000 (x); V 806°, 20 (z2); 950°, 1 (z2); *n*-Heptanoic acid A 523°, N (l); 1-Heptene A 332°, N (l); 263°, 66000 (x); α -*n*-Heptylene (see 1-Heptene); Hexachlorobutadiene A 618°, 6000 (x); Hexachlorodiphenyl oxide A 628°, 600 (x); *n*-Hexadecane A 230°, 66000 (x); 232°, N (y1); *iso*-Hexadecane A 484°, N (y2); 1-Hexadecene A 240°, 78000 (x); 253°, N (y1); Hexahydrobenzene (see *cyclo*Hexane); Hexahydrophenol (see *cyclo*Hexanol); Hexamethylbenzene O 375°, N (b); Hexamethylene (see *cyclo*Hexane); *n*-Hexane O 296°, N (b); A 487°, N (a); 520°, N (l); 248°, N (n1); 261°, N (n5); 261°, 30000 (x); V 828°, 20 (z2); 1015°, 1 (z2); *iso*-Hexane O 268°, N (a);

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284°, N (e); 2,5-Hexanedione (see Acetylacetone); 1-Hexene A 272°, 72000 (x); Hexone (see *iso*-Butylmethyl ketone); *n*-Hexyl alcohol O 300°, N (e); V 801°, 20 (z4); 970°, 1 (z4); *iso*-Hexyl alcohol V 800°, 20 (z4); 963°, 1 (z4); Hexylene O 325°, N (b); Hydrazine A 270°, N (c12); Hydrocyanic acid A 538°, N (i1); Hydrogen O 560°, N (j); A 572°, N (g3); V 610°, 20 (z1)*; 700°, 1 (z1)*; Hydrogen sulphide O 220°, N (g2); A 292°, N (u2); Hydroquinone O 630°, N (b); 2-Hydroxyethylamine (see Monoethanolamine); 4-Hydroxy-4-methyl-2-pentanone (see Diacetone alcohol); α -Hydroxytoluene (see Benzyl alcohol); *m*-Hydroxytoluene (see *m*-Cresol); Isophorone O 322°, N (c1); A 462°, N (c1); Isoprene O 440°, N (b); Kerosine O 270°, N (a); A 295°, N (a); 254°, N (i1); 249°, 66000 (x); V 806°, 20 (z2); 999°, 1 (z2); Ketohexahydrobenzene (see *cyclo*Hexanone); *dl*-Limonene A 263°, 30000 (x); Linseed oil A 438°, N (i2); Mesitylene A 621°, N (l); Mesityl oxide A 344°, N (i2); V 823°, 20 (z5); 1037°, 1 (z5); Methanamide (see Formamide); Methane O 556°, N (g2); A 632°, N (v); 537°, N (i2); V 961°, 20 (z1); 1050°, 10 (z1); Methanol (see Methyl alcohol); Methone A 506°, N (l); *o*-Methoxyaniline (see *o*-Anisidine); 2-Methoxyethanol (see Ethyleneglycolmonomethyl ether); Methyl acetate A 654°, N (l); 502°, N (i3); V 816°, 20 (z5); 1028°, 2 (z5); Methyl alcohol O 555°, N (a); 500°, N (b); 461°, N (c1); A 574°, N (l); 470°, N (i3); 464°, N (n5); V 820°, 20 (z4); 1040°, 1 (z4); Methylamine O 400°, N (c1); A 430°, N (c1); Methylaniline (see Toluidine); 2-Methylbiphenyl A 502°, 12000 (x); Methyl bromide A 537°, N (n1); 2-Methylbutane O 294°, N (c1); A 420°, N (c1); 427°, 6000 (x); 2-Methyl-2-butanol (see *tert*-Amyl alcohol); 3-Methyl-1-butanol (see *iso*-Amyl alcohol); 3-Methyl-1-butene A 374°, 6000 (x); 1-Methyl-2-*tert*-butylcyclohexane A 314°, 12000 (x); 1-Methyl-3-*tert*-butylcyclohexane (high boiling isomer) A 304°, 12000 (x); 1-Methyl-3-*tert*-butylcyclohexane (low boiling isomer) A 291°, 24000 (x); Methylbutyl ketone A 533°, N (c9); Methyl cellosolve (see Ethyleneglycolmonomethyl ether); Methyl chloride A 632°, N (n1); Methyl cyanide (see Acetonitrile); Methylcyclohexane O 285°, N (c); A 265°, 108000 (x); Methylcyclohexanone A 598°, N (l); Methylcyclopentane O 329°, N (c); A 323°, 6000 (x); V 812°, 20 (z2); 1013°, 1 (z2); 2-Methyldecane A 231°, N (y1); Methylene dichloride (see Methylene chloride); 1-Methyl-3,5-diethylbenzene A 461°, 12000 (x); Methylene chloride O 606°, N (c1); A 642°, N (c1); 662°, N (i2); V 902°, 20 (z3); 1085°, 2 (z3); Methyl ether (see Dimethyl ether); 1-Methyl-2-ethylbenzene A 447°, 18000 (x); 1-Methyl-3-ethylbenzene A 485°, 18000 (x); 1-Methyl-4-ethylbenzene A 483°, 12000 (x); Methylethyl ether A 190°, N (i2); Methylethyl ketone A 514°, N (c9); 505°, N (n4); V 804°, 20 (z5); 975°, 1 (z5); 2-Methyl-3-ethylpentane A 461°, N (r); Methyl formate A 236°, N (n1); 449°, N (i2); V 797°, 20 (z5); 1026°, 2 (z5); Methylheptenone A 534°, N (l); Methylhexyl ketone A 572°, N (l); Methylisopropylcarbinol (see *sec*-Amyl alcohol); Methyl lactate A 385°,

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N (n5); 1-Methylnaphthalene A 566°, N (r); 547°, 24000 (x); 553°, N (yl); 2-Methylnonane A 214°, 102000 (x); 2-Methylpropanal (see *iso*-Butyraldehyde); 2-Methyloctane A 227°, 66000 (x); 3-Methyloctane A 228°, 60000 (x); 4-Methyloctane A 232°, 6000 (x); 2-Methylpentane O 275°, N (e); A 306°, N (c12); 307°, 6000 (x); 3-Methylpentane A 304°, 12000 (x); 2-Methyl-1-pentene A 306°, 6000 (x); 4-Methyl-1-pentene A 304°, 12000 (x); 4-Methyl-3-pentene-2-one (see Mesityl oxide); 2-Methyl-1-propanol (see *iso*-Butyl alcohol); α -Methylpropyl alcohol (see *sec*-Butyl alcohol); 2-Methyl propane (see *iso*-Butane); 2-Methylpropene A 465°, N (c12); Methylpropionate A 469°, N (c12); Methyl-*n*-propyl ketone A 505°, N (c9); V 832°, 20 (z5); 1020°, 1 (z5); 2-Methylpyridine (see α -Picoline); Methyl salicylate A 454°, N (n2); 2-Methyltetrahydrofuran (see Tetrahydrosylvan); Monoethanolamine V 780°, 20 (z3); 1006°, 1 (z3); Monoisopropylxylenes V 798°, 20 (z2); 1040°, 1 (z2); Naphthalene O 630°, N (b); 560°, N (c6); A 587°, N (c6); 568°, N (i2); Neatsfoot oil A 442°, N (i2); Neohexane (see 2,2-Dimethylbutane); Nicotine O 235°, N (c7); A 244°, N (c7); Nitrobenzene A 556°, N (l); 482°, N (n2); V 706°, 20 (z3); 884°, 1 (z3); Nitroethane A 415°, N (i2); V 623°, 20 (z3); 762°, 1 (z3); Nitroglycerol A 270°, N (i2); Nitromethane A 419°, N (i2); V 684°, 20 (z3); 784°, 1 (z3); 1-Nitropropane A 417°, N (i2); 2-Nitropropane A 428°, N (i2); *o*-Nitrotoluene V 672°, 20 (z3); 837°, 1 (z3); *m*-Nitrotoluene V 711°, 20 (z3); 911°, 1 (z3); *n*-Nonadecane A 237°, N (yl); *n*-Nonane A 285°, N (s); 234°, 66000 (x); *n*-Octadecane A 235°, N (yl); 1-Octadecene A 251°, N (yl); Octadecyl alcohol O 270°, N (b); Octahydroanthracene O 315°, N (b); *n*-Octane O 208°, N (c1); A 458°, N (l); 218°, N (c1); 240°, 54000 (x); *iso*-Octane (see 2,2,4-Trimethylpentane); 1-Octene A 256°, 72000 (x); Octyleneglycol A 335°, N (i2); Olive oil A 441°, N (i2); Oxalic acid O 640°, N (b); Oxybutyraldehyde (see Aldol); Palm oil A 343°, N (i2); Paraldehyde A 541°, N (l); 242°, N (i1); V 846°, 20 (z5); 1064°, 1 (z5); *n*-Pentane O 300°, N (b); 258°, N (c1); A 579°, N (l); 290°, N (c1); 284°, 24000 (x); *iso*-Pentane (see 2-Methylbutane); 1-Pentene A 298°, 18000 (x); 1-Pentanol (see *n*-Amyl alcohol); 2-Pentanone (see Methylpropyl ketone); γ -Pentylene oxide (see Tetrahydrosylvan); Perfluorodimethylcyclohexane A 651°, 6000 (x); *p*-Phenetidine V 822°, 20 (z3); 1004°, 1 (z3); Phenol O 574°, N (a); 500°, N (k); A 715°, N (a); Phenylamine (see Aniline); Phenylaniline (see Diphenylamine); Phenylbromide (see Bromobenzene); Phenyl carbinol (see Benzyl alcohol); Phenyl chloride (see Chlorobenzene); *N*-Phenyldiethylamine (see Diethylaniline); Phenylethane (see Ethylbenzene); Phenylethylene (see Styrene); Phenylmethyl ether (see Anisole); Phenylmethyl ketone (see Acetophenone); Phosphorus (yellow) A 30°, N (i2); Phosphorus (red) A 260°, N (i2); Phosphorus sesquisulphide A 100°, N (i2); Phthalic anhydride A 584°, N (i2); α -Picoline A 538°, N (i2); V 846°, 20 (z3); 1037°, 2 (z3); Picric acid A 300°, N (i2); Pinene O 275°, N (e);

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A 263°, 60000 (x); V 797°, 20 (z2); 1039°, 1 (z2); Propane O 468°, N (c1); A 493°, N (c1); 466°, N (i2); 504°, 6000 (x); 1-Propanol (see *n*-Propyl alcohol); 2-Propanol (see *iso*-Propyl alcohol); 2-Propanone (see Acetone); Propenal (see Acrolein); Propene A 458°, N (c9); Propen-1-ol (see Allyl alcohol); Propene oxide (see Propylene oxide); Propionaldehyde A 419°, N (l); *n*-Propionic acid A 596°, N (l); *n*-Propyl acetate O 388°, N (c1); A 662°, N (l); 450°, N (c1); V 828°, 20 (z5); 1060° 2 (z5); *iso*-Propyl-acetate O 448°, N (c1); A 572°, N (c1); 460°, N (i2); 476°, N (c12); *n*-Propyl alcohol O 445°, N (a); 370°, N (b); 328°, N (d); A 505°, N (a); 540°, N (l); 439°, N (c1); 433°, N (i3); V 811°, 20 (z4); 1007°, 1 (z4); *iso*-Propyl alcohol O 512°, N (a); A 590°, N (a); 620°, N (l); 456°, N (i3); V 811°, 20 (z4); 1050°, 1 (z4); *n*-Propylamine A 318°, N (c12); *iso*-Propylamine A 402°, N (c12); *n*-Propylbenzene A 456°, 12000 (x); *iso*-Propylbenzene (see Cumene); 2-Propylbiphenyl A 452°, 18000 (x); Propyl bromide O 255°, N (c1); A 490°, N (c1); Propyl chloride A 520°, N (c1); *iso*-Propyl chloride A 593°, N (i2); Propylcyclopentane A 285°, N (r); Propylene (see Propene); Propylenealdehyde (see Crotonaldehyde); Propylene dichloride A 557°, N (c9); V 790°, 20 (z3); 1012°, 2 (z3); Propylene glycol O 392°, N (c1); A 421°, N (c1); Propylene oxide V 748°, 10 (z4); 870°, 1 (z4); *iso*-Propyl ether (see Diisopropyl ether); *n*-Propyl formate A 455°, N (c12); *iso*-Propyl formate A 485°, N (c12); 4-*iso*-Propylheptane A 288°, N (y1); *p*-*iso*-Propyltoluene (see *p*-Cymene); Pseudocumene (see *pseudo*-Cumene); Pulegon A 426°, N (l); Pyridine A 482°, N (n2); 574°, N (i2); V 745°, 20 (z3); 1014°, 1 (z3); Pyrogallol O 510°, N (b); Quinoline A 480°, N (c12); Quinone O 575°, N (b); Rape seed oil A 446°, N (i2); Rosin oil A 342°, N (i2); Salicylaldehide V 772°, 20 (z5); 1015°, 1 (z5); Soya bean oil A 445°, N (i2); Stearic acid O 250°, N (b); A 395°, N (i1); Styrene O 450°, N (c1); A 490°, N (c1); V 777°, 20 (z2); 1065°, 1 (z2); Sugar O 378°, N (a); A 385°, N (a); Sulphur A 232°, N (i2); Tannic acid A 527°, N (i2); Tartaric acid A 428°, N (i2); Tetraaryl salicylate A 577°, 6000 (x); *n*-Tetradecane A 232°, N (y1); 1-Tetradecene A 239°, 66000 (x); 255°, N (y1); 1,2,3,4-Tetrahydrobenzene (see *cyclo*Hexene); Tetrahydrofurfuryl alcohol O 273°, N (c1); A 282°, N (c1); V 793°, 20 (z4); 980°, 1 (z4); Tetrahydronaphthalene O 420°, N (b); A 423°, 6000 (x); V 819°, 20 (z2); 1030°, 1 (z2); Tetrahydro-sylvan V 794°, 20 (z5); 1025°, 1 (z5); Tetraisobutylene A 415°, N (y2); Tetralin (see Tetrahydronaphthalene); Tetramethylbenzene V 791°, 20 (z2); 1030°, 1 (z2); 2,2,3,3-Tetramethylpentane A 430°, N (c12); 452°, 42000 (x); 516°, N (y2); 2,3,3,4-Tetramethylpentane A 437°, 24000 (x); 514°, N (y2); Toluene O 552°, N (a); 640°, N (b); 516°, N (f2); A 810°, N (a); 633°, N (l); 552°, N (i3); 540°, N (c12); 568°, 48000 (x); 635°, N (y1); V 830°, 20 (z2); 1057°, 1 (z2); *o*-Toluidine A 537°, N (l); 482°, N (n2); V 832°, 20 (z3); 1040°, 3 (z3); *m*-Toluidine A 580°, N (l); V 846°, 1 (z3); 1062°, 2 (z3); *p*-Toluidine A 482°, N (i1);

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Tributyl citrate A 368°, N (i2); Trichloroethylene O 419°, N (c1); A 463°, N (c1); V 771°, 10 (z3); 950°, 1 (z3); Trichloro-1-(pentafluoroethyl)-4-(trifluoromethyl) benzene A 568°, N (y3); Tricresyl phosphate A 600°, N (x); Triethyleneglycol O 244°, N (c1); A 371°, N (c1); Triethylenetetramine A 338°, N (i2); Triisobutylenes A 413°, N (y2); V 789°, 20 (z2); 1060°, 1 (z2); 1,2,3-Trimethylbenzene A 479°, 24000 (x); 510°, N (y1); 1,2,4-Trimethylbenzene A 521°, 24000 (x); 528°, N (y1); 1,3,5-Trimethylbenzene A 559°, 48000 (x); 577°, N (y1); 2,2,3-Trimethylbutane A 454°, 18000 (x); 2,3,3-Trimethyl-1-butene A 383°, 12000 (x); 2,5,5-Trimethylheptane A 485°, N (y1); 2,2,3-Trimethylpentane A 436°, 24000 (x); 2,2,4-Trimethylpentane O 283°, N (c1); A 561°, N (l); 434°, N (c1); 447°, 12000 (x); 515°, N (y1); V 786°, 20 (z2); 996°, 2 (z2); 2,3,3-Trimethylpentane A 430°, 12000 (x); 2,3,4-Trimethyl-1-pentene A 257°, 12000 (x); 2,4,4-Trimethyl-1-pentene (cf. Di-isobutylenes) A 420°, 12000 (x); 2,4,4-Trimethyl-2-pentene (cf. Di-isobutylenes) A 308°, 30000 (x); 3,4,4-Trimethyl-2-pentene A 330°, 24000 (x); 2,4,6-Trimethyl-1,3,5-trioxane (see Paraldehyde); Trinitrophenol (see Picric acid); Trioxane A 424°, N (c1); 414°, N (i2); Tritolyl phosphate (see Tri-cresyl phosphate); Tung oil A 457°, N (i2); Turkey red oil A 445°, N (i2); Turpentine A 252°, N (n3); 253°, N (i3); 255°, N (n5); V 780°, 20 (z2); 996°, 1 (z2); Vinyl acetate A 427°, N (i1); Vinylcyclohexene A 269°, N (i2); Vinyl ether (see Divinyl ether); Vinylethyl ether A 201°, N (i2); Vinyl-2-ethylhexyl ether A 201°, N (i2); Vinylisopropyl ether A 272°, N (i2); *o*-Xylene A 496°, N (i3); 501°, 30000 (x); 551°, N (y1); *m*-Xylene A 563°, 54000 (x); 652°, N (y1); *p*-Xylene A 618°, N (l); 564°, 42000 (x); 657°, N (y1); Zinc stearate A 421°, N (i2).

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(Cross-references to the main list of references at the end of the AGARDograph are given in square brackets.)

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- ^{f1} MOORE, H. [see ref. 194]
- ^{f2} MOORE, H. [see ref. 198]
- ^{g1} DIXON, H. B. and HIGGINS, W. F. [see ref. 61]
- ^{g2} DIXON, H. B. and COWARD, H. F. [see ref. 56]
- ^{g3} COWARD, H. F. [see ref. 41]
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- ^s LEWIS, J. S. [see ref. 172]
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- ^{z2} MULLINS, B. P. [see ref. 212]
- ^{z3} MULLINS, B. P. [see ref. 213]
- ^{z4} MULLINS, B. P. [see ref. 214]
- ^{z5} MULLINS, B. P. [see ref. 215]

EFFECT OF FUEL ADDITIVES

1. INTRODUCTORY REMARKS

THE search for fuel additives that bring about beneficial effects received a tremendous stimulus in 1922 when MIDGLEY¹⁸⁰ discovered the remarkable anti-knock effect of traces of lead tetraethyl, and the activity in this field of investigation has shown no signs of abating since then. Fuel additives may exert various effects; they may impart stability to the fuel during storage, reduce the corrosiveness of the fuel, improve the fuel's lubricating properties, reduce the freezing point or alter the ignitability of the fuel. It is this last effect which is of interest here and the change in the ignition temperature of the fuel may be taken as a measure of it. This effect should strictly be assessed from tests in which the ignition delay time is carefully measured and arranged to be constant, or, better still, the effect may be fully represented by a comparison of ignition delay *v.* temperature curves, under the same conditions of mixture strength and static pressure. Fortunately, many of the ignition tests that have been reported, though not specifying the ignition delay, probably have been made under approximately constant conditions of ignition delay, and so a comparison of ignition temperatures, in these instances, does indicate the true effect of the fuel additive.

This chapter will consist of a review of the knowledge of the effect of additives upon the ignition temperatures of fuels*, mainly hydrocarbon fuels. The influence of such additives upon the behaviour of engines, on the other hand, comprises one of the topics discussed in Chapter 14.

Separate sections will be devoted here to lead tetraethyl and the organic nitrous and nitric esters on account of the large effects produced by these substances and the considerable amount of research undertaken with them.

2. LEAD TETRAETHYL

ORMANDY and CRAVEN²²⁰ in 1924 reported that lead tetraethyl at a concentration of $2\frac{1}{2}$ g/l. *decreased* the spontaneous ignition temperature of heptane by some 14° as determined in the Moore apparatus in a current of oxygen. WEERMAN²²¹ carried out tests with petrol in 1925 which he reported on two years later; he found quite definitely that lead tetraethyl at a concentration of 2 g/l. *raised* the ignition temperature by some 100° the actual increase depending somewhat upon the volume of

* There are no means for calculating the effects of additives and so this knowledge is based entirely upon experiments.

oxygen per gram of petrol used in the tests. All subsequent research workers working with other than pure oxygen have confirmed that lead tetraethyl tends to *increase* ignition temperatures.

EGERTON and GATES⁷³ reported in 1927 that lead tetraethyl at a concentration of $2\frac{1}{2}$ g/l. raised the ignition temperature of benzene by 18°, cyclohexane by 27°, methylcyclohexane by 92°, pentane by c. 80°, isohexane by 46°, heptane by 83°, petrol by 82°, ether by 65°; amyl alcohol, dimethylaniline and carbon disulphide were unaffected by this concentration of lead tetraethyl. Typical curves showing how lead tetraethyl suppresses the combustion of a combustible vapour were presented by these authors in *Fig. 1* of their paper; they found by recording the deflection of a galvanometer connected to a thermocouple arranged to show the difference in temperature between the walls of the pot and the bulk of the gas, that 1 per cent of lead tetraethyl caused the temperature rise starting at 544° C to be even smaller than that observed in the absence of the additive and starting at 456° C.

TANAKA and NAGAI²⁹⁵ noted that the ignition temperature of ethyl alcohol was abnormally high when determined in a crucible that had been used for studying the effects of lead tetraethyl upon various combustibles. They concluded that this was due to the after-effects of lead tetraethyl upon the surface of the platinum crucible used.

EGERTON⁷² in 1928 concluded that in lead tetraethyl, the organic radicals have only a secondary effect and that the influence of lead tetraethyl is inhibited by the addition of ether due to the formation of a stable oxidation product; this also explains the results of Ormandy and Craven noted above.

LAYNG and YOKER¹⁶³ and MARDLES¹⁶³ have described the effect of lead tetraethyl upon the slow oxidation of liquid hydrocarbons. GILL, MARDLES and TETT⁹⁹ noted that lead tetraethyl suppressed the cool-flame formation during the slow (low temperature) combustion of carbon disulphide-, ether- and acetaldehyde-air mixtures, a result which was similar to that noted more recently by MULLINS³⁰⁵ for kerosine and gas oil and supported by emission spectrographic evidence.

MOHR¹⁹² reported that the self-ignition points of lead tetraethyl and 'Ethyl fluid' were both 150°, yet addition to motor benzine raised the self-ignition points from 300° to a maximum of 350° with 0.5 per cent 'Ethyl fluid' and to a maximum of 430° with 15 per cent of lead tetraethyl. Further evidence of the inhibiting influence of lead tetraethyl upon hydrocarbon ignition is afforded by the more recent work of SORTMAN, BEATTY and HERON²⁸³ (using the drop method and a steel crucible), ONO²²⁸ (using a crucible method due to YAMAKITA²²⁸), JOVELLANOS *et al.*¹⁸¹ (using the M.I.T. adiabatic compression method in which the effect of lead tetraethyl upon delay time is much less marked) and FRANK and BLACKHAM^{86, 87} (using a modified Moore type apparatus and *n*-dodecane as parent fuel).

OTHER ADDITIVES

3. ORGANIC NITRITES AND NITRATES

MARDLES¹⁸³ in 1928 reported that a small quantity of isoamyl nitrite reduced the spontaneous ignition temperatures of fuels, and in 1932 HELMORE¹¹⁰ filed a patent describing the use of small proportions of methyl and ethyl nitrates in a high boiling point fuel oil to improve its ignition properties in internal combustion engines. Since then many investigators have studied the influence of various organic nitrites and nitrates upon the ignition of hydrocarbon fuels under a variety of laboratory and engine conditions. In most cases appreciable effects were observed and these have been attributed largely to the influence on the combustion chain mechanism of the nitrogen peroxide formed during the decomposition of the organic esters.

PRETTRE, DUMANOIS and LAFFITTE²⁵² found that amyl nitrite accelerated the velocity of propagation of a pentane-air flame, and BATT¹⁵ found, using the same mixture and additive, greatly enhanced violence of the explosions occurring in the first zone of ignition.

JOST and RÖGENER¹⁴⁸ investigated the effect of amyl nitrite and ethyl nitrate on the final temperature and the induction time of heptane-air mixtures ignited by adiabatic compression; both additives strongly accelerated the ignition, especially the latter one. A similar result with a compression-ignition apparatus was reported by JOVELLANOS *et al.*¹⁸¹, who determined that increasing the concentration of ethyl nitrite in triptane progressively decreased both the delay time and the critical explosion pressure.

There is abundant evidence in the scientific and patent literature that organic nitrites and nitrates, especially the lower homologues, are capable of reducing the ignition delay of hydrocarbon fuels under Diesel engine running conditions. Two references only will be given here, the second of which is a very comprehensive survey of the literature relating to ignition accelerators for compression-ignition engine fuels; see THIEMANN²⁰², and BOGEN and WILSON²⁰.

Recently MULLINS²¹⁰ made a systematic study of the effect of ethyl nitrate, ethyl and amyl nitrites in various concentrations upon the ignition delay of kerosine-vitiated air mixtures at atmospheric pressure. He found that the nitrate was very much more effective than the nitrites, but that for all three additives, under the continuous flow test conditions employed, concentrations less than 1 per cent produced negligible effects upon the ignition delay. For blends containing up to 50 per cent (vol.), however, the ignition delay progressively decreased.

4. OTHER ADDITIVES

EGERTON and GATES⁷² in 1927 reported the results of a very comprehensive investigation into the effects of metallic vapours on the ignition of substances and found that, in general, oxidation of the combustible,

and therefore ignition, was delayed. An exception to this rule occurred when the fuel was an alcohol, the metal having little effect upon the ignition in this case. These workers ⁷⁵ also measured the rise in the igniting temperature of acetaldehyde and of petrol produced by aniline, quinone and other organic substances added to the combustible in various concentrations up to 10 per cent by volume.

WEERMAN ³²¹ tested many organic compounds of 22 elements which included lead, iron, mercury, nickel, selenium, boron, chromium, tin, zinc, bismuth, silicon, cobalt, aluminium and sulphur as petrol additives, and reported that the spontaneous ignition temperature was increased by varying amounts up to 170 C° (for iron carbonyl); four substances did, in fact, reduce the S.I.T. of petrol by 10 C°, these being boric triethyl, zinc diethyl, aluminium triethyl and silicon tetraethyl. GREBEL ¹⁰⁴ found, as also did Weerman, that small quantities of iron carbonyl raised the spontaneous ignition point of petrol more than did lead tetraethyl. GREBEL ¹⁰⁵, using the Krupp modification of a Moore type apparatus, systematically determined the effect of various organic additives including acetone, acrolein, ethyl alcohol, acetaldehyde, benzene, ether and aniline upon the spontaneous ignition temperature of various petroleum blends. He also measured ¹⁰⁶ the effects of mixtures of ethyl alcohol and benzene and of mixtures of acetone and aniline upon the ignition temperature of a fuel blend comprising 50 per cent gasoline, 30 per cent benzene and 20 per cent ethyl alcohol; 1 per cent acetone plus 1 per cent aniline was more effective in raising the ignition temperature than 2 or 5 per cent acetone alone.

FRANK and BLACKHAM ⁸⁷ determined the effect of many amines, phenols, hydrocarbons, alcohols, carbonyl compounds, halogen compounds and other organic compounds, when added in 5 per cent molar concentration, upon the spontaneous ignition temperature of *n*-dodecane. Lead tetraethyl was easily the most effective in raising the S.I.T., and the aromatic amines were also quite potent in this respect. Several compounds lowered the S.I.T. slightly, viz. *p*-nitroaniline, biphenyl, benzaldehyde, carbon tetrachloride, nitrobenzene and cumene hydroperoxide. One compound, *tert*-butyl peroxide, lowered the S.I.T. by 33 C°.

MULLINS ²¹⁰ has presented ignition delay *v.* temperature curves for kerosine with and without various additives which included *tert*-butylhydroperoxide, diethylether, acetaldehyde, propylene oxide, nitrobenzene and carbon disulphide. Diethylether was the most effective of these substances at 5 per cent (vol.) concentration, appreciable reductions in ignition delay being noted. It is instructive to compare the effects of these additives with the ignition delay *v.* temperature curves of the pure additives reported by the same author ²¹²⁻²¹⁵.

FACTORS AFFECTING IGNITION DELAY

IN THIS chapter the more important factors that affect the ignition delay of a combustible mixture, excluding temperature and fuel composition, are reviewed briefly. The effects of fuel structure and temperature are, of course, of primary importance, and these are inevitably dealt with automatically in the other chapters of the AGARDograph.

1. SURFACES

A careful investigation of the effects of surface temperature and composition upon the auto-ignition temperatures in air of various combustibles was made by MASSON and HAMILTON¹⁸⁷. They made that part of the surface upon which the drop fell essentially the hot junction of a thermocouple and this enabled an accurate measurement of the surface temperature, just prior to contact with the drop, to be obtained. For materials of high heat capacity the loss of heat from the plate to the drop was sometimes so great that no flash occurred or only after a long (5 to 6 sec) time interval. When the surface is below the auto-ignition temperature an immediate lowering of the temperature of the plate was noted due to the cooling effect of contact with the liquid; later a temperature rise due to combustion took place. Masson and Hamilton found that ignition temperatures determined on one type of surface differed considerably from those obtained on another, owing to differences in catalytic activity of the surfaces. If, at a given temperature, a surface of low activity gives a flash, no flash is observed on a surface of higher activity, it being necessary to raise the temperature of the latter surface in order to cause sufficient combustion to take place in the gaseous phases to produce a flash. However, the catalytic activity of a surface is a function of the temperature, in general, approaching a maximum value for each case; at high (incandescent) temperatures these distinctions disappear. Since the range of auto-ignition temperature is below the temperature of maximum catalytic activity for most substances, differences in auto-ignition temperatures with different surfaces are to be expected. A surface of zero catalytic activity and zero temperature coefficient of activity should give an A.I.T. value which approaches the ignition temperature of the corresponding gaseous mixture. Many test results using platinum, gold, silver and Pyrex glass surfaces were tabulated by Masson and Hamilton; for example, the A.I.T.s of *n*-heptane on these four surfaces are, respectively, 451° C, 477° C, 474° C, and 476° C, whereas for benzene they are, respectively,

FACTORS AFFECTING IGNITION DELAY

656° C, 618° C, 656° C, and 649° C. Not only must the effect of fuel structure be taken into account in estimating catalytic activity, but also the change in catalytic activity with temperature just mentioned: it was not possible in these experiments to keep the surface temperature constant and so this factor complicates the interpretation and generalization of the results obtained. Generally A.I.T.s on glass were lower than A.I.T.s on platinum, a surface of greater catalytic activity; *n*-heptane, 1-heptene and *p*-cymene were exceptions to this rule.

LEWIS¹⁷¹ measured the ignition points of various hydrocarbon-oxygen mixtures in heated vessels and made a special study of the catalytic effect of surfaces with the following results: powdered glass and pumice increased the ignition point of paraffins; charcoal caused an increase for paraffins and a decrease for olefines; metals either had no effect (tin, zinc and aluminium) or caused an increase (silver, platinum, lead and copper).

The influence of wall material upon the position of the spontaneous ignition *v.* delay curves was investigated for various combustibles by ONO²²⁸. He used crucibles made of alumina, porcelain, quartz, terex glass, aluminium and stainless steel and these gave approximately identical curves, whereas crucibles of platinum, copper, and nickel gave different curves owing to catalytic or catalyst poisoning effects. Potassium chloride coatings on terex glass or on platinum did not affect the ignition of *iso*-octane but strongly inhibited the ignition of ethyl alcohol.

HIKITA¹¹⁹ recently described an apparatus for measuring the ignition temperature of a sample of an explosive compound and with this apparatus determined the effect of metal surfaces.

The effect of the *condition* of a metal surface on the spontaneous ignition temperature of hydrocarbons was studied by FRANK and BLACKHAM⁸⁷ two years ago. They reported differences between polished stainless steel and stainless steel in different degrees of oxidation. Thus *p*-xylene had an S.I.T. (with 125 c.c./min. air flow) of 657° C on bright stainless steel, whereas on highly oxidized stainless steel the S.I.T. was 697° C, 708° C, and 710° C in three successive tests in the same vessel. On the other hand, a change in the metal surface had substantially no effect on the S.I.T. of those compounds which undergo spontaneous ignition below 290° C. Metals included in the latter studies were stainless steel, copper, aluminium, black iron, brass, Inconel, aluminium alloy (24-S) and magnesium.

2. PRESSURE

There is a dearth of experimental data upon the influence of pressure upon the spontaneous ignition of fuels, which is all the more felt by combustion engineers in view of the importance of this variable in engines and the impossibility of applying generally the over-simplified

PRESSURE

theory represented by such equations as those of Semenov and of Hinshelwood referred to in Chapter 2. The theoretical difficulties arise because of the chemical complexity of the combustion reactions preceding ignition; the nature of these reactions may be subject to change during the induction period and so, therefore, may the reaction rate and activation energy of reaction vary with time; furthermore, these reactions are usually of the chain type. At present exact knowledge of the effect of static pressure upon the ignitability of fuels has to be determined experimentally if it is to be obtained at all. The present section therefore reviews the experimental data obtained in the cases of specific reactions under specified conditions.

ZAGULIN²³⁸ has studied a number of combustion reactions over a range of pressures and has presented the results in the form of figures and tables. He gives values of (E/R) for H_2-Cl_2 , H_2-Br_2 , CS_2-O_2 , CH_4-O_2 , Cl_2-O_2 , $C_2H_6-O_2$, $C_3H_8-O_2$, and $C_5H_{12}-O_2$ mixtures. Further work on the effect of pressure upon the spontaneous inflammation of the last-named mixture within the pressure range 5 to 112 cm mercury has been published by NEUMANN and ESTROVICH²²⁴.

TOWNEND and COHEN²¹⁴ have determined the influence of pressure on the ignition points of a 6.5 per cent (vol.) gasoline-air mixture and have noted the occurrence of cool flames. In this and much similar work in which pressure-temperature ignition regions have been delineated for various combustible mixtures, the ignition delay time has not generally been measured accurately and often has not been controlled or measured at all. Many such diagrams have been summarized in Chapter 11 (section C) of the book by JOST¹⁴³.

Gaseous paraffin hydrocarbons have been investigated at various pressures by TOWNEND and CHAMBERLAIN²¹², who reported that pressure-temperature curves for constant delay times less than 2 sec showed a marked pressure minimum at about 410° C. NAYLOR and WHEELER²²⁰ found that for methane-air mixtures near a heated surface, the delay increased with reduction in pressure and suggested that this was because the reaction ceased to be a surface reaction; at a given pressure the delay increased with the methane concentration.

LAURE¹⁸⁰, using gas oil in his heated cylindrical bomb at reduced pressures, found that the ignition temperature fell as pressure increased according to a hyperbolic law.

PESCHARD²²⁹ studied *n*-heptane, *iso*-octane, gasoline, benzene and ethyl alcohol at pressures between 3 cm and 160 cm mercury and reported activation energy values. He found that below 440° C, $E = 3.4$ kcal/mole and above 440° C, $E = 30.6$ kcal/mole for *n*-heptane-oxygen mixtures.

Much valuable spontaneous ignition data at high pressures has been obtained by use of the adiabatic compression technique. Sources of such data may be obtained by reference to Chapter 6. In interpreting this

data it should be borne in mind that a different pressure in a given apparatus is usually accompanied by a different working temperature because of the nature of the technique used.

Recently MULLINS²¹¹ determined ignition delay *v.* temperature curves for several combustible gases in vitiated air at various reduced pressures. Generally, it was found that, at a given temperature, $\tau P^n = \text{constant}$, but the value of the pressure exponent n differed from fuel to fuel. The dependence of n upon temperature, within the ranges of temperature covered, was also measured in some cases. Pressure exponents for acetylene and methane were less than unity; pressure exponents for carbon monoxide and hydrogen varied strongly with temperature; pressure exponents for ethane, calor gas and buta gas exceeded unity. The pressure exponent for kerosine was reported by MULLINS²⁰⁹ as unity.

3. FUEL CONCENTRATION

MASON and WHEELER¹⁸⁵ found experimentally that an increase in hydrocarbon concentration tended to reduce the auto-ignition temperature of a hydrocarbon-oxygen mixture whereas change in the oxygen concentration produced a much smaller effect. They ascribed these results to the fact that the component with the greater 'stopping power' for radiant energy, such as could 'activate' it, increased the rate of reaction with the concentration. Alternatively, in terms of the chain theory, the increase in the concentration of hydrocarbon molecules would augment the number of chains formed in unit time and hence the number of active centres.

On the other hand, TIZARD and PYE³⁰⁶ put forward some evidence showing that the rate of reaction of a fuel-air mixture upon sudden compression was independent, within wide limits, of the concentration of the combustible gas and only depended upon the oxygen concentration. MULLINS²⁰⁹ also found that the ignition delay of *weak* kerosine-air mixtures did not depend upon the mixture strength; his method of observation attempted to eliminate the effect of mixture gradients in the neighbourhood of the fuel injector.

This lack of dependence of ignition delay upon the fuel/air ratio within the weak range is not hard to understand. There are relatively very few fuel molecules present and it will take approximately as long for three or four of them to become 'conditioned' for reaction (by collision) as for one of them to be so 'conditioned'. The exact nature of the 'conditioning' process does not affect this argument so long as it involves no appreciable interchange (e.g. of energy) between fuel molecules. An appreciable increase in fuel concentration would not increase the fuel-oxygen collision rate of *each* fuel molecule, but might increase the ratio of fuel-fuel to fuel-oxygen molecular collisions so much that sufficient 'conditioned' fuel molecules for the occurrence of ignition

OXYGEN CONCENTRATION

were formed more quickly—perhaps by energy interchange between fuel molecules, the energy deriving from preflame (slow combustion) reactions. When the fuel/air ratio is excessively great (i.e. very rich mixtures) it is conceivable that the fuel-oxygen molecular collision rate would fall so much, due now to the weak oxygen concentration, that the ignition delay would again be larger. These simple considerations suggest that in homogeneous combustion as the mixture ratio is steadily varied the ignition delay would pass through a minimum value.

This is a branch of the subject in which there is very little definite experimental information. This is probably, in part, due to the great experimental difficulties in suddenly producing a fully mixed, homogeneous fuel-air mixture at a high temperature.

GERSTEIN⁹⁸ recently referred to some tube experiments with propane-air mixtures in which the variation of ignition delay with fuel concentration was studied. He found the strongest dependence occurred in the weak mixture range, but here, again, the existence of mixture gradients ahead of the prepared mixture through which observations were made, may have affected the results, especially those with the richer mixtures.

4. OXYGEN CONCENTRATION

Ignition temperatures of combustibles in oxygen are generally somewhat lower than corresponding ignition temperatures in air as may be seen by referring to the data in Chapter 11 above. There have been a number of investigations into the effect of oxygen concentration upon the ignition temperature, or at constant temperature upon the ignition delay of fuels, and these investigations, some of which have taken the oxygen concentration below 21 per cent (vol.), are reviewed and discussed below.

As mentioned in the preceding section, TIZARD and PYE³⁰⁶ have shown by their adiabatic compression method that the reaction rate of a fuel-air mixture depends on the oxygen concentration. LEWIS¹⁷¹, using a heated cylindrical glass bulb technique, showed that the influence of oxygen concentration was fairly small (7° to 17° C) and that in the particular case of amylene, this showed practically no change of ignition temperature when exploded in various concentrations of oxygen.

Concentrations of oxygen intermediate between 21 per cent and 100 per cent were studied by PAHL²³¹, who led known mixtures of purified air and oxygen through a heated copper tube into an ignition block containing an 11 c.c. combustion chamber provided with a small orifice for the introduction of the fuel under investigation. The block was electrically heated and ignition temperatures were measured at various oxygen concentrations. With allyl alcohol the ignition temperature fell regularly from c. 450° C for 20 per cent oxygen to 393° C for 100 per cent oxygen; with benzene a gradual fall from 840° C for

10 per cent oxygen to c. 700° C for 100 per cent oxygen was observed. The time from the fall of a drop of fuel into the combustion chamber until ignition occurred was taken as the delay; this increased with the decrease of the oxygen content as well as the ignition temperature.

ZERBE, ECKERT and JENTZSCH³⁴¹ found that increased oxygen concentration caused a lowering of the auto-ignition temperatures of fuels as determined in the Jentzsch type of apparatus, although JOHNSON, CRELLIN and CARHART¹³⁸, who also used this type of apparatus, say that the ignition delay is much more dependent on the temperature than on oxygen concentration.

DYKSTRA and EDGAR⁷¹ reported on the variation in ignition temperature for *iso*-octane and a gasoline, using Dixon's concentric tube method and different oxygen-nitrogen-fuel proportions.

BARON and LAFFITTE^{9, 10} have presented data upon the ignition temperatures of diethyl ether-oxygen-nitrogen (or carbon dioxide) mixtures. They found that the ignition temperature increased slightly as $p_N/(p_E + p_O)$ decreased, $(p_E + p_O)$ being constant, and decreased more markedly as $(p_E + p_O)$ increased, $p_N(p_E + p_O)$ being constant.

The specific nature of the influence of oxygen concentration on spontaneous ignition phenomena is illustrated by the work of REUTENAUER²⁵³ who passed gaseous mixtures of oxygen, nitrogen and hydrocarbons through an enclosure the temperature of which rose slowly. With ketene and decahydronaphthalene the temperatures limiting the two ignition zones varied little with composition. With dipentene, on the other hand, an increase of oxygen concentration in a mixture containing 2.9 per cent of the hydrocarbon reduced greatly the range of the second ignition zone, due, Reutenauer believes, to the formation of intermediate compounds such as aldehydes and peroxides.

Evidence concerning the influence of oxygen concentration upon the ignition delay as determined by the bomb method was obtained by LONN¹⁷⁸ who, using hydrocarbon fuels, found that if the oxidant consisted of mixtures of oxygen and nitrogen the ignition delay was controlled by the partial pressure of the oxygen. He also discovered that addition of large amounts of carbon dioxide decreased the ignition delay, whereas small amounts of carbon dioxide had the opposite effect.

MULLINS²⁰⁶ investigated the effect of oxygen concentration in the range 8 per cent to 13 per cent upon the ignition delay of kerosine-vitiated air mixtures by the N.G.T.E. method of test, the low oxygen partial pressures being obtained by water injection, since preliminary tests had shown that the effect of water addition itself was not large. At a given temperature the ignition delay was found to vary according to the inverse square power of the oxygen concentration.

BROATCH²⁴ has measured the effect upon the ignition delay of a bipropellant fuel system of gradually replacing with nitrogen the oxygen in the surrounding air. He brought the fuel and oxidizer

WATER VAPOUR

together by allowing two jets of liquid to impinge. The two liquids used in this study were, respectively, 80 per cent hydrogen peroxide and a mixture of hydrazine, methyl alcohol and water.

5. WATER VAPOUR

The effect of water vapour on spontaneous ignition temperatures and ignition delays is rather complex and sometimes specific in its action. This has been known for nearly seventy years in the special case of carbon monoxide-oxygen mixtures through the work of DIXON⁵², though even for inflammable liquids the effects of water vapour were studied as long ago as 1926 by TANAKA and NAGAI²⁹⁴.

JONES and SEAMAN¹⁴⁰ determined the difference between the ignition temperatures of dry and moist (saturated with water vapour at room temperature) methane-air mixtures and found this to vary with the mixture composition, reaching a maximum of 11 C° for a mixture containing 4 per cent methane. The effect of amounts of water vapour less than 20 per cent saturation was too small to be measured. The water vapour had no appreciable effect upon the ignition delay, however. BUNTE and BLOCH²⁸ also made measurements of the ignition temperatures of dry and moist methane-air mixtures and studied ethylene-air, carbon monoxide-air, and hydrogen-air mixtures similarly. The effect of water vapour on the ignition zones of the last-named mixture has been investigated more recently by NALBANDYAN²¹⁶.

The complex and specific nature of the effect of water vapour on hydrocarbon oxidation has been illustrated by CHIRKOV²⁶ in his studies upon ethane. Upon investigating the dependence of the ignition induction period upon pressure with and without the addition of water vapour, he found that when the temperature was less than 600° C water vapour reduced the delay period, the reduction being smaller the higher the temperature. At 630° C addition of 3.6 per cent water vapour was without effect.

The effect of added water vapour upon the ignition delay of carbon-monoxide-vitiated air mixtures under continuous flow short delay conditions was measured by MULLINS²¹¹. He found that the addition of c. 2 per cent (by wt.) water vapour reduced the ignition delay to a half and a quarter of its previous values at 750° C and 800° C, respectively—notwithstanding the fact that the oxygen concentration was diminished by c. 1 per cent in the process. Generally the effectiveness of the added water was greatest at the highest air temperatures. By contrast, addition of water to Calor gas-vitiated air mixtures made little difference to the ignition delays within the temperature range 850° to 1000° C.

APPLICATIONS

1. STATIC FIRE HAZARDS

AIRCRAFT fires occur because of three main causes: (i) explosions of inflammable fuel vapour-air mixtures in an enclosed space such as the vapour space in a fuel tank, and (ii) ignition of vapours from leaking or spilt liquid fuel by sparks or flames, and (iii) spontaneous ignition of liquid fuel through contact with a hot surface in the presence of air. Fires of origin (i) depend upon the existence of a mixture ratio which falls between the so-called weak and rich limits of inflammability and the minimum fuel concentration will be achieved at lower temperatures the more volatile the fuel. Fires of origin (ii) again depend upon the rate of vapour release which is a function of fuel volatility and which is assessed by the 'flash-point' test. POMEROY²⁴⁸ has stated an approximate working rule that the spontaneous ignition temperatures of petroleum oils are inversely proportional to the flash points. Fires of origin (iii) depend upon fuel properties that are involved in the types of test described in Chapters 3, 4, 5 and 9 and which are expressed by a spontaneous ignition temperature. Such fires may occur after a long delay time (i.e. more than 1000 msec) and thus much of the data summarized in Chapter 11 is relevant in this connection. Such spontaneous ignition temperature data obtained by the same test method does indicate the order of the various liquid fuels with respect to danger from fire due to contact with, for example, a hot exhaust pipe.

2. SPARK-IGNITION ENGINES

A very clear and up-to-date survey of the problem of engine knock and the relation of auto-ignition to this phenomenon has been published by EGERTON and MOORE⁷⁶ in which the contrast between ordinary adiabatic ignition and the conditions in the engine end-gas is one of numerous points dealt with. They state that in ordinary ignition by adiabatic compression the cold charge rises in temperature until in some regions the chemical reaction rate overcomes the local heat loss (or produces a critical concentration of active radicals), and ignition results; when once a flame has appeared it travels through the rest of the mixture which has undergone only slight change. In an engine, the mixture has been exposed to other influences, the hot exhaust valves, some radiation from the flame front, and hot products diffused from the flame and spread by the turbulence of the mixture; these cause some change in the

chemical state of the gases, 'presensitization' as it is called. When the ignition of the end-gas occurs, owing to presensitization, the flame may travel somewhat like a true detonation and certainly much more rapidly than in ordinary adiabatic ignition. Egerton and Moore conclude their survey by stressing the distinction that should be made between ignition and inflammation. The smooth combustion of the charges in a spark-ignition engine is true inflammation of an entirely different character from the combustion of the end-gas which is an ignition—an auto-ignition with its definite delay period. The SOKOLIK and YANTOVSKII²⁸² description of the two-stage nature of this knock producing spontaneous ignition in engines has already been summarized in Chapter 6, but it is necessary to mention here the elegant experimental proof of BARBER, MALIN and MIKITA⁷ that such spontaneous ignitions are entirely responsible for knock. They demonstrated that knock does occur if a combustible air-fuel vapour mixture resides for an appreciable time at combustion chamber temperatures and pressures, and conversely that the operation of a C.F.R. engine, specially modified so that such residence time is vanishingly small, was quite independent of the octane or cetane numbers of the fuel used.

Of the many earlier surveys relating to the mechanism of operation of spark-ignition engines, several have dealt particularly with the significance of ignition delay and ignition temperatures in this connection. ZEISE²³⁹ treated the question from the physico-chemical standpoint and regarded the formation of intermediate combustion products as critically important for spontaneous ignition, a view which the present writer shares. EGERTON and GATES⁷⁴ showed that ignition temperatures of fuels could be related to their knocking characteristics in engines. JOST¹⁴⁴ developed Semenov's chain theory of combustion and showed that the resulting induction period reaction rates were consistent with known engine behaviour of fuels, at any rate in so far as the influences of pressure, temperature and activation energy were concerned.

PESCHARD^{225, 226}, SCHMIDT²⁶⁴ and later WITSCHAKOWSKI²²¹ proposed to characterize a fuel's anti-knock quality in terms of its ignition delay values, or more explicitly, by the three constants in Semenov's equation. Attempts to correlate engine behaviour (octane ratings) of fuels with only one constant, such as the activation energy, were not successful and PESCHARD²²⁵ expressed this, by inference, when he stated that the study of pressure limits of ignition should be complemented by a study of the period of *induction* preceding ignition.

It should be mentioned, however, that partial success was obtained by several research workers who attempted to correlate knocking properties with auto-ignition temperatures. Among these people were MASSON and HAMILTON¹⁸⁸, SCHÄFER²⁶¹ and HERSTAD^{118, 119}. MACCORMAC and TOWNEND¹⁷⁹ attempted a similar correlation but carried out their

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laboratory spontaneous ignition tests under pressure, whilst YAMAKITA^{335, 337} based his work on spontaneous ignition versus ignition delay time curves.

Recently two new spontaneous ignition parameters have been taken as criteria of the engine knock ratings of fuels. BARUSCH and PAYNE¹⁴ measured the position of formation of cool flames produced at atmospheric pressure in a 1 in. diameter glass tube flow system, and DOWNS and WHEELER⁶⁶ have made use of auto-ignition ratings obtained in a motored engine.

3. COMPRESSION-IGNITION ENGINE

The link between the ignition quality (cetane number) of a diesel fuel and the spontaneous ignition properties is very direct since cetane number is defined as the percentage of cetane in that blend with α -methylnaphthalene which gives the same ignition delay as the test fuel in the standard test engine. Cetane number is a measure of the tendency of a fuel to give rough running and diesel knock in a compression-ignition engine and also gives some indication of the ease with which a given fuel permits starting at low temperatures. These two statements are not always true, however, if the fuel contains some additive, such as ethyl nitrate, to improve ignition quality. There is little doubt, that, as in the case of the spark-ignition engine, preflame reactions of the fuel play an important role in determining the rapidity of the initial combustion and hence the ignition quality of the fuel.

Many research workers have obtained a fairly good correlation of this ignition quality with the results of spontaneous ignition tests by bomb techniques (see Chapter 6)—see also, for example, the papers by WOLFER³³³ and by MIKHAILOVA and NEIMAN¹⁹¹. On the other hand, it has been reported by others that such correlations of engine fuel performance with laboratory determined ignition delay data are imperfect (HUM and SMITH¹³⁷) or even of little value (LINDNER¹⁷³).

CLERGET³⁷ showed that the relation between ignition delay and cetane number of nine fuels was not linear, even when the ignition delay was measured under engine conditions. DUMAÑOIS and DESBROSSE⁶⁹ suggested that the relation between ignition delay in a compression-ignition engine, τ , and the cetane number C_N was of the form

$$C_N (\tau - a) = b \quad \dots \dots (30)$$

where a and b are constants, and for an equimolar mixture of two fuels the relation was expressed by the equations:

$$\frac{2}{\tau - a} = \frac{1}{\tau_1 - a} + \frac{1}{\tau_2 - a} \quad \dots \dots (31)$$

and

$$C_N = C_{N_1} + C_{N_2} \quad \dots \dots (32)$$

where suffixes 1 and 2 refer to the two fuels.

The effect of additives upon ignition delay and ignition temperatures is dealt with in Chapter 12; the effect of additives on cetane number may be very great indeed; much information on this topic is summarized in the comprehensive paper by BOGEN and WILSON²⁰. WIDMAIER³²⁶ noted that when an additive was admitted with the intake air of a compression-ignition engine starting was much improved. More generally, GARNER *et al.*⁹⁴ found that admission of an additive in the vapour phase in this way was more effective, both as regards cold starting and cetane rating, than when added in the liquid phase to the fuel; they attributed this to the initiation of preflame reactions during the compression stroke.

4. CETANE AND OCTANE RATING RELATIONSHIPS

DUMANOIS⁶⁷ in 1933 measured the ignition quality of a diesel fuel by tests in a spark-ignition engine. The test fuel was blended to a given percentage in a petrol of known octane number and the variation in octane number was measured. The more the octane number decreased, the higher the ignition quality of the fuel. For several fuels this form of test yielded results that correlated well with measurements in compression-ignition engines.

From numerous tests with gasolines and gas oils from crude shale, ISIBASI¹²⁸ established the following simple relation between cetane number, C_N , and octane number O_N :

$$C_N + O_N = K' \quad (33)$$

where K' is a constant with a value of about 110 for most crude petroleum oils and about 100 for certain cracked shale oils. WILKE³²⁸ gave the following approximate relation two years later:

$$O_N = 120 - 2 C_N \quad (34)$$

whilst DUMANOIS⁶⁸, in common with these two authors, established a linear connection between C_N and O_N .

WIDMAIER³²⁵, NYGAARD *et al.*³²⁷ and TREER³²⁶ have also reported the results of correlating cetane and octane numbers, the last two papers giving graphical correlations and including a treatment of cetane number also. It is possible to connect C_N and O_N from the recently published ignition data of FRANK and BLACKHAM⁸⁶ since correlations exist between their measured spontaneous ignition temperatures and both cetane and octane ratings.

5. GAS TURBINE

The possible significance of spontaneous ignition as a factor controlling the performance of a gas turbine was first discussed in 1945 by LLOYD¹⁷⁸. In the typical gas turbine combustion chamber, combustion is initiated

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by means of a spark in a turbulent primary zone into which a portion of the total inlet air is admitted, and is continued in a secondary zone after injection of most of the remaining air. The stability and completeness of combustion are determined by these primary (piloting) and secondary reaction zones. In the piloting zone there is a recirculation of hot gases, which, mixing with the entering air and fuel spray, continuously rekindle the flame; this ignition may be true spontaneous ignition or inflammation in the sense defined by EGERTON and MOORE⁷⁶ and referred to earlier in this chapter, and is very rapid, the reaction time available being a few milliseconds only. In the secondary zone all the combustible material from the primary zone—and this includes unburned fuel and intermediate combustion products—has to be burned completely if 100 per cent combustion efficiency is to be achieved. Here again there occurs a spontaneous ignition process complicated by the presence of flame; the gas transit time through this zone in aircraft gas turbines is of the order of 10 msec. The basic characteristics of the combustion process in gas turbines may be listed as follows: continuous, near atmospheric pressure level; heterogeneous mixture; short reaction time and complications associated with the omnipresence of flame in some regions of the combustion system.

The only relevant ignition temperature measurements are those reported by LLOYD^{176, 177} and by MULLINS²⁰⁸⁻²¹⁵, since only these were made at short delay times, low pressures and under continuous flow conditions. The data cited by HOWES and RAMPTON¹²⁴, for example, in a paper dealing with the properties of gas turbine fuels, are quite inapplicable for many reasons, two of which are that oxygen was the oxidant and delay times were in the range 3000 to 23,000 msec.

The fact that Mullins' data was obtained with vitiated air, i.e. air which had been heated by the combustion of some kerosine in it, is especially appropriate from the point of view of gas turbine applications as may be judged from the following considerations: flame is omnipresent in the reversal region of a primary zone and hence some stationary concentration of reaction products must exist there together with an atmosphere deficient in oxygen; the secondary zone lies in the wake of the primary zone and hence part of the air entering the secondary zone must be heavily vitiated; gas turbine systems employing reheat (fuel injection after the turbine) possess an ignition zone into which only vitiated air is fed; the later combustion zones of any continuous flow gas turbine combustion system employing fuel injection at several successive axial planes are fed with vitiated air; finally, many gas turbine combustion systems that are planned or are in operation (see, for example, BUCHER²⁷ and CROWE⁴⁶) employ deliberate recirculation of a portion of the exhaust gas into the combustion chamber primary or secondary zones producing conditions there that are even more heavily vitiated than usual.

6. ROCKET MOTOR AND PULSE-JET

Ignition delay in rocket motors may result in ultimate violent ignition followed by undesirable explosion of the fuels used. KISTIAKOWSKY¹⁸⁶ has patented a method by which these troubles may be avoided in the case of gasoline-fuming nitric acid mixtures in rocket motors. BROATCH²⁴ has described an apparatus for measuring the ignition delay of two components (fuel and oxidizer) in which the two liquids are projected horizontally through glass capillaries so that they impinge. A new method of studying the ignition of bipropellant mixtures was reported last year by GREGORY and CALCOTE¹⁰⁷ who allowed a single droplet of one reactant to fall through a known length of the gaseous phase of the other reactant with provision for observing the time of fall before ignition, determined by two photocells.

Little is known about the combustion mechanism of the pulse-jet and so it is not known in particular to what extent the process is governed by or affected by the spontaneous ignition delay times and temperatures of the fuels used. Recently however some evidence has come to light, which should as yet only be regarded as circumstantial, that the pulse-jet combustion performance may be appreciably governed by the spontaneous ignition characteristics of the fuel. The evidence takes the form of a reasonably good correlation between the O.N.E.R.A. pulse-jet performance index for various fuels and the corresponding global activation energies of reaction calculated by Mullins from spontaneous ignition tests by the N.G.T.E. method²⁰⁷. These findings have been recently published (BARRÈRE¹² and BARRÈRE, RAPPENAU and MOUTET¹³).

CONCLUSIONS

THE spontaneous ignition of combustible mixtures has formed the study of much research work since the beginning of the present century and most of the experiments have aimed at determining ignition temperatures. Although the concept of the ignition delay has been clearly recognized for nearly fifty years, many of the experiments have been conducted without special regard to this variable; had ignition delay been measured or controlled in these cases, the value of the experimental work would have been much greater.

Because of its intimate dependence upon delay time as well as many other factors such as pressure, presence of surfaces and method of introduction of fuel into the measuring apparatus, the spontaneous ignition temperature of a combustible mixture is not an absolute property. If care be taken in considering the precise conditions for ignition provided by any given test method, the spontaneous ignition data available can be very valuable especially when it is important to know the *relative* ignitabilities of different fuels under various conditions. Spontaneous ignition temperatures themselves are useful if interpreted carefully in this way—and to assist this interpretation the numerous test methods have been described in some detail in this AGARDograph—although ignition temperature *v.* delay curves are superior and should be consulted for preference when they exist.

The role of spontaneous ignition in spark-ignition and compression-ignition engines has been very fully studied and is, in consequence, better understood than the part that spontaneous ignition plays in gas turbines, rocket motors and pulse-jets. These questions are being tackled and must be regarded as worthy of investigation, for a detailed understanding of the mechanism of combustion in any prime mover must result in a more rational and, therefore, a better understanding of its design problems.

There are still several notable gaps in our fundamental knowledge of the spontaneous ignition *behaviour* of fuels some of which have recently been thrown into relief by a consideration of the combustion processes in the newer prime movers. Knowledge of the effects of fuel concentration and extremes of pressure (down to 0.1 and up to 20 atm.) upon the ignition delay *v.* temperature curves of combustible mixtures and the effect of high temperatures (over 1000° C) upon the ignition delays of homogeneous and heterogeneous combustible mixtures are some of these.

CONCLUSIONS

Finally, it is clear that all theoretical attempts to describe the diverse spontaneous ignition phenomena exhibited by different fuels in different atmospheres (oxidizers) are, at best, qualitative in form. Detailed attempts to describe the rate processes occurring during induction periods have been frustrated by the extreme complexity of the chemical reactions involved and the lack of knowledge of them. It is true to say that only one combustion reaction is well understood from the chemical standpoint, the hydrogen-oxygen reaction, but even in this case many minor features of the reaction scheme are still in doubt. Physical-chemical knowledge of the *mechanism* of spontaneous ignition is thus still well short of enabling ignition temperatures and delays to be calculated *ab initio*, and investigation in this field is truly of a long-term nature.

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