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A THESIS

entitled

THE SPARK IGNITION OF SOME
HYDROCARBONS IN AIR

by

JOHN THOMAS HEDGER

Submitted for the
Degree of Doctor of Philosophy
at
The City University

ABSTRACT

A systematic study of the variation of the minimum energy for ignition of n-decane/air and 2,2,5-trimethyl-hexane/air mixtures, by single electrical capacitor discharges, has been made. In addition the lower limits of flammability of selected hydrocarbons have been determined, both individually and admixed, under conditions of limiting ignition energy. The lower limits of flammability determined for single and multi-component fuels has been related to the more commonly determined flash point.

An introduction (Section 1) describes the hazards associated with hydrocarbon fuels, the common methods of hazard detection and prevention and the classical theories of the ignition process. Expressions relating the flammable properties of fuels to their physical properties and the effects of physical conditions on the ignition of a flammable mixture are discussed in detail.

The experimental apparatus and procedures are described in detail (Section 2). For flammability determinations the apparatus consisted essentially of a combustion tube 120 cm., long and 5 cm., in diameter. Detection of the passage of a flame was by thermocouples.

The results obtained are presented and discussed in Section 3. It is shown that the energy required for ignition rises very rapidly as the lower limit of flammability is approached. It is also shown that under conditions of limiting ignition energy (i.e. ca. 2 J) one observes some degree of

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dependency of the lower limit of flammability with molecular structure. This is qualitatively correlated with the spontaneous ignition temperature and octane numbers of the fuels chosen and is quantitatively related to an alkylperoxy mechanism of oxidation.

From the lower limits of flammability of mixtures it is shown that, under the ignition conditions employed, all constituent fuels are consumed in the ignition process, i.e. Le Chatlier's rule for the lower limits of flammability of multi-component fuels is shown to apply to the mixtures investigated.

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My thanks go to [REDACTED] [REDACTED] and [REDACTED] [REDACTED] for their guidance and interest and to [REDACTED] [REDACTED] [REDACTED] for his assistance. Thanks are also due to my colleagues for their help and forbearance and particularly to my wife for her infinite patience.

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The dependance of the Industrial World upon crude oil was recently high-lighted by the energy crisis. The enormous monetary problems involved in securing future supplies of this raw material provide a yardstick by which the importance of oil may be measured. In the development of North Sea Oil the United Kingdom is committed to an investment of over £1800 million in an attempt to become a self-sufficient oil producing nation.

The consumption of oil on such a massive scale as both a fuel and as feedstock for the petro-chemical industry has resulted in the storage and transportation of highly flammable materials on an unprecedented scale. It has recently been reported that the U.K.'s strategic reserves of petroleum based fuel total 24.7 million tons. The hazards associated with such an undertaking is principally that of accidental release of a flammable vapour, admixture with air and subsequent ignition.

There are many well documented case histories¹ of such catastrophies involving such substances as liquified petroleum gas (L.P.G.), liquified butane and liquified natural gas. In the event of a tank rupture these highly volatile fuels may form vapour clouds several feet deep and covering thousands of square yards. It is perhaps ironic that normal safety precautions e.g. no naked flames, no smoking etc., may in fact allow such flammable gas clouds to achieve much greater proportions than would otherwise have occurred.

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In the actual use of a fuel or flammable solvent the hazard involved may be on a smaller scale than that illustrated above. For example, fuel spillage in an engine room, fuel build-up in an unignited boiler or residual fuel in a fuel tank. Such hazards have the common denominator of being confined and as such provide the possibility of rupturing or fragmenting their container in the event of an explosion. There is also the possibility of the container being above ambient temperatures or containing hot pipes or machinery, all of which may render a normally 'safe' fuel unsafe, due to the increase in vapour pressure creating an ignitable fuel/air mixture.

In an attempt to remove the hazards associated with any fuel there are several fundamental questions which must be answered:

- What are the flammable fuel/air compositions?
- What are the physical circumstances that may give rise to a flammable mixture?
- What are the possible sources of ignition?

The answers to these questions provide a qualitative guide to the type of hazard one is dealing with and suggest means of eliminating that hazard.

Since many questions of this type were first asked in the mining industry, it is perhaps not surprising to find that a great deal of work has been conducted by such institutions as the Safety in Mines Research Establishment in Sheffield and the Bureau of Mines in Pennsylvania. Much of the information obtained has been

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reviewed by several authors whose critical assessments of that information have allowed a more confident application of the results.

It is the purpose of this thesis to both extend the above information and to allow a more fundamental understanding of the physical and chemical parameters involved in characterising and assessing a potentially hazardous situation.

1.2 CLASSIFICATION OF HAZARDS

An awareness of the hazard associated with the handling and use of any flammable material is an obvious prerequisite of safety and a means of comparing the hazard of one compound to that of another would be an advantage.

Since no single parameter is sufficient to describe the hazard associated with each of the many situations in which they may be employed, it has become necessary to adopt several parameters as a means to this end. The most commonly employed parameters are the flash point, flammability limits and spontaneous ignition temperatures.

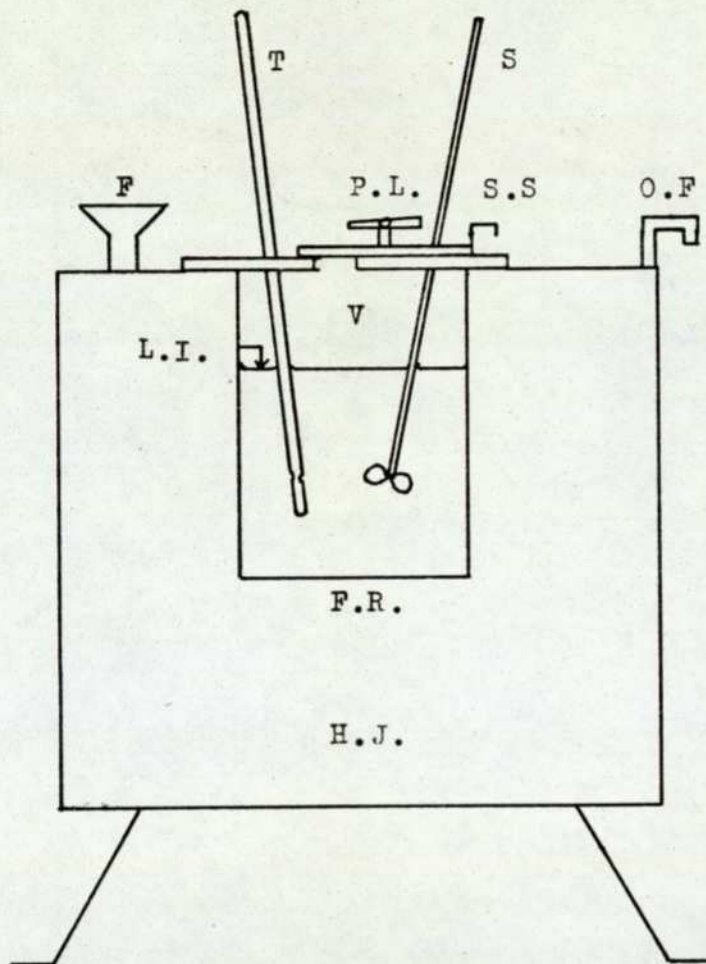
1.2.1 Flash Points

The flash point of a liquid is defined as the lowest temperature at which that liquid will produce sufficient vapour to form a flammable mixture with the air immediately above its surface.

There are several commercially available instruments with which the flash point may be determined; of these the 'Abel' and 'Pensky Martin' are the most widely used. These differ only in the range of temperatures over which they are designed to operate, the Abel being for flash points between -17.7°C and $+71^{\circ}\text{C}$ and the Pensky-Martin for flash points in the range 20°C to $>100^{\circ}\text{C}$.

The main features of these instruments are shown in Figure 1.1. Both are of the 'closed cup' type, in that the test liquid is contained in a vessel (F.R.) which has a removable but close fitting lid, into which a mechanical

Figure 1.1
Flash Point Apparatus



Key

H.J. - Heating Jacket	S - Stirrer
F.R. - Fuel Reservoir	T - Thermometer
L.I. - Level Indicator	P.L.- Pilot Light
V. - Vapour Space	S.S.- Sliding Shutter
F. - Funnel	
O.F. - Over Flow	

shutter (S.S) is incorporated. The instrument is so engineered that opening the shutter allows a small flame (P.L) to be inserted into the air space (V) above the liquid. The fuel vessel is surrounded by a metal jacket, the annular space((H.J) of which may be filled with either a 'dry ice'/ glycerol mixture, air or water depending upon the value of the flash point being obtained. A small stirrer (S) is located in the test liquid to ensure an even temperature distribution and a thermometer (T) records the actual temperature. Heat is supplied indirectly by a small bunsen burner placed beneath the annular space.

The temperature of the test liquid is allowed to rise at a specified rate and the flame is introduced into the liquid vessel at specific intervals of temperature increase.

The exact description and standard mode of operating the various instruments is laid down by the Institute of
¹⁰
 Petroleum.

From the above description and the definition of flash point, one can appreciate that this procedure is limited to materials which are liquids at normal temperatures and pressures. Further, the flash point is a function of the vapour pressure of the liquid and if its vapour pressure/temperature relationship is known (viz. the Antoine equation) the fuel concentration at the flash point may be calculated. The calculated value will, in fact, be slightly high, since the above procedure is dynamic and, hence, the

liquid and its vapour will not be in equilibrium.

The virtue of the flash point for hazard classification is that for a particular instrument consistent results may readily be obtained and the value determined is sensitive to volatile flammable impurities in the bulk liquid. Consequently, flash points are widely used as a standard by which handling and storage precautions are taken for bulk liquids and as a rapid check on quality.

The disadvantages of flash point datum is that:

- It provides no information on the extent of the flammable range,

- It is only applicable to liquids,

- Instruments of different design do not provide comparable results, as shown in Table 1.1.^{11,12}

Considerably more information may be obtained by a study of the limits of flammability.

1.2.2 Limits of Flammability

The limits of flammability of gaseous fuel in air are the highest and lowest concentrations of that fuel which will support combustion in air. These are known respectively as the upper and lower limits of flammability and the intervening range of fuel/air concentrations is termed the flammable range.

This definition is illustrated by the following examples, determined at 20°C and 1 atmosphere pressure.

Table 1.1

Fuel	Method of Determination		
	Abel [*] (°F)	Pensky Martin [*] (°F)	Cleveland Open Cup (°F)
White Spirit	94	105	115
Kerosine	127	135	140
Gas Oil	—	195	200
Lubricating Oil	—	400	402

*Closed cup methods.

Table 1.2

Fuel	Lower Limit of Flammability (%v/v)	Upper Limit of Flammability (%v/v)
methane	5.3	14
hydrogen	4.0	75
n-pentane	1.5	7.8

The above limits of flammability were determined in 'standard' apparatus which consists of a 5 cm. diameter glass tube, 120 cm. long open at the lower end. The mixture under test is ignited by a small flame or an electric spark at the lower end so that upward propagation of flame results. This apparatus evolved from early work in the field of flammability limits,¹⁴⁻¹⁷ and yields results which correspond closely to those found in practical situations.

It is, in any event normal practice to allow a safety factor of 2:1 in industries where a flammable gas hazard exists. For example, in the coal mining industry men are withdrawn from the coal face if the methane concentration rises above 2.5% v/v, whilst the lower limit is 5% v/v. Such safety factors are necessary as the limits of flammability determined in the laboratory, are not a fundamental property of the gaseous mixture but are dependant upon a number of physical factors which are described in detail in Section 1.4.5.

Of all the factors which affect flammability limits, temperature is the most interesting from the present point of view. At normal ambient temperatures some liquid fuels will not have a sufficiently high vapour pressure to produce a flammable mixture, but raising the temperature will ultimately allow the required vapour pressure to be achieved. This is obviously an alternative description of the flash point.

If one now considers the effect of temperature upon the flammable range of a particular fuel one would observe, up to a temperature of ca. 100°C , a gradual widening of the flammable range. If the temperature is increased further, there are indications that this range widens more dramatically^{18,19} due to the upper limit being raised, while the lower limit remains relatively constant.

If the temperature is raised sufficiently, however, ignition may occur spontaneously. The lowest temperature at which spontaneous ignition occurs is the basis of the method of hazard classification known as the spontaneous ignition temperatures (S.I.T.).

1.2.3 Spontaneous Ignition Temperature.

The spontaneous ignition temperature is the lowest temperature to which a volume of combustible gas must be heated to cause ignition without the need for any other external source of energy, such as a flame or an electric spark.

This particular property has been determined by
many authors²⁰ for a wide range of fuels in many different
types of apparatus. This work has shown that the lowest
values for spontaneous ignition temperatures are obtained in
large spherical vessels. The spontaneous ignition temperature
is very dependant upon the physical size, shape and material
of the reactor in which the experiments are performed.

One is primarily concerned with spontaneous
ignition temperatures in those situations where accidental
over-heating of a combustable gas mixture can occur, for
example, in engine crank cases and gear boxes, engine rooms
and fuel storage depots where handling machinery exists.
The range of fuel concentrations over which spontaneous
ignition can occur is typically from a few per-cent to
over 90% v/v.¹⁸

1.3 METHODS OF DETECTION OF HAZARDOUS ATMOSPHERES.

Whilst the use of flash points, flammability limits and spontaneous ignition temperatures enable one to define the conditions under which a flammable mixture can be formed and ignition of that mixture can occur, one also requires to know when a critical situation is arising. For example, if a leakage of fuel developed in an engine room a means of detecting the increased fuel vapour concentration in the air would serve both to indicate that the leak existed and the extent of the hazard produced i.e. whether the lower limit of flammability had been exceeded.

Indication of a possible hazard can be obtained by a variety of methods, from simple temperature measurement, for example, placing thermocouples in mechanical bearings, to taking air samples and analysing them chromatographically.

A very common and relatively inexpensive method of flammable gas detection for concentrations up to the lower limit of flammability is by the so-called pellistor. This device consists of a bead of catalyst coated, refractory material supported upon a platinum coil. The flammable gas is oxidised on the catalyst surface and the heat of reaction causes the bead temperature to rise, thus changing the resistance of the platinum wire. This change in resistance is proportional to the gas concentration and may be displayed on a meter. Such devices first found application in the mining industry and have more recently found extensive application in detecting dangerous concentrations of natural gas in building basements. This latter situation has arisen

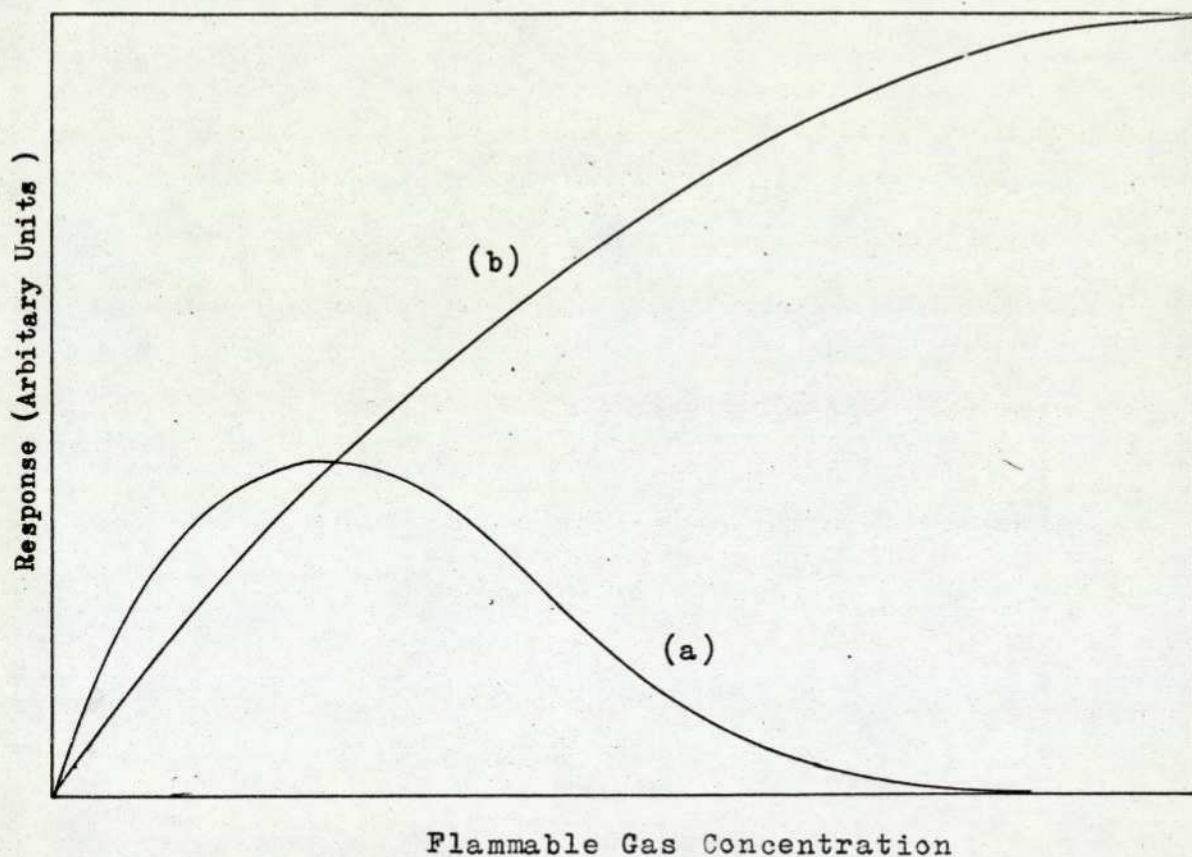
because of the nature of gas-main pipe jointing methods, which were satisfactory for town gas but allow considerable leakage of natural gas. Several explosions have occurred due to such leakages, notably those at the telephone exchanges in Glasgow in 1973.

The main advantages of the pellistor device are that it can detect a wide range of flammable gases and operates in a diffusion mode, thereby simplifying the mechanical construction compared with alternatives such as thermal conductivity devices. The use of thermal conductivity devices is in fact usually restricted to the detection of hydrogen and methane in low cost instruments. Other gases can of course be detected by this technique, but the instrument costs rise dramatically.

Thermal conductivity devices consist of a heated platinum wire which is enclosed in a chamber and surrounded by air. If the air is admixed with a flammable vapour the rate at which heat will be lost from the wire will depend upon the thermal conductivity of the resultant gaseous mixture and hence the change in resistance of the platinum can be directly related to the vapour concentration. Such devices operate on a purging/measuring cycle and are therefore slow. They do, however, have the advantage over the catalytic bead technique that they give an unambiguous signal over the entire 0-100% v/v fuel concentration range, whereas the bead gives an increasing signal up to the stoichiometric ratio and thereafter a decreasing signal. Typical response curves are given in Figure 1.2.

Figure 1.2

Typical Response Curves for the Pellistor and
Thermal Conductivity Chamber.



Legend:

- (a) Response curve for a pellistor
- (b) Response curve for the thermal conductivity chamber.

The above methods of flammable gas detection are usually calibrated in terms of 0-100% of the lower explosive limit i.e. up to the lower limit concentration, and have resolutions of typically $\pm 5\%$ f.s.d. Detection of gases in low concentrations e.g. up to 1000 p.p.m., requires more sophisticated instrumentation and is catered for by the flame ionisation detector and non-dispersive infra-red (N.D.I.R.) techniques. More recently materials which exhibit semi-conductor properties when exposed to low concentrations of gases have been discovered. The most commonly used material is stannic oxide heated to 300-600°C, at which temperature the electrical resistance of the oxide is reduced by ca. 50% when exposed to 100 p.p.m. methane in air.

The mechanism by which this process occurs is little understood, but is believed to be similar to that involved for electrical semi-conductors, in that a gas molecule absorbed on to the oxide surface will either liberate or absorb an electron which will stimulate a small current and, hence, reduce the oxide resistance at a constant potential. ²¹ Whatever the mechanism the responses so far achieved are comparable to the F.I.D. and do not suffer the necessity of a hydrogen supply.

The usefulness of the detector is, however, limited by its non-linear response but may find extensive application as a detector of small fuel leaks from pipe-lines and container vessels.

1.4 IGNITION

A gaseous mixture of a fuel and air may ignite either spontaneously if all, or part, of the mixture is raised to a sufficiently high temperature, or if it is brought into contact with a source of ignition, i.e. a spark or flame. There are, however, several differences between these modes of ignition. Thus, the range of composition which will ignite spontaneously is much wider than that for ignition by an external source.¹⁸

The temperature at which spontaneous ignition of a hydrocarbon/air mixture will occur is typically above 200°C whereas induced ignition is limited only by the vapour pressure of the particular fuel in that it must be sufficient to produce a flammable mixture with air.

In general terms, however, one may regard each mode of ignition as a different manifestation of the same phenomena over a wide spectrum of temperatures. Spontaneous ignition, for example, does not occur uniformly throughout a reaction vessel, unless the vessel is very small. Due to convection and conduction of the heat of reaction, temperature gradients are established and ignition usually occurs at a hot spot in the vessel and spreads as a wave reaction throughout the mixture.¹³

In a similar way a spark will heat a small volume of gas (ca. 0.04 c.c.) to a very high temperature (ca. 10,000°K) for a short period of time (ca. 10^{-8} sec.) and generate a combustion wave which will propagate through the mixture if the composition is within the flammable range.

A further point to consider is that spontaneous ignition will only occur after a period of time termed the ignition delay (or induction period) which may be as short as a second or may last many minutes; ignition by a spark also suffers a delay in that the combustion wave does not appear until several milli-seconds² after the passage of the spark. The inference from this is that although one is allowing two different time and temperature scales the essential phenomena is the same viz. the reaction of a small volume of gas to produce a self-sustaining combustion wave.

One may further draw a comparison between these two means of ignition in that the spontaneous ignition temperature constitutes a limiting condition and, similarly, an electrical discharge must be a certain minimum energy to be effective and also constitutes a limiting condition. In contrast to this ignition by a small flame is the result of a high temperature ca. $2,000^{\circ}\text{K}$, and comparatively long time ca. 1 sec., and, hence, provides an excess of energy for ignition and is not a limiting condition.

A consequence of this view is that phenomena observed during ignition by the passage of a spark may be explained by the general theories of ignition as derived from spontaneous ignition studies. The theories are summarised below and, as is conventional, a distinction is drawn between a thermal theory and a chain-radical theory. This distinction is purely for convenience and in practice the actual mechanism of the reaction will probably involve radical species, the actual identity of which will depend upon the temperature. The essence of a unified chain-thermal theory is given at the end.

1.4.1 Thermal Theory of Ignition

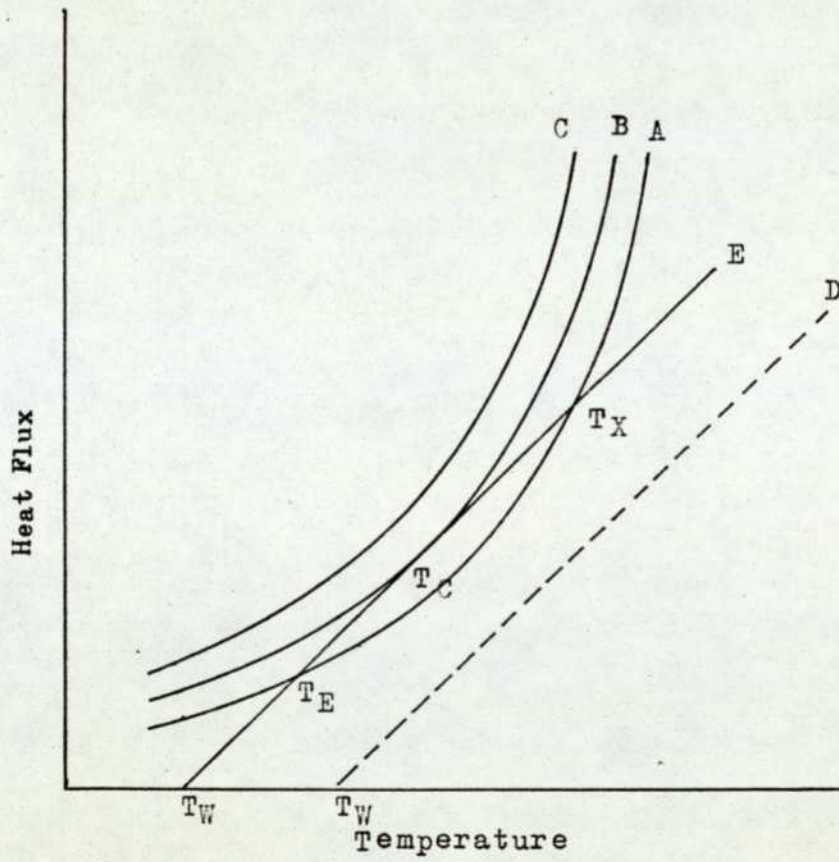
The prime requisite for the ignition of any fuel is that it should undergo an exothermic reaction on oxidation. If one, therefore, considers a gaseous mixture of a fuel and an oxidant at a temperature T_F , enclosed in a vessel of temperature T_W , then oxidation of the fuel will result in the release of heat which will be conducted to the walls of the vessel and will subsequently be lost to the surroundings.

If the rate of heat release by the reacting mixture is equal to the rate of heat loss at the walls of the vessel, the temperature of the gas, T_F , and the rate of chemical reaction will remain constant, i.e. an equilibrium state will be achieved. However, since the rate of reaction increases exponentially with temperature if the heat release exceeds the heat loss, T_F will increase and lead to a subsequent increase in the rate of reaction in the body of the gas and may result in an explosion. Furthermore, since the rate of heat loss from the vessel walls is a linear function of temperature and the rate of reaction an exponential function of temperature, the conditions for ignition may be expressed graphically as shown in Figure 1.3.

The line E represents the rate of heat lost by a vessel as the temperature increases, while the curves A, B and C represent the rate of heat release by the reaction. If the initial conditions are such that the vessel wall is at T_W and the gas mixture is represented by the extreme left hand side of curve A, then the gas is releasing heat

Figure 1.3

Heat Balance for an Exothermic Reaction in a
Spherical Vessel.



faster than the vessel is losing heat and, hence, the vessel and gas temperatures will rise until the temperature given as T_E is achieved and the rates of heat release and heat loss are equal. The system will then maintain equilibrium at that temperature. Had the initial condition of the gas been defined by points on curves A and E between T_E and T_X then the vessel would have lost heat faster than the reaction could have supplied it and the temperature of the system would have fallen, again to T_E . An initial condition described by any point on curves A or E above T_X would indicate that heat is being supplied by the chemical reaction faster than it is lost by the vessel and the reaction would autoaccelerate giving an explosion. Referring to curve C one observes that any initial condition described by any point on curve C gives a spontaneously ignitable mixture, because for all gas mixtures on this curve the heat release is in excess of the heat lost by the vessel. Curve B represents a critical condition in that curve B is tangential to E and it is the temperature T_C that represents a minimum temperature for spontaneous ignition.

This latter critical condition has been the basis of attempts to characterise different fuels with respect to the fire hazard they present, on the basis of the value of T_C , referred to as the spontaneous ignition temperature (S.I.T.) or the self-ignition temperature. This particular criterion is not used extensively, since it is not an intensive property of the fuel. This is easily illustrated if one considers that the position of curves of the type A, B and C

is a function of pressure, volume and fuel concentration each of which alter the rate of heat transfer from the gas to the vessel walls. Similarly, any alteration in the size, shape, material or environment of the vessel will change the position of the curve E, for example, to position D.

This qualitative description of a thermal theory²² of ignition has been developed by Semenov²³⁻²⁶ and Frank-Kamenetsky into a series of quantitative equations for a variety of combustion vessel shapes. However, since these equations apply specifically to ignition at constant volume, and where any rise in temperature is the result of chemical reaction, they will not be further discussed since these conditions do not exist in the current experiments.

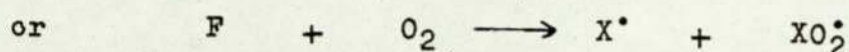
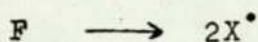
1.4.2 Radical Theory of Ignition.

This theory postulates a radical chain mechanism for spontaneous ignition. The critical condition between slow combustion and ignition is a function of the relative importance of the chain branching step in the chain reaction. The major types of reaction forming the overall chain reaction are illustrated below for a general case.

Initiation Reaction

In the absence of any chemical initiation such as peroxides or azo-compounds, free radicals may be produced by the reaction of a fuel molecule with oxygen or by the spontaneous decomposition of the parent fuel molecule. This

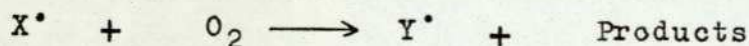
may be expressed as:



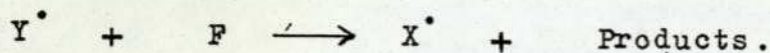
where F is the parent compound and $X^{\bullet}$ is any radical species. Such reactions are highly endothermic with an activation energy of $50-100^{\circ}\text{Kcal.mole}^{-1}$ and, hence, the rate of reaction will be slow below 400°C .

Propagation Reactions

The radical chain is propagated by a radical species reacting with a parent molecule e.g. oxygen, to furnish a second radical:

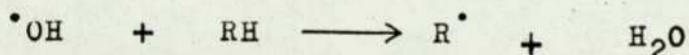
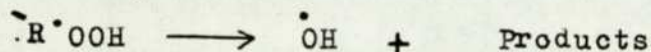
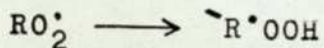
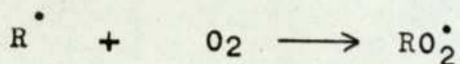


$X^{\bullet}$ and $Y^{\bullet}$ are usually different species and $X^{\bullet}$ is usually regenerated by the reaction of $Y^{\bullet}$ with a fuel molecule:



These reactions have activation energies typically of $0-20^{\circ}\text{Kcal.mole}^{-1}$ and are consequently fast even at temperatures below 300°C .

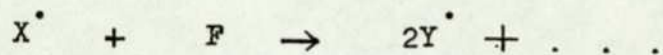
An example of a typical propagation scheme is given by the hydroperoxy mechanism for alkane oxidation: 27



In this scheme the $R^{\bullet}$ radical is regenerated via an hydroxyl radical.

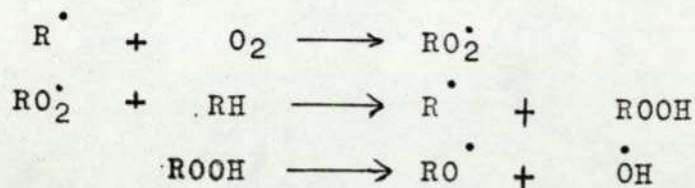
Branching Reaction

The branching reaction is a special case of the propagation reaction in which a radical reacts with a parent molecule to yield two or more radical species:



Since this reaction increases the number of chain carriers, it does not have to occur frequently to significantly affect the overall rate of reaction. Such reactions typically have activation energies of 30-40 kcal.mole⁻¹.

The above reaction is termed a linear branching reaction, but other forms of branching occur, of which the most important is degenerate branching. This occurs when a stable intermediate formed in the propagation reaction either decomposes or reacts with a free radical to provide more than one free radical as products. For example, if one refers to the oxidation of an alkane, the following scheme would be an example of degenerate chain branching:²⁷



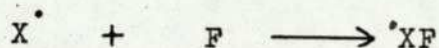
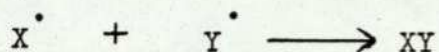
If, however, the radical concentration had increased without going via the stable hydro-peroxy intermediate then the branching would have been described as linear.

Termination Reactions

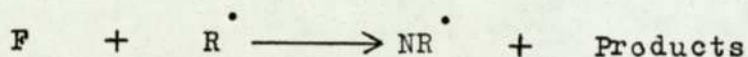
Free radicals are removed from the reaction by reacting with a second radical or a molecular species, the latter yielding a less reactive radical incapable of

propagating the chain. For small radicals the former requires a 'third body' to be present to remove the energy released by the reaction. For larger radical species the molecule formed may be able to stabilise itself by the redistribution of energy throughout its many bonds and subsequently lose energy by normal molecular collisions. Termination can also occur at the walls of the reaction vessel, the efficiency of the process depending upon the surface material and the reactants pressure. For example, at low pressures the number of molecular collisions a molecule will suffer prior to reaching the vessel wall will be less than at higher pressures, consequently, high energy molecules will lose their excess energy via molecular collisions as the pressure increases and, hence, the effect of the surface on termination will decrease in importance.

Termination reactions may be summarised as:



In the explosive region (i.e. above the S.I.T.) of a particular system the above series of reactions may be generally summarised as:



where $R^{\cdot}$ refers to any free radical and N is called the multiplication factor and takes the following values for each type of reaction in the overall chain reaction:

N	$>$	1	chain branching
N	$=$	1	chain propagation
N	$=$	0	chain termination.

Hence, we may define a term ϕ_g , called the branching factor, by the following equation:

$$\phi_g = \frac{(N - 1)}{\bar{t}_r} \quad (1)$$

where ϕ_g = the branching factor in the gas phase.

$\bar{t}_r$ = the mean lifetime of the active centres.

Since radicals will also be removed at the walls of the vessel, a net branching factor will be given by:

$$\phi = \phi_g - \phi_w \quad (2)$$

where ϕ_w = the rate of loss of radicals by wall termination.

The rate of increase of the radical concentration, n , will be given by:

$$\frac{dn}{dt} = n_0 + \phi n \quad (3)$$

where n_0 = the rate of initiation of free radicals in unit volume per unit time.

Integration of this expression yields:

$$n = \frac{n_0}{\phi} (e^{\phi t} - 1) \quad (4)$$

if $n = 0$ at $t = 0$ and if ϕ is independent of time. This equation indicates an exponential increase in the radical concentration with time in the explosive region.

In the explosive region, $\bar{t}_r$ will be very small, therefore, as can be seen from equation (1), $(N - 1)$ needs only to be slightly positive to give a high value of ϕ_g .

ϕ will also be large, since ϕ_w will be lower than ϕ_g in the explosive region, since the mean time a molecule will take to diffuse to the walls will be long compared to $\bar{t}_r$. In the slow combustion region, i.e. below the S.I.T., a steady state will occur, i.e. $dn/dt = 0$.

An expression for the limiting condition between slow combustion and an explosion may be obtained from the rate expression for each of the above reactions:

Initiation: $\frac{d[X^\cdot]}{dt} = I_0$ i.e. rate of initiation

(N.B. $I_0 \neq n_0$ due to the temperature difference):

Propagation:

$$\frac{d[P]}{dt} = f_p [X^\cdot]$$

Branching:

$$\frac{d[X^\cdot]}{dt} = f_b (N - 1) [X^\cdot]$$

Termination:

$$\frac{-d[X^\cdot]}{dt} = f_g [X^\cdot] \quad - \text{ gas phase}$$

$$\frac{-d[X^\cdot]}{dt} = f_w [X^\cdot] \quad - \text{ vessel wall}$$

where f_b , f_p , f_g and f_w contain the respective kinetic rate constants and concentration terms. At the steady state all the $d[X^\cdot]/dt$ terms must sum to zero:

$$I_0 + f_b(N - 1) X^\cdot = (f_w + f_g)[X^\cdot]$$

therefore:
$$[X'] = \frac{I_0}{(f_w + f_g) - (N - 1)f_b}$$

Since:

$$\frac{d[P]}{dt} = f_p[X']$$

the overall reaction rate is given by:

$$\frac{d[P]}{dt} = \frac{f_p I_0}{(f_w + f_g) - (N - 1)f_b} \quad (5)$$

Hence, as long as $N < 1$ a steady state situation i.e. slow combustion will occur. The limit between slow combustion and an explosion will occur when the steady state equation breaks down i.e. when:

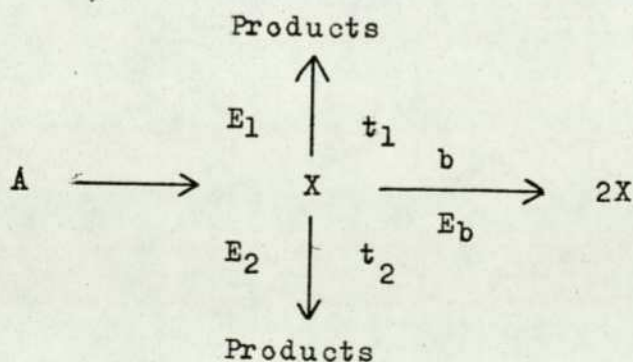
$$(N - 1)f_b = f_w + f_g$$

This will occur for flammable gas mixtures when a suitable ignition source is available. This equation does not allow any accurate prediction of ignition limits or flammability limits, since f_b , f_w and f_g will probably be complex functions of temperature and pressure, however, at low pressures f_w will predominate as the termination mechanism due to easier diffusion to the vessel walls. This may be the factor responsible for the convergence of the lower and upper limits of flammability at low pressures. (See Section 1.4.5.2). Upper and lower limits similarly will be respectively the enhanced effect of f_g at high fuel concentrations and the reduced effect of f_b at low fuel concentrations.

1.4.3 Unified Theory of Ignition.

If one considers the temperature/pressure ignition diagrams for the hydrocarbons one observes that (except for the simplest molecules) at reduced pressures and elevated temperatures the ignition boundary is not a smooth curve but contains an additional area outside the ignition boundary. A typical curve is shown in Figure 1.4. The additional area is caused by the phenomena known as the 'cool flame' in which a wave of low temperature combustion will pass through a reaction vessel whilst not consuming all the reactants. Within the cool flame area several regions are distinguished by the number of cool flames that will propagate under these exact conditions. Such behaviour is not predicted by either the thermal or radical chain theories of ignition but has been successfully explained by a unified theory of ignition^{28,29} as predicted by Gray and Yang.

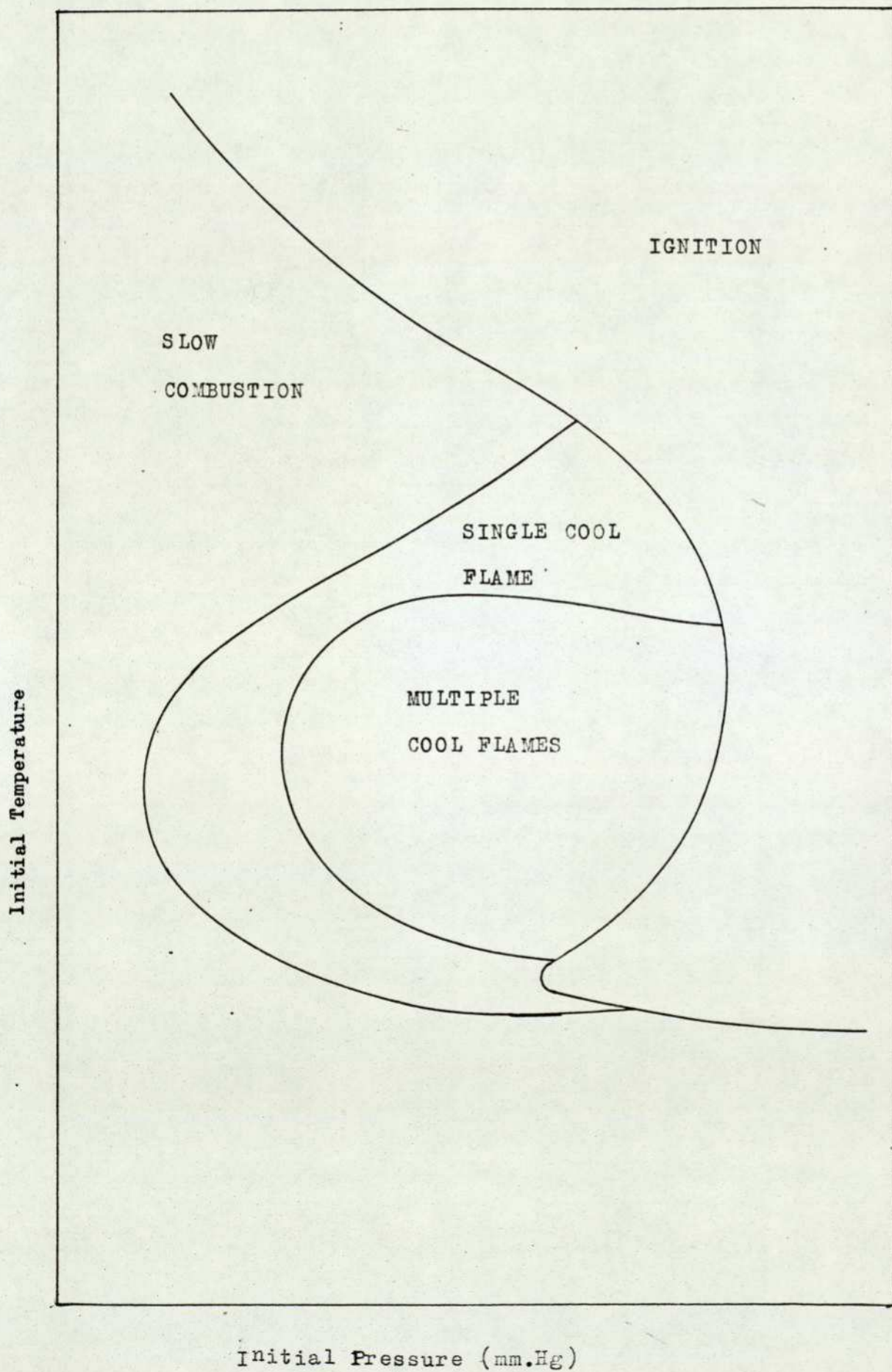
The basis of this theory is that a chain carrier, X, can undergo any one of the several possible radical reactions at different temperatures. This is shown schematically below:



If $E_1 < E_b < E_2$ and t refers to a termination reaction and b a branching reaction, then at low temperatures reaction t_1

Figure 1.4

Typical Ignition Diagram for a Hydrocarbon/Air Mixture.



will occur leading to slow combustion; at higher temperatures reaction b will occur leading to an explosion, but the increased rate of reaction caused by reaction b will raise the temperature and will allow reaction t_2 to occur which will deplete the concentration of X to a level where the rate of reaction b will be reduced, hence, the temperature will fall and slow combustion will again occur. Gray and Yang^{30, 31} have extended this theory to a general case of several chain carriers and have successfully predicted the multiple cool flame phenomena.

This theory has illustrated the profound effect of temperature upon the course of a reaction. It is indeed as a result of extensive studies of the occurrence and analysis of the products of cool flames that has led to the present understanding of the mechanism of hydrocarbon oxidation. This subject is discussed more fully in Section 3.

1.4.4 Induced Ignition

A fuel/air mixture at room temperature and one atmosphere pressure may only be ignited by an external source e.g. a flame or spark if the composition of the mixture is within the flammable range and the ignition source is of sufficient energy. Under such conditions slow combustion of the mixture is so slow as to be immeasurable and spontaneous ignition will never occur. One may assume, therefore, that an external ignition source must either raise an element of gas to a sufficiently high temperature or provide sufficient radical species to increase the rate of

reaction to the point where the reaction will auto-accelerate if a combustion wave is to be formed. It is, however, possible to render a mixture, which is within the flammable range, non-ignitable by, for example, reducing the energy of the ignition source or reducing the physical dimensions of the combustion chamber. The different phenomena that may be observed when physical parameters are varied should be carefully distinguished. If one considers the limits of flammability as those compositions outside of which no mixture may be ignited to produce a stable combustion wave, then any apparatus which will permit ignition to occur but will prevent a combustion wave from propagating will measure limits of propagation and not limits of flammability. Alternatively if the apparatus is such that ignition is prevented until (say) the ignition energy reaches some critical value, then one observes limits of ignitability. Both situations may be realised in practice and the factors which give rise to their occurrence are summarised in the following section.

1.4.5 Factors Affecting Limits of Flammability

1.4.5.1 Source of Ignition

The criteria for a source of ignition used in the determination of flammability data is that it should:

- (a) be of sufficient energy that all flammable mixtures under 'standard' conditions will be ignited,

- (b) not be so large as to cause appreciable heating or turbulence of the gas mixture,
- (c) be instantaneous.

The use of a small town gas or methane/air flame is common, but has the disadvantage that neither can be employed in situ, but have to be introduced to the gas mixture through some form of removable aperture.⁸ This is undesirable due to the ingress of air and limits the temperature range over which the apparatus can be employed, (cf. flash point apparatus).

The lack of any control over the energy imparted by a flame to the gas mixture is also a hindrance, since it is often desirable to regulate this parameter. Large flames are obviously to be avoided as they will not satisfy condition (b) above.

The most easily controlled source of ignition is the electrical capacitor discharge across a pair of electrodes. The energy released is a simple function of the value of the capacitor and the voltage to which it is raised and is given by the relationship:²

$$E = CV^2/2$$

where E = energy in joules,
 C = capacitance in farads,
 and V = voltage.

The discharge may be employed in-situ and may be regarded as instantaneous, since its duration will only be of the order of 10^{-8} - 10^{-7} secs. This time interval has been

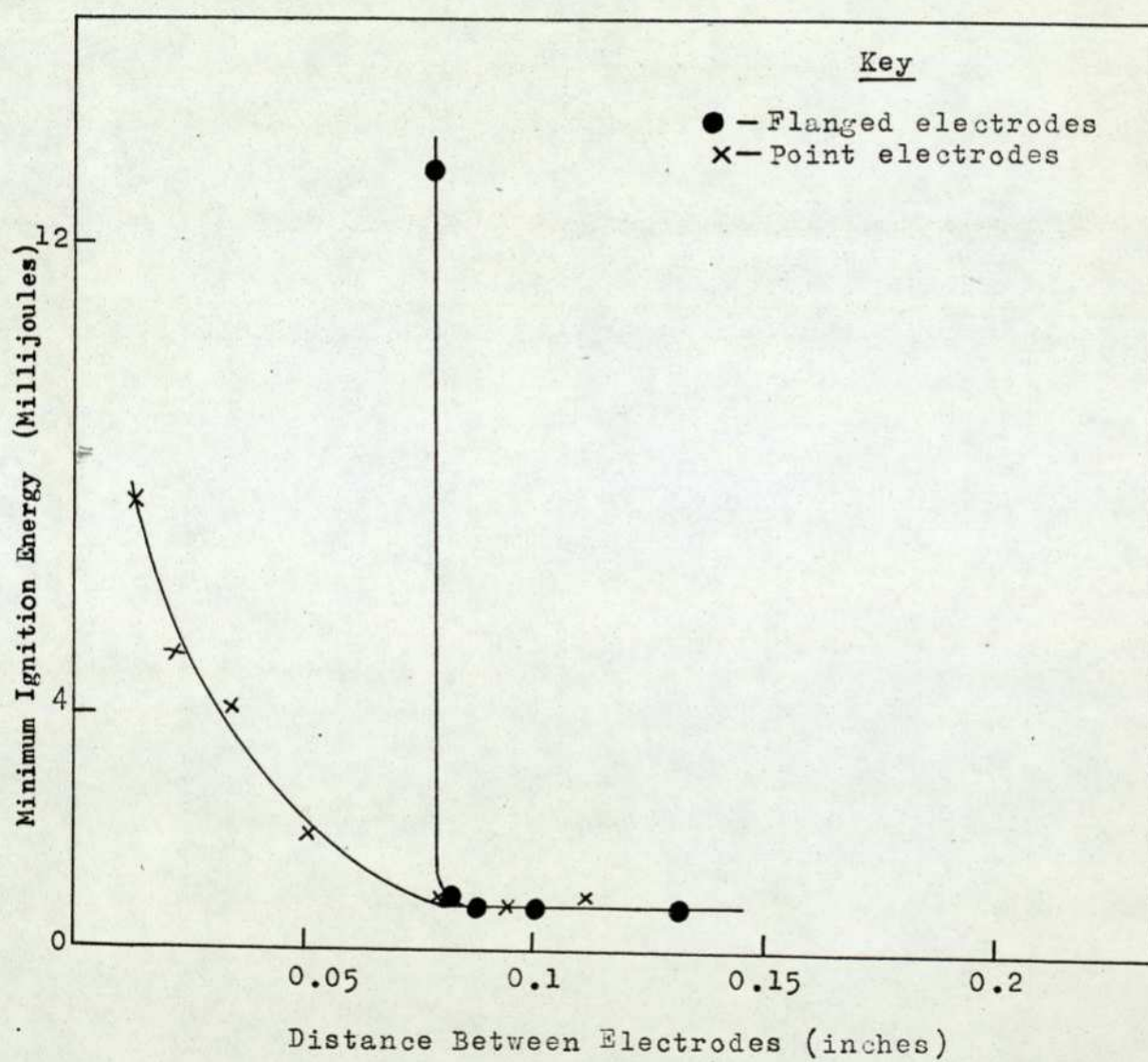
shown to be orders of magnitude shorter than the time taken for the development of the combustion wave,⁸¹ hence, if one determines the smallest spark capable of causing ignition of a mixture, the energy imparted to the mixture must be the minimum energy that can ignite that mixture. This conclusion has been deduced from work conducted on solid explosives and flammable gas mixtures where the energy required for ignition has been introduced at varying, controlled rates.^{32,33} This work has been reviewed by Lewis and von Elbe² along with their own and other's work on the spark ignition of flammable gas mixtures. The essential conclusions of the various experiments are that below a certain electrode separation, termed the quenching distance, the electrodes will cause the ignition energy of a mixture to rise.

Typical curves of electrode separation versus ignition energy for different electrode geometries are reproduced in Figure 1.5.

For the n-alkanes a plot of ignition energy versus fuel/air stoichiometric ratio for each member exhibits a minimum value (Figure 1.6).³⁴ For methane this minimum exists slightly below the stoichiometric ratio whilst for higher alkanes it occurs above stoichiometric. This phenomena may be explained on the basis of the higher diffusivity of methane compared to air and the lower diffusivity of the higher alkanes. In the former situation, methane will diffuse towards the flame front rendering the gas mixture stoichiometric, whilst in the latter case air will diffuse towards the flame thus achieving

Figure 1.5

Variation of Minimum Ignition Energy with
Electrode Separation.



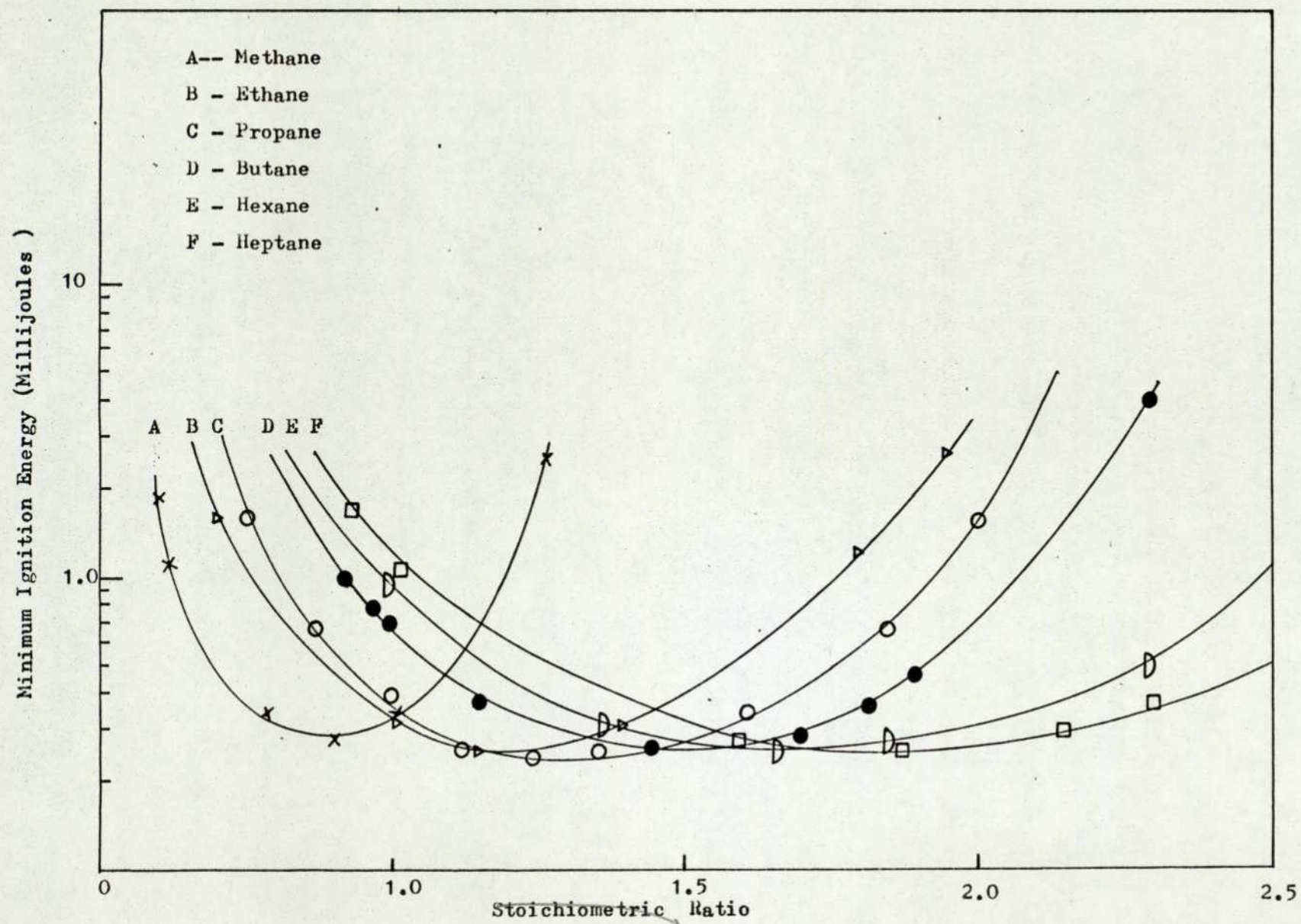


Figure 1.6
Variation of Minimum Ignition Energy with
Stoichiometry for some n-Alkanes

the same effect.

The actual value of the minimum ignition energy for the n-alkanes (up to n-heptane), in air remains remarkably similar at between 0.2×10^{-3} and 0.3×10^{-3} joules. For other fuels the above curves may be far more complicated^{35,36} showing several minima at different energy values.

For the n-alkanes the minimum ignition energy is found to decrease with increasing oxygen content reaching typical values of 0.002×10^{-3} joules in pure oxygen, and to increase at reduced pressure, (Figures 1.7 and 1.8).

Evidence as to the actual amount of energy imparted to a gas mixture from a spark is rather contradictory. The actual energy distribution within the discharge is not fully understood³⁶ and it has been shown that for large energy sparks some loss of energy occurs in the form of a shock wave.³⁷ The question of energy loss to the electrodes has also resulted in several contradictory results, the most recent of which states that the minimum energy required for ignition of a particular mixture depends upon the melting point of the electrode material.³⁶ The authors arrived at the conclusion that the function $\frac{1}{2}CV^2$ is an acceptable equation for the energy of a discharge, but that it is not equal to the energy required for ignition.

Other workers have usually been interested only in the limits of flammability and as such have used high energy sparks of tens or hundreds of joules.^{7,38} Although it is known that the energy for ignition increases as the limits of flammability are approached the rate of this rise is not known

Figure 1.7

Variation of Minimum Energy with Oxygen Partial Pressure
for Ethane, O₂ and N₂, at 1 Atmosphere Pressure

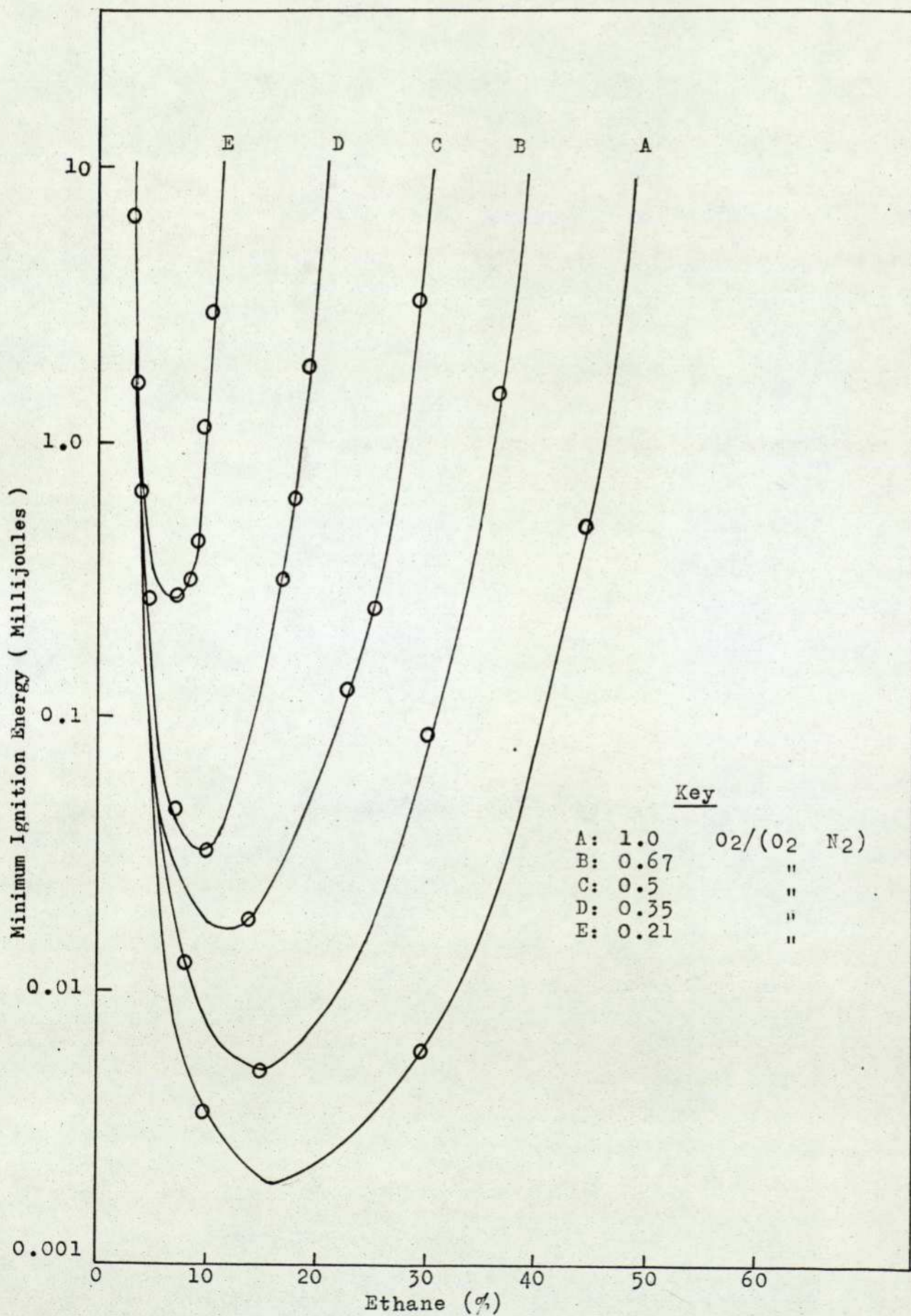
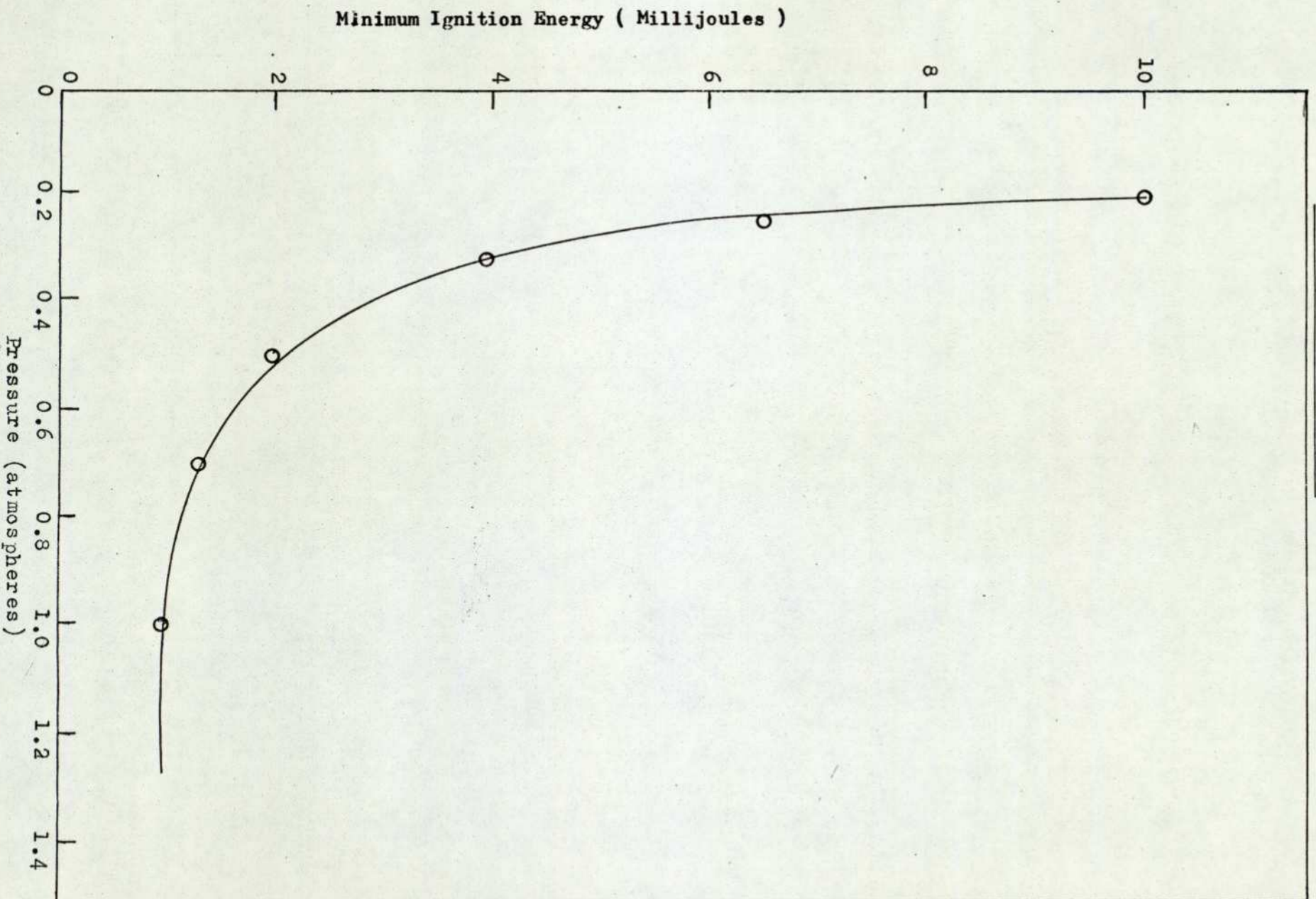


Figure 1.8

Variation of Minimum Energy with Pressure for
10 %v/v Ethane in Air



and, hence, from a safety concern one is unable to evaluate the safety of any discharge in any near limit atmosphere.

Other types of electrical discharge which may be encountered are inductive or static in nature.^{39,40} Both are capable of causing ignition and it has long been standard practice in the oil industry to provide an electrical contact to earth for all oil transfer vessels because of the build-up of static charge. Inductive arcs are used in most internal combustion engines although there is currently a trend towards capacitor discharges in high performance engines. The electrical parameters involved in the incendivity of an inductive coil discharge have been discussed by Bradford and Finch.⁴¹

Other sources of ignition which have been employed include hot wires, exploding wires and gun cotton.^{2,42} The effect of a hot wire is similar to the hot vessel used in S.I.T. determinations and although the heat release can be carefully controlled, it is unreliable in weak mixtures due to the convection currents which are set up. These currents prevent an element of gas from maintaining its S.I.T. for the period of its ignition delay. Partial oxidation of the fuel also alters the gas composition giving spurious results. Exploding wires have a special application for igniting mists, where the small diameter of the wire does not cause the mist to coalesce.⁴³ The wire is exploded by passing a very high current, which causes the metal to rapidly vaporise. Gun cotton (cotton soaked in nitro-glycerine), has been used infrequently to ensure that sufficiently high ignition energy

was obtained to ignite limit mixtures.² Local heating of the gas mixture and subsequent expansion of the gases render it of limited use for flammability limit determinations.

1.4.5.2 Quenching.

15,16
Payman et.al. in 1919, whilst working on flames in narrow tubes, observed that as the combustion tube was narrowed the limits of flammability are also narrowed until at a limiting diameter no flame could be propagated. Later work by Lewis and von Elbe showed that the minimum ignition energy of a mixture was a function of both the shape and separation distance of the electrodes when igniting by condenser-discharge. These workers were, in fact, observing the effects of quenching of the flame by a solid body.

The results of Lewis and von Elbe are reproduced in Figure 1.5. Curve A shows the variation of minimum ignition energy using needle point electrodes with change in electrode separation. Curve B represents similar results using electrodes with glass flanges parallel to each other. This curve shows a sharp increase in the minimum ignition energy at point C and represents the quenching distance of the gas mixture at that temperature, pressure and electrode configuration. Not all fuels give such simple curves as those in Figure 1.5. Thus, for example, some fuels have less clearly defined quenching distances and other fuels have several minima e.g. methyl ethyl ketone, a phenomenon for which no explanation exists. The quenching distance is also known to vary over the whole flammable range.^{35,44}

Although the evidence is rather scarce, the material used as the flange on the electrode does not appear to alter the quenching distance for a given mixture.⁴⁵ This is explained on a thermal theory by assuming that heat loss to the solid is the cause of quenching and that, since the heat capacity of any solid is orders of magnitude greater than that for a gas, the heat capacity differences for different materials has a negligible effect.

There is some evidence¹³ to suggest that the quenching distance for flammable mixtures increases markedly as the observed limit of flammability is approached and such limits are, more correctly, quenching limits, where the quenching distance is similar in magnitude to the dimensions of the containing vessel. Such an argument may explain the wider limits observed using flat flame burners as compared to those determined in tubes, although this is not supported by observations in large vessels.⁴⁶ This may be an example of limits of propagation rather than limits of flammability.

The effect of such variables as temperature, pressure and flame speed on quenching distances within the normal range is more important. Thus, for example, the quenching distance determined by using flanged electrodes is known to widen with an increase in initial temperature.⁴⁷ Similarly, if a flame is propagating towards an orifice one requires to know the orifice diameter and length which will extinguish the flame front. The former dimension is known to decrease with increasing flame speed and the latter increase.²⁰

Such knowledge is extremely important when machinery

is operating in a hazardous area and hot surfaces and stray sparks may occur in flammable atmospheres. It is frequently necessary to allow air to reach machinery as a coolant and, in order to render the situation safe, a flame arrester is constructed around the machinery such that any ignition taking place will be quenched.

Such an arrester must also have sufficient mechanical strength to contain any explosion that may occur. Sintered metal is frequently used in this application due to its porosity, narrow pore size distribution in the micron range and good mechanical strength.

A great deal of work has been conducted on this subject and this has been reviewed elsewhere by Lewis and von Elbe² and by Palmer⁹. The conclusions drawn regarding the mechanism of quenching are often contradictory, but the results obtained have allowed the calculation of safe gaps and flame path lengths, the application of which is strictly governed by legislation⁴⁸ and is discussed in Section 1.5.

1.4.5.3. Combustion Vessel Dimensions

One of the requisites of Coward and Brinsley's¹⁷ definition of a flammable gas mixture is that it should be able to support a combustion wave indefinitely. The most conveniently shaped vessel in which to observe such a combustion wave, and hence in which to determine limits, is a tube. In practice these authors found that a flame which propagates over 120 cm. along an open tube with an unbroken flame front will continue to do so indefinitely and, hence, this may be

considered to be the minimum length of a vessel for flammability limit studies.

The width of the tube is also found to be important^{8,38} and, in general, the limits of flammability are wider for increasing diameter tubes. This is very important for small tubes (< 1 cm.),^{15,16,49} but becomes negligible for tubes over 5 cm. in diameter and, hence, this is the normal diameter employed.

For a tube of the above dimensions the material of construction is, largely, unimportant although borosilicate glass is usually employed, since this is resistant to thermal shock, has a relatively low thermal conductivity and allows visual observation of the combustion wave.

Recent work by Furno, Cook, Kuchta and Burgess⁴⁶ using a spherical combustion vessel, 12 feet in diameter, has given some interesting results for flames in the absence of confining tube walls. These workers found that flames propagated spherically away from an ignition source only for mixtures in the middle of the flammable range; limit mixtures propagated as a mushroom shaped cap of flame in an upward direction effectively forming their own 'tube' of gas. The limits so found were not significantly different from those found in 5 cm. diameter tubes, indicating that the tube walls do not materially influence the limits.

If instead of a propagating flame moving through a stationary volume of gas, one considers a body of gas moving towards a stationary flame, then essentially the process is the same. Such a situation exists with the so-called flat flame

burner, which consists of a vertical tube up which the gas mixture flows. Streamlined flow is obtained by passing the gas through a matrix of small diameter tubes within the main burner rim. In controlled environments with low flow velocities and heated burner rims to prevent quenching, it has been possible to maintain flames on fuel/air mixtures outside the normal flammable range.^{6,45} Such results confirm that the limits of flammability determined in the tubes are not absolute values, but in any event the above observations must be regarded as laboratory phenomena.

1.4.5.4 Direction of Propagation

The limits of flammability for upward propagation of a flame in a tube are invariably wider than those for downward propagation, hence, for safety purposes it is always the former that are quoted in the literature. Experiments in large vessels⁴⁶ have substantiated this observation and have shown that spherical propagation of flame only occurs for a range of fuel concentrations in the centre of the flammable range. As the limits of flammability are approached so only upward propagation of flame is observed.

The generally accepted explanation of this is that at low burning velocities (the velocity of propagation normal to the flame front and relative to the ambient gases) convection will assist heat transfer to the unburnt layer of gas in upward propagation, but will not assist downward propagation.

The limits for horizontal propagation are intermediate to those for upward and downward propagation, as would be expected. Furno et.al.⁴⁶ have observed that it is only between the upper and lower limits of flammability for downward propagation that a detonation wave can be initiated. Between these propagation limits at constant volume only moderate pressures are developed and only a fraction of the total fuel is consumed.⁵⁰ Such observations have led Goldman⁵¹ to suggest that a more rigid definition of the limit of flammability should be the downward propagation limit. However, Coward and Jones⁸ have commented that ... "It is inconceivable that anyone who has seen a 5.6% methane/air flame travelling up a long tube would term this mixture non-flammable." The lower limit of methane in air for upward propagation is quoted by these authors as 5.3%.

1.4.5.5 Molecular Structure

Lewis and von Elbe^{2,52} determined the variation of minimum ignition energy with fuel/air composition for the n-alkanes up to n-heptane, (Figure 1.6). These results showed that the minimum of these curves occurred at a constant value of the ignition energy but at progressively higher stoichiometric ratios for increase in molecular weight. Similar types of curves have been obtained for a wide variety of compounds^{35,44,53-55} and correlations of the variation of minimum ignition energy with structure have been made. Calcote et. al.,³⁵ for example, have compared the minimum ignition energy at the stoichiometric ratio for groups of structurally similar compounds and have

53

shown that general trends can be established. These may be summarised for isomeric compounds as:

- (a) the minimum ignition energy at stoichiometry increases with the extent of branching;
- (b) the minimum ignition energy at stoichiometry decreases with the degree of unsaturation.

It is interesting to attempt to draw correlations between limits of flammability, spontaneous ignition temperatures and minimum ignition energies and typical results are given in Table 1.3. One also observes that the S.I.T. is very sensitive to the degree of branching of the molecule. This is not so for the lower limit of flammability although a marginal decrease in the limit is observed for some isomers. The latter observation would indicate that a group of isomers should have identical curves of the type given in Figure 1.6. This inference is not supported by the results of Calcote³⁵ which show that the ignition energy for stoichiometric mixtures increases with the degree of branching, and from which one would expect the lower limit to also increase. No explanation of these anomalies could be found in the literature.

1.4.5.6. Temperature

Normal ambient temperature variations do not measurably affect the limits of flammability of a particular fuel. Experimental results^{38,56} indicate that the variation of the limits up to ca. 100°C is almost linear; the limits varying by ca. 8% of their value at 25°C for each 100°C rise in temperature. Later work has shown that at higher temperatures

Table 1.3

Fuel	L.L.F. ⁸ (% v/v)	S.I.T. ⁶⁵ (°C)	M.I.E. ⁵² at $\phi=1$ (10^4 J)
n-butane	1.9	410	—
iso-butane	1.8	460	5.2
n-pentane	1.5	260	5.1
iso-pentane	1.4	420	7.0
2,2-dimethyl propane	1.4	450	15.7
n-hexane	1.2	230	—
2,3-dimethyl butane	1.2	290	—
2,2-dimethyl butane	1.2	425	16.4

Legend:

L.L.F. = lower limit of flammability under
standard conditions

S.I.T. = spontaneous ignition temperature at
1 atmosphere pressure

M.I.E. = minimum ignition energy at the
stoichiometric ratio

this linear relationship is not obeyed by the upper limit for hydrocarbons higher than propane, the limits widening considerably over a small range of temperatures.^{18,19} Typical results are shown in Figure 1.9.

The most dramatic effect of temperature is on the vapour pressure of high boiling fuels, where raising the temperature by a few degrees can increase the vapour pressure sufficiently to cause the occurrence of a flammable mixture in air (cf. flash points). This effect is explained by the shape of the vapour pressure versus temperature curve.

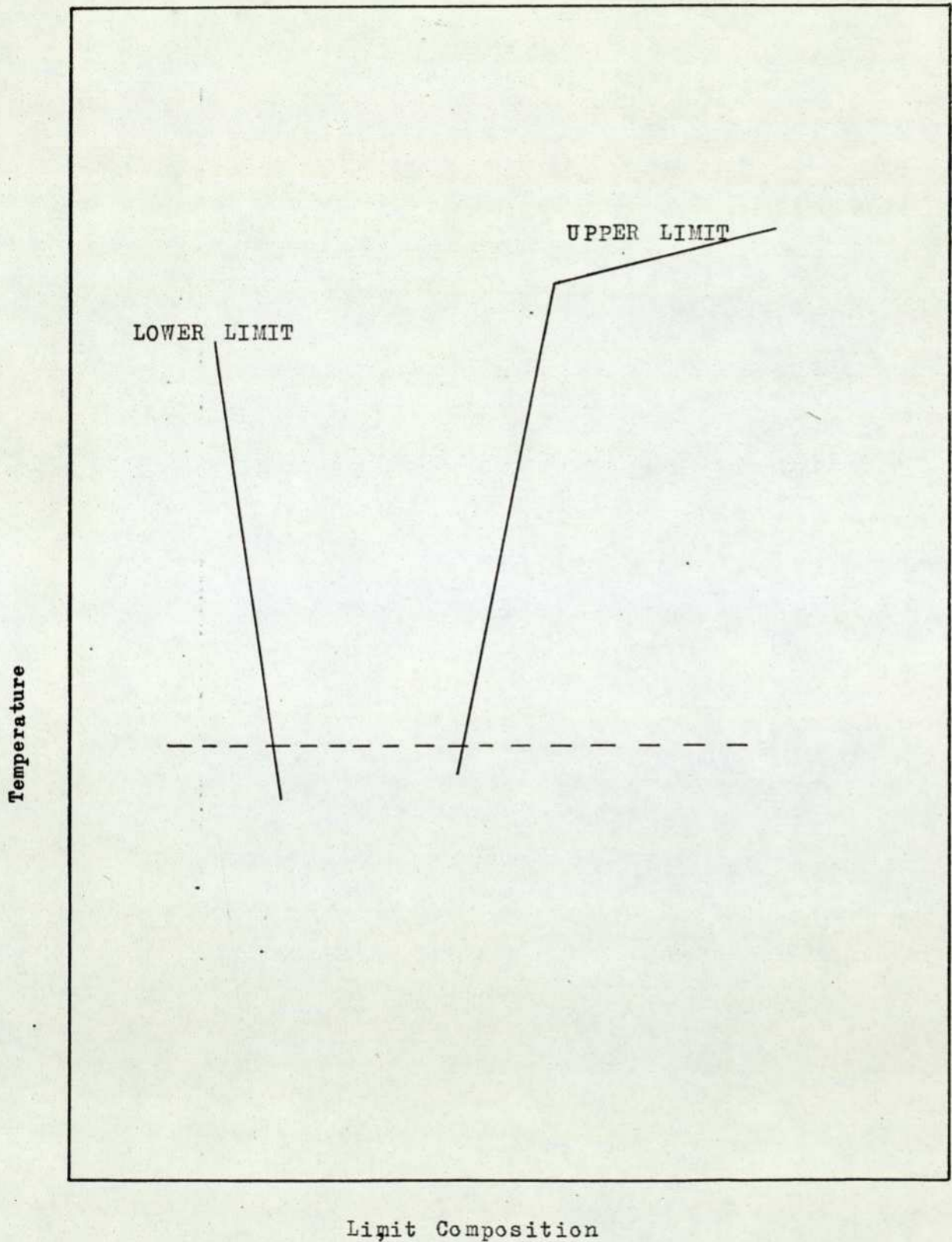
In general, the effect of temperature is consistent with a thermal theory of propagation on the basis that in order for a flame to propagate, the burning layer of gas must raise the adjacent layer of unburnt gas to a temperature at which it will rapidly ignite. The amount of heat required to achieve this temperature will be less if the initial temperature of the gas is raised and consequently mixtures which would not normally sustain propagation are able to do so.⁵⁷

1.4.5.7 Pressure

Moderate changes in pressure i.e. normal atmospheric variations, do not affect the limit of flammability.⁸ Burgoyne⁵⁸ and Lovachev et. al.⁷ have reviewed the data relating to a wide range of pressures and reveal that a number of phenomena occur. In general, reducing the pressure results, ultimately,¹⁸ in a coincidence of the limits and increasing the pressure (over several atmospheres) initially narrows and then widens the flammable range. At the low pressure limit several

Figure 1.9

Variation of Upper and Lower Limits of Flammability
with Temperature



fuel →

59-61
 authors have observed the existence of a pressure peninsular, for both hydrogen and methane/air mixtures, although some results⁶² suggest that the peninsular only occurs in narrow tubes. The general variation of limits of flammability with pressure are shown in Figure 1.10. It has been noted by Lovachev et. al.⁷ that the effect of pressure is more pronounced on the limits for downward propagation than for upward propagation. This indicates that convection currents, from the hot combustion products, are an important parameter in the mechanism of flame propagation at both super and sub-atmospheric pressures. Lewis and von Elbe² have also shown that at reduced pressures the minimum ignition energy increases; an observation that is consistent with the increase in S.I.T. at reduced pressures.

1.4.5.8. Turbulence

The effect of turbulence on the limits of flammability and minimum ignition energies has not been widely studied, but Wheeler¹⁶ and Coward and Jones⁸ have shown that mild turbulence lowers the minimum ignition energy and widens the limits for methane/air mixtures, whilst vigorous agitation has the opposite effect. Furthermore, increasing the velocity of the gaseous mixture in the combustion tube does not affect the limits of flammability until the Reynolds Number^a of the

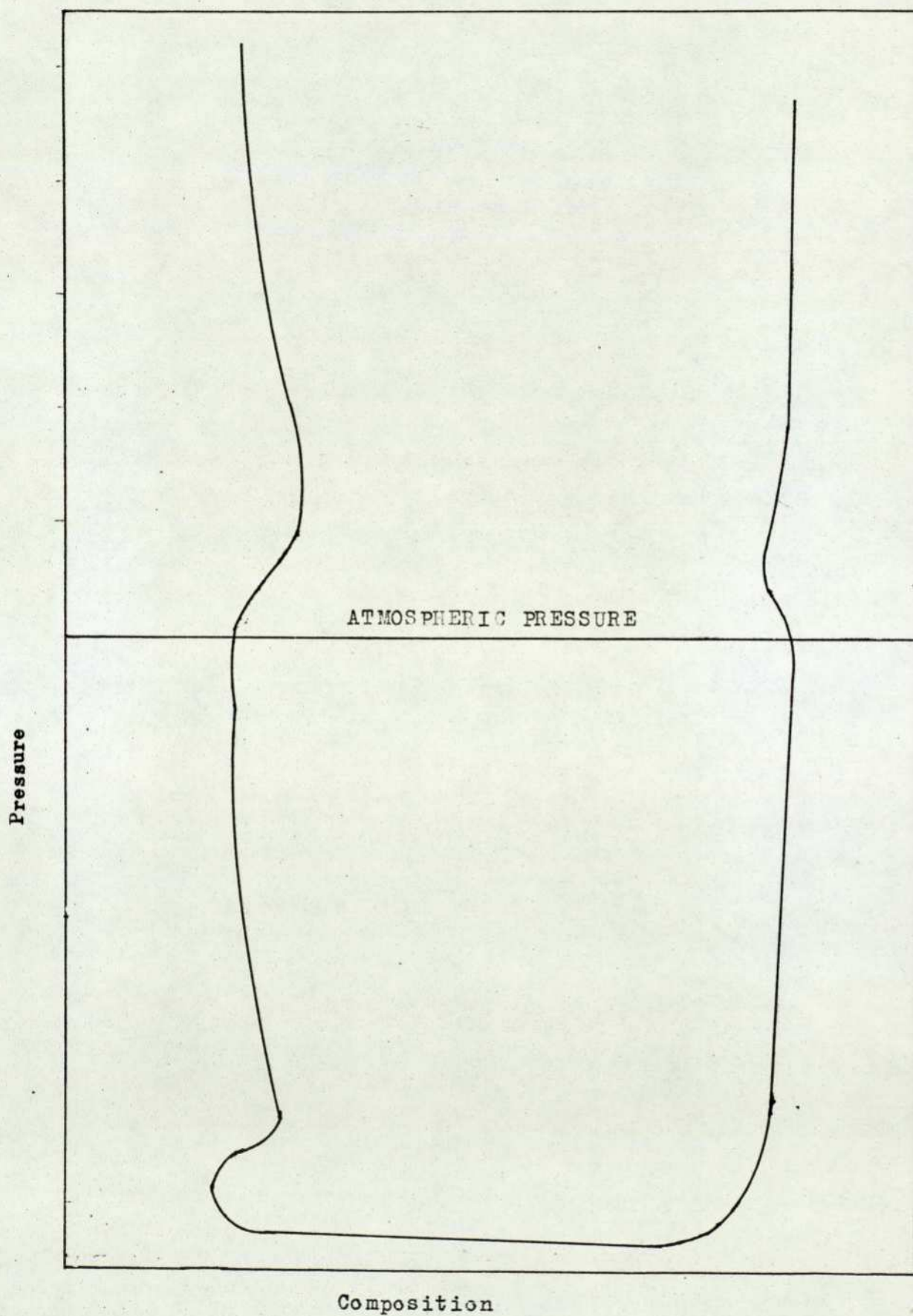
a: The Reynolds Number is a dimensionless group which describes the dynamic similarity of fluid flow. The number is given by:

$$N_{Re} = (LV\rho)/\mu$$

where: L = characteristic dimension; V = fluid velocity;
 ρ = density; μ = dynamic viscosity.

Figure 1.10

Variation of Limits of Flammability with Pressure.



2
mixture reaches a value of 2,000 i.e. the onset of turbulence.
Such results indicate that mild turbulence exists in heat
and radical transfer thus promoting flame propagation, but
severe turbulence destroys this effect. More importantly,
from a safety aspect, however, is the observation that for
ignition of a constant volume mixture, turbulence increases
both the rate of pressure rise and the ultimate pressure
attained.^{9,45} This further indicates that although severe
turbulence may reduce the flammable range, once ignition is
achieved propagation progresses far more rapidly than in a
quiescent system.

1.5 SUPPRESSION OF A FLAMMABLE HAZARD

The creation of flammable atmospheres is either necessary (i.e. chemical feedstocks, gas fires, welding torch) or accidental. In the former case, the mixture is usually consumed as it is formed, as in a diffusion flame, or it is handled in such a way that should ignition occur, the explosion will be either contained or vented so as to cause minimal damage. The key to the success of either of these operations is a knowledge of the pressure that will be generated as a result of ignition. In the latter case, some environments are more likely to contain a flammable atmosphere than others and some gases and vapours are more liable to create a hazardous situation than others. Hence, to provide protection for all possible situations the Factory Inspectorate has divided the majority of flammable gases and vapours into two groups, namely;

group I, which is for the mining industry only and contains only firedamp (methane) and groups II A, B and C, which apply to general industry.

The distribution of gases and vapours within group II depends upon their minimum ignition energies, quenching distances, flammable range and spontaneous ignition temperature. The complete list is given in B.S. 4683,⁴⁸ but an illustrative extract is given in Table 1.4. It is the responsibility of the Factory Inspectorate to decide in which grouping a particular environment falls. Once a group is appropriated all electrical and mechanical equipment within that area must conform to the requirements of B.S. 4683 and must be either

Table 1.4Summary of Hazardous Classification After B.S. 4683

Group I	firedamp (methane)
Group IIa	methane, natural gas
Group IIb	alkanes, alkenes, alcohol ketones etc.
Group IIc	hydrogen, town gas, water gas, producer gas and acetylene

flameproof or intrinsically safe with respect to a particular fuel. For example, a group 1 flameproof enclosure, when filled and surrounded by a 9% methane in air mixture, must neither explode nor cause the surrounding mixture to ignite when the inside mixture is ignited with a spark. Similarly, a group 1 intrinsically safe electrical circuit is one that under no circumstances can produce a spark in excess of the minimum ignition energy of methane in air, viz. 0.2 mJ.

Obviously, in all such classified areas, smoking and naked lights are forbidden and the philosophy is one of 'remove all possible sources of ignition.'

The methods of detection of a flammable hazard have been mentioned earlier (Section 1.3) and given such warning, adequate dilution either with air or with some inert gas to ensure that the fuel concentration is below the lower limit of flammability is usually relatively easy. In the circumstance where either ventilation or inerting is not possible e.g. some mining applications or 'close down' conditions on defence vessels (i.e. hermetically sealed engine rooms etc.) one is forced to construct to either intrinsically safe or flameproof specifications. In this context, following explosions in the holds of several large oil-tankers, it has become standard practice to fill empty holds with engine exhaust. Similarly, filling the ullage space above a liquid fuel in a closed container with an inert gas prevents a flammable atmosphere forming.

A novel method of reducing a flammable hazard has
63
been illustrated by Huggett, who has shown that artificially

created atmospheres can support life but not combustion; thus, for example, a rabbit lived in an atmosphere containing 21% O_2 ; 21% C_2F_6 and 58% N_2 without any ill effects, but neither filter paper nor cotton cloth would burn. An extension of this work could provide a habitable atmosphere in which fuel gases are not ignitable.

The flammable hazard of a particular gas could be reduced if either its flammable range are narrowed or its lower limit was raised. Both of these effects were obtained in the case of hydrogen, for example, if it is diluted with methane; similarly mixtures of methane and carbon monoxide have a lower limit between that of methane (5.0%) and carbon monoxide (12.5%). (It is this combination of methane and carbon monoxide that causes the lower limit of natural gas to be between 6 and 6.5%). This effect was first observed and stated quantitatively by Le Chatelier¹⁴ and is discussed by Zebatakis²⁰ and Jones⁶⁵ in conjunction with other facets of flammability and their practical applications. One may find many examples, as above, of the practical application of derived physico-chemical relationships which are discussed in the next section.

1.6 PHYSICO-CHEMICAL RELATIONSHIPS

1.6.1 General

Over the years general relationships have been observed between the flammable properties and various intrinsic properties of many gases and vapours. These relationships become very evident within any homologous series and are particularly well documented for the n-alkanes.

Although such relationships are usually qualitative they are important since they provide a guide to the flammable characteristic of an unstudied fuel from a knowledge of its position in the homologous series and its intrinsic properties. Some of the more common relationships obtained for the n-alkanes are discussed below.

1.6.2 Single Component Fuels

From literature data^{2,4,8,9,66} several equations can be derived which relate carbon number to primary functions of the n-alkanes, such as molecular weight, boiling point and molar heat of combustion. A graphical procedure has been adopted by Affens⁶⁷⁻⁷¹ to derive the following equations;

$$M = 14.027n + 2.016 \quad (1)$$

$$(t_B + 293.2)^2 = 21,580n \quad (2)$$

$$\Delta H = 146.91n + 47.496 \quad (3)$$

where; n = carbon number, M = molecular weight, t_B = boiling point and ΔH = heat of combustion.

These equations represent the lines of 'best fit' for the data relating M , t_B or ΔH to n . Similarly, equations relating the upper and lower limits of flammability to carbon number have been derived:

$$1/L = 0.1347n + 0.4353 \quad (4)$$

$$1/U = 0.01337n + 0.05151 \quad (5)$$

where; L = lower limit of flammability and U = upper limit of flammability. It should be noted that, in general, data for lower limits is more numerous and more consistent than that for upper limits. Equation (5) is, therefore, open to some error and one must question the validity of quoting the correlation factor to five decimal places.

From equations (3) and (4) it can be shown that:

$$L \Delta H = 1091 \quad (6)$$

A relationship of this form has been observed by several authors^{8,71-73} and has led to the general conclusion that the observed limits of flammability are the result of a thermal mechanism; a conclusion which is substantiated by the very similar temperatures of flames of limit mixture compositions.^{42,57}

Using available data,^{8,38,56} Affens has also derived an equation to describe the variation of the lower limit with temperature (see Section 1.4.4.6):

$$L_t = 1.02L(1 - 7.75 \times 10^{-4}t) \quad (7)$$

where L_t = lower limit at $t^\circ\text{C}$ and L = lower limit at 25°C .

Due to insufficient data this equation may not be particularly accurate, but since the lower limit only varies by about 8% for a 100°C change in temperature, this is not of great importance. The usefulness of equation (7) is that it permits

the derivation of equations which relate temperature variable functions such as vapour pressure to flash points. Figure 1.11 shows a typical vapour pressure versus temperature curve.

Vapour pressure data may be calculated from the
66
equation viz:

$$\log_{10} P = -(0.2185A/T) + B \quad (8)$$

where P = partial pressure, T = temperature and A and B are constants. If the lower limit of flammability is known, the temperature at which flammable mixtures will be produced can be interpolated.

A graphical method of determining the flash point is illustrated by Figure 1.11, in which the vapour pressure versus temperature curve is bisected by a lower limit versus temperature curve; the point of intersection (A) allows the flash point to be read off. From a series of such graphs Affens has determined the following equation for the relationship between the flash point and carbon number, for the n-alkanes:

$$(F.P. + 277.3)^2 = 10,410n \quad (9)$$

Table 1.5 shows actual and theoretical values of flash points. In general, the above expression is verified, but several anomalies exist due to the wide discrepancies for flash point values found in the literature.

Affens has further combined equations (4) and (9) for the n-alkanes to eliminate n and hence obtain:

$$(F.P. + 277.3)^2 = 77,291(1/L) - 3365$$

Thus a plot of $(F.P. + 277.3)^2$ versus $1/L$ should yield a straight line. This relationship is given in Figure 1.12 and shows good agreement. Hence, although the limits of

Figure 1.11

Variation of Vapour Pressure and Lower and Upper Limits of Flammability with Temperature.

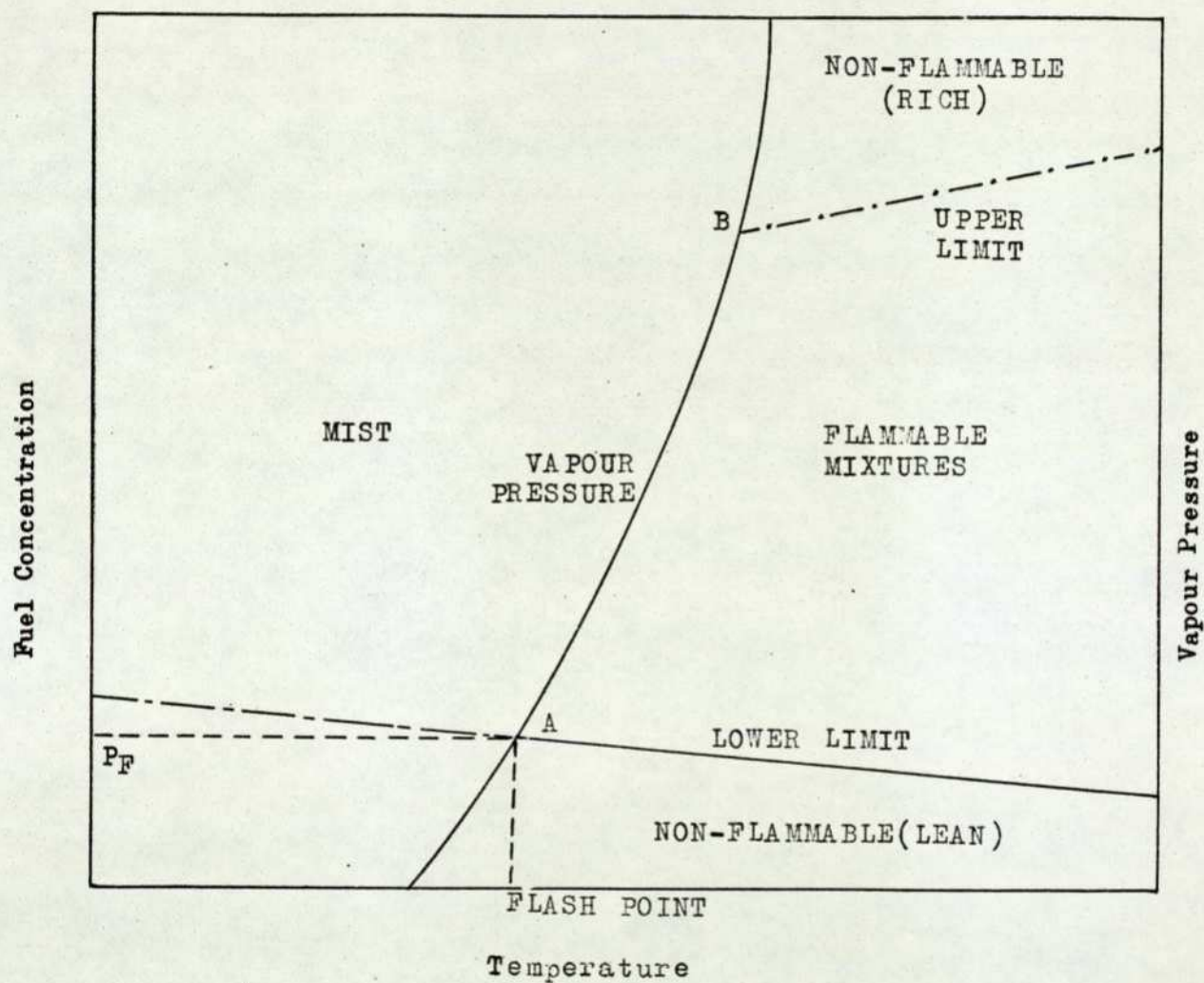


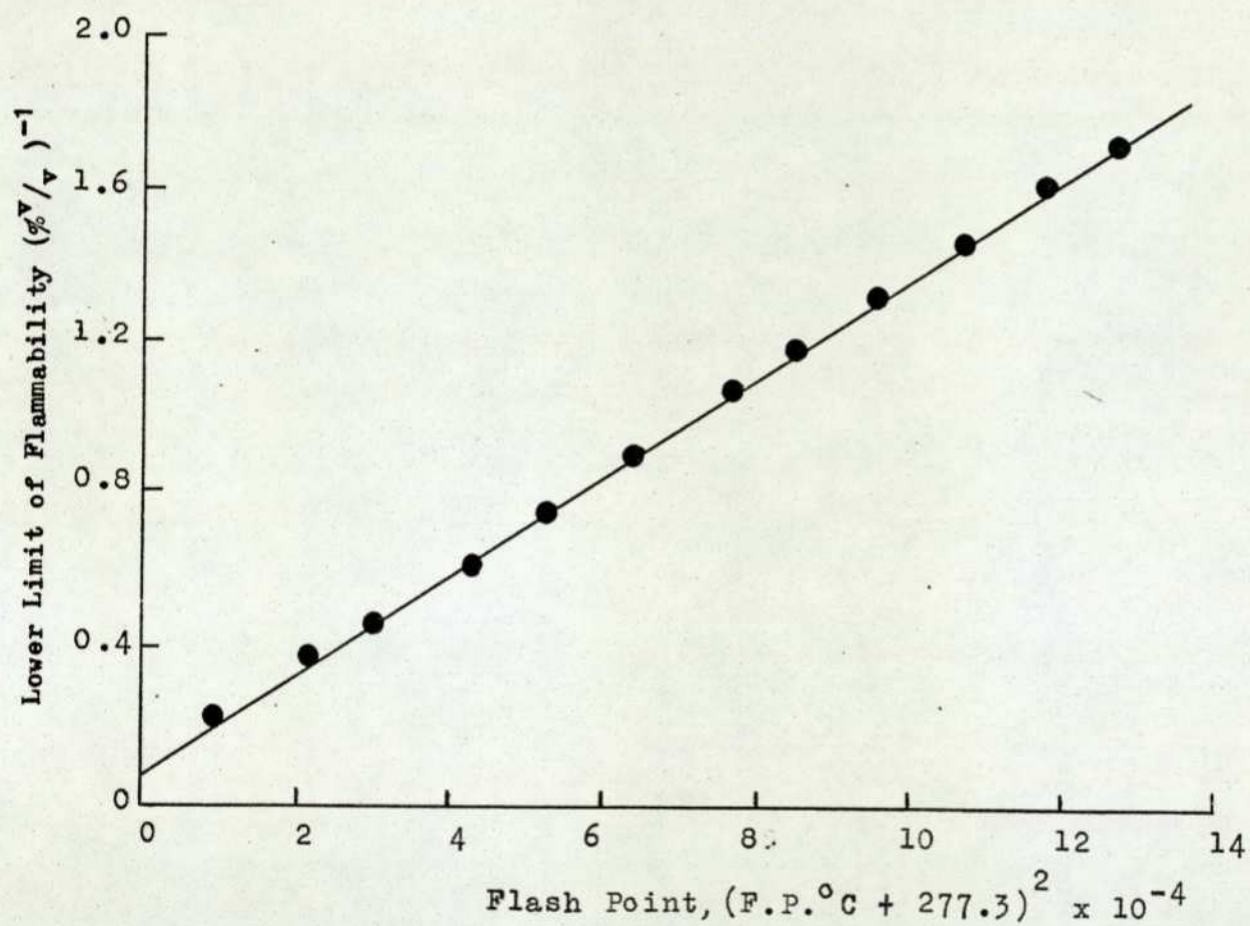
Table 1.5Actual and Theoretical Flash Points

Fuel	Actual F.P. [†] °C	Calculated F.P. °C
n-pentane	-49	-49
n-hexane	-23	-27
n-heptane	-3	-7
n-octane	14	11
n-nonane	31	29
n-decane	46	45

[†] Literature average.

Figure 1.12

Variation of Lower Limit of Flammability with
Flash Point for the n-Alkanes (from ref. 71)



flammability of the n-alkanes are well documented, similar equations for other homologous series give a rapid and reasonably accurate means of determining the lower limit of flammability from the more readily obtainable flash point data.

1.6.3 Multicomponent Fuels

The importance of the effect of one component upon the flammability of a second component in a fuel mixture has long been realised and the advent of fuel blending to obtain fuels with specific properties has increased the necessity for knowledge in this field.⁶⁴

Le Chatelier¹⁴ in 1891 formulated the following principle; a flammable mixture is formed from two flammable gases, when the sum of the ratios of the actual concentrations to the concentration at the lower limit of flammability for each gas is unity. This is expressed more conveniently as;

$$\frac{C_A}{L_A} + \frac{C_B}{L_B} + \dots = 1 \quad (10)$$

where C = the molar concentration and L = lower limit of flammability. Coward, Carpenter and Payman⁷⁴ derived an alternative form of this expression by algebraic rearrangement viz.:

$$\frac{1}{L_M} = \frac{N_A}{L_A} + \frac{N_B}{L_B} + \dots \sum_i \frac{N_i}{L_i} \quad (11)$$

where N_i = mole fraction of a component in the total fuel vapour, L_i = lower limit of flammability of that component and L_M = lower limit of flammability of the total mixture.

Several authors have tested the validity of the above expressions and have shown that they hold for such adverse mixtures as $H_2 + CO + CH_4 + AIR$; in addition to multi-component hydrocarbon mixtures.^{65,75-78} Analogous expressions exist for the upper limit of flammability but these have not been so extensively studied.⁶⁹

For binary mixtures equation (10) may be expressed in the form:

$$C_B = L_B - (L_B/L_A) \cdot C_A \quad (12)$$

i.e. a plot of C_B versus C_A is a straight line (see Figure 1.13) thus providing a simple means of experimental verification.

Equation (11) gains wider application if the lower limit is related to the liquid composition from whence the vapour came. This may be achieved by application of Raoult's^{20,79} and Dalton's Laws. These may be expressed respectively as:

$$p_i = P_{oi} M_i$$

where p_i = partial pressure of component i , P_{oi} = vapour pressure of pure compound i and M_i = mole fraction of i in the liquid; and:

$$P = P_A + P_B + \dots \sum_i p_i \quad (13)$$

where P = total vapour pressure of mixture and p_i = partial pressure.

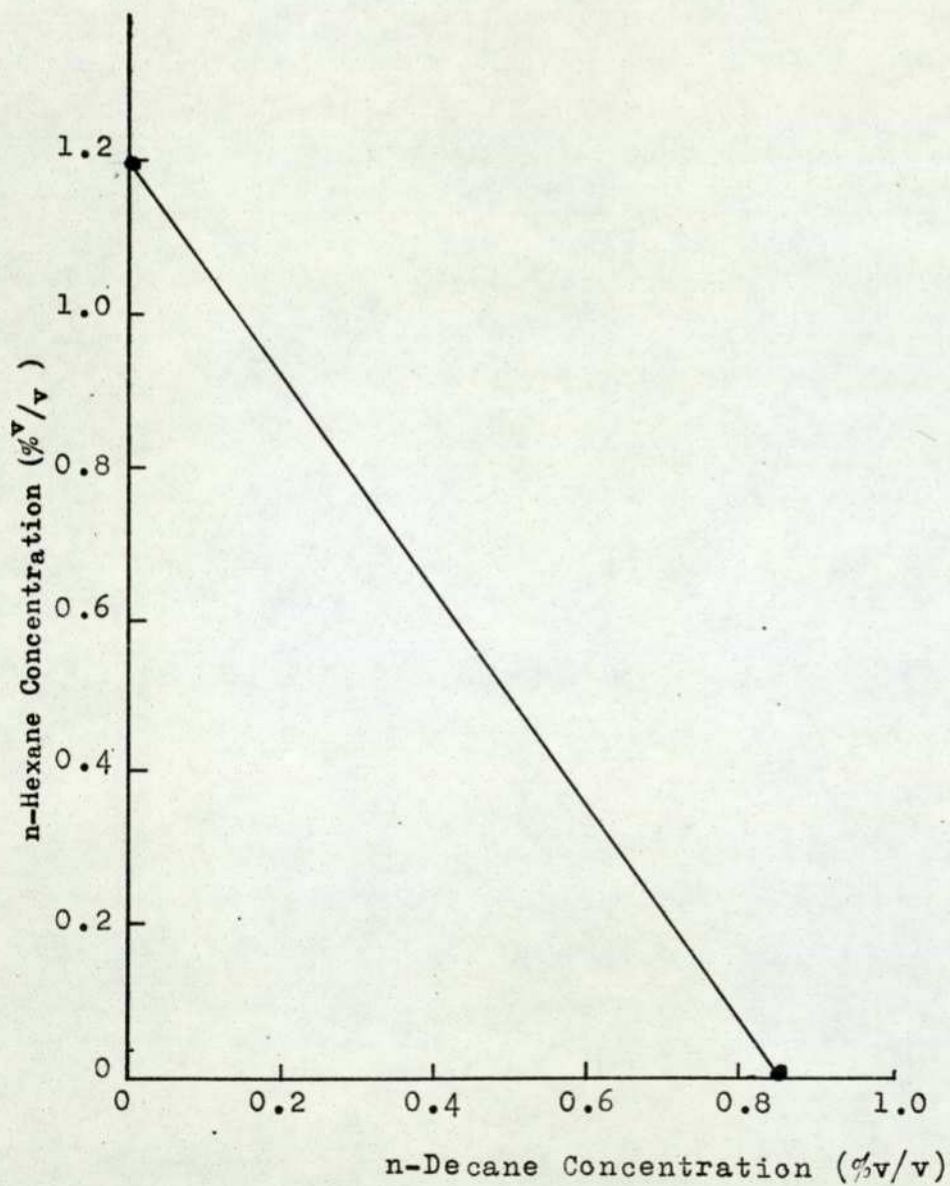
These equations may be combined to give:

$$N_i = \frac{M_i P_{oi}}{\sum_i M_i P_{oi}} \quad (14)$$

(The distinction between N_i , the mole fraction in the vapour, and M_i , the mole fraction in the liquid should be noted.)

Figure 1.13

Theoretical Lower Limit Compositions of Mixtures
of n-Hexane and n-Decane in Air



Substitution of (14) into (11) gives:

$$\frac{1}{L_m} = \frac{\sum_i (M_i P_{oi}) / L_i}{\sum_i M_i P_{oi}} \quad (15)$$

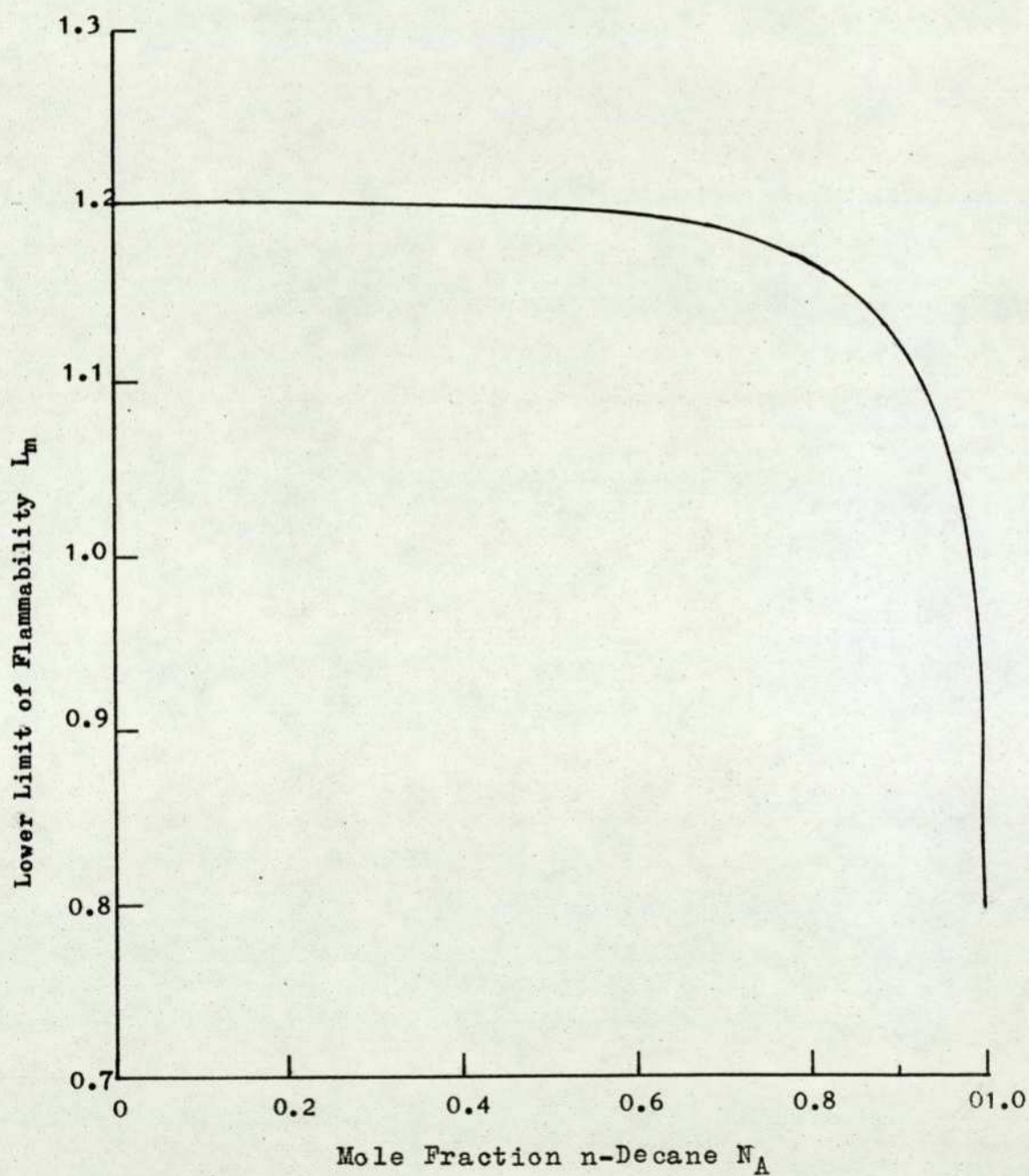
which for a binary mixture becomes:

$$\frac{1}{L_M} = \frac{M_A P_{oA} / L_A + M_B P_{oB} / L_B}{M_A P_{oA} + M_B P_{oB}} \quad (16)$$

The variation of L_M with N_M is plotted in Figure 1.14 for theoretical mixtures of n-hexane and n-decane at 60°C. It should be noted that the abscissa could equally well be the flash point of the mixtures. Either indicates the influence of a small concentration of a lower boiling paraffin on a higher member of the homologous series. Since, this situation is readily realised in practice, a knowledge of the flammability of such mixtures is invaluable for safety reasons. A limited amount of work has been conducted in this field^{64,80} and is extended in the present work.

Figure 1.14

Variation of the Lower Limit of Flammability
with Liquid Composition for a Binary Mixture



SECTION 2
EXPERIMENTAL

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2.1. GENERAL

The apparatus was designed and constructed within the general specifications of the 'standard' apparatus as described by Coward and Brinsley.¹⁷ Several innovations were included which were designed to reduce experimental errors e.g. on-line analysis of fuel/air mixtures, or to reduce the experimental time required e.g. the auxiliary discharge circuit. Due to these innovations several preliminary experiments were necessary to ensure their reliability.

The description of the apparatus is divided into two parts entitled 'The Flow System' (Section 2.3.) and 'The Static System' (Section 2.5.) The former system employed a dynamic method of mixing the fuel and air. This mixture had an upward velocity of ca. 1cm./sec. in the combustion tube. These experimental conditions were chosen as they were thought to conform most closely to the conditions prevailing in an engine room or similar environment. This apparatus was, however, rather tedious to operate and the results varied only slightly from those obtained under static conditions.

Further, it was required to produce mixtures containing more than one fuel component which on the flow apparatus was extremely difficult. For these reasons a static apparatus was designed which allowed greater flexibility of operation.

2.2. MATERIALS

2.2.1. Fuels

(i) Liquids

n-Hexane, n-decane, 2,2,5-trimethylhexane, hex-1-ene and 2,2-dimethylbutane were obtained from Koch Light Laboratories Ltd. They were all 'puriss' grade supplied at not less than 99.9% pure. Analysis by gas/liquid chromatography showed no measurable impurities.

(ii) Gases

n-Butane and 2,2-dimethylpropane were supplied by British Oxygen Co., Ltd., as 'pure' grade gases of not less than 99.5% purity. Again no significant impurities were found.

2.2.2. Permanent Gases

Air and helium were supplied by British Oxygen Company (Industrial Gases) Ltd., as commercially pure gases (99% purity) and were dried before use by passage through a column of type 4A molecular sieve.

2.3. THE FLOW SYSTEM

2.3.1. Preliminary Experiments

2.3.1.1. Fuel/Air Mixture Preparation

1. Injection Technique

Several attempts were made to prepare fuel/air mixtures by the direct injection of liquid fuel into a heated gas stream after the method employed by Zebatakis et. al.³⁸

The initial apparatus consisted of a Perkin Elmer 452 chromatograph, with a 5 cm., 3 mm outside diameter stainless steel tube in place of a column to ensure a rapid response. No column was needed as only one compound was introduced. Nitrogen was used as the carrier gas and a Taylor-Servomex type Mk. 158 micro-kathrometer as the detector.

A 5 ml., syringe containing the fuel was located in a Baird and Tatlock continuous liquid injector, model 6230. The needle of the syringe was inserted directly into the injection part of the chromatograph. The output from the chromatograph was fed to an Hitachi flat bed recorder and the system was allowed to stabilise until a steady baseline was recorded.

The continuous injector was then switched on and after some initial large fluctuations the baseline appeared as an irregular 'saw-tooth' type trace. Adjustment of the injection port temperature and syringe needle size failed to eliminate these irregularities and it was concluded that either droplet formation was occurring or the syringe plunger was not in fact moving at a uniform speed.

Modification to the apparatus included;

(i) incorporating a heated mixing chamber prior to injection into the chromatography system;

(ii) passing the fuel/nitrogen mixture through a sample loop and analysing the contents of the sample loop independently; and

(iii) using different syringe sizes and designs.

None of these measures were effective in obtaining a consistent fuel/nitrogen ratio, therefore this method of mixture preparation was abandoned.

2. Saturation of Air with Fuel Vapour.

A flow of dried air controlled by a needle valve and flow meter, was passed into an oven which was set at room temperature. The air was preheated by passage through a glass coil and then passed through three 250 ml. Dreschel bottles in series. The Dreschel bottles were filled with fuel and their downpipes were filled with No. 1 porosity glass scinters.

The resultant fuel/air mixture was taken from the oven via a heated tube, through a heated sample loop and then vented to atmosphere. The sample loop was fitted with Rotaflow greaseless taps such that a sample of the fuel/air mixture could be removed for analysis using a Perkin Elmer 452 gas chromatograph. Stringent precautions were taken to ensure that no fuel condensed in the sample loop or inter-connecting tubing.

The theoretical fuel concentration for any fuel/air mixture was calculated from the partial pressure of the fuel at the temperature of the oven, using available literature data.⁶⁶ The fuel concentration, determined by

experiment, was obtained from the expression:

$$\%v/v = (N \times 22.414 \times 100) / V$$

where N = moles of fuel in sample taken

V = volume of sample loop.

The value of N was obtained by the method of peak areas, following calibration of the chromatograph with known samples of liquid fuel.

Initial experimental results showed that the fuel/air mixtures obtained did not contain the theoretical amount of fuel. This discrepancy was attributed to adsorption of the fuel into the butyl rubber tubing which was used as the connection between the Dreschel bottles. This tubing was observed to swell during the passage of the fuel/air mixture. All such connections were replaced by glass tubing and Young's greaseless joints.

The above analysis was then repeated and the fuel/air mixtures contained a partial pressure of the fuel in excess of that calculated. Such results are similar to those obtained by Irshad⁹⁵ and later by Cole,⁹⁶ both of whom have shown that the effect is dependent upon the flow ratio of the air and may be due to pneumatic transport of fuel droplets.

The system was subsequently modified to that described in section 2.3.2.4.

2.3.1.2. Electrical Breakdown of the Electrode Separation.

The voltage at which sparks spontaneously passed between the electrodes was obtained for a range of electrode separations. The lowest voltage at which electrical breakdown could be induced by the method described in Section 2.4.6. was also determined. By ensuring that the applied voltage was always between these values a discharge could be obtained when required by energising the auxiliary ignition circuit described in Section 2.3.2.6. These results are given in Table 2.1.

2.3.1.3. Capacitor Measurement.

A Wain Kerr capacitance bridge was used to measure the total capacitance of the main discharge circuit (Section 2.3.2.6.). This was necessary since the connecting wires in the circuit and the electrodes can create a capacitance of several pico-farads which could be significant compared with the lower values of capacitance employed in the circuit. In addition, since the capacitors in the main circuit were supplied with a tolerance of $\pm 10\%$ on their nominal values, it was required to determine the actual 'in circuit' capacitance of each unit. These results are given in Table 2.2. and the total capacitance measure, C_{actual} , was the figure employed in calculating the energy of a given discharge.

Table 2.1.

Variation of Maximum and Minimum Breakdown Voltages
With Spark Gap.

Spark Gap m.m.	Minimum Voltage Capable of Causing a Spark. kV.	Maximum Voltage Possible to Avoid Multiple Sparks. kV.
0.5	2.5	3.5
1.0	2.6	4.25
1.5	2.8	5.5
2.0	3.0	6.8
2.5	4.0	8.0

Table 2.2.Nominal and Actual Capacitance Values.

C nominal	C actual
25 μF	26 μF
50 μF	49 μF
100 μF	112 μF
300 μF	287 μF
500 μF	560 μF
1000 μF	1120 μF
0.01 μF	0.0123 μF
0.2 μF	0.2 μF

2.3.2. The Apparatus.

The apparatus is shown in Plate 2.1. and schematically in Figure 2.1. Essentially it consists of a system of ovens in which fuel and air are mixed, passed into a combustion tube and ignited by an electric spark. Facility exists for analysing the fuel/air mixture.

External to the ovens is the electrical circuitry which monitors the energy of the igniting spark and the passage of a flame if produced.

The gaseous exhaust from the combustion tube was removed via a metal hood and flexible ducting to an adjacent fume cupboard. This prevented any possible build up of flammable gas/air mixtures.

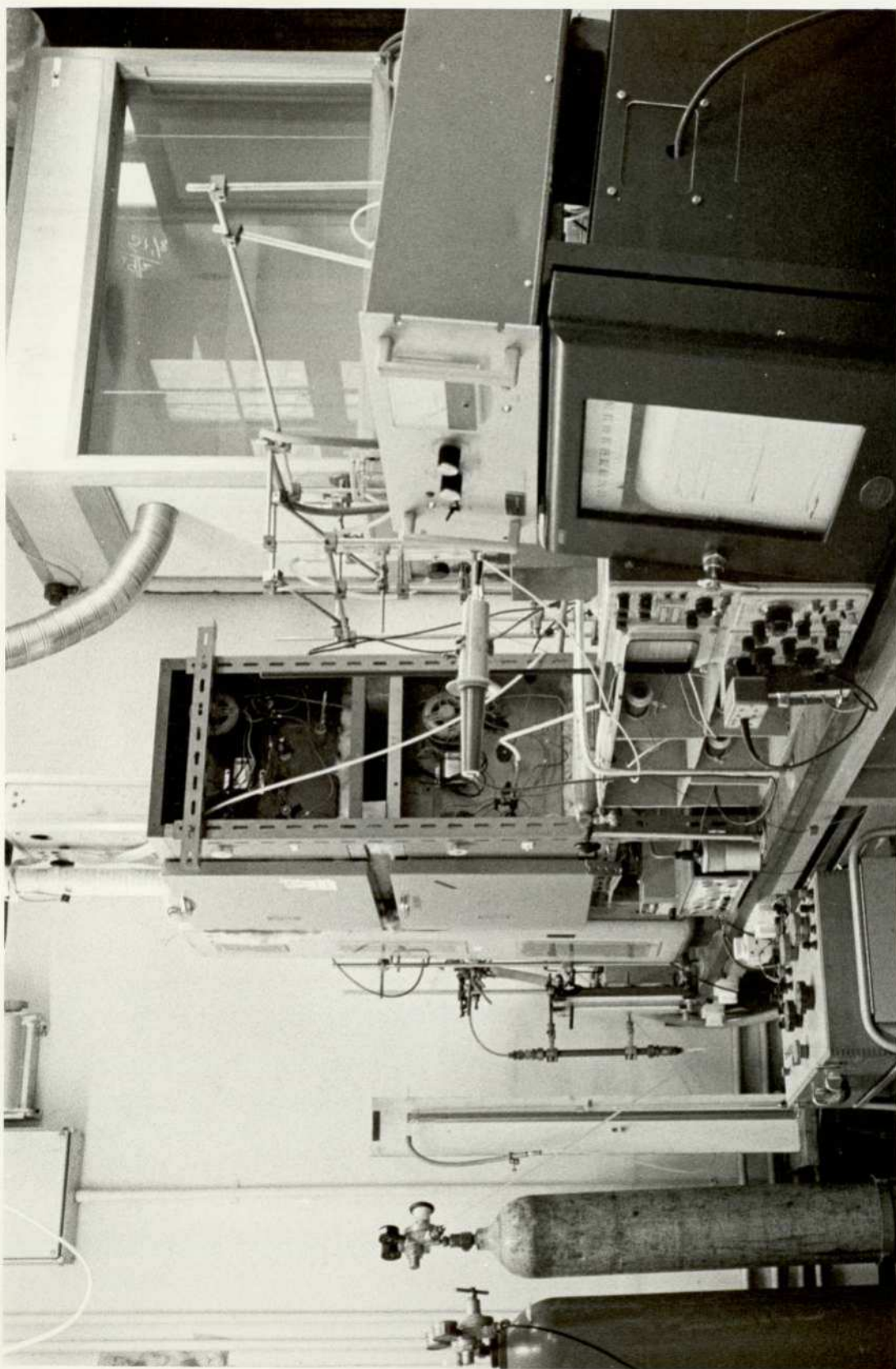
The individual components of the system are described in the following sections.

2.3.2.1. The Combustion Tube.

The combustion tube was manufactured from Pyrex glass tubing, 130 cm. long, 5 cm. outside diameter and 2 mm. wall thickness. Gases were admitted to the tube at its base via a 6 mm. outside diameter glass tubing. Two B.24 Quickfit ground glass sockets were glass welded to the tube 5 cm. above its base such that one socket was 180° relative to the other in a horizontal plane. These sockets acted as supports for the main electrodes.

A B.10 Quickfit ground glass socket was mounted at 90° to these sockets and in the same horizontal plane in order to support the auxiliary electrode.

Plate 2.1



General View of Apparatus

Legend for Figure 2.1

A ₀	-	auxiliary oven
M ₀	-	main oven
T	-	combustion tube
S	-	sample valve
C	-	chromatography column
I	-	sample injection port
K	-	katharometer
R	-	rotameters
D	-	drying tubes
F.C.	-	Brooks flow controller
F.T.	-	flame trap
SAT	-	device for saturating air with fuel vapour - see text
CON	-	device for condensing excess fuel held in air - see text
1,2 & 3	-	needle valves

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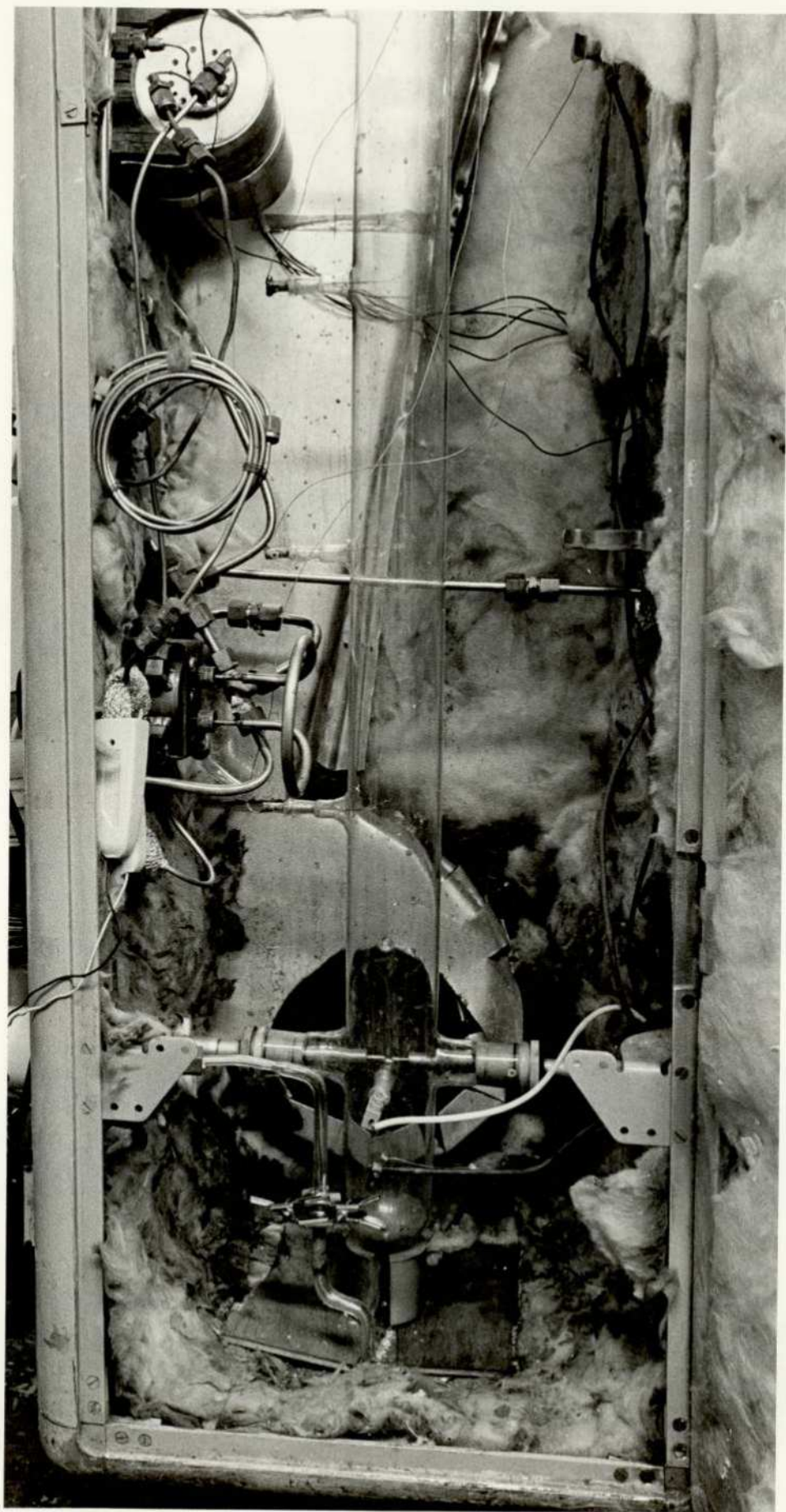
Five further B.10 Quickfit ground glass sockets were mounted horizontally onto the combustion tube at distances of 15, 30, 60 and 120 cm., vertically above the centre line of the main electrode supports, to accommodate micro thermocouples which recorded the speed and extent of flame propagation. Plate 2.2. shows the lower half of the combustion tube and its immediate surroundings in detail. The combustion tube was open to atmosphere at its upper end.

2.3.2.2. The Main Oven.

The combustion tube was mounted vertically in an oven to facilitate measurement at elevated temperature. No oven of the required dimensions was commercially available and one was, therefore, constructed as follows. A metal cabinet 22 cm x 22 cm x 100 cm was lined with a 5 cm. layer of glass fibre. A Perkin Elmer 1 KW heating element was mounted onto an asbestos board and fixed to the rear wall of the case, 18" above the base. A Perkin Elmer turbo fan was mounted near to the bottom of the rear case wall and was shaft driven from an externally mounted electric 240v A.C. fractional horsepower motor.

By means of suitably formed aluminium sheeting air was forced over the heating element by the turbo-fan and circulated rapidly around the oven. The temperature was controlled to within $\pm 0.5^{\circ}\text{C}$ by connecting the heating element via a platinum resistance thermometer to a Sirect, Mark 2, proportional temperature controller. It was found that a temperature gradient of only 1°C at 100°C

Plate 2.2



The Combustion Tube

could be achieved over the whole length of the oven in this way.

Since this oven case was the largest available it was necessary to cut a hole in the top and mount the combustion tube with ca. 30 cm., of its upper end protruding. This exposed length of tube was heated independently by the following method. The tube was wrapped in asbestos tape and a heating coil of nichrome wire was wound over the asbestos. The voltage across the heating coil and, hence, the temperature in the upper part of the tube, was regulated by means of a Veriac transformer.

By use of this heating arrangement it was possible to obtain a temperature distribution of better than $\pm 1^{\circ}\text{C}$ inside the whole length of the combustion tube for a main oven temperature of 100°C .

2.3.2.3. The Auxiliary Ovens.

Two auxiliary ovens (Holbeck-Leba Junior), were mounted adjacent to the main oven (see plate 21). These ovens were thermostatically controlled, but were found to have a temperature variation of $\pm 2^{\circ}\text{C}$ at 50°C over their heating cycle. This was reduced to less than $\pm 1^{\circ}\text{C}$ at 50°C by the incorporation of motor driven fans. This measure was considered necessary, since the temperatures in these ovens were used to regulate the fuel/air composition on the basis of the partial pressure of the liquid fuel.

Connections between the main and auxiliary ovens were obtained using specially made open ended Dewar tubes.

These ensured that no cold-spots existed along inter-connecting fuel/air lines.

2.3.2.4. Fuel/air Mixtures Preparation.

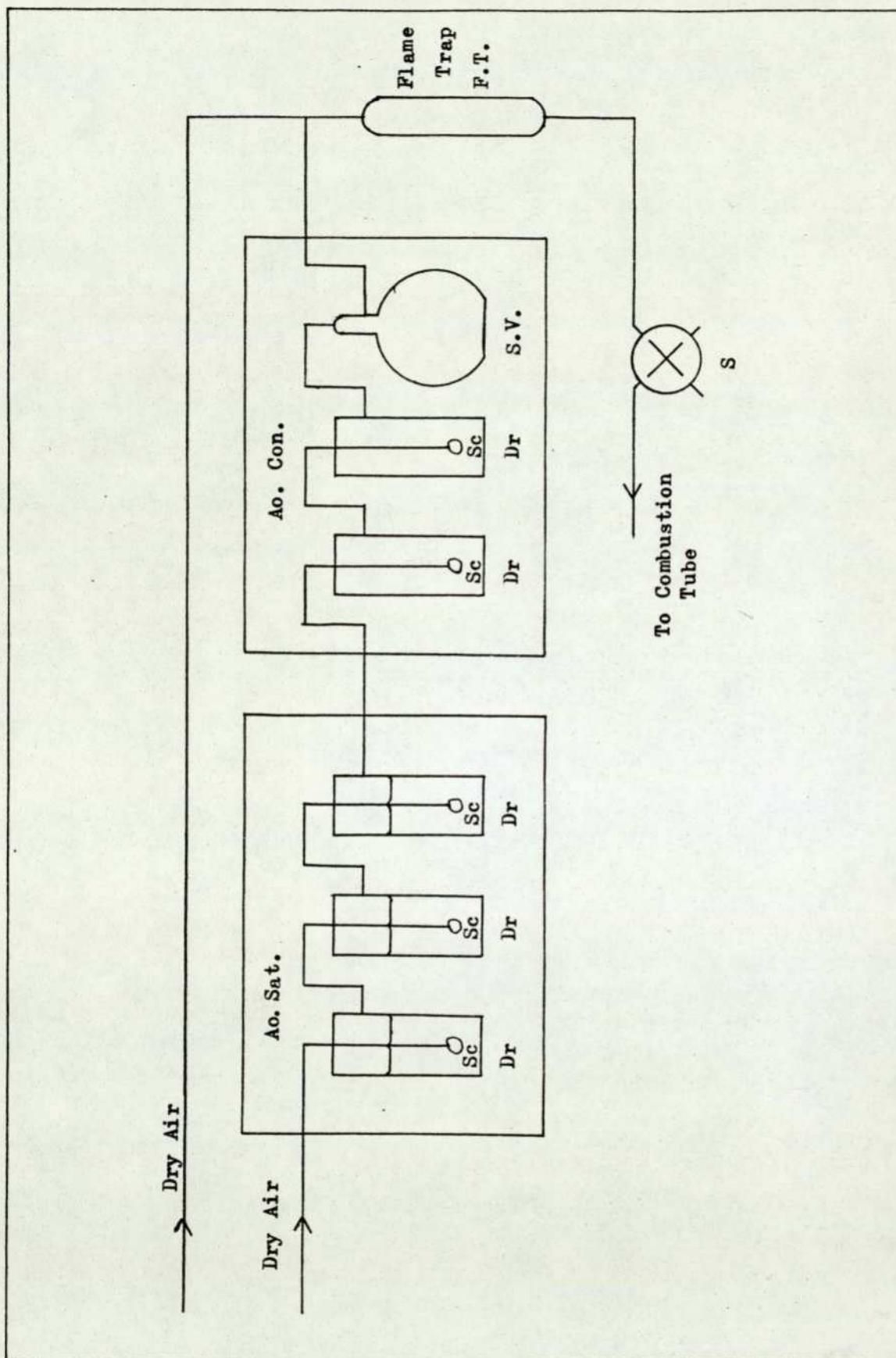
The apparatus for preparing fuel/air mixtures of known concentrations is shown schematically in figures 2.1. and 2.2. The preliminary experiments which resulted in this design have been described in Section 2.3.

Air taken from a pressurised cylinder, via a pressure regulator, was dried over type 4A Molecular Sieve and regulated by a needle valve and flow meter assembly. The air was then passed through the main oven, which acted as a preheater, and into one of the auxiliary ovens. Three 500 ml., Dreschel bottles, fitted with grade 3 porosity glass scinters, were mounted in the auxiliary oven. Each bottle was filled with liquid fuel and arranged so that the air passed through the liquid in each bottle in turn.

The fuel/air mixture obtained was then passed, via the main oven, to the second auxiliary oven in which two empty 500 ml., Dreschel bottles, again fitted with glass scinters, and a 500 ml., spherical flask were mounted (plate 2.3.). The temperature in this oven was always lower than that maintained in the first oven so that the fuel/air mixture would enter the second oven with a fuel vapour pressure in excess of that possible at the lower temperature. Consequently, fuel would condense out from the mixture to leave the air saturated with fuel vapour at the temperature

Figure 2.2

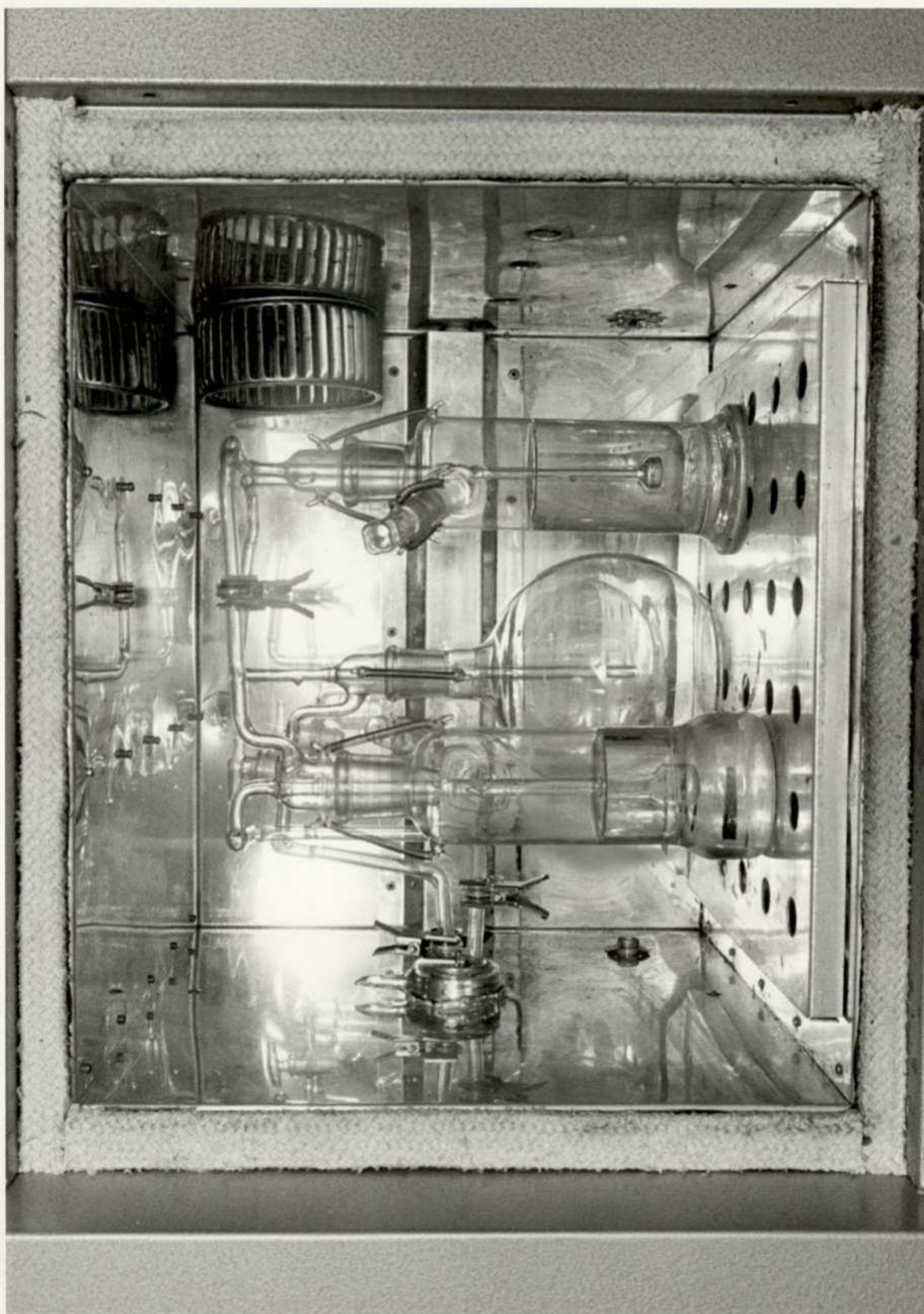
Fuel/Air Mixture Preparation Apparatus



Legend for Figure 2.2

Ao. Sat	-	auxiliary oven containing saturaters
Ao. Con	-	auxiliary oven containg condensers
Dr	-	Dreschel bottles
Sc.	-	No. 3 porosity glass scinters
F.T.	-	flame trap and mixing vessel
S	-	6-way sample valve
S.V.	-	500 ml. spherical vessel

Plate 2.3



Fuel/Air Mixture Preparation Apparatus

of the second auxiliary oven. Only in this way was it possible to obtain fully saturated air whilst avoiding supersaturation.

The fuel/air mixture was then passed back through the main oven, the temperature of which was in excess of both auxiliary ovens and through a mixing chamber consisting of a Pyrex glass tube 150 mm. x 25 mm., packed with 3mm., glass beads. This chamber also acted as a flame trap. The resulting fuel/air mixture was finally passed through a Perkin-Elmer Six Port Valve and into the combustion chamber.

This system was modified slightly for fuels with a lower flammability temperature^a of less than 40°C. For such fuels the second auxiliary oven was set at 40°C, (the lowest stable temperature obtainable) and the resultant fuel/air mixture was diluted with dry, preheated air prior to entering the mixing chamber. The diluent air was regulated by a needle valve and flow meter assembly.

2.3.2.5. The Fuel/Air Mixture Analysis System

The fuel concentration in any fuel/air mixture was determined chromatographically. The system which is shown schematically in Figure 2.1., consisted of a Servomex Micro-Katharometer type MK. 158, (K), a Perkin-Elmer 6-port valve, (S), a liquid injection port, (I), and

a. The lower flammability temperature is defined as the temperature at which the saturation vapour pressure of the fuel is able to form a lower limit mixture at one atmosphere pressure.

a stainless steel chromatographic column 2 metres long and 3mm., outside diameter. The liquid phase used was silicon grease adsorbed onto a stationary phase of Chromasorb 'P', 100 mesh in the ratio 1:9 w/w.

The column material was prepared by dissolving the required weight of silicon grease in methanol and adding the required amount of Chromasorb 'P' to the solution with thorough mixing. The methanol was removed under partial vacuum on a rotary evaporator. It was found necessary to resuspend the resulting solid in methanol and remove the methanol on the rotary evaporator several times before a material of uniform size was obtained.

The carrier gas employed was helium, which was taken from cylinders and dried over type 4A Molecular Sieve contained in a high pressure drying tube. The helium was passed at a pressure of 70 p.s.i.g. , to a Brooks Flow Controller, (see Figure 1 (D) and (F.C.) respectively). The volumetric flow rate of the gas was measured on a Series 1100 Rotameter, (R), calibrated against a bubble flow meter. The helium flow was maintained accurately at 100 mls./min. To protect the katharometer device the gas was filtered through a scintered stainless steel filter.

The katharometer was connected to a Taylor Servomex supply/attenuator circuit, which had a facility for supplying a constant voltage to the katharometer, balancing the wheatstone bridge circuit in the detector and attenuating the signal from the detector. The detector output was recorded on an E.M.I. Series 0 ⁺ 1 mV recorder.

Calibration of the katharometer response to a particular fuel was carried out by direct injection of liquid samples. To facilitate rapid evaporation of injected samples the injection block was heated separately to ca. 200°C with commercial heating tape. When injected samples of less than 1 µl were required the fuel was diluted in a suitable solvent, such as n-pentane, and injected in a corresponding volume.

The Perkin-Elmer 6-port valve was fitted with a 5 ml., sample tube. This tube was continuously flushed with fuel/air mixture, except when a sample was required for analysis. By operating the valve the helium was used to flush a 5 ml., sample of fuel/air mixture into the analysis system. This valve was protected from damage by solid by solid particles by scintered stainless steel filters placed in both the helium and fuel/air inlet connectors.

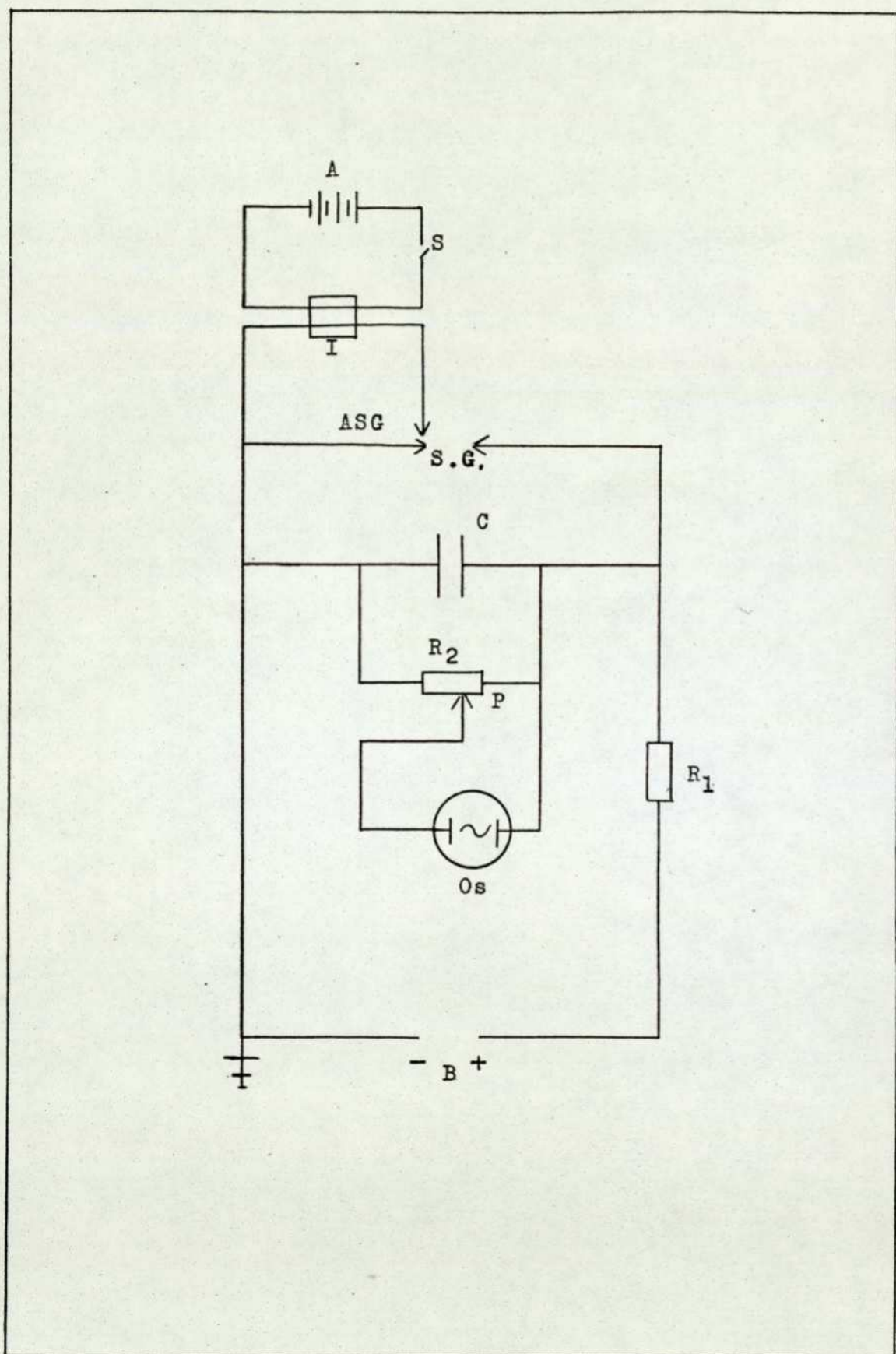
2.3.2.6. The Capacitor Discharge Circuit.

The electrical circuit employed to obtain a single spark of known energy is shown in Figure 2.3.

The capacitor, C, was either a single capacitor or several capacitors connected in series which produced the total capacitance required. The individual capacitors were mounted on insulating boards such that each board contained a specific total capacitance. The boards were mounted in a rack such that any board could be connected in circuit by a simple push connector.

The power supply, B, was a Brandenburg Stabilised

Figure 2.3.

Capacitor Discharge Circuit.

Legend for Figure 2.3

A - 12 volt accumulator.

S - switch

I - inductance coil.

ASG - auxiliary spark gap.

S.G.- main spark gap.

C - capacitor.

R_1 - 30 K Ω 10 w resistor.

P - potential divider.

Os - oscilloscope.

B - H.V. power supply.

high voltage unit which could supply a continuously variable voltage from 2.5 to 30 kV. The resistor, R, was used to slow down the rate of charge of the capacitor, C. This prevented the passage of a succession of sparks when the capacitor was discharged across the spark gaps, using the auxiliary ignition circuit.

The auxiliary ignition circuit comprising the accumulator, A, switch, S, and induction coil, I, was employed to produce a low energy discharge across the auxiliary spark gap, A.S.G. This discharge was induced by switching S on and off once, rapidly, this caused a momentary current to flow through the primary windings of the induction coil, thus inducing a high voltage in the secondary windings of the coil. This high voltage caused a discharge across the auxiliary spark gap which was maintained at 0.25 mm. The auxiliary spark did not cause ignition of any gas mixture. This was proven by experiment and could be predicted because:

- (a) the energy of a discharge is given by $\frac{1}{2}CV^2$ and since the auxiliary ignition circuit had virtually no capacitance the auxiliary spark was therefore of very low energy - certainly below the minimum energy of the fuel/air mixture.
- (b) the auxiliary spark gap was chosen so that it was less than the quenching distance for any fuel/air mixture, thereby preventing ignition occurring.

The object of this small spark was to provide electrically conductive species which reduced the spontaneous breakdown voltage of the main spark gap. This technique enabled discharges to be obtained across the main electrodes at voltages which would otherwise have necessitated closing the main spark gap to distances within the quenching distances of the fuel/air mixtures employed.

2.3.2.7. The Electrodes.

The geometry and construction of the electrodes is shown in Figure 2.4. and Plate 2.4. The main electrodes were machined from $\frac{3}{8}$ " diameter, 316 stainless steel rod. The extended tips of the electrodes were 0.5" long and 0.1" in diameter. One electrode was machined flat with a polished face whilst the other was pointed at an angle of 45° .

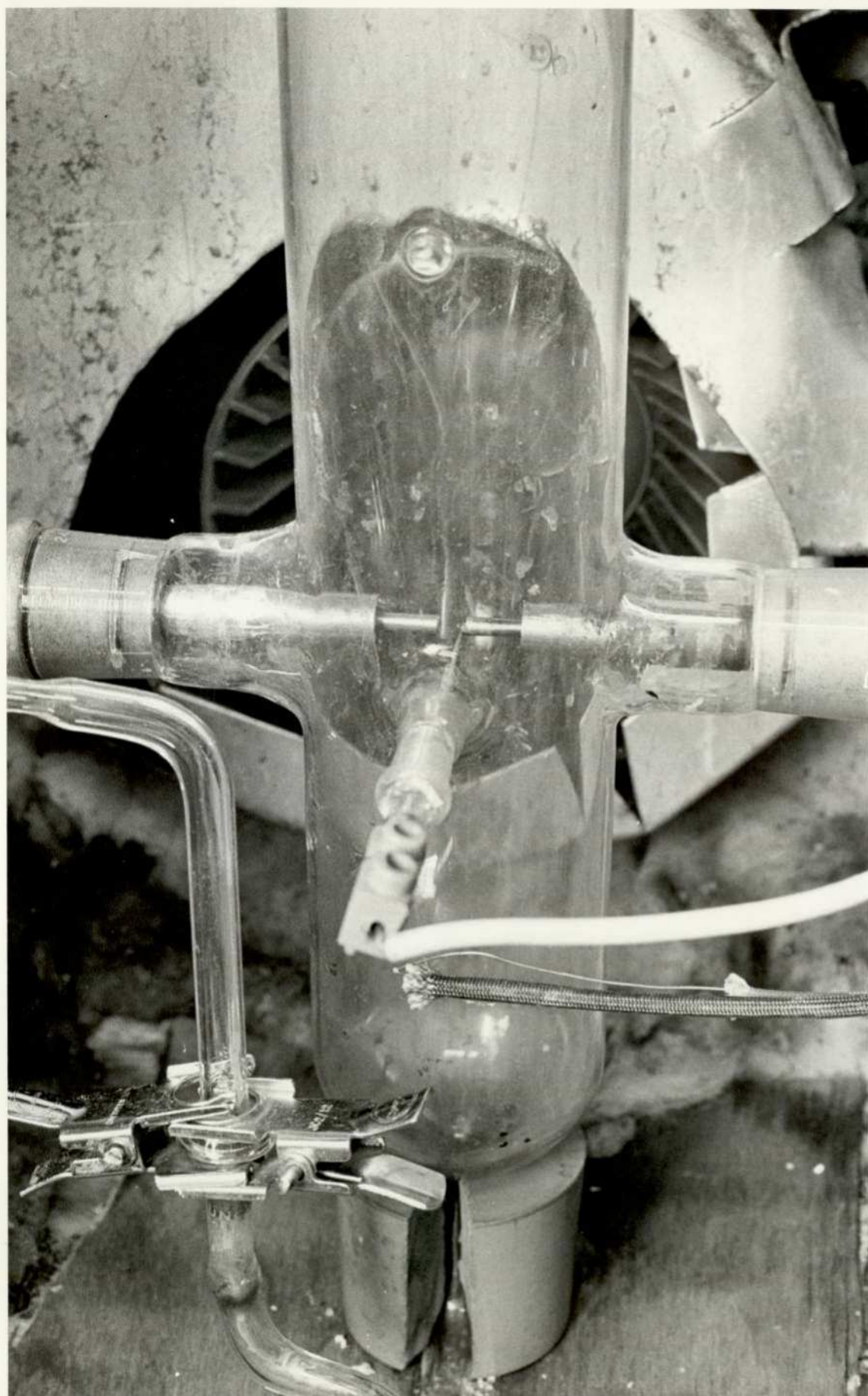
The bodies of the electrodes were machined such that they were an interference fit onto the stems of the two micrometer heads (M). The insulating cones I, were manufactured from P.T.F.E., and were machined to be an interference fit onto the micrometer barrels B. Grooves were machined into the P.T.F.E. to accept viton 'O' rings. This was found to be necessary due to the high coefficient of thermal expansion of the P.T.F.E. which either caused the electrodes to 'creep' apart as they were heated or shattered the retaining B. 19 glass sockets. The viton rings also ensured a gas-tight seal.

The auxiliary electrodes A, consisted of a

Legend for Figure 2.4

- E - main electrode
- I - P.T.F.E. insulating material shaped to
fit B.19 sockets
- M - micrometer heads
- A - auxiliary electrodes
- S - B.12 Pyrex ground glass cone welded to
auxiliary electrode
- Vi - Viton 'O' rings
- B - micrometer barrel
- C - electrical connections

Plate 2.4



Electrode Configuration

tungston rod insulated along the centre portion by a glass sheath. This electrode was glass welded into a B. 10 Pyrex ground glass cone, S.

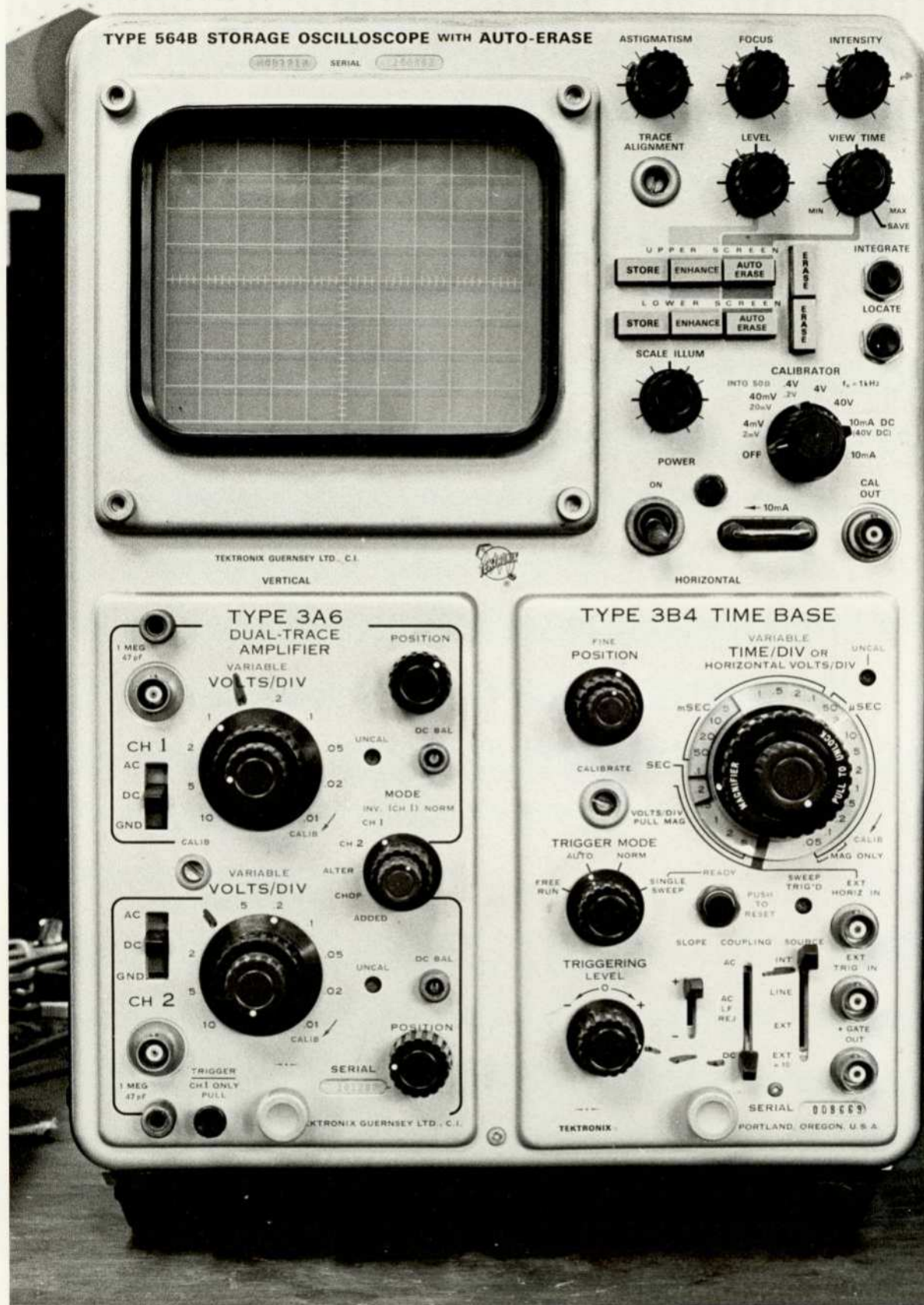
The respective electrode separations were selected by bringing the auxiliary and earthed main electrodes into contact and then separating them by ca. 0.25 mm., by adjustment of the micrometer head. The non-earthed main electrode was then brought into contact with the earthed electrode and adjusted back to give the required main electrode gap.

Electrical connections were made through the screw connectors, C, and were ensured to be screwed tight to provide good electrical contact. Provision was made in the wall of the main oven for a P.T.F.E. insulating collar to extend around the non-earthed electrode, (see Figure 2.4). Heat loss from the oven was minimised by a glass fibre plug which was inserted into the collar.

2.3.2.8. The Oscilloscope.

This instrument was a Tektronix 564B storage oscilloscope incorporating a type 3A6 dual trace amplifier (see Plate 2.5). The oscilloscope was used to measure the voltage across the capacitor, C, (see Figure 2.3) via a $10^3:1$ attenuator. The voltage was displayed as a simple vertical movement of the oscilloscope trace. The passage of a spark was also recorded by the oscilloscope, the display showing a very rapid decrease in the voltage across the capacitor followed by a slow increase up to the original

Plate 2.5



The Oscilloscope

voltage. This is illustrated in Figure 2.5.

If the oscilloscope was taken to the limits of its resolving power then a display as shown in Plate 2.6 was obtained. This type of display has been discussed previously in Chapter 1, under 'Source of Ignition', it will suffice here to say that the voltage drop experienced by the capacitor is clearly defined.

The outputs from several 40 s.w.g. chromel-alumel thermocouples located in the combustion tube were displayed on channel 2. These thermocouples had a common cold junction and were connected in parallel, hence, their combined outputs were additive.

The output from the thermocouples was amplified on a separate D.C. amplifier and then fed into the oscilloscope. The passage of a flame past each thermocouple caused a vertical displacement on the oscilloscope, as shown in Plates 2.7 (a) and (b).

By selection of a suitable 'triggering' arrangement (i.e. a suitable means of causing the oscilloscope spot to sweep across the screen), on the 3B4 time base, a discharge between the main electrodes produced a signal which was fed into channel 1 of the 3A6 amplifier. This signal was not recorded but triggered channel 2 to begin its recording sweep. In this way a record of the flame behaviour was achieved from the moment of the spark discharge and not from the time the flame reached the first thermocouple as would otherwise be the case. .

Figure 2.5
Typical Voltage/Time Oscillographs for
Capacitor Discharge

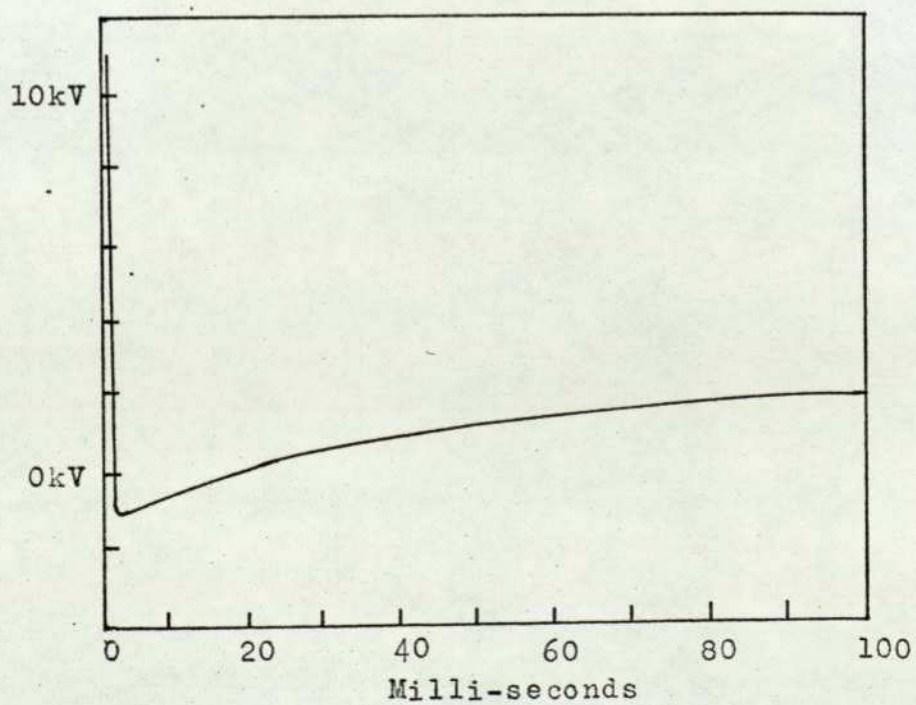
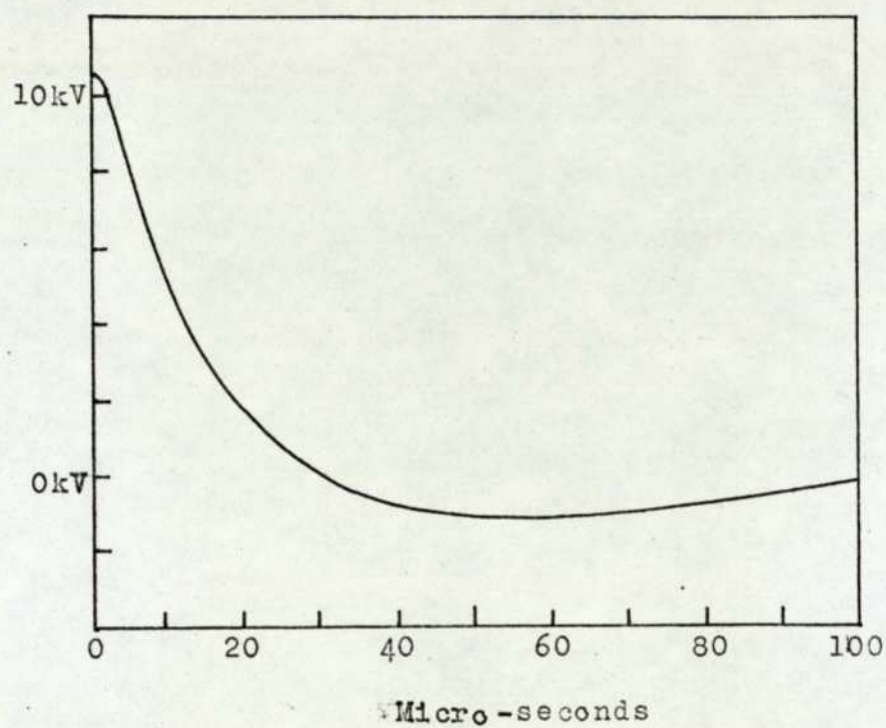
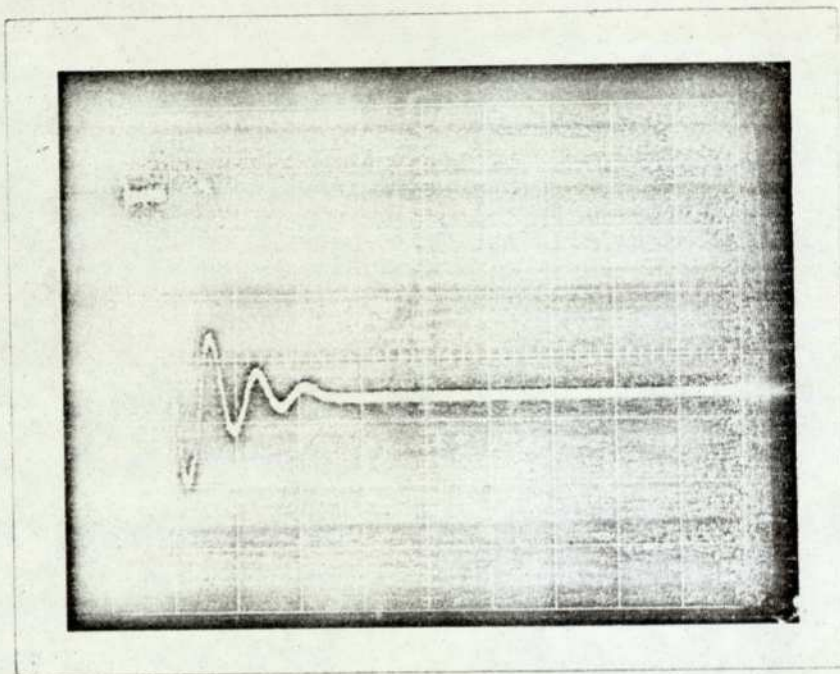


Plate 2.6.

Voltage/Time Record of the Discharge
of an 0.2 μ F Capacitor Charged to 7 KV.

2 volts/
division

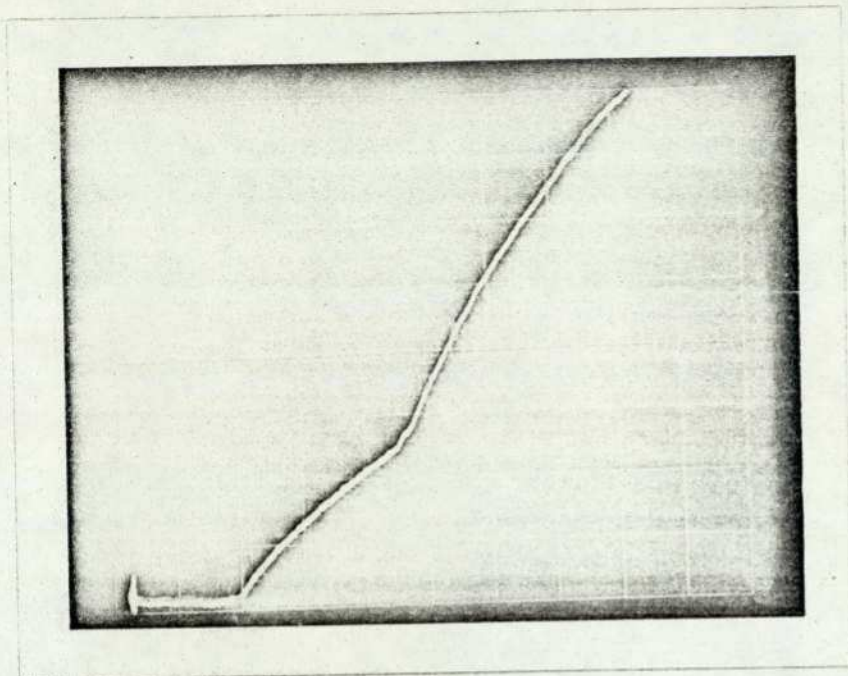


10 μ s/division

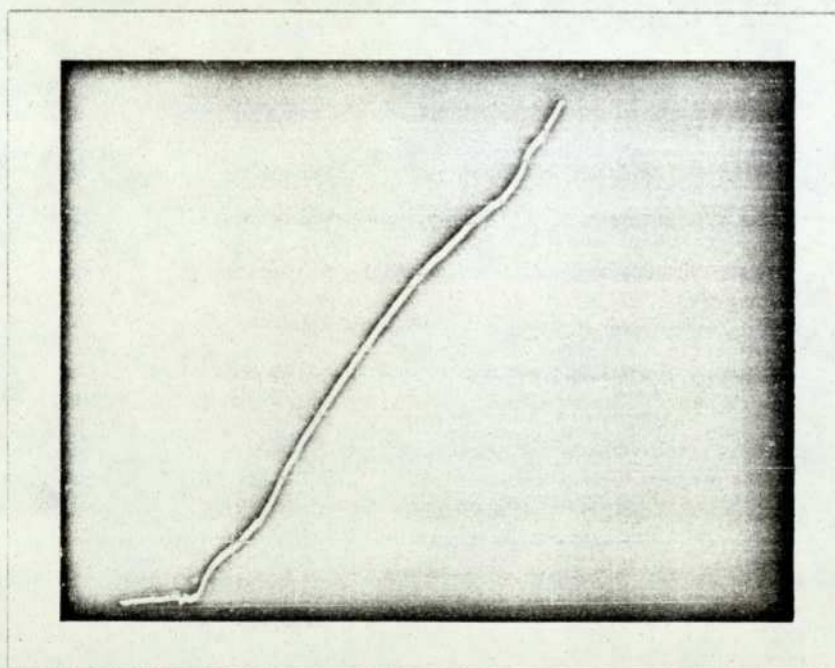
Voltage attenuation $10^3:1$

Plate 2.7

Oscillograph of Thermocouple Outputs



(a)



(b)

2.4. EXPERIMENTAL PROCEDURE

The Dreschel bottles in the auxiliary oven (A_0) were filled with the fuel under investigation. The main oven (M_0) was heated to a constant temperature of $100 \pm 1^\circ\text{C}$ the temperatures required in the auxiliary ovens were selected and the system was allowed to stabilise at these temperatures.

Helium was supplied to the katharometer unit (K) and allowed sufficient time to purge the unit before electrical power was turned on.

All electrical equipment was allowed to attain its normal working temperature.

The katharometer was left until no baseline drift was observed on the recorder unit and was then calibrated by injection of known volume samples of the fuel under investigation.

The main electrodes were set to the required gap and the smallest capacitor, 25 pF, was connected into the discharge circuit C, (see Figure 2.3). The high voltage probe (P) was connected across the terminals of the capacitor and the output from the probe connected to the oscilloscope (O_s).

Air was then passed through the system, as indicated in Figure 2.1, and samples were taken via the six-port valve, of the fuel/air mixture produced. These were analysed and the fuel concentration calculated.

Sufficient fuel/air mixture was then passed through the combustion tube to purge the tube six times.

The capacitor in the main discharge circuit was charged to the minimum breakdown voltage from the Brandenburg power supply. The auxiliary discharge circuit was then rapidly switched 'on' and 'off' causing a small spark to pass across the auxiliary electrode gap.

A discharge across the main electrodes occurred and the event was recorded. The passage or not of a flame up the combustion tube was also recorded. If ignition of the gas did not occur the voltage across the main capacitor was increased by 500 volts and the process repeated. The voltage across the main capacitor was then increased in units of 500 volts until the maximum breakdown voltage was achieved across the main electrode or until the passage of a flame was recorded.

If no flame occurred before the maximum breakdown voltage was reached the voltage supply to the capacitor was removed. The capacitor was then discharged to earth via a 9mm. stainless steel rod with an insulating handle, and replaced by a unit of higher value. This procedure was repeated until the passage of a flame was recorded.

A record of the time intervals at which the flame reached each thermocouple in the combustion tube was made. The mean flame speed was calculated from this data. The voltage and capacitance of the main capacitor at the time of ignition were also recorded, this enabled the minimum ignition energy for that mixture to be calculated.

The combustion tube was then purged with fuel/air mixture and the entire procedure was repeated until a

consistent value of the minimum ignition energy was obtained for that mixture.

The procedure was then repeated for various main electrode gaps to ensure that the minimum ignition energy was determined under non-quenching conditions, (Chapter 1, Section 1.4.4.2).

The fuel/air composition was then altered by adjustment of the auxiliary oven temperature or by dilution of the fuel/air mixture with air, as described previously. The above procedure was again repeated. By this method it was possible to construct diagrams of the variation of minimum ignition energy with fuel/air composition.

These results are given in Chapter 3.

2.5. THE STATIC SYSTEM.

2.5.1. General

In many details the apparatus for investigating static fuel/air mixtures was similar to that previously described for the flow system in Section 2.3.

For convenience only the differences between the two systems will be described here.

A schematic diagram of the 'static' apparatus is given in Figure 2.6.

All interconnecting tubes were $\frac{1}{4}$ " outside diameter 316 stainless steel and connections were made using either Simplifix, Swagelok or Drallim tube couplings. All the regulating valves were supplied by Hope International Ltd. These valves were manufactured from stainless steel and both coarse and fine adjustment types were used.

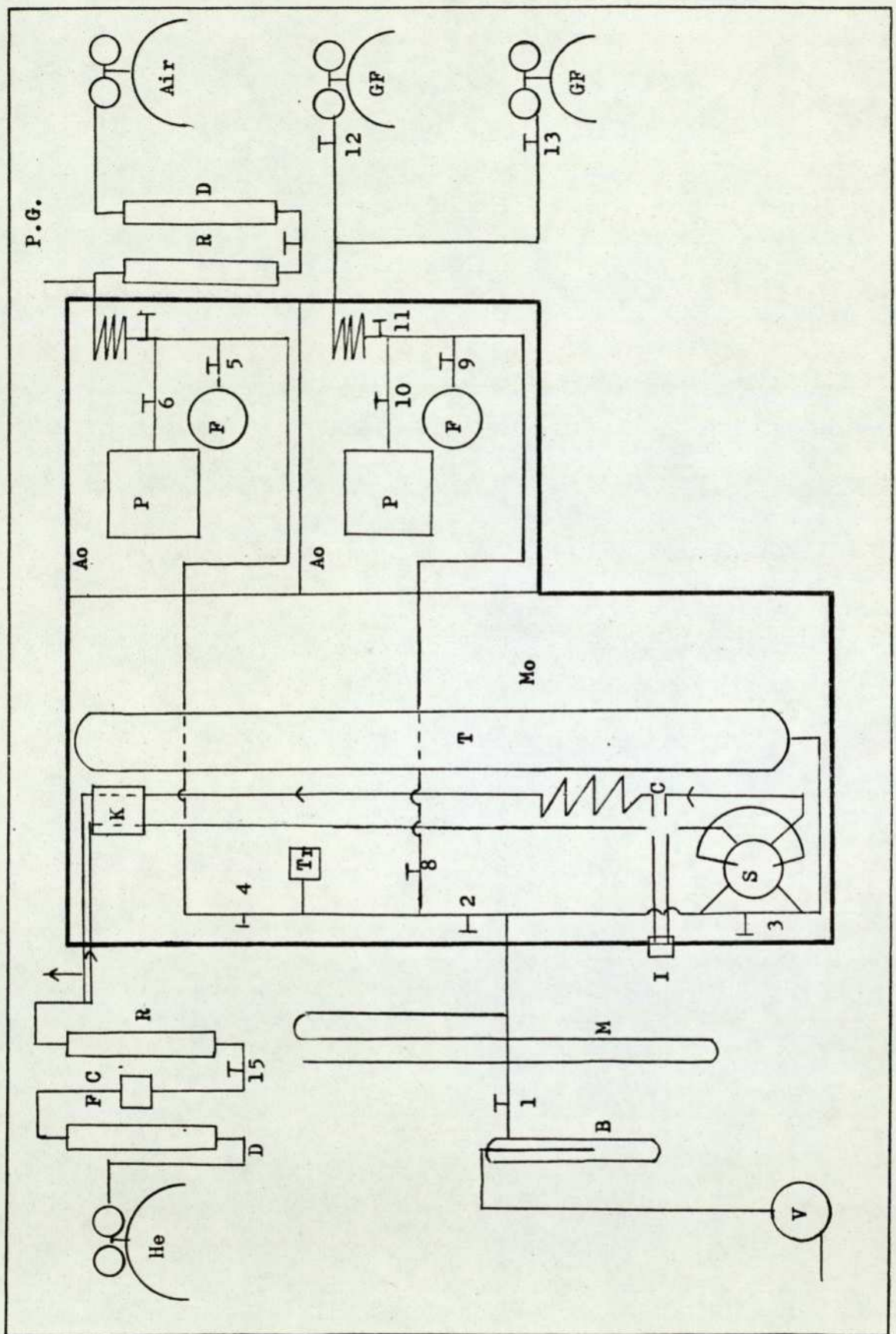
The apparatus consisted of an Edwards High Vacuum type EDM2 pump connected to a combustion tube as previously described but with the addition of a glass top joined to the combustion tube by a ground glass flange. This enabled the combustion tube to be evacuated. Also connected to the vacuum pump were two stainless steel premix vessels of 4 litres capacity, each of which was mounted in an auxiliary oven.

Fuel/air mixtures were prepared in these premix vessels at several atmospheres pressure and then transferred to the combustion tube for investigation.

Pressure measurements in the apparatus were made using a Bell and Howell type 4-366 pressure transducer, which

Figure 2.6

Schematic Diagram of the Static System



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Legend for Figure 2.6

V	-	vacuum pump
B	-	cold trap
M	-	mercury manometer
I	-	injection port
S	-	six-port sample valve
C	-	chromatography column
K	-	micro-katharometer
Tr	-	pressure transducer
D	-	drying tube
F.C.	-	Brooks flow controller
R	-	rotameter flowmeter
Mo	-	main oven
Ao	-	auxiliary ovens
T	-	combustion tube
P	-	premix vessel
F	-	liquid fuel reservoir
G.F.	-	gaseous fuel cylinders
P.G.	-	Budenberg pressure gauge

gave a 0-40 mV output over a 0-50 p.s.i. pressure range. This unit was calibrated by a mercury in glass manometer, M, for pressures up to atmospheric and by a 0-30 p.s.i. Brandenburg pressure guage (P.G.). The output from the transducer was measured on a Croyden Precision Instrument Ltd., type P.3. Potentiometer and was found to be linear.

2.5.2. Fuel/Air Mixture Preparation.

The desired fuel/air mixtures were prepared by the method of partial pressures in stainless steel premix vessels mounted in the auxiliary ovens (Plate 2.8) which were maintained at 80°C to prevent any fuel condensation. Each vessel was fitted with internal paddles and a magnet mounted on a spindle, see Figure 2.7.

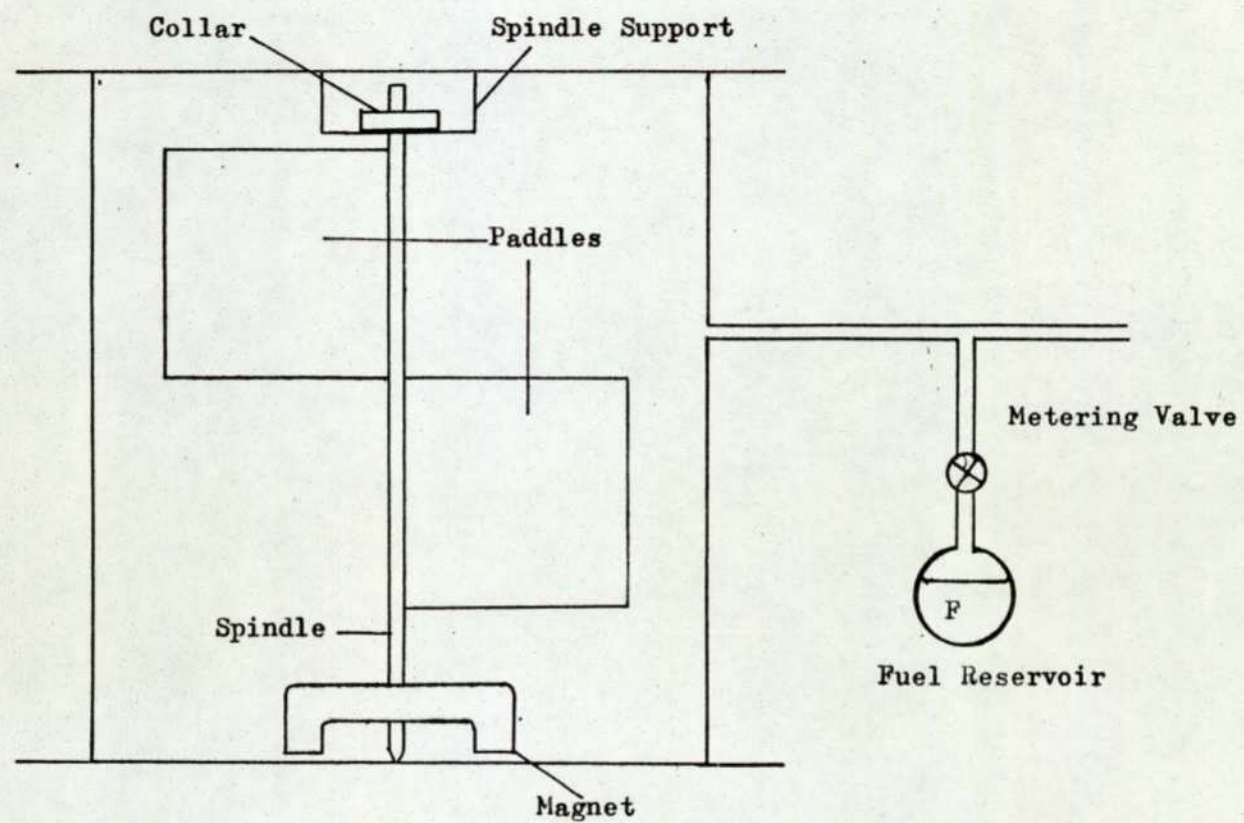
It was intended to place an electric motor with a second magnet mounted on the output shaft beneath the premix vessel and by magnetic induction rotate the paddles to ensure homogenous gas mixtures. Unfortunately, in practice no motor could be found which would operate under these high temperature conditions. It was found, however, by analysis on the on-line G.L.C. system, that for n-butane/air mixtures identical results were obtained for several samples taken from one gaseous mixture which had been allowed to equilibrate for 15 minutes.

The procedure of allowing gas mixtures to stand for at least 15 minutes was therefore adopted.

The premix vessels were thoroughly degreased by washing with tri-chlorethylene prior to final assembly.

Figure 2.7

Details of Premix Vessel



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The required partial pressure of fuel was introduced into the premix vessel by evaporation from a fuel reservoir, F, which was connected to the premix vessel via a Hoke micro-adjustable valve and a Youngs 'O' ring joint.

2.6. EXPERIMENTAL PROCEDURE.

2.6.1. Fuel/Air Mixture Manufacture.

Liquid fuels were placed in the reservoir (Plate 2.8) and degassed by repeatedly freezing and thawing under vacuum to remove all dissolved air. The reservoir was then allowed to achieve the temperature of the auxiliary oven.

The premix vessel was evacuated and a measured partial pressure of fuel vapour was introduced via a micro-valve which gave fine control. Dry air was then introduced into the premix vessel until the pressure was achieved which gave the required fuel/air ratio. This mixture was allowed to equilibrate for 15 minutes.

The combustion tube was then evacuated and subsequently filled with the fuel/air mixture. The glass cap was removed from the combustion tube and the minimum ignition energy was determined, as described under the flow system.

If a gaseous fuel was used it was introduced into the premix vessel up to the required pressure, direct from the cylinder. Multicomponent mixtures were prepared by adding each component successively except when both components were liquids. In this case a mixture of the two liquids was manufactured in the ratio which would give the required composition of the vapour.

Plate 2.8High Pressure Fuel/Air Mixture and Liquid Fuel Reservoirs

The apparatus employed was the standard Abel Flash
Point Apparatus¹⁰ shown schematically in Figure 1.1.

In this apparatus a measured volume of fuel is placed in the container, which is surrounded by a heating jacket, HJ. A stirrer and thermometer are inserted into the fuel via the fuel container lid on which is mounted a sliding plate to give access to the vapour space above the fuel. When the sliding plate is withdrawn the test flame is caused to dip into the fuel vapour space.

The operational procedure is fully described in the literature¹¹ and consists of heating the fuel at a specific rate and introducing the test flame into the vapour space at specific temperature intervals.

Samples prepared for flash point measurements were prepared in sealed, capped bottles to prevent any evaporation of volatile components and were analysed on a Perkin Elmer Automatic G.L.C. apparatus. Cooling of the test samples was achieved, where necessary, by either ice/water or solid carbon dioxide/acetone mixtures depending upon the temperature required.

SECTION 3

RESULTS AND DISCUSSION

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3.1 IGNITION OF HYDROCARBON/AIR MIXTURES

It is well known that the spontaneous combustion of a hydrocarbon/air mixture can exhibit several phenomena including cool flames, two-stage ignition (ignition preceded by a cool flame) and single-stage ignition. The phenomena observed will depend upon the structure of the hydrocarbon, the nature of the reactor, the stoichiometry and the pressure and temperature to which the mixture is subjected. At sufficiently high pressure (1 Atm.) and temperature ca. 600°C ignition will occur very rapidly for all flammable mixtures without the formation of any cool flames since sufficient energy is available for initial pyrolysis of the fuel to occur, thus giving rise to high radical concentrations and high rates of reaction. At lower temperatures i.e. 200 - 500°C, the available energy is only sufficient to break the weaker carbon-hydrogen bonds by oxygen attack and results in relatively low radical concentrations and low rates of reaction which lead to the formation of intermediate, oxygenated products. This mode of initiation is characterised by long delays before ignition occurs, cool flames and a high dependence of these phenomena on fuel structure.

An analogous situation to the effect of temperature on spontaneous ignition may be envisaged when ignition is induced by a localised source of energy. A very high energy source, such as a flame, will ignite any fuel/air mixture within the flammable range of that fuel and no significant difference between the lower limits of flammability of its isomers will be observed. ^{2,8,38} In contrast, a low energy source

of ignition ($< 2J$) might be expected to exhibit a dependence of the limit of flammability observed on molecular structure. A limited amount of evidence for such a dependence does exist,^{35,86} but the results, herein, present a systematic study of selected fuels from which a strong correlation is observed between the lower limit of flammability and molecular structure if the mechanism of oxidation is assumed to proceed via the alkylperoxy radical mechanism, as elucidated from studies of the spontaneous ignition of hydrocarbons.

3.2 VARIATION OF MINIMUM IGNITION ENERGY WITH FUEL CONCENTRATION

Figures 3.1 and 3.2 show the variation of minimum ignition energy with concentration at 100 °C for n-decane/air and 2,2,5-trimethylhexane/air mixtures respectively. These results were obtained under minimum quenching conditions and typical curves of minimum ignition energy versus electrode separation are shown in Figure 3.3. The errors involved in the results in Figures 3.1 and 3.2 are $\pm 5\%$ of the value stated for the concentration terms, this being the limits of accuracy of the analysis system, and $\pm 10\%$ of the value stated for the minimum ignition energy, this being the limit of resolution of the applied voltage.

The ignition diagrams show three distinct regions:

1. At lean fuel concentrations a very rapid fall in ignition energy occurs as the concentration of the fuel increases above that of the lower limit. Thus, for n-decane the ignition energy falls from >1 J to 1 mJ for a change in fuel concentration from 0.85 %v/v to 1.0 %v/v.

2. As the fuel concentration is increased further the ignition energy falls, to a minimum of 0.2 mJ at a concentration in excess of the stoichiometric ratio.

3. Thereafter the ignition energy increases until the upper limit of flammability is reached. (Unfortunately this portion of the curve could not be studied during the present work due to experimental limitations.)

To interpret these ignition diagrams it is necessary to consider the sequence of events following the passage of the spark. Several authors ^{2,81} have taken direct photographs

Figure 3.1.

Variation of Minimum Ignition Energy with

Fuel Concentration for n-Decane/Air Mixtures at 100 °C.

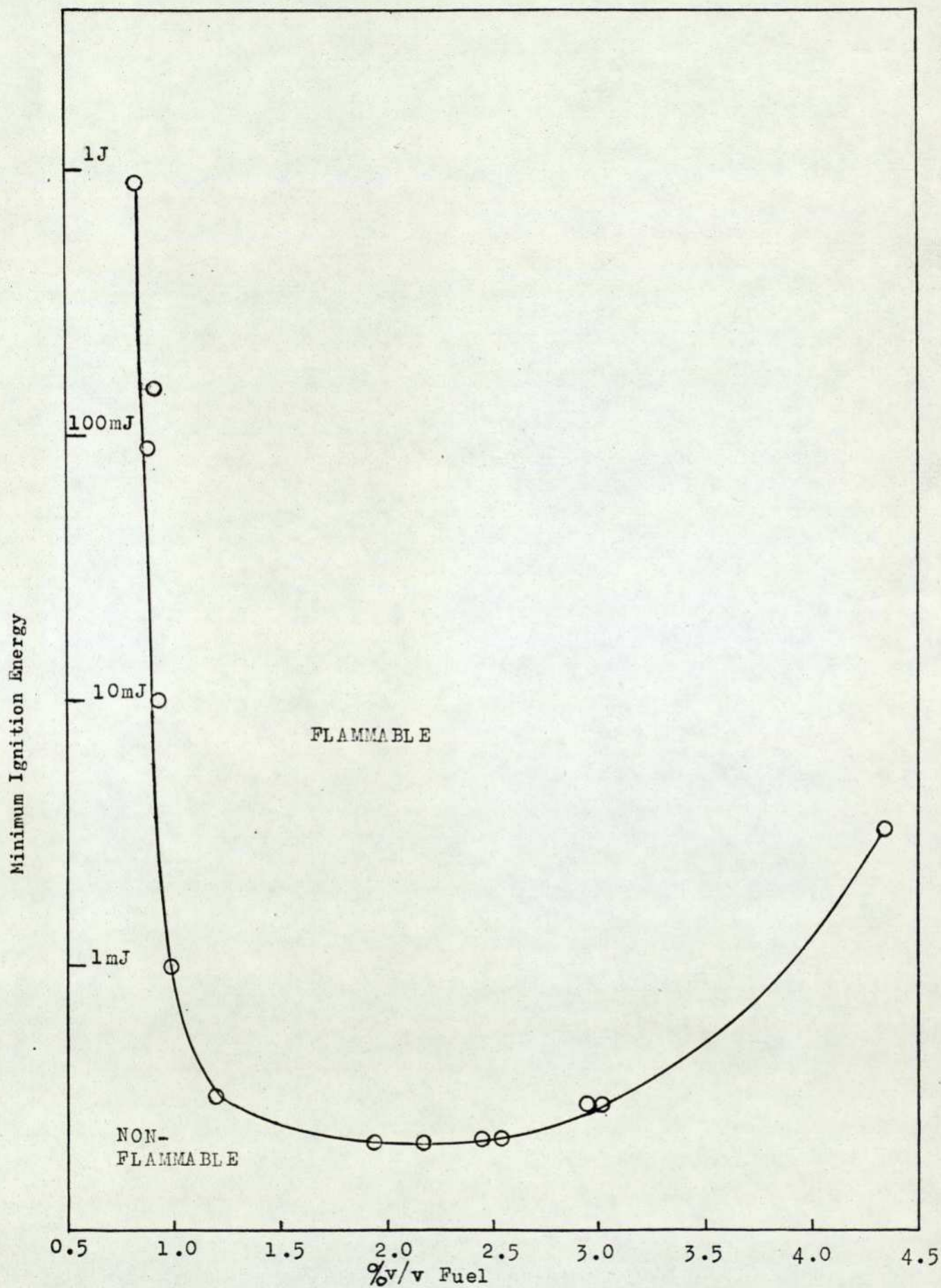


Figure 3.2.

Variation of Minimum Ignition Energy with Fuel/Air
Concentration for 2,2,5-Trimethylhexane /Air mixtures at 100°C.

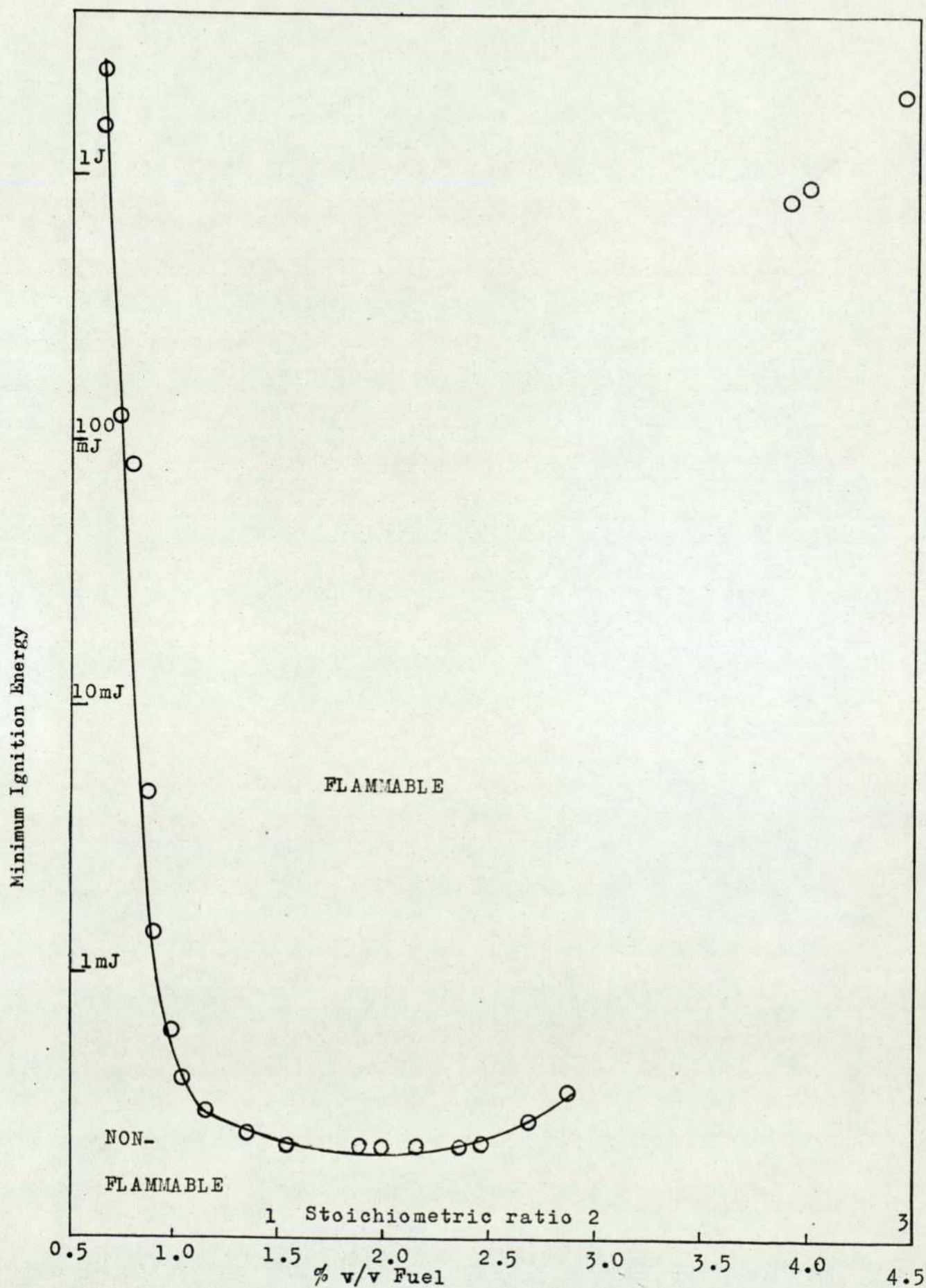
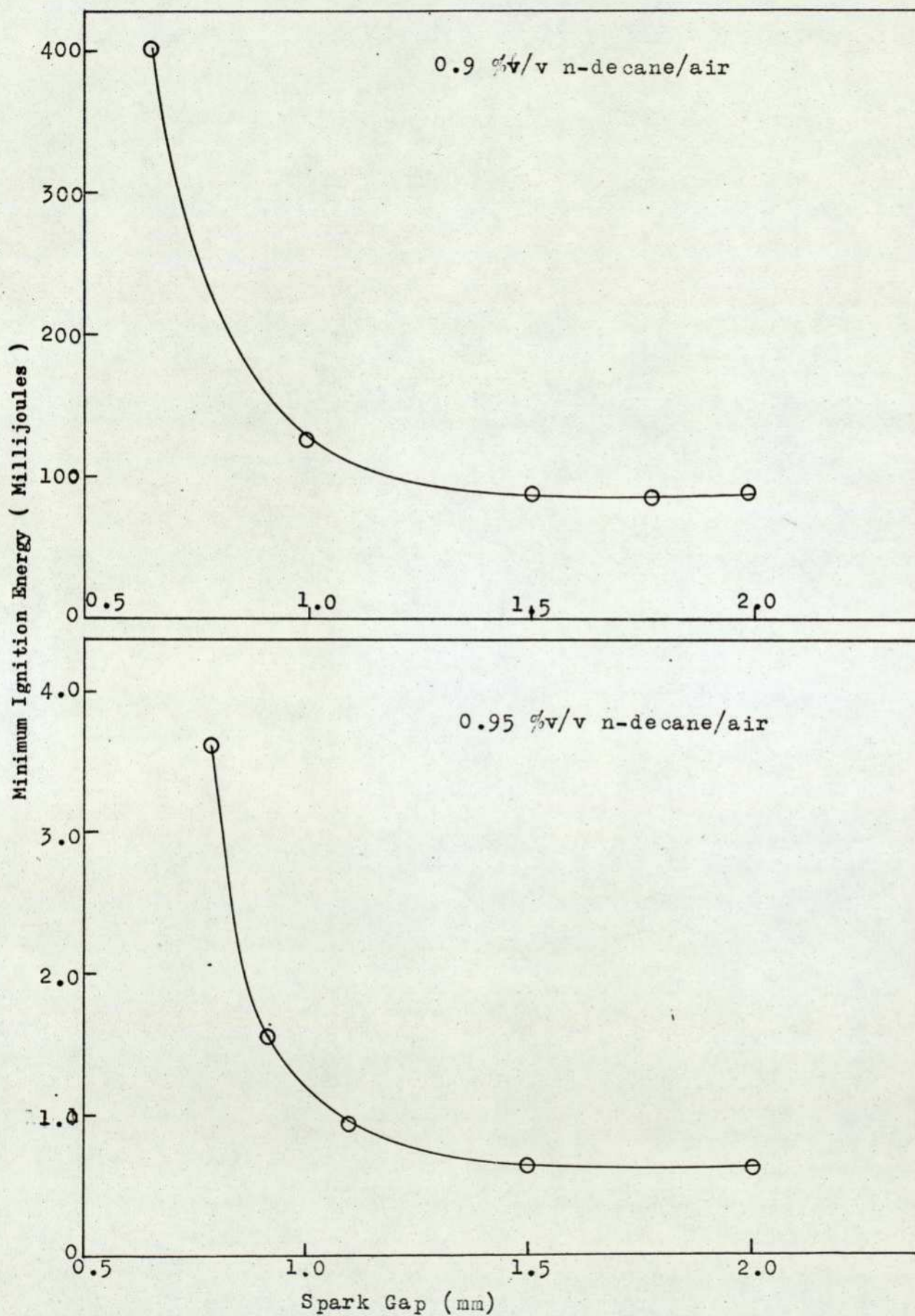


Figure 3.3

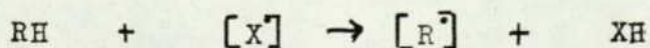
Typical Curves of Variation of Minimum Ignition
Energy with Spark Gap.



of this event and their conclusions are summarised below:

1. The passage of a spark occurs in ca. 10^{-7} secs. A cylindrical volume of reacting gas is created, centered around the spark path.^{82,83}
2. The initial reacting volume increases rapidly in size for ca. 100 μ secs., and assumes a spherical shape.
3. The rate of volume increase falls and a difference is observed between flames which will propagate and those which will be extinguished, in that the rate of reacting volume increase is lower for the latter.
4. After 1 m.sec., the rate of growth of a propagating flame falls to its' lowest level, but increases after 3 m.sec., and reaches the value expected for a steady state flame after 5 m.sec.
5. The non-propagating flames become turbulent after 1 m.sec., diffuse after 2-3 m.sec., and disappear after 5 m.sec.

These events were observed for both methane and propane (but not for hydrogen) and led the authors to conclude that after a period of approximately 1 m.sec., a critical flux of heat and radicals (F_c) must exist across the reaction boundary to permit a true propagation wave to develop. The minima observed in Figures 3.1 and 3.2 correspond to the minimum energy capable of achieving F_c for these fuels. The achievement of F_c no doubt corresponds to some critical rate of fuel consumption via the reaction:



and hence the critical rate of reaction will be given by:

$$R_c = k[RH]^a[X^\bullet]^b$$

As the lower limit of flammability is approached so $[RH]$ decreases; in order to maintain R_c the ignition energy must be raised to increase $[X^\bullet]$. The very large increase in ignition energy for small changes in RH at the lower limit shows that R_c is very sensitive to $[RH]$ i.e. $a > b$.

As the upper limit is approached so the ignition energy again increases. In fuel rich mixtures it is probable that radical-radical termination reactions are competing effectively against the propagation reaction, thus necessitating an increase in the ignition energy to maintain the supply of the radical species.

The ignition diagrams given in Figures 3.1 and 3.2² are known to be typical of many systems. Lewis and von Elbe obtained similar diagrams for several n-alkanes (Figure 1.6) and showed that only in the case of methane does the minimum occur at less than the stoichiometric ratio. This is believed to be due to the high diffusion coefficient of methane which allows fuel molecules to diffuse into the reaction zone, thereby increasing $[RH]$.

3.3 LOWER LIMITS OF FLAMMABILITY OF HYDROCARBON/AIR MIXTURES IGNITED BY SINGLE SPARKS OF 2 J. ENERGY

From the ignition diagrams for n-decane and 2,2,5-trimethylhexane it appeared that the lower limit of flammability could be determined using a spark of ca. 2 J., energy. The lower limits of flammability of a range of hydrocarbons were therefore determined using such a spark in the static vacuum apparatus previously described. These results obtained are shown in Table 3.1 and Figure 3.4 where they are compared with literature values obtained using either a flame or continuous D.C. arc as the source of ignition.

The lower limits of flammability determined for the n-alkanes are, within experimental error, the same as those reported in the literature,^{8,38} but the lower limits for the isomers were found to vary from that of the n-alkane and from the values quoted in the literature. The literature values of the lower limits of the branched isomers are either the same as the parent n-isomer or marginally lower, whereas in the present work the values for branched isomers were always found to be higher than the n-isomer except for 2,2,5-trimethylhexane which was lower than the literature value for n-nonane.

Evidence for structural dependancy has also³⁵ been obtained by Calcote et al., who determined the minimum ignition energy for a wide range flammable compounds at the stoichiometric ratio in air. Some of the results are given in Table 3.2 and show that in each case the branched isomer had a higher ignition energy than the n-isomer.

Table 3.1

Lower Limits of Flammability

Fuel	This Work				Literature	
	Determined at 100°C		Calculated at 25°C		Determined at 25°C	
	Flow	Static	Flow	Static	Flow ¹	Static ²
n-butane	—	1.7	—	1.8	1.8	1.9
n-pentane	—	—	—	—	1.4	1.5
2,2-dimethyl propane	—	1.6	—	1.68	1.4	1.4
n-hexane	—	1.25	—	1.32	1.31	1.2
2,2-dimethyl butane	—	1.35	—	1.43	1.2	1.2
hex-1-ene	—	1.25	—	1.32	—	—
2,2,5-tri- methylhexane	0.67	—	0.72	—	—	—
n-decane	0.9	0.85	0.96	0.89	0.78 ^e	0.8
n-nonane	—	—	—	—	0.87 ^e	—

Legend:

e: estimated

1: reference No. 38. Ignition source: continuous
D.C arc.

2: reference No. 8. Ignition source: small flame.

Figure 3.4.

Variation of Lower Limit of Flammability
with Carbon Number at 25°C.

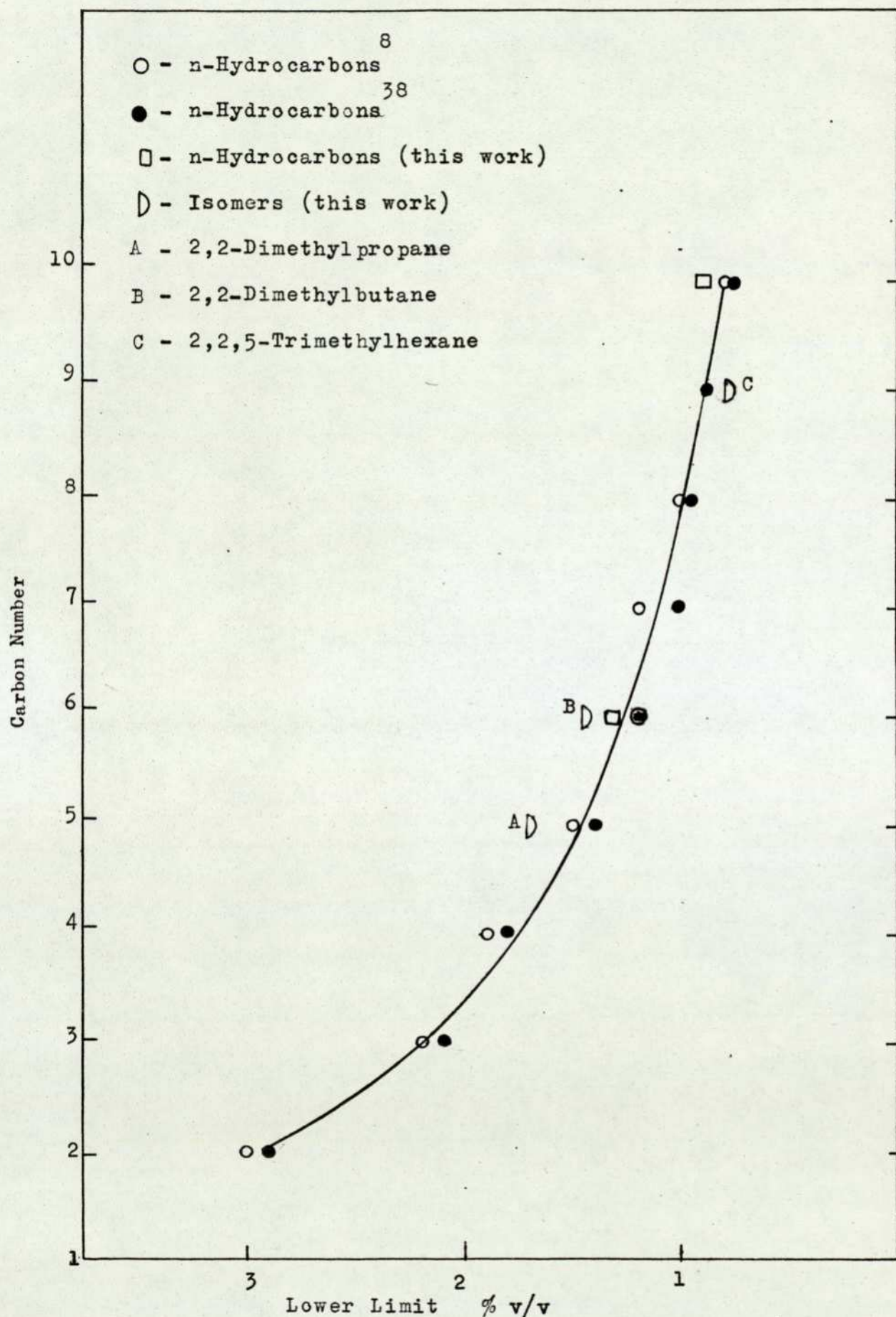


Table 3.2

Minimum Ignition Energy at Stoichiometric Ratio
For Some Hydrocarbons

Minimum Ignition Energy(10^{-4}J) at Stoichiometric Ratio			
Fuel	ref.35	Lower Limit	ref.34
propane	3.05	2.1	4.0
n-butane	4.0 ^e	1.9	7.2
iso-butane	5.2	1.8	—
n-pentane	5.1	1.4	—
iso-pentane	7.0	1.3	—
2,2-dimethyl propane	15.7	—	—
n-hexane	6.0 ^e	1.2	9.5
2,2-dimethyl butane	16.4	—	—
n-heptane	7.0	1.1	10.0
2,2,3-tri-methylbutane	10.0	—	—
2,2,4-tri-methylpentane	13.5	—	—

e = estimated value

Lewis and von Elbe suggest that the fuel concentration at the minimum of the ignition curve is determined by the diffusion coefficient of the fuel, thus this minima would be expected to be coincident for any group of isomers. It appears, therefore, that the ignition curves of isomers are coincident at their minima and at the lower limit for high energy ignition sources, but that between these two values (i.e. on the lean side of the minimum) each isomer has its own ignition curve and thus exhibits structural dependence (Figure 3.5). Since the majority of previous studies have been aimed at either determining the minimum ignition energy or the lower limit using high energy sources, it is hardly surprising that the structural dependence reported herein and by Calcote at stoichiometry has previously been overlooked.

Figure 3.5 clearly illustrates the dependence of the lower limit of flammability on structure for ignition sources of ca. 1 J. This dependence may be correlated with the molecular structure of the compound as shown in Figure 3.6. Thus, for example, it can be seen that the minimum ignition energy increases with increase in C number for any homologous series irrespective of the degree of branching of the carbon chain and with increase in the degree of branching at a given carbon atom for a series of isomers. Furthermore, substitution by a second methyl group has considerably more effect than the substitution by the first, as would be expected. Thus, for example, substitution of a hydrogen at the 2- position in n-pentane increases the

Figure 3.5

Variation of Minimum Ignition Energy with Concentration
for n-Pentane and 2,2-dimethylpropane

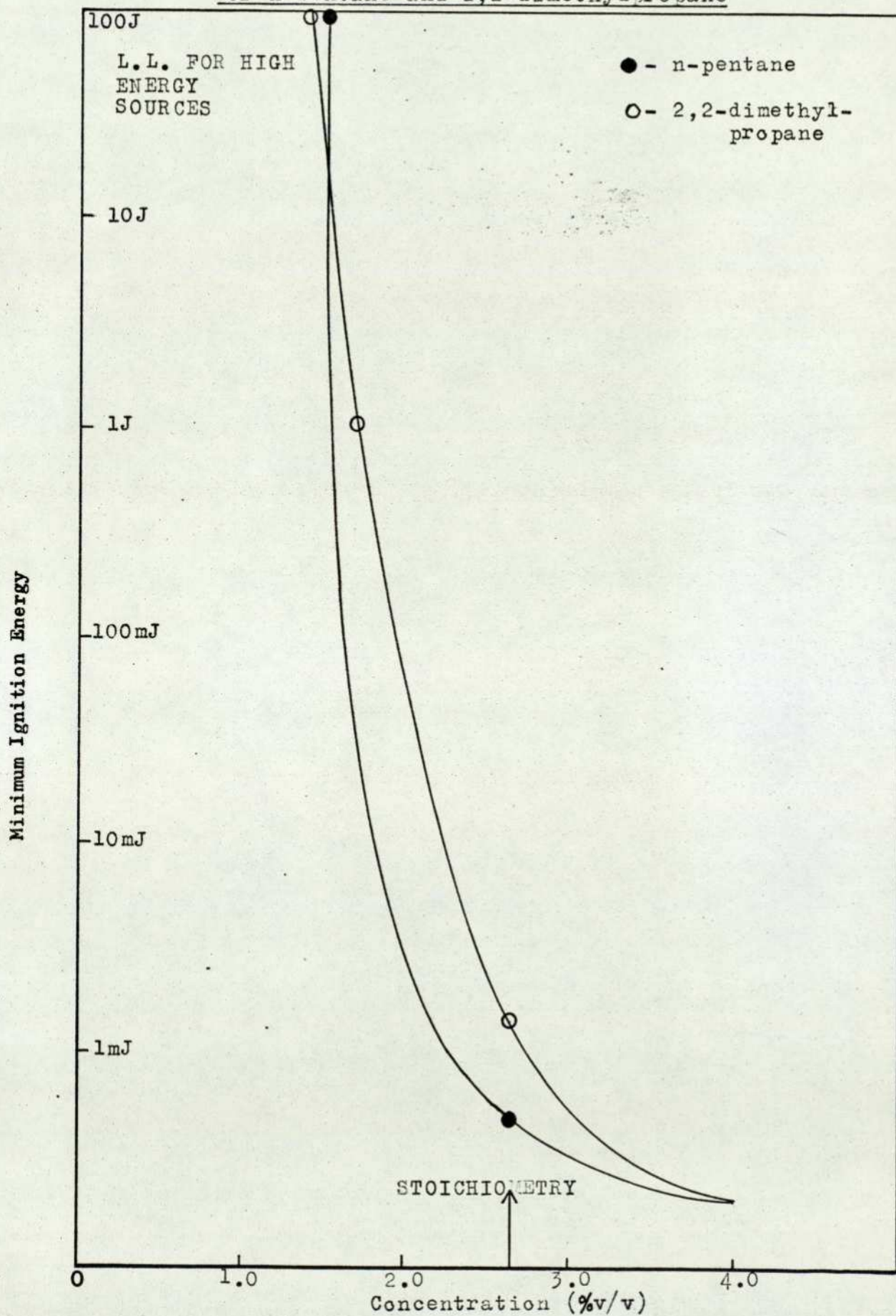
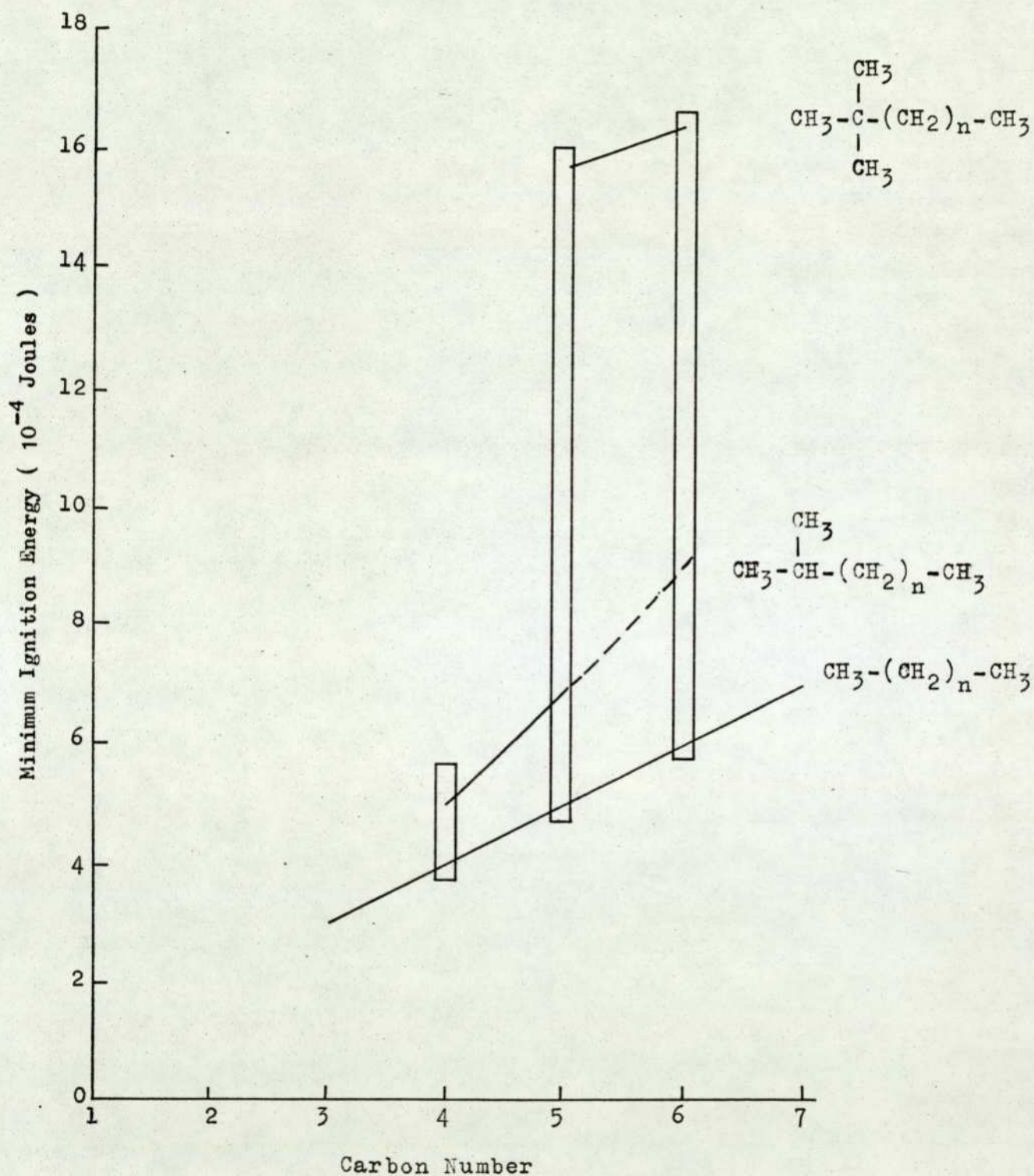


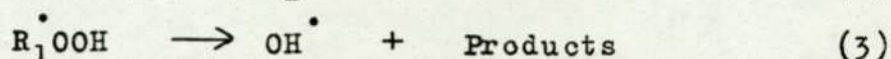
Figure 3.6

Variation of Minimum Ignition Energy at Stoichiometry
with Carbon Number and Molecular Structure.



minimum energy from 5×10^{-4} mJ to 7×10^{-4} mJ, whereas substitution of the second hydrogen increases the minimum energy from 7×10^{-4} mJ to 15.7×10^{-4} mJ for a stoichiometric mixture.

Such a correlation is found to be consistent with a low temperature oxidation mechanism proceeding via alkylperoxy radicals,^{13,84} the rate of which is known to depend upon the molecular structure of the fuel. Thus, the propagation²⁷ reactions may be summarised as follows:

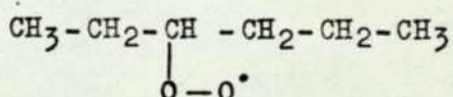


Of these steps it is reaction (2) which introduces the element of structural dependence because the activation energy of this reaction depends upon:

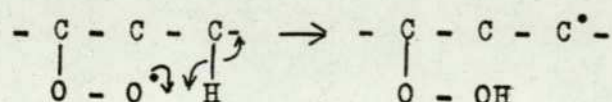
(a) the size of cyclic intermediate that must be formed, and

(b) the nature of the C-H bond broken.

This may be illustrated as follows for the hex-3-ylperoxy radical:



In principle, isomerisation may occur by abstraction of a hydrogen from any of the remaining carbon atoms, but that involving 1:5 H transfer, viz:



is energetically the most favoured route because of the lower

strain energy of the six membered ring ($0.6 \text{ kcal.mole}^{-1}$) compared with that of a four (2.6), five (6.5) or seven (6.5) membered ring. For the hex-3-ylperoxy radical the most favoured sites for hydrogen abstraction are either the one or five positions. The nature of the carbon-hydrogen bond, however, is different at these positions being primary (1°) at the 1- position and secondary (2°) at the 5- position. Abstraction of a 1° hydrogen requires an activation energy of $14.6 \text{ kcal.mole}^{-1}$ compared with $11.1 \text{ kcal.mole}^{-1}$ at a 2° hydrogen with the result that, for the hex-3-ylperoxy radical, isomerisation is most favoured via hydrogen abstraction from the 5- position. Estimated values for different isomerisations are given in Table 3.3.⁸⁵

Clearly, therefore, from such considerations it is possible to deduce for each particular group of isomers the ease of ignitability.

Thus, it is apparent that oxidation via this mechanism will become easier with increasing molecular weight due to the increase in the number of $2^\circ \text{ C} - \text{H}$ bonds and the number of possible 1:5 hydrogen transfers from them. Such an effect is indeed observed, using both high energy and low energy ignition sources, for an homologous series, as shown in Figure 3.4, where the lower limit of flammability decreases with increasing molecular weight, whilst the alkylperoxy mechanism readily explains this effect for low energy ignition sources it is unlikely to apply to high energy ignition sources. In this case, the explanation probably lies in increased susceptibility to fragmentation of high molecular

Table 3.3

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Activation Energy for Cyclisation of RO₂ Radicals
at 600°K

Nature of C-H bond broken	Position of C atom from which H is removed	Size of transition ring	E kcal.mole ⁻¹
Primary	α or δ	5 or 7	20.5
	β	6	14.6
	δ	8	24.0
Secondary	α or δ	5 or 7	17.0
	β	6	11.1
	δ	8	20.5
Tertiary	α or δ	5 or 7	14.2
	β	6	8.3
	δ	8	17.7

weight molecules when heated.

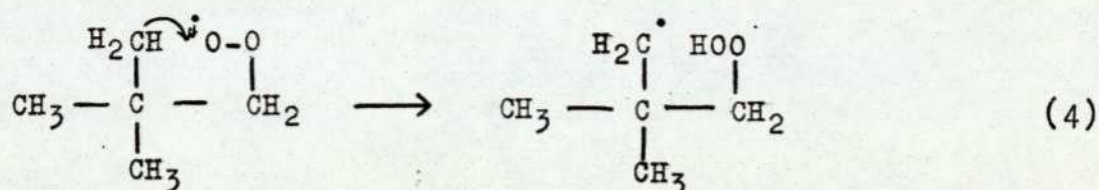
In an attempt to quantify the relationship between molecular structure and the lower limit of flammability in terms of an alkylperoxy radical mechanism of oxidation, the fuels studied herein are considered individually below.

3.4 CORRELATION OF LOWER LIMIT OF FLAMMABILITY WITH OXIDATION MECHANISM

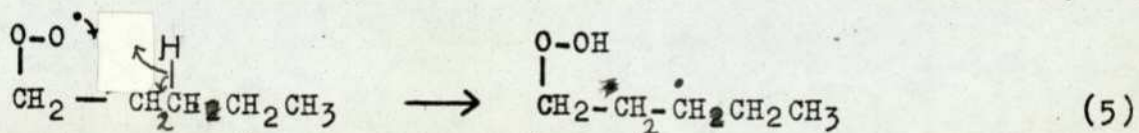
3.4.1 Pentane Isomers.

The lower limits of flammability, using high and low energy sources, and the possible routes for 1:5 isomerisation of the possible alkylperoxy radicals of n-pentane and 2,2-dimethylpropane are given in Table 3.4.

If the initial attack on a fuel molecule involves unselective abstraction of a hydrogen atom (as is generally believed) the only radical possible from 2,2-dimethylpropane is 2,2-dimethylprop-1-yl and addition of oxygen will yield the 1-peroxy-2,2-dimethylpropyl radical. Isomerisation of this radical can only proceed via a 1^{y} 1:5 internal hydrogen abstraction with one of nine possible hydrogen atoms:



For n-pentane, however, initial attack at the 1-, 2-, 4- or 5- positions will give a peroxy radical capable of isomerising via 1:5 H transfer involving a 2^{y} C-H bond, e.g.



It has been estimated that $E_4 - E_5 = 3.5 \text{ kcal.mole}^{-1}$ indicating that reaction (5) will proceed more rapidly than reaction (4) and this is reflected in the value of the lower limit under low ignition energy conditions for 2,2-dimethylpropane as compared with that obtained for both isomers under high ignition energy conditions.

Table 3.4

Correlations Between Lower Limit of Flammability
and Alkylperoxy Radical Formation for Pentane
Isomers

Fuel	L.L. at 25°C		No. of H atoms for initial attack	Peroxy radical	Type of 1:5 isom.	No. of H atoms available for isom.
	Lit ⁸	This work				
n-pentane	1.5		6	1-yl	2 ^y	2
			4	2-yl	2 ^y	2
			2	3-yl	1 ^y	6
2,2-di- methyl propane	1.4	1.68	12	1-yl	1 ^y	9

3.4.2 Hexane Isomers

The lower limits of flammability and the possible routes for 1:5 isomerisation of the possible alkylperoxy radicals of n-hexane and 2,2-dimethylbutane are given in Table 3.5.

The preponderance of 1:5 internal hydrogen abstractions involving 2^{y} C-H bonds for n-hexane is readily correlated with the lower value of the lower limit compared with 2,2-dimethylbutane. From this table it would appear that the total number of hydrogen atoms which may take part in 1:5 isomerisation is less important than the number of C-H bonds available for initial attack in the fuel molecule which will give rise to a radical capable of 2^{y} 1:5 isomerisation. Initial attack at any C-H bond in n-hexane yields a radical capable of 2^{y} 1:5 isomerisation whilst only the 1-peroxy-2,2-dimethylbutyl radical from 2,2-dimethylbutane is able to undergo this reaction.

3.4.3 n-Alkanes and Their Isomers

It will be seen from Table 3.1 that for the n-alkanes of carbon number greater than six the lower limit does not vary greatly. This effect is observed for limits determined with both low and high energy ignition sources and is readily reconciled with a low temperature mechanism, since the addition of successive methylene groups will have progressively less effect upon the number of available alkylperoxy radical isomerisation routes involving 1:5 2^{y}

Table 3.5

Correlations Between Lower Limit of Flammability
and Alkylperoxy Radical Formation for Hexane

Isomers

Fuel	L.L. at 25°C		No. of H atoms for initial attack	Peroxy radical	Type of 1:5 isom.	No. of H atoms available for isom.
	Lit ⁸	This work				
n-hexane	1.20	1.25	6	1-yl	2 ^y	2
			4	2-yl	2 ^y	2
			4	3-yl	2 ^y	2
					1 ^y	3
2,2-di- methyl butane	1.20	1.43	9	1-yl	2 ^y	2
					1 ^y	6
			2	3-yl	1 ^y	9
			3	4-yl		nil

hydrogen transfer. The addition of each successive methylene group after n-hexane gives two additional 2^y C-H bonds for initial attack, the peroxy radical from which, has four 2^y hydrogen atoms available for 1:5 transfer. This is perhaps best illustrated by considering the number of individual C-H bonds open to initial attack which lead to corresponding alkylperoxy radicals capable of isomerisation by 1:5, 2^y hydrogen transfer and the number of hydrogen atoms available for that transfer as shown in Table 3.6.

Consideration of the possible isomers that may exist reveals that for any branched isomer the number of possible 2^y 1:5 hydrogen transfer isomerisation routes (and consequently the ease of oxidation) is reduced compared with the normal isomer. This is illustrated for several isomers in Table 3.7. It will be observed that the effect of branching is less pronounced for the high molecular weight compounds than for those of low molecular weight. This correlates with the result obtained herein for the lower limit of 2,2,5-trimethylhexane, which is, within experimental error, the same as the literature value for n-nonane, whereas that for 2,2-dimethylpropane is significantly different from n-pentane.

Table 3.6Structurally Effective C-H Bonds for the n-Alkanes

Fuel	No. C-H bonds ^a	No. H atoms ^b
propane	—	—
butane	6	2
pentane	10	2
hexane	14	2
heptane	14 2	2 4
octane	14 4	2 4
nonane	14 6	2 4
decane	14 8	2 4

Assuming unselective initial attack:

a: No. of C-H bonds the initial attack of which ultimately leads to an alkylperoxy radical capable of 1:5 2^{Y} -H transfer.

b: No. of H atoms available per radical for 1:5 2^{Y} -H transfer.

Table 3.7

Comparison of Structurally Effective C-H Bonds for
Some n-Alkanes and an Isomer

Fuel	No. C-H bonds ^a	No. H atoms ^b
n-pentane	10	2
2,2-dimethyl propane	-	-
n-hexane	14	2
2,2-dimethyl butane	9	2
n-octane	14	2
	4	4
2,2-dimethyl hexane	16	2
n-decane	14	2
	8	4
2,2-dimethyl octane	20	2
	2	4

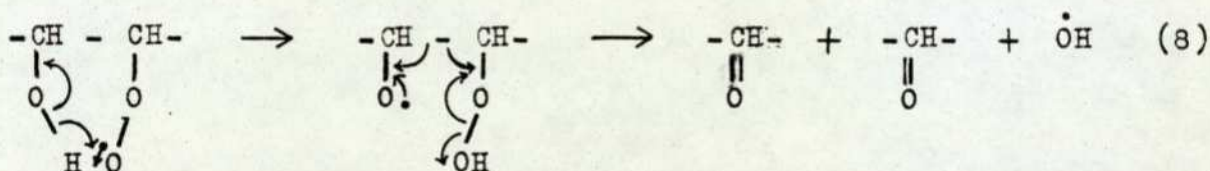
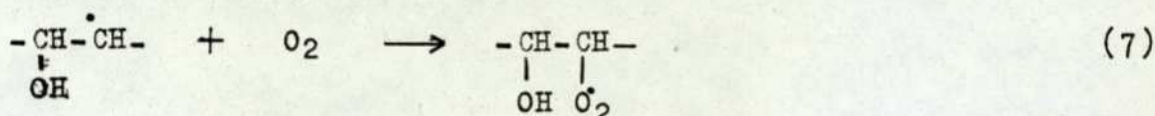
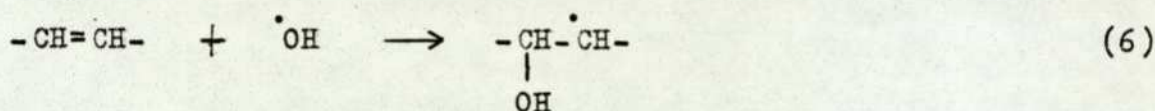
a: No. of C-H bonds the initial attack of which ultimately leads to an alkylperoxy radical capable of 1:5 2^{y} -H transfer.
b: No. of H atoms available per radical for 1:5 2^{y} -H transfer.

3.4.4 Hex-1-ene

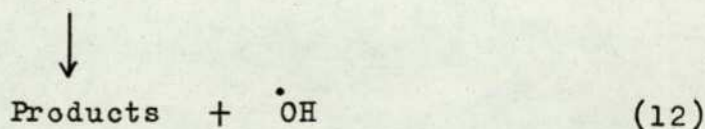
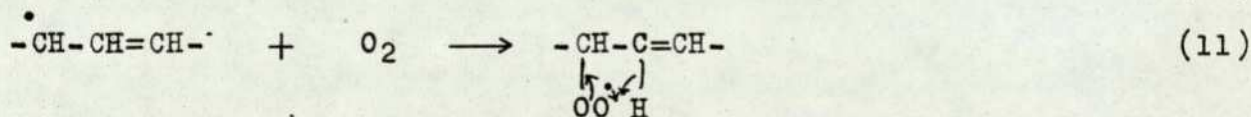
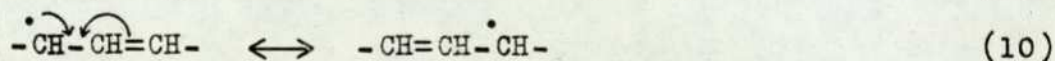
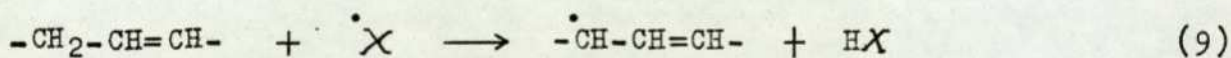
The lower limit of flammability of hex-1-ene is 1.25%^v/_v at 100°C (calculated as 1.32%^v/_v at 25°C). Surprisingly no literature value exists for this compound. The above value is, however, the same as that determined for n-hexane, a fact which can be accounted for by the similarity of the oxidation process.

The oxidation of an alkene proceeds via either an additive or abstractive mechanism.^{87,88} The general reaction schemes are:

Additive



Abstractive



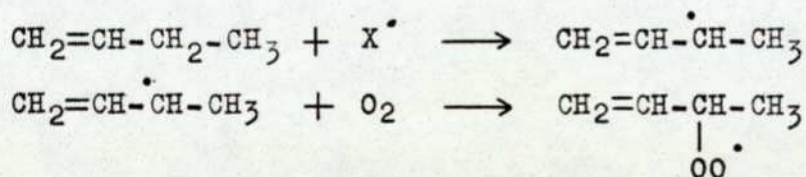
In the additive mechanism the hydroxyperoxy radical in reaction (8) isomerises via a 1:5 hydrogen transfer which is similar to that described previously for alkylperoxy radicals.

As mentioned previously a six membered cyclic transition state is the most favoured configuration; in this case, the activation energy will be at least 6 kcal.mole⁻¹ larger than the least favoured 1:5 hydrogen transfer for alkylperoxy radicals (namely those involving 1^y C-H bonds) due to the higher bond strength of the -O-H bond:⁸⁴

$$D [\overset{\cdot}{O}_2 C_n H_n O-H] = 104 \text{ kcal.mole}^{-1}, \quad D [-CH_2-H] = 98 \text{ kcal.mole}^{-1}.$$

It is probably significantly higher than 6 kcal.mole⁻¹, however, due to the higher strain energy of the cyclic complex.

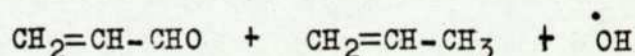
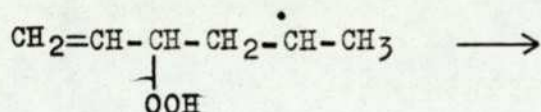
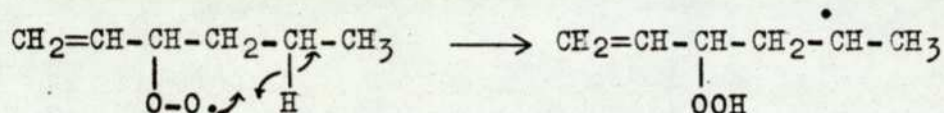
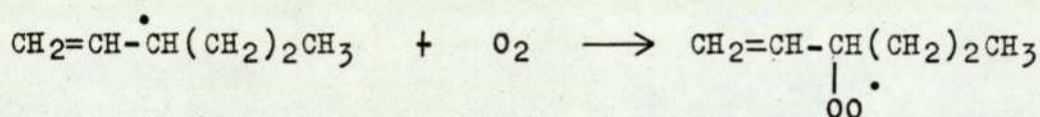
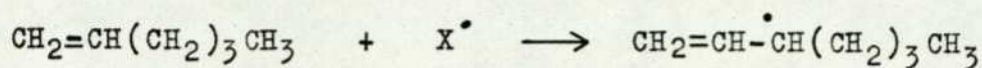
The abstractive route becomes important when the alkene possesses an α -CH₂ group, since the strength of the α -C-H bond is only 85 kcal.mole⁻¹ i.e. it is 6.8 kcal.mole⁻¹ weaker than a 3^y C-H bond in a saturated hydrocarbon. But-1-ene is the lowest molecular weight alkene which possesses an α -CH₂ group:-



Addition of oxygen yields an alkylperoxy radical which can only isomerise by a five membered ring and involves the breaking of a 1^y C-H bond; both of which are energetically unfavourable compared with the additive mechanism and, hence, the additive mechanism will predominate. With an increase in molecular weight, however, more facile isomerisations are possible and the abstractive mode of attack becomes more important.

Hex-1-ene is the first member of the homologous

series which contains both an α and γ -CH₂ group; hence, not only can it undergo ready hydrogen abstraction at the α -CH₂ but the subsequent alkenylperoxy radical has a 2^y CH₂ group available for the facile 1:5 hydrogen transfer reaction:



It can be seen, therefore, that the low temperature mechanism of oxidation of hex-1-ene is not substantially different from that of n-hexane. It is difficult from theoretical considerations to predict whether hex-1-ene would be expected to be more, or less, readily oxidised than n-hexane since several factors mitigate for and against, viz:

- two facile modes of oxidation can occur,
- initial hydrogen abstraction at the -CH₂ is faster, but;
- the cyclic transition state in the additive route is energetically less favourable than the analogous one for the hexylperoxy radical isomerisation;
- the alkenyl radical is resonance stabilised;

-the alkenylperoxy radical has fewer modes of isomerisation and subsequent decomposition open to it than the hexylperoxy radical.

It may be concluded, however, that the ease of oxidation of hex-1-ene is unlikely to be significantly different from its parent alkane particularly in a spark induced process where the initial attack on the fuel is unselective.

Literature data on the limits of flammability for alkenes is very limited and the only relevant data obtained is given below:

Alkene	L.E.L. (%v/v)	Parent Alkane L.E.L. (%v/v)
Propene	2.4	2.2
But-1-ene	1.6	1.9
But-2-ene	1.8	1.9

The presence of an α -CH₂ in but-1-ene may be correlated with its low value of the lower limit compared with n-butane; an effect which is not so apparent for but-2-ene. The higher, lower limit for propene than for propane may also be correlated with the mechanism of oxidation since:

(a) an abstraction mechanism is unlikely due to the absence of an α -CH₂;

(b) a hydroxylperoxy radical isomerisation via an addition mechanism has previously been shown to be more difficult than the possible 1;5 hydrogen transfer for the n-alkane via an alkylperoxy mechanism.

3.5 CORRELATIONS BETWEEN OCTANE NUMBER, SPONTANEOUS IGNITION TEMPERATURE AND LOWER LIMIT OF FLAMMABILITY

The octane number of a fuel is defined as: "the whole number nearest to the percentage by volume of iso-octane (2,2,4-trimethylpentane) in the blend of iso-octane and n-heptane which the fuel matches in knock characteristics when compared by the specified procedure."

Thus, by definition n-heptane has an octane number of 0 and iso-octane an octane number of 100; n-heptane being very susceptible to knock and iso-octane very resistant. The term 'knock' is often used loosely to describe a multitude of phenomena but within the context of octane number it has a definite meaning. During the power stroke of an internal combustion engine the fuel gases are compressed in the cylinder head and ignited by a spark slightly prior to the piston reversing direction at the end of the compression stroke, i.e. just prior to top dead centre. The combustion wave created propagates from the spark towards the piston crown which is, itself, still rising, the effect is to heat and compress the unburnt gases between the piston crown and combustion wave. If these effects cause the unburnt gases to spontaneously ignite, prior to the exhaust cycle, then knocking occurs. Consequently, one would anticipate a correlation between octane number, spontaneous ignition temperature and the lower limit of flammability. In general, for the n-alkanes qualitative correlations do exist as can be seen in Table 3.8. As the molecular weight increases, so the fuel becomes more easily oxidised and the octane number, spontaneous ignition

Table 3.8

Variation of Spontaneous Ignition Temperature,
Octane Number and Lower Limit of Flammability for
the n-Alkanes

n-alkane	L.L.F. ^a	O.N. ^b	S.I.T. ^c
propane	2.1	102	466
butane	1.8	94	405
pentane	1.4	62	258
hexane	1.2	25	223
heptane	1.05	0	223
octane	0.95	—	220
nonane	0.85	—	206
decane	0.75	—	208

a: reference no. 42

b: reference no. 92

c: reference no. 20

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temperature and lower limit of flammability all decrease.

Furthermore, from the extensive data on octane numbers one may generalise that as the degree of branching increases so the octane number increases with respect to the n-isomer. This observation is supported by a similar, though less well documented, trend for spontaneous ignition temperatures and by the results presented herein, (except for 2,2,5-trimethylhexane) in that the lower limit of flammability rises with increased branching under the experimental conditions employed (Table 3.9).

Attempts to interpret the octane number of a particular isomer in terms of molecular structure, as done previously for the lower limits of flammability, shows that it is sensitive both to the degree of branching and to the position of the side arms. Such an observation is consistent with a low temperature mechanism but attempts at explanations for individual molecules are difficult, especially at high molecular weight.

Thus, although the present results show the lower limits of n-hexane and hex-1-ene to be the same, their octane numbers are 24.8 and 78.4 respectively, which would indicate that n-hexane should have a somewhat lower, lower limit of flammability than hex-1-ene. Consideration of the octane numbers of the isomers hex-1-ene (24.8), hex-2-ene (92.7) and hex-3-ene (94.0), however, is consistent with an abstractive mechanism of oxidation in that hydrogen abstraction is only able to proceed via oxygen addition and a 2° 1:5 hydrogen transfer for hex-1-ene resulting in its lower octane number.

Table 3.9

Variation of Spontaneous Ignition Temperature,
Octane Number and Lower Limit of Flammability For
Some Branched Alkanes

Fuel	L.L.F. ^d	O.N. ^b	S.I.T. ^c
n-butane	1.8	94	405
n-pentane	1.4 ^a	62	258
2,2-dimethyl propane	1.7	85.5	450
n-hexane	1.3	25	223
2,2-dimethyl butane	1.4	92	425

a: reference no. 38

b: reference no. 93

c: reference no. 20

d: this work

3.6 LOWER LIMITS OF FLAMMABILITY OF MULTICOMPONENT HYDROCARBON/AIR MIXTURES

3.6.1 Binary Mixtures

The lower limits of flammability of a range of vapour mixtures of n-decane with n-butane, 2,2-dimethylpropane, n-hexane, hex-1-ene and 2,2-dimethylbutane were determined using the static apparatus described in Section 2.5 and a spark of 2.5 J energy obtained from an 0.1 uF capacitor charged to 5 kV. The results are given in Table 3.10. (a - e).

The modified form of Le Chatelier's equation⁷⁴ derived by Coward et. al., which was discussed previously (Section 1.8.3) is given by:

$$\frac{N_A}{L_A} + \frac{N_B}{L_B} = \frac{1}{L_M} \quad (1)$$

where N_A and N_B are the mole fraction of A and B in the vapour; L_A and L_B are the lower limits of flammability of the components A and B and L_M is the lower limit of the mixture.

Since: Since:

$$N_A + N_B = 1 \quad (2)$$

rearrangement of (1) gives;

$$N_A = \frac{L_A \cdot L_B}{L_M(L_B - L_A)} + \frac{L_A}{(L_B - L_A)}$$

Hence, a plot of N_A versus $1/L_M$ should give a straight line if this equation is valid. Figures 3.7 and 3.8 show unequivocally that the above equation is indeed applicable to these mixtures under conditions of low energy ignition.

Table 3.10(a)

Composition of Limit Mixtures of n-Butane and
n-Decane in Air at 100° C

n-decane (%v/v)	n-butane (%v/v)	Mole fraction n-decane	1/L _M
0.85	0.0	1.0	1.18
0.73	0.19	0.79	1.05
0.7	0.2	0.78	1.05
0.33	1.06	0.23	0.72
0.15	1.4	0.1	0.65
0.0	1.7	0.0	0.59

Table 3.10(b)

Composition of Limit Mixtures of 2,2-Dimethyl-
Propane and n-Decane in Air at 100° C

n-decane (%v/v)	2,2-dimethyl propane (%v/v)	Mole fraction n-decane	1/L _M
0.85	0.0	1.0	1.18
0.82	0.2	0.8	1.06
0.56	0.47	0.54	0.93
0.45	0.89	0.34	0.81
0.17	1.4	0.11	0.69
0.0	1.6	0.0	0.63

Table 3.10(c)

Composition of Limit Mixtures of n-Hexane and
n-Decane in Air at 100° C

n-decane (%v/v)	n-hexane (%v/v)	Mole fraction n-decane	1/L _M
0.85	0.0	1.0	1.18
0.64	0.3	0.68	1.06
0.58	0.54	0.52	0.99
0.51	0.57	0.47	0.97
0.45	0.64	0.41	0.95
0.25	0.85	0.28	0.9
0.0	1.25	0.0	0.8

Table 3.10(d)

Composition of Limit Mixtures of 2,2-Dimethyl-
Butane and n-Decane in Air at 100° C

n-decane (%v/v)	2,2-dimethyl butane (%v/v)	Mole fraction n-decane	1/L _M
0.85	0.0	1.0	1.18
0.72	0.14	0.84	1.11
0.61	0.34	0.64	1.02
0.52	0.51	0.5	0.96
0.38	0.61	0.38	0.91
0.29	0.93	0.24	0.84
0.23	1.06	0.18	0.82
0.0	1.35	0.0	0.74

Table 3.10(e)

Composition of Limit Mixtures of Hex-1-ene and
n-Decane at 100°C

n-decane (%v/v)	hex-1-ene (%v/v)	Mole fraction n-decane	1/L _M
0.85	0.0	1.0	1.18
0.75	0.18	0.81	1.1
0.7	0.22	0.76	1.08
0.55	0.45	0.55	1.01
0.31	0.8	0.28	0.91
0.24	1.0	0.19	0.87
0.0	1.25	0.0	0.8

Figure 3.7

Variation of $1/L_M$ with the Mole Fraction of n-Decane
for Mixtures of n-Decane and some Alkanes

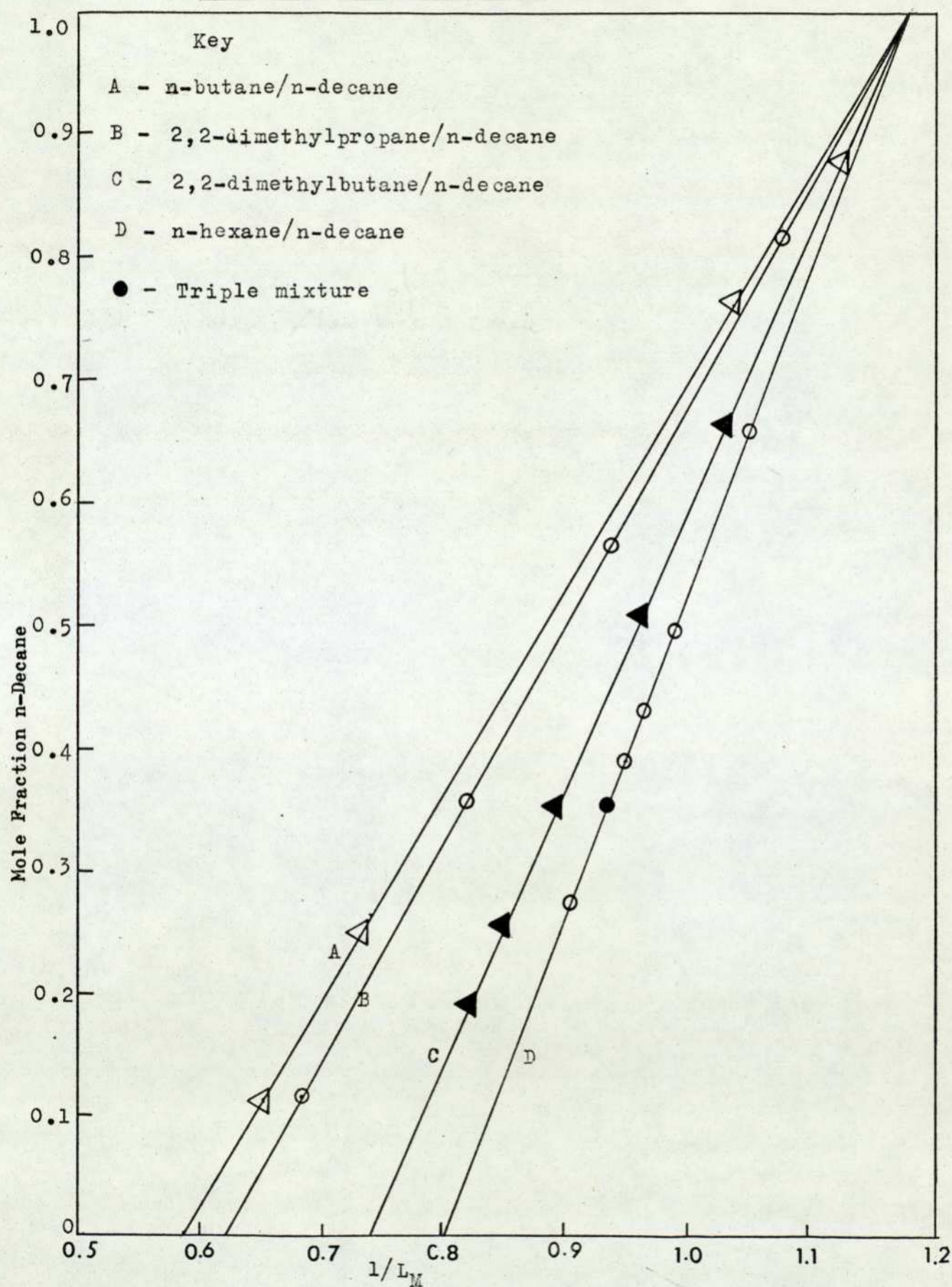
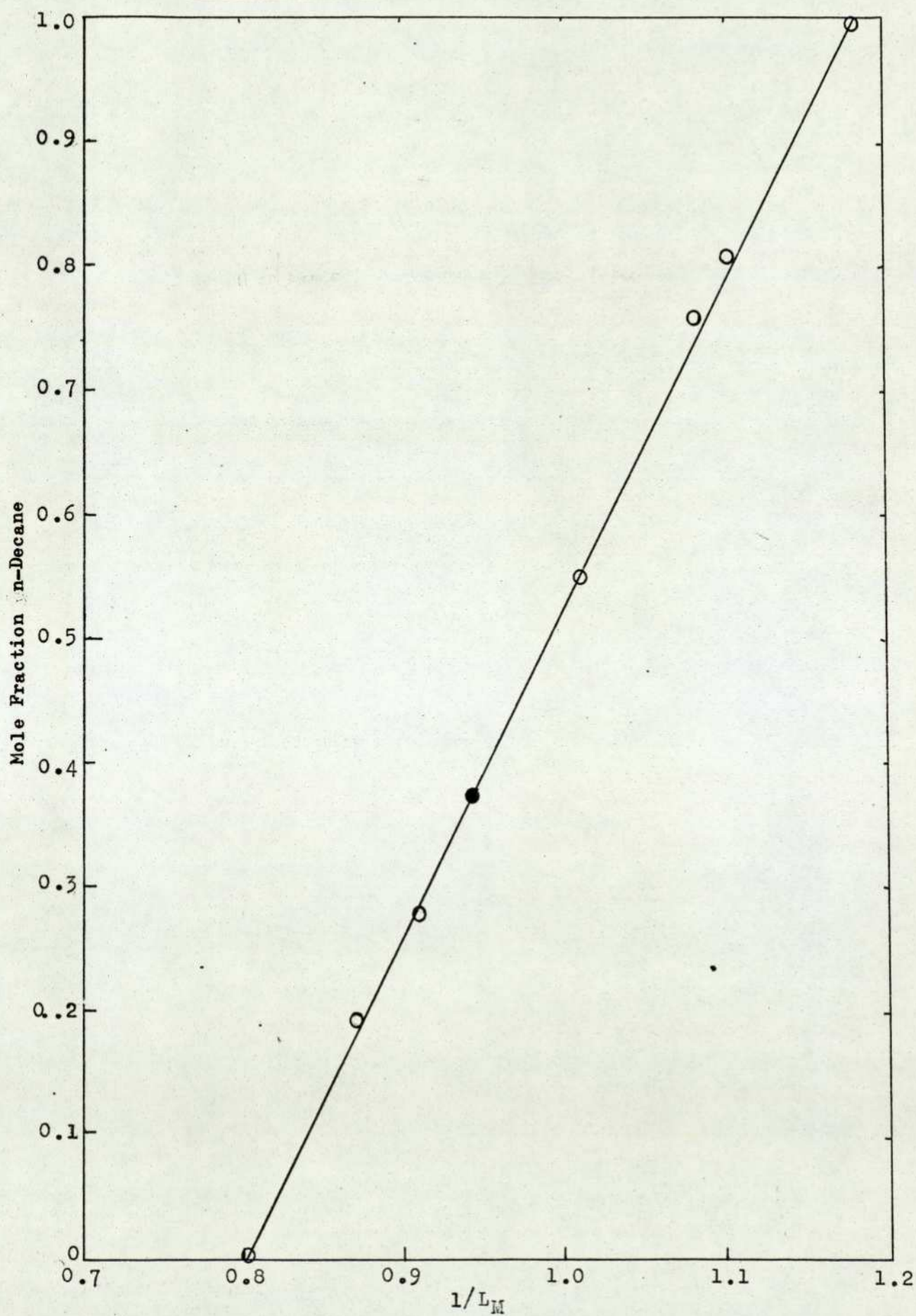


Figure 3.8

Variation of $1/L_M$ with the Mole Fraction of n-Decane
for n-Decane and Hex-1-ene Mixtures



3.6.2 Tertiary Mixtures

Lower limit tertiary mixtures in air were prepared from the following fuels - n-decane, - n-hexane, - hex-1-ene and - n-decane, + n-hexane, + n-butane. The exact compositions are given in Table 3.11a and Table 3.11b.

The former mixture was specifically used in order to test whether the substitution of hex-1-ene for n-hexane affected the lower limit of n-decane, + n-hexane mixtures. Clearly, if the lower limit of hex-1-ene and n-hexane are the same, as the previous results show, then the lower limit of the ternary mixture should fall exactly on the line obtained for the $1/L_M$ versus composition for the binary mixture. The result is plotted in Figure 3.7 and clearly confirms that the lower limit for the alkane and its conjugate alkene are identical when ignited by a low energy source.

The results for the n-decane + n-hexane + n-butane mixtures prepared are shown in Figure 3.9. These show that Le Chatelier's rule may be extended to triple fuel mixtures, i.e.

$$\frac{1}{L_M} = \frac{N_A}{L_A} + \frac{N_B}{L_B} + \frac{N_C}{L_C}$$

which rearranged gives:

$$N_C = \frac{1}{L_M} \frac{N_A}{L_A} + \frac{L_B L_C - L_C(1 - N_A)}{L_B - L_C}$$

which is of the form:

$$N_C = 1/L_M \cdot X + C$$

for $N_A/L_A = \text{constant}$.

Table 3.11(a)

Composition of Limit Mixture of n-Decane,
n-Hexane and Hex-1-ene at 100° C

n-decane (%v/v)	n-hexane (%v/v)	hex-1-ene (%v/v)	Mole fraction			1/L _M
			n-decane	n-hexane	hex-1-ene	
0.39	0.32(5)	0.32(5)	0.38	0.31	0.31	0.941

Table 3.11(b)

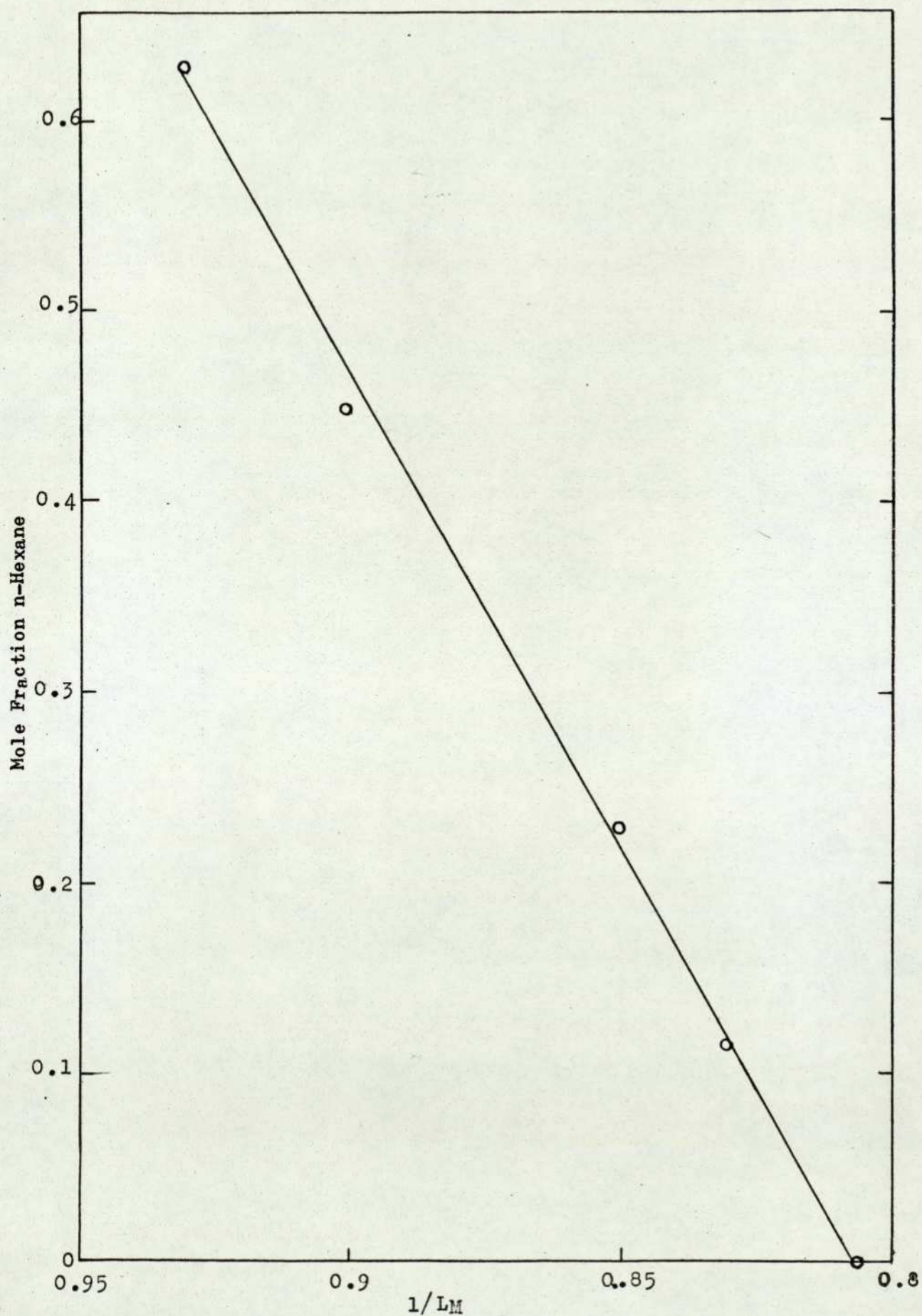
Composition of Limit Mixtures of n-Decane,
n-Hexane and n-Butane at 100° C

n-decane (%v/v)	n-hexane (%v/v)	n-butane (%v/v)	Mole fraction			1/L _M
			n-decane	n-hexane	n-butane	
0.45	0.0	1.13	0.37	0.0	0.63	0.81 ⁺
0.45	0.26	0.44	0.39	0.23	0.38	0.85
0.45	0.14	0.63	0.37	0.11	0.52	0.83
0.44	0.54	0.22	0.37	0.45	0.18	0.9
0.45	0.79	0.0	0.37	0.63	0.0	0.93 ⁺

+ from Figure 3.7

Figure 3.9 .

Variation of $1/L_m$ with the Mole Fraction n-Hexane for
n-Decane, n-Hexane and n-Butane Mixtures at 100 C.



Hence, since the mole fraction of n-decane was kept constant, a plot of N_C (the mole fraction of n-hexane) versus $1/L_M$ should yield a straight line as found.

3.6.3 Discussion of the Lower Limit of Flammability of Multicomponent Hydrocarbon/Air Mixtures

Le Chatelier's rule has been shown to apply for selected fuel/air mixtures by other authors but only when employing high energy sources of ignition. The present work extends this information to the binary and tertiary mixtures described above and further shows that the rule applies when ignition sources of limiting energy are used. Furthermore, from Figures 3.1 to 3.3 the lower limit of flammability of lean mixtures is observed to vary by only a few tenths of a per-cent for several orders of magnitude change in minimum ignition energy. From this one may conclude that Le Chatelier's rule will apply without any major error for a wide range of ignition energies.

The results of a number of authors^{87,94} who have studied the spontaneous ignition mixtures of both alkanes and alkenes, at a variety of temperatures, have shown that the interaction during pre-flame reaction is varied and complex. For mixtures of n-heptane and hept-1-ene in oxygen, for example, the alkene is not involved in the pre-flame reaction at temperatures below 300°C, whilst at temperatures above 300°C both fuels are consumed equally. Salooja has also shown that for a variety of binary fuel mixtures at 750°C, in some cases the more easily ignitable compound disproportionately affected ignition, whilst in others the mixture was more easily ignitable than either of the components.

In the present work the validity of Le Chatelier's rule shows that both components contribute to the ignition process in direct proportion to the ratio of their concentrations to their lower limits of flammability. From this one may conclude that the temperature which exists at the critical phase of flame development is sufficient for both fuels to react significantly i.e. at least of the same order as the spontaneous ignition temperature of the least easily ignitable compound. The compound with the highest spontaneous ignition temperature is 2,2-dimethylpropane at 450°C . Most certainly the temperature could be considerably in excess of this, but at significantly lower temperatures the rate of reaction of 2,2-dimethylpropane would be insufficient to make a contribution to the ignition process in proportion to its concentration.

3.7

DESCRIPTION OF THE IGNITION OF A FLAMMABLE MIXTURE
BY A SPARK

From the results presented herein and the results of other workers, it would appear that the following sequence of events occurs when the ignition source is a spark of < 1 J:

(a) The passage of the spark will occur during 10^{-7} to 10^{-8} secs., and create a region of very high temperature and high radical concentration along a small volume termed the spark channel.^{2,81}

(b) The reacting volume will expand and the temperature within it will drop dramatically until a critical state is achieved after 10^{-2} to 10^{-3} sec. At this stage a minimum rate of reaction is required to sustain a critical energy flux across the reaction boundary. The temperature is ca. 500 to 600°C and the reactions are those showing a structural dependence typical of the mechanism of low temperature hydrocarbon oxidation.

(c) If the critical rate of reaction is achieved, the adjacent layer of unburnt gas will ignite, leading to a self-sustaining propagation wave. The period taken for a flame to develop is long compared with the duration of the spark, thus, one is unlikely to observe a flame which is incapable of being self-sustaining as is possible with high energy ignition sources (i.e. flames; continuous discharges).

From this sequence of events it is apparent that structural dependence of the lower limit due to low temperature combustion will not be observed if either flames or continuous electric discharges are used for ignition, since their duration will be sufficiently long to obliterate the critical phase. A number of other factors which affect the lower limit of flammability are explicable by this process of ignition. Thus, raising the temperature of the gas mixture will reduce the energy required to ignite the unburnt layer of gas during the critical phase. The phenomena of quenching is similarly explained since the presence of a solid body will act as a heat and radical sink during the critical phase. In this respect, needle pointed electrodes will be less effective than flanged electrodes, since the reacting volume will rise by convection, thus, reducing their effect, (see Figure 1.5).

3.8 FLASH POINTS

3.8.1 Single Components

The flash point of a pure compound is defined as the temperature at which the vapour pressure of a liquid is just sufficient to produce a lower flammability limit mixture in air. The vapour pressure versus temperature curves for n-hexane, hex-1-ene, 2,2-dimethylbutane, 2,2,5-trimethylhexane and n-decane are given in Figure 3.10, from which the theoretical flash points of these compounds are obtained by inspection and the equation:

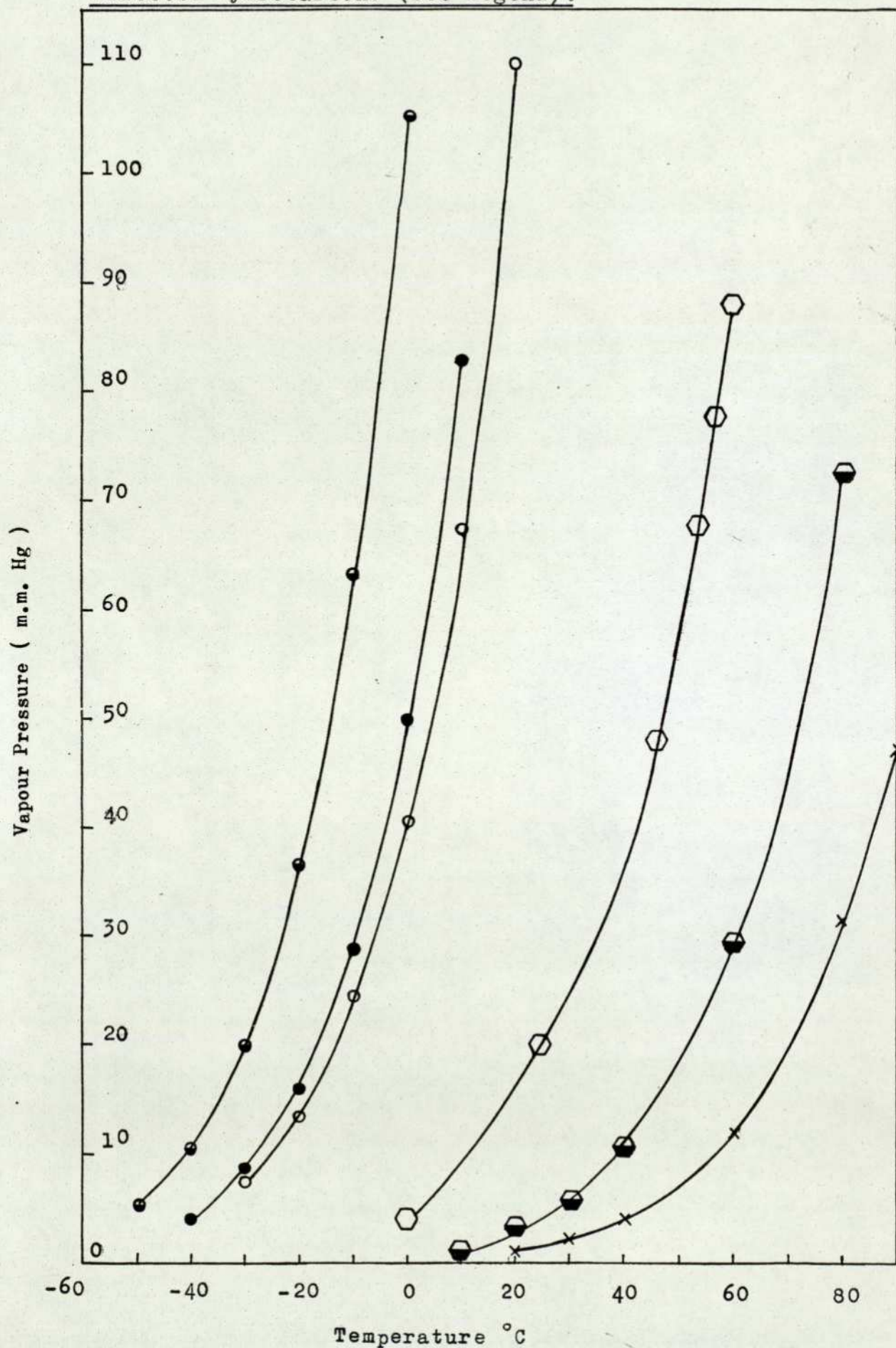
$$\frac{P.100}{760} = L$$

where L = the lower flammability limit at the flash point temperature, expressed in %v/v; and P = the partial pressure of the fuel. Theoretical flash points and literature values are given in Table 3.12, the latter being taken from the Koch Light Laboratories Catalogue 1973⁸⁹ and the Laboratory Safety Handbook,⁹⁰ since these appeared to be the most consistent available. The theoretical values were obtained from literature values of the lower limit of flammability and, for comparison, the lower limit values determined in this work. Also included in Table 3.12 the flash points determined, in this work, using an Abel flash point apparatus.

Comparison of Figure 3.10 with Table 3.12 shows the profound effect of vapour pressure upon the flash point. It also illustrates the errors to which the flash point is subject, particularly for highly volatile compounds. For example, the literature flash points of -30°C and -23°C

Figure 3.10.

Variation of Vapour Pressure with Temperature for
Selected Hydrocarbons (see Legend).



Legend for Figure 3.10

● - 2,2-dimethylbutane

● - hex-1-ene

○ - n-hexane

⬡ - 2,2,5-trimethylhexane

× - n-decane

◐ - n-nonane

Table 3.12

Theoretical and Actual Flash Points for some Fuels

Fuel	Lit. flash point ($^{\circ}\text{C}$)		Theoretical flash point($^{\circ}\text{C}$)		Flash points($^{\circ}\text{C}$)
	ref.1	ref.2	lit,	this work	This work Abel method
2,2-dimethyl butane	-32	-48	-43 ⁴	-40	—
n-hexane	-23	-30	-26 ³	-25	—
hex-1-ene	-26	—	—	-28	—
n-nonane	31	—	31 ³	—	—
2,2,5-tri-methylhexane	13	—	7	3	12 $\pm$ 3
n-decane	46	46	46 ³	48	49 $\pm$ 1

1: reference no. 89

2: reference no. 90

3: reference no. 20

4: reference no. 38

for n-hexane corresponds to calculated lower limits of flammability of 1.0%v/v and 1.45%v/v respectively. Furthermore, it can be seen that lower limit mixtures are created at vapour pressures which occur on that part of the vapour pressure/temperature curve with a shallow gradient; consequently the flash point is a very inaccurate way of confirming the lower limit of flammability for a 'hot' ignition source.

Although the flash point is unreliable for highly volatile compounds such as 2,2-dimethylbutane, it becomes more useful for less volatile compounds such as n-nonane, n-decane.

Since the flash point is dependent on the vapour pressure, adulteration of a high boiling point liquid with a small amount of a low boiling point compound would be expected to dramatically alter its flammable properties. This conclusion is verified by the following results.

3.8.2. Binary Fuel Mixtures

The application of Le Chatelier's rule to the multiple hydrocarbon vapour/air mixtures under consideration has been previously proven (Figures 3.7 and 3.8) and hence, using Raoult's law we may write:

$$\frac{100M_A P_{oA}}{760L_A} + \frac{100M_B P_{oB}}{760L_B} = 1$$

where: M_A and M_B = Mole fractions of the compounds in the liquid.

P_{oA} and P_{oB} = Vapour pressures of the pure compounds.

L_A and L_B = Lower limits of flammability of A and B.

At any temperature T, P_{OA} and P_{OB} can be obtained from Figure 3.10. The variation of the lower limit of flammability with temperature is given by Affens⁶⁷ as:

$$\frac{L_T}{L} = 1.02 - 0.000721T$$

where: L_T = lower limit at $T^{\circ}\text{C}$; and L = lower limit at 25°C .

A series of binary component fuels of n-decane with n-hexane, hex-1-ene, 2,2-dimethylbutane and 2,2,5-trimethylhexane were made up and their composition determined by G.L.C. The flash points of these fuels were then determined using an Abel flash point apparatus and compared with the calculated values (Figures 3.11 to 3.14).

For synthetic fuels whose constituents have widely differing boiling points, such as 2,2-dimethylbutane (B.pt 49.7°C) and n-decane (B.pt 174.1°C), small concentrations of the low boiling constituent dramatically lowers the flash point (Figure 3.13). The effect is, predictably, less severe for fuels whose constituents have similar boiling points, such as 2,2,5-trimethylhexane and n-decane (Figure 3.14). It should also be noted, however, that the discrepancy between the theoretical and practical curves is greatest for the fuels whose constituents have the most dissimilar vapour pressures, viz. Figure 3.13. and for mixtures of dissimilar vapour pressure the actual flash point is lower than the calculated flash point. Whilst a discrepancy between the actual and theoretical flash points may differ by a few degrees for a pure hydrocarbon, e.g. n-decane $46-49^{\circ}\text{C}$ for the sythetic fuels studied here the discrepancy can be as large as 10°C .

Figure 3.11

Variation of Flash Point with Mole Fraction of
n-Decane for n-Decane/n-Hexane Mixtures.

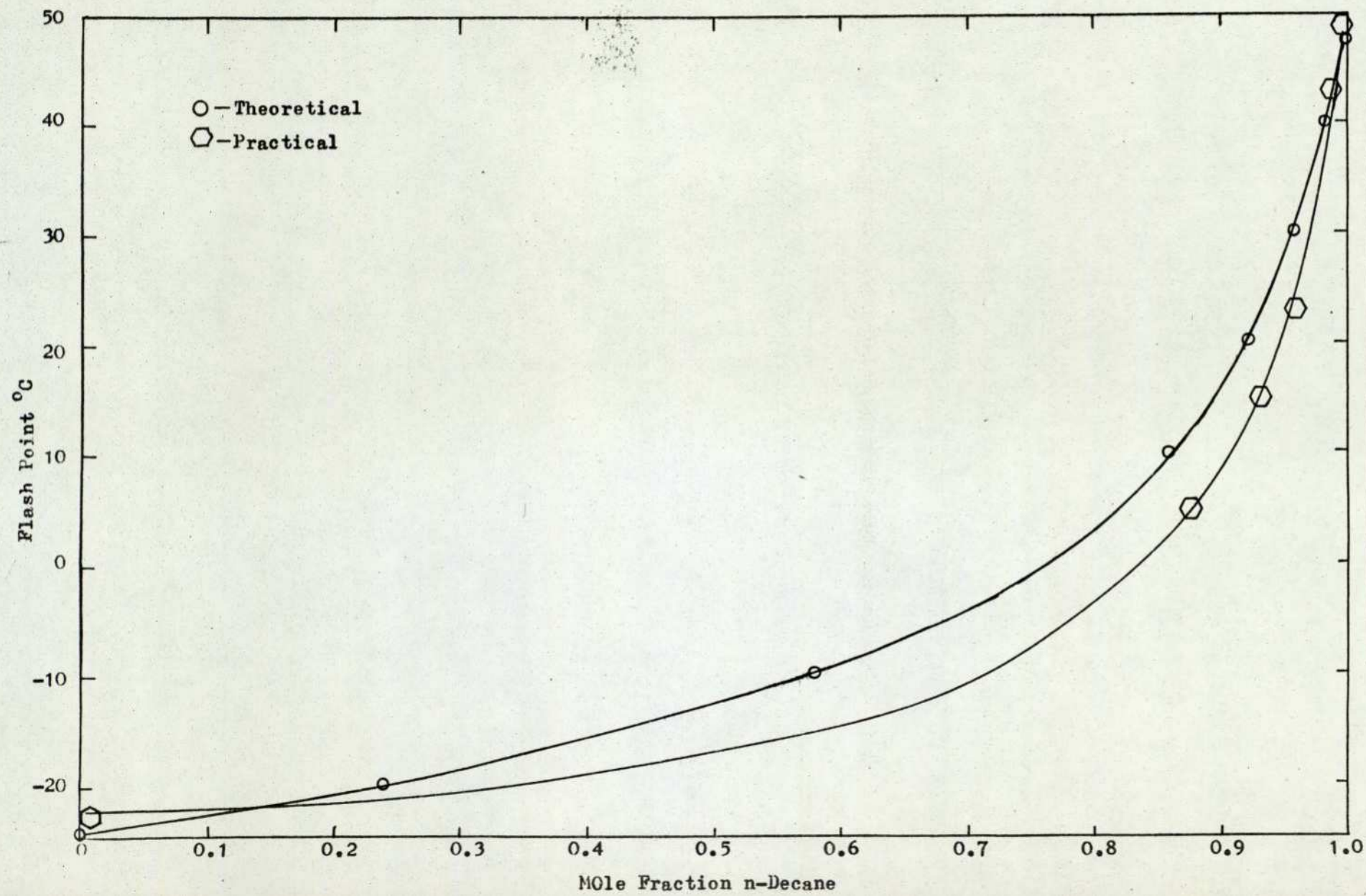


Figure 3.12

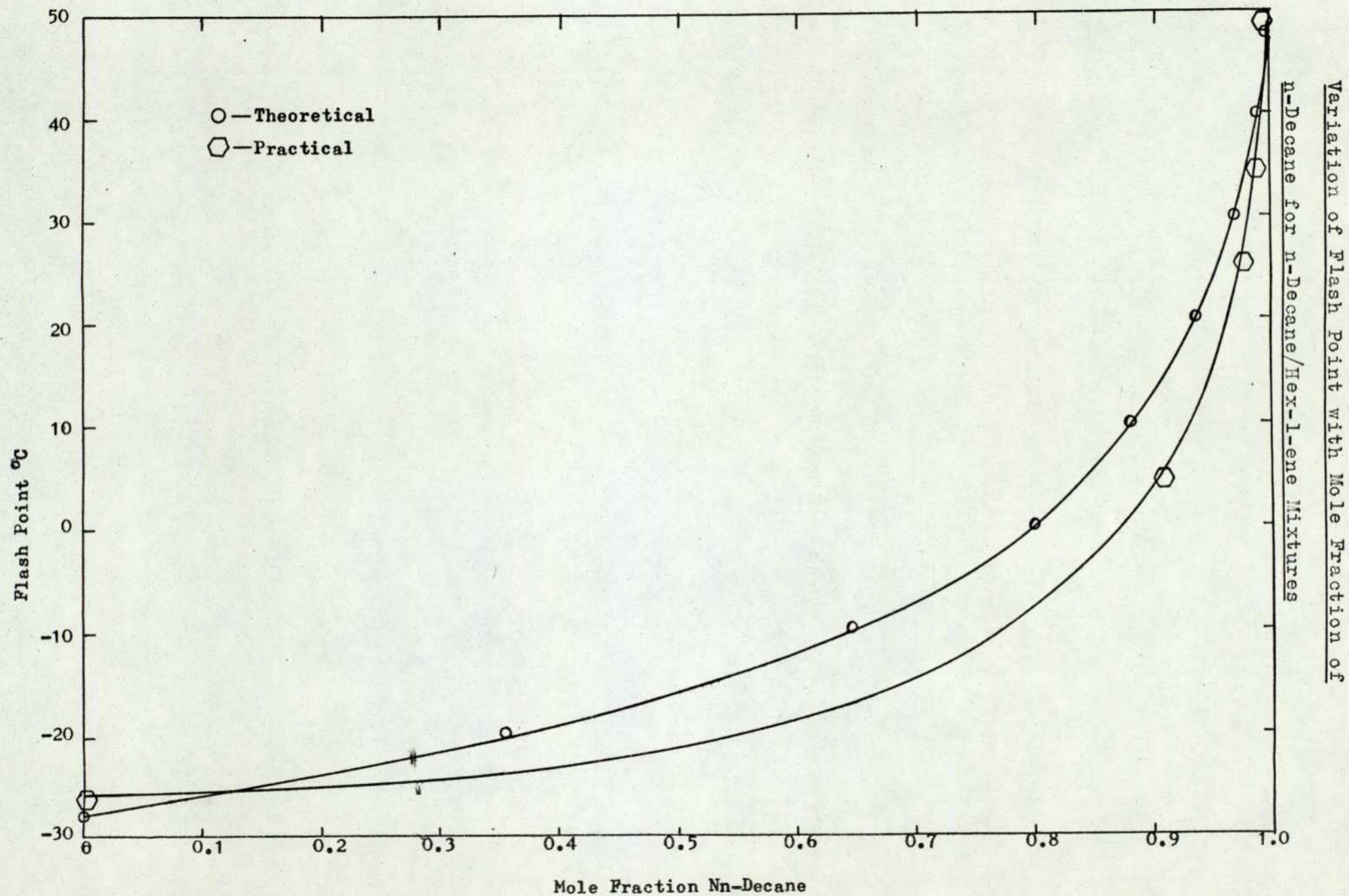


Figure 3.13

Variation of Flash Point with Mole Fraction of
n-Decane for n-Decane/2,2-Dimethylbutane

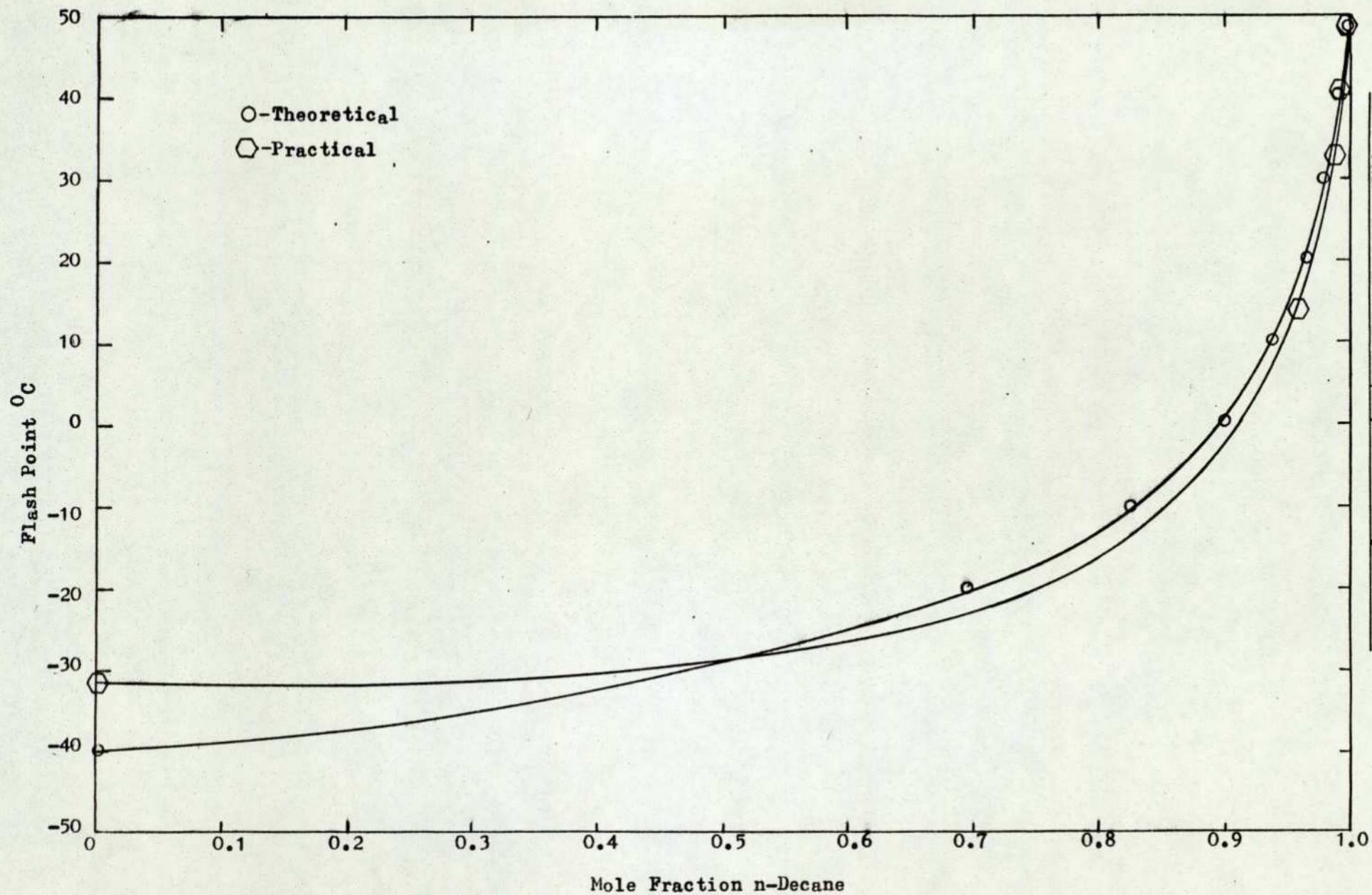
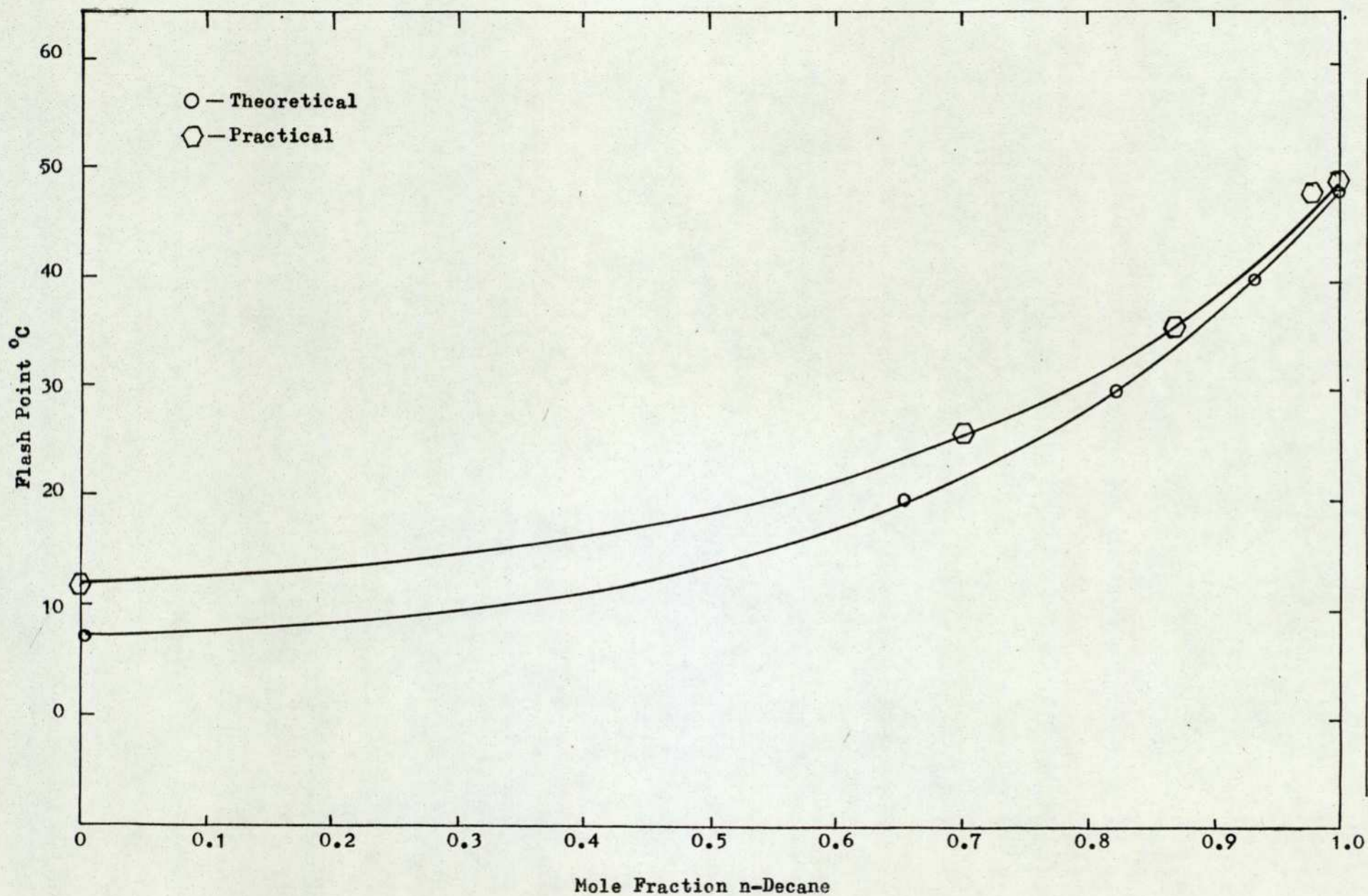


Figure 3.14

Variation of Flash Point with Mole Fraction of
n-Decane for n-Decane/2,2,5-trimethylhexane Mixtures



The above phenomena is explained by the dynamic method of flash point determination which inevitably causes temperature gradients to occur within the liquid sample. For single components this is not important since the vapour pressure is relatively insensitive to temperature at low vapour pressures, as mentioned previously. However, for a volatile component at a relatively high temperature one is at a position on the vapour pressure/temperature curve where the gradient is very steep and, hence, the vapour pressure is very sensitive to small temperature variations.

The temperature of a liquid sample during a flash point determination is taken in the centre of the sample and consequently at the vessel walls a higher temperature (and, hence, a higher vapour pressure) will prevail, causing the flash point to be lower than that calculated. However, it does give a good qualitative guide to fuel blending.

This conclusion is the antithesis of the conclusion
91
drawn by Affens who found that within experimental error the calculated and actual flash points of mixtures of n-butane and n-octane in n-undecane were the same. This discrepancy between the two sets of results may have arisen because Affens has calculated theoretical flash points from a complex single equation which, "is based on the assumption that the vapour pressure - temperature relationships are known and that the system obeys the laws of Raoult, Dalton and Le Chatelier!" For hydrocarbon mixtures the laws of Raoult and Dalton would be expected to be obeyed and, further, Le Chatelier's law has been proven to be obeyed. However,

any equation describing the vapour pressure - temperature relationship will only apply with a given set of coefficients over a limited range of temperatures and for any mixture the temperature range covered must be that which describes a vapour pressure change for the higher boiling component from 0 to 5 - 15 torr. This region is particularly difficult to describe by an equation, since the gradient of the curve changes very little initially and then increases abruptly. This effect is not encountered in the present work since the vapour pressure is measured direct from the vapour pressure/temperature curve and whilst this is not so neat a solution, it is felt to be the more accurate. Furthermore, the compounds investigated were of higher molecular weight, C_8 to C_{12} , with consequently smaller differences in vapour pressure.

It may be concluded, therefore, that hydrocarbon mixtures so far tested obey Raoult's, Dalton's and Le Chatelier's laws. For high boiling point (i.e. flash point $>0^{\circ}C$) mixtures one may use these laws to predict their flash point from the individual component properties, as shown by Affens. For low boiling mixtures non-equilibrium effects produce low flash points due to selective vapourisation of low boiling constituents. The dangers associated with contamination of a fuel by low boiling components is, therefore, to be emphasised, and adequate precautions should be taken to ensure any volatile components are retained in samples taken for flash point and other flammability tests.

3.9 GENERAL OBSERVATIONS

During any series of experiments, such as those reported herein, one makes observations that, whilst falling outside the intended sphere of measurement, are still of sufficient merit to warrant reporting. Such data as was collected, and the general observations made are summarised below.

3.9.1 Near Limit Phenomena

The following sequence of events was observed for mixtures near the limit of flammability in the combustion tube. A concave flame would propagate upwards, but not downwards, from the source of ignition for approximately 60cm., the flame would then remain stationary momentarily, as a flat, blue, luminous disc. This disc then moved downwards for ca. 10cm., after which it abruptly changed direction again and accelerated upwards before disintegrating prior to reaching the top of the tube.

These observations are explained by the interaction of the surface area of the flame and, hence, the rate of formation of hot combustion products and the area of tube available for cooling the hot gases. It should, of course, be remembered that although the spacial velocity of the flame (i.e. relative to the tube) changes dramatically, the burning velocity (i.e. the flame speed in relation to the unburnt gas) remains constant. No flame will reach the top of the combustion tube when a flame reversal is achieved since the fuel/air mixture in the upper portion of the tube

will be diluted below the lower limit of flammability by ingress of ambient air during the downward movement of the flame.

The time taken for the first reversal in the direction of flame propagation to occur is also important, since it is well known that in industrial explosions structural damage is often more severe due to the subsequent contraction of gases than the initial expansion. Furthermore, if preventative measures are taken e.g. bursting discs are provided in a closed tunnel, disc rupture occurring on the initial pressure pulse may, in fact, assist flame propagation by preventing the retarding effect of 'hot product' contraction from occurring.

If the present work, thermocouples located up the combustion tube permitted mean spatial velocities of flame fronts to be calculated. In all cases, the observations were for near limit flames, since it was only for these compositions that the phenomena was observed; higher concentrations gave flame speeds which took the flame to the top of the tube before contraction could occur. The spacial velocity was calculated by dividing the distance between thermocouples into the time taken for the flame to pass from one to the next as measured on an oscilloscope. The occurrence of flame reversal between any two thermocouples obviously dramatically reduced the mean flame speed. Care was also exercised to ensure that spurious outputs from downward moving flames were not recorded.

For any given combustion tube diameter the time before contraction remains reasonably constant because two opposing factors operate. On the one hand, the greater the

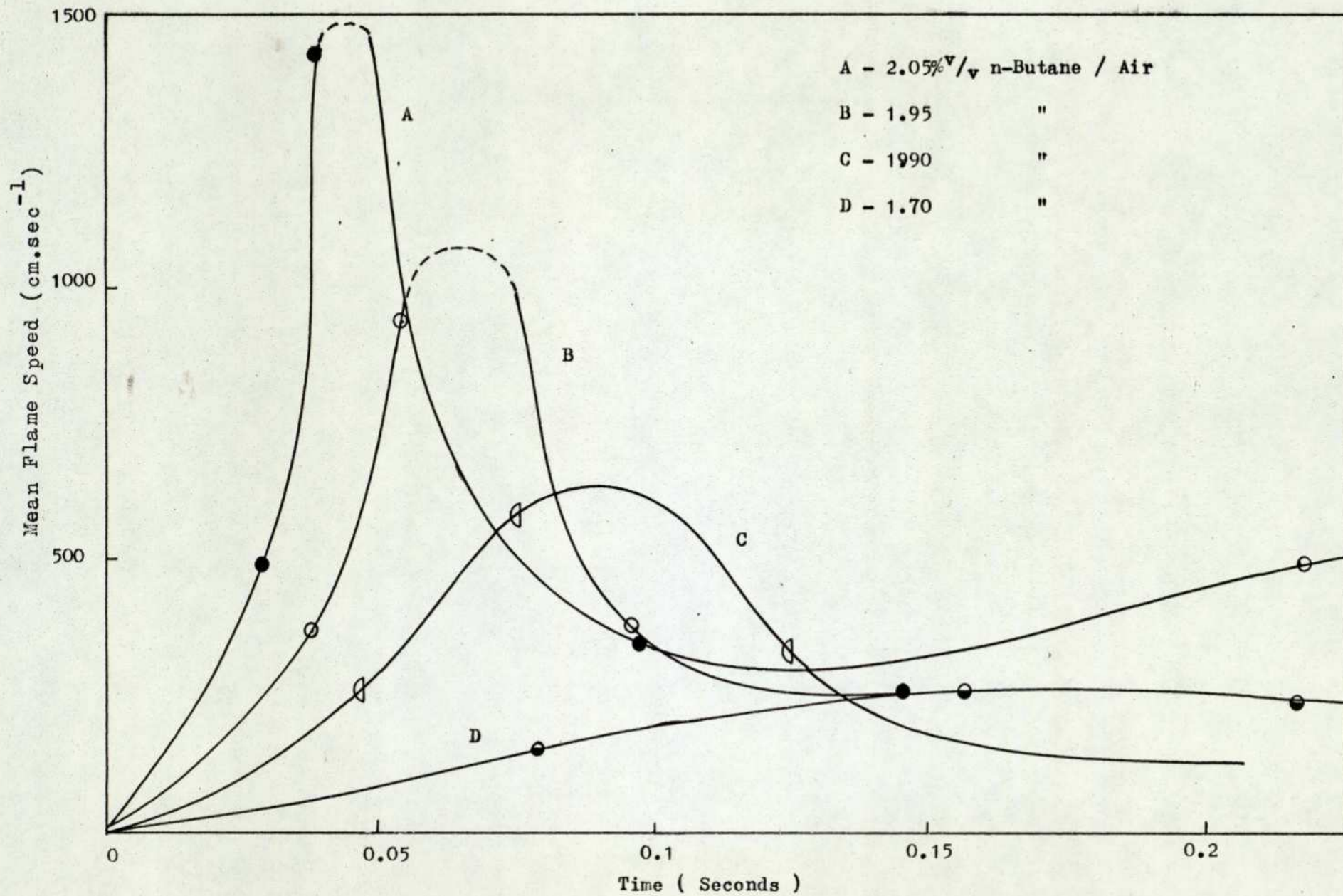
flame speed the greater the surface area of the tube for heat loss and, hence, the shorter the interval before contraction, while, on the other hand, a high flame speed will be associated with an increased burning velocity, which will produce more combustion products and increase the supply of heat, thereby increasing the time interval. The actual interval before contraction could not accurately be determined due to the wide separation of the thermocouples, but some data for near-limit butane/air mixtures is given in Figure 3.15.

3.9.2 Flames Within the Flammable Range

It was observed that flame speeds increased dramatically as the fuel concentration increased until a maximum was reached at the most easily ignited mixture, after which it decreased. Thus, by reference to Figure 3.1, lean mixtures which could be ignited by sparks of less than 100 mJ energy gave a mild report, whilst all those mixtures which could be ignited by very small sparks, i.e. less than 10 mJ, gave a very violent report. All lean mixtures gave a characteristic blue flame, which was clearly defined. Rich mixtures gave a yellow flame and at high concentrations this was slow moving and behaved in a similar manner to a bubble rising through water leaving a long luminous tail. After such flames substantial soot deposition was observed.

Figure 3.15

Variation of Mean Flame Speed with Time for
Various n-Butane/Air Mixtures.



3.9.3 Occurrence of Ignition

Ignition of a near limit mixture either exhibited the oscillatory nature described previously, or it did not ignite at all. The former case was taken as a limit condition, although the requisite 120 cm., of flame propagation, as defined for a 'standard' limit,¹⁷ was not achieved. This was considered acceptable, since flame extinction was thought to be due to dilution of the fuel/air mixture (see Section 3.9.1.) rather than an inability of the flame to propagate. It would appear, therefore, that the apparatus described by Jones⁶⁵ consisting of a short tube, 30 cm., long, of 5 cm., diameter, immersed in a heating/cooling bath and employing a capacitor discharge as the source of ignition, would provide a perfectly adequate and considerably simplified means of determining lower limits of flammability of normal isomers.

The ignition energy versus composition diagrams for lean mixtures of n-decane and 2,2,5-trimethylhexane have been constructed for single electric discharges up to an ignition energy of 2.5 J. Sparks of this energy have been used to determine the lower limits of flammability of the following compounds: n-decane, n-hexane, n-butane, 2,2-dimethylpropane, 2,2-dimethylbutane, 2,2,5-trimethylhexane and hex-1-ene.

The values obtained for the isomers 2,2-dimethylpropane and 2,2-dimethylbutane are higher than those given in the literature. Literature values for 2,2,5-trimethylhexane and hex-1-ene are not available for comparison. These differences are attributed to the difference in the source of ignition and the results obtained correlate well with current theories of the low temperature mechanism of oxidation. Qualitative correlations have also been obtained between the lower limit of flammability results obtained and literature values of spontaneous ignition temperatures and octane numbers.

It has been shown that Le Chatelier's Rule of Limit Mixtures can be applied to a wide range of binary fuel mixtures and can be extended to tertiary fuel mixtures when ignited by sparks of 2.5 J. energy.

Correlations have been drawn between the lower limits of flammability and the flash points of the compounds given above. The flash point is found to be insensitive to small variations in the lower limit of flammability. Flash points of binary fuel mixtures have been determined

and the profound effect of a small concentration of a high vapour pressure liquid in a low vapour pressure liquid has been demonstrated. This data enables fuels whose individual properties of lower limit of flammability, flash point and vapour pressure are known to be blended to achieve a fuel of specified flash point or flammability limit.

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