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Citation: Foster, C. D. (1974). The spontaneous ignition of hydrocarbons in air. (Unpublished Doctoral thesis, The City University)

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A THESIS

entitled

THE SPONTANEOUS IGNITION OF
HYDROCARBONS IN AIR

by

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

ABSTRACT

Studies have been made of the combustion of relatively high molecular weight alkanes (especially n-decane) at sub-atmospheric pressures and in the temperature range 480 to 620°K. Special attention has been paid to the variation with n-decane:air ratio of the spontaneous ignition temperature limits and the effect on these limits of replacing some or all of the n-decane by a highly branched alkane, 2,2,5-trimethylhexane. In addition, the variation with molecular weight and molecular structure of the alkane of the spontaneous ignition temperature limits has been investigated. Studies have also been made of the initial conditions required to cause spontaneous ignition in asymmetrically heated n-decane-air mixtures.

The Introduction (Section 1) outlines the hazards associated with unwanted ignition in hydrocarbon fuels, with particular reference to spontaneous ignition. Methods of classifying flammable and explosive gas mixtures are briefly reviewed, and ways in which the ignition tendency of these mixtures may be reduced are described in terms of the influence of experimental conditions on thermal balance and on the chemistry of the combustion reactions.

The Experimental Section (Section 2) describes the vacuum apparatus and the procedures used. Temperature and pressure changes accompanying combustion reactions were monitored using fine thermocouples and a strain-gauge pressure transducer

respectively. Asymmetric heating of n-decane-air mixtures was achieved using a hot tube contained in a cooler spherical vessel.

The Results Section (Section 3) describes the temperature/pressure ignition profiles for n-decane-air mixtures, and the slow-combustion/cool-flame boundaries obtained with several other alkanes. Overall changes in the nature of the combustion reactions are related to the variation with initial temperature and pressure of the induction period preceding and pressure change accompanying the passage of cool flames. Temperature profiles across the vertical diameter of the reaction vessel show the existence of maximum stable temperature rises at the centre of the vessel under slow-combustion/cool-flame boundary conditions for n-decane-air mixtures; these measurements also indicate the extent of natural convection in such mixtures.

For the hot-tube-in-a-sphere studies, the minimum tube temperature required to cause spontaneous ignition of n-decane in air is shown to depend on vessel temperature and tube diameter. Induction periods preceding, and pressure changes accompanying ignition are shown to be very sensitive to changes in tube temperature.

Finally, in the Discussion Section (Section 4) it is shown that lobes occurring on the two-stage ignition profile for n-decane-air mixtures probably result from changes with temperature of the chain-branching reactions and that the overall activation energy is related to these reactions. The ignitability of fuel-air mixtures containing n-decane and 2,2,5-trimethylhexane is shown to be influenced largely

by the more readily ignitable component, n-decane.

Under conditions where heat transfer in the reacting gases takes place purely by conduction, cool-flame limits are in excellent agreement with predictions according to the conductive theory of thermal ignition. A computer programme based on thermal ignition theory is presented which predicts reasonably accurately for alkanes with carbon number not greater than ten the autoignition temperatures at atmospheric pressure, and the limiting conditions for cool flames. When convective heat transfer is significant, the critical condition for ignition is a function of the Rayleigh number of the gas. The overall activation energy for cool-flame combustion is shown to be a parameter characteristic of the ignitability of an alkane.

Spontaneous ignition in asymmetrically heated gaseous reactants is unlikely to occur unless a critical amount of heat is supplied to the gas which is consequently raised above a critical temperature.

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ACKNOWLEDGEMENTS

The research for this thesis was carried out under the direction of Professor C.F. Cullis in the Combustion Research Laboratory of the City University. I would like to thank my colleagues for providing such a stimulating and congenial atmosphere in which it was a pleasure to work.

My special thanks go to [REDACTED] for the help and guidance he has given me throughout this work and in many other ways, and [REDACTED] [REDACTED] [REDACTED] for the interest which he has shown in this work. I would like to acknowledge the financial support given by The Admiralty Oil Laboratory, to whom I am indebted.

Finally, I would like to thank my wife for her patience and for the encouragement which she has given me throughout.

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INTRODUCTION

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1.1 Introduction

The combustion of hydrocarbons in air is a chemical reaction of tremendous technological and economic importance, and is at present used very largely as a source of heat and mechanical energy. Indeed, energy statistics released for 1971 show that petroleum fuels (which consist almost exclusively of hydrocarbons) were responsible for more than 45% of the total energy consumed in the United Kingdom.¹

A recent report given by the Under Secretary for Trade and Industry showed that oil companies had already invested over £300 million in North Sea projects, and that a further £200 million was already scheduled for expenditure mainly on oil. Furthermore, plans have been made to spend £1500 million on oil development, so that by 1980, the North Sea could provide one half of the supplies and one quarter of the energy requirements of the United Kingdom.

As a result of the increase in the United Kingdom oil output, it follows that there must also be an increase in the bulk movement and storage of petroleum. Thus, in 1971, as much as 162 million tons of bulk petroleum were moved throughout the United Kingdom, of which 57 million tons were transported by road, 16 million tons by rail and the rest by water and pipeline.¹ By handling such large quantities, in particular of volatile hydrocarbons and combustible gases, industrial organisations face the risk of explosion caused by the accidental release of these substances, their admixture with air and subsequent ignition. One class of such explosions, namely

those which occur in the open air, has the potential of being very dangerous and expensive.² The reason for this is simply that larger and larger quantities of dangerous materials are being handled, shipped or stored in bulk, and the chance of a large release of fuel (as an unconfined vapour cloud) before ignition has thereby increased tremendously. Three notable cases of unconfined vapour cloud explosions have occurred quite recently in the United States.

In 1962, a 7,000 gallon road tanker was involved in an accident in the town of New Berlin, New York.³ As a result of the accident, the tanker ruptured and released a vapour cloud which was 80 feet deep, and covered an area of 200,000 square feet before it ignited. The explosion and resulting fire killed ten people and caused \$200,000 damage. The second incident occurred in Crescent City, Illinois in 1970.⁴ A train containing ten 33,000 gallon tank trucks was derailed in the centre of the town. The vapour cloud explosion triggered off fire and subsequent explosions which destroyed the business section of the town, although fortunately no fatalities were reported. The third incident, which also took place in 1970, involved an 8-inch diameter, 40 year old pipeline, and occurred near Port Hudson, Missouri.⁵ The pipeline, which contained liquid propane, burst at a cold stitch weld and released 550,000 cubic feet of propane gas before ignition occurred thirteen minutes later. It was estimated that the vapour cloud covered approximately ten acres when ignition occurred, but damage was slight owing to the isolated location of the incident.

Although unconfined vapour cloud explosions usually have disastrous consequences, they fortunately tend to occur less frequently than other types of accidental explosions, such as those occurring in fuel tanks, machinery spaces or engine rooms in ships and aircraft, or in chemical plant.

In recent years, therefore, a considerable amount of research has been specifically concerned with the assessment of such explosive hazards as these, and, in particular, with the reduction of the tendency of hydrocarbon fuels to undergo spontaneous ignition. Whilst this research has led to a far better understanding of the dependence of spontaneous ignition temperature limits on the chemistry of the combustion reactions, there have been relatively few attempts to quantify the hazards.

1.2 Methods of classifying flammable and explosive gas mixtures

In the past, several experimental techniques have been developed which provide a means of measuring the range of flammability and the ignition hazard of combustible gases and liquids. These techniques have subsequently been standardised in order that they may provide a basis for the classification of a flammable liquid or gas from a legal standpoint, and from the point of view of laying down codes of practice. In the following Sections, some of these experimental techniques will be described.

1.2.1 Flammability limits

A mixture of a combustible gas or vapour and a gaseous supporter of combustion (e.g. air) may be diluted with one of its components, or a third component, until a limiting composition is reached, whereupon further dilution renders the mixture incapable of propagating a flame. For each combination of combustible gas and supporter of combustion there exist two such limiting compositions known as the upper and lower limits of flammability. For example, all n-decane + air mixtures at a temperature of 100°C and in the limiting composition range 0.77 to 5.35 vol % n-decane, have been shown to be flammable;⁶ where 0.77 and 5.35 vol % n-decane represent the lower and upper limits of flammability respectively.

Flammability limits are usually measured using a homogeneous, quiescent gas mixture contained in a vertical tube of at least 5 cm. diam. and 120 cm. length. The gas mixture may

be ignited by a spark or flame introduced into the top or bottom of the tube, causing downward or upward flame propagation respectively. From the point of view of ignition hazard, it is generally safer to consider the limits for upward flame propagation since these limits are wider than those for downward flame propagation. A large amount of data on the flammability limits of numerous combustible gases and vapours has been collected by Coward and Jones.⁶

Studies have also been made of the flammability limits of mists and sprays.⁷ In these studies, it was shown that the flammable properties of a suspension of particles of tetrahydronaphthalene, of diameter less than 10 microns, was identical to that of a vapour. However, in a suspension of particles of diameter greater than 40 microns, the particles burnt individually. From the point of view of explosion hazards, it is noteworthy that coarser aerosols maintain a flame at substantially lower fuel-air ratios than do fine aerosols or gaseous mixtures.

1.2.2 Flash points

The flash point of a flammable liquid is the temperature to which the liquid has to be heated so that it releases sufficient vapour to form a mixture with air which can be momentarily ignited by a flame. Continuous burning takes place at a slightly higher temperature, known as the 'fire point', which is the lowest temperature at which the liquid gives off vapour at a rate great enough to support a continuous flame, after the original flame has been removed.

Flash points may be measured using closed or open cup methods. In principle, both methods are similar and involve heating a prescribed volume of liquid at a standard rate in a cup of standard dimensions. A test flame is applied to the vapour space at given intervals of time, and the flash point is the temperature of the liquid at which a flame is first observed to propagate through the vapour space.

The concept of flash point was introduced into the 1862 Petroleum Act, and developed in subsequent legislation. As recently as 1967, it has been shown that the standard methods of determining open flash points suffer from defects of design, and consequently their use may give misleading results.⁸ Further to this, it is shown that the open flash point is an arbitrary quantity, which does not relate to any specific hazard. In contrast, however, if the temperature of a liquid exceeds its closed flash point, then the concentration of the vapour near the liquid surface exceeds the lower flammability limit.

1.2.3 Ignition by electric sparks

Small electric sparks may be passed through a potentially explosive gas mixture without causing ignition. However, if the energy of this spark is increased, a threshold energy is reached which causes the gas to ignite in the vicinity of the spark, and a flame to propagate throughout the volume of the gas. The threshold spark energy is a definite function of the properties of the explosive gas mixture and of the configuration of the spark gap. Threshold

spark energy determinations are usually carried out in vertical tubes or spherical vessels, and the results show continuous limits for the variation of threshold spark energy with composition of the explosive gas mixture.

1.2.4 Spontaneous ignition temperature

The spontaneous ignition temperature is the temperature to which a combustible gas mixture must be heated so as to cause the gas to ignite in the absence of a separate ignition source, such as a spark or flame. Spontaneous ignition temperatures are a function of several variable parameters including the size, shape and nature of the containing vessel or heat source, and the pressure, composition and chemical nature of the gas mixture. Studies which are made to assess the tendency of a gas mixture to undergo spontaneous ignition should be carried out in large spherical vessels, in which it has been shown that ignition takes place more readily than in vessels of any other shape or size.⁹

Spontaneous ignition in gases is accompanied by the release of a large amount of heat and a sudden increase in the number of molecules present. Thus, a closed reaction vessel equipped with pressure and temperature measuring devices will provide a convenient method of detecting whether or not spontaneous ignition is taking place.

When the temperature of the containing vessel is below the spontaneous ignition temperature of the gas mixture, slow combustion reactions will take place accompanied by a slow release of heat

which is quickly dissipated through the gas and lost at the vessel walls. When the temperature of the reaction vessel is raised to the spontaneous ignition temperature of the gas mixture, the rate of heat release becomes greater than the rate of heat dissipation, causing self-heating of the gases and self-acceleration of the reaction and resulting in the propagation of a flame throughout the gas mixture.

The spontaneous ignition of a gas mixture is associated with a finite delay time which corresponds to the extent of occurrence of pre-ignition reactions which must take place before a flame can propagate. This delay time decreases with increasing temperature of the gas mixture, and thus the maximum delay time will correspond to the minimum spontaneous ignition temperature. Since in practical situations, a given volume of flammable gas is usually moving continuously, ignition of this gas volume will be subject to it remaining in contact with a hot surface for a time which at least equals the ignition delay.

The spontaneous ignition temperatures of a considerable number of hydrocarbons and other compounds have been determined by several workers.¹⁰⁻¹³ In these studies, the test liquid is normally introduced in drop form into a heated reaction chamber or crucible, and its spontaneous ignition temperature is then measured. Since, in some of these experiments, the ignition chambers were small and the air or oxygen flowed at a controlled rate through the chamber, the measured spontaneous ignition

temperatures of the compounds tested were considerably higher than those which would be expected had the studies been made under static conditions, and in large spherical vessels. Thus, whilst these numerous studies provide good comparisons for the relative tendencies of the compounds to undergo spontaneous ignition, the values reported are not reliable measures of their ignition hazard.

1.3 Examples of the accidental spontaneous ignition of hydrocarbon-air mixtures

The accidental spontaneous ignition of hydrocarbon-air mixtures is still an all too frequent occurrence. Recently published figures have shown that between 1967 and 1969, there has been a 40% increase in the number of fires in oil refineries and chemical plants.¹⁴ Furthermore, at least 40% of the 52 fires which occurred in oil refineries and chemical plants in 1969 were initiated by spontaneous ignition or by hot pipes.

The large scale use of hydrocarbon fuels and lubricants in ships presents a significant explosive hazard. Crankcase explosions are just one example, and after such an incident in 1947, resulting in the loss of twenty-eight lives, a comprehensive investigation was undertaken. The results of this investigation indicated that the occurrence of crankcase explosions is likely to be associated, in a majority of cases, with the formation and subsequent spontaneous ignition of a lubricating oil mist in contact with an over-heated engine part.¹⁵ In a more recent publication, one of those responsible for the above investigation has outlined the initiation and development of gaseous explosions in ships, considering in turn the explosive medium, the source of ignition and the behaviour and control of the explosion flame.¹⁶ In this paper, mention is made of a survey of 16 serious explosions which have occurred in ships since the Second World War. The survey showed that the cause of half the cases was spontaneous ignition resulting from the exposure of hydrocarbon vapours in air to high temperatures in hot spaces or near

over-heated surfaces. Two of the cases involved crankcases.

In recent years, a considerable number of studies have been made of the spontaneous ignition characteristics of aviation fuels.¹⁷⁻²⁴ Some of these studies have been concerned with aspects of safety in supersonic flight, during which skin temperatures of Mach 3 aircraft have been reported to be as high as 250°C. This temperature is greater by tens of degrees than the spontaneous ignition temperature of several aviation fuels given in Table I. Hence, if any fuel came into contact with areas of the aircraft skin at these elevated temperatures, a flammable vapour-air mixture might be formed and may subsequently ignite. Although only a few examples of fire and explosive hazards have been described above, it is clear that these have stimulated a considerable number of investigations into the spontaneous ignition behaviour of hydrocarbon fuels and lubricants. The results of these investigations, along with flammability limit and flash-point values, provide some quantitative assessment of the ignition and explosion hazards of a particular hydrocarbon fuel. Thus, the effectiveness of a method chosen to reduce these hazards may also be evaluated.

TABLE I

The spontaneous ignition temperatures in air and at atmospheric pressure of some aviation fuels.

Fuel	Spontaneous ignition temperature (°C)	Experimental conditions	Reference
Jet, J.P. 6.	230	200 cm ³ spherical vessel	23
A.V.T.U.R.	210	18 in. diam. spherical vessel	22
Kerosene, SR 312	210	6 in. diam. spherical vessel	18

1.4 Methods of altering the spontaneous ignition characteristics of hydrocarbons

1.4.1 Introduction

Before considering ways in which the spontaneous ignition characteristics of hydrocarbons may be modified, it would be helpful to outline briefly the chemical nature of combustion reactions, and to indicate the types of combustion phenomena which may be observed. A comprehensive account of the chemistry of combustion reactions will be given later.

The non-isothermal oxidation of a hydrocarbon, taking place in a closed vessel, is accompanied by a transient pressure change, the characteristics of which may serve to classify the various types of combustion behaviour.

There are four classes of combustion behaviour, viz.

- slow combustion - an almost isothermal phenomenon giving rise gradually to a small pressure increase;
- single or multiple cool flames - pressure fluctuations superimposed on slow combustion;
- two-stage ignition - a cool flame followed by a large pressure pulse which represents an explosive consumption of reactants;
- single-stage ignition - a large pressure pulse representing explosive reactant consumption.

Whether or not any one type of combustion behaviour will take place depends on the ratio of hydrocarbon to oxidant, the initial temperature and pressure of the reactants and the size, shape and nature of the reaction vessel. The variation with temperature and

pressure of the several types of combustion behaviour form an ignition profile, a typical example of which is given in figure 1.1. The several types of combustion behaviour are separated by well-defined limits and, in figure 1.1, the variation with pressure of the spontaneous ignition temperature limit is represented by the line ABC.

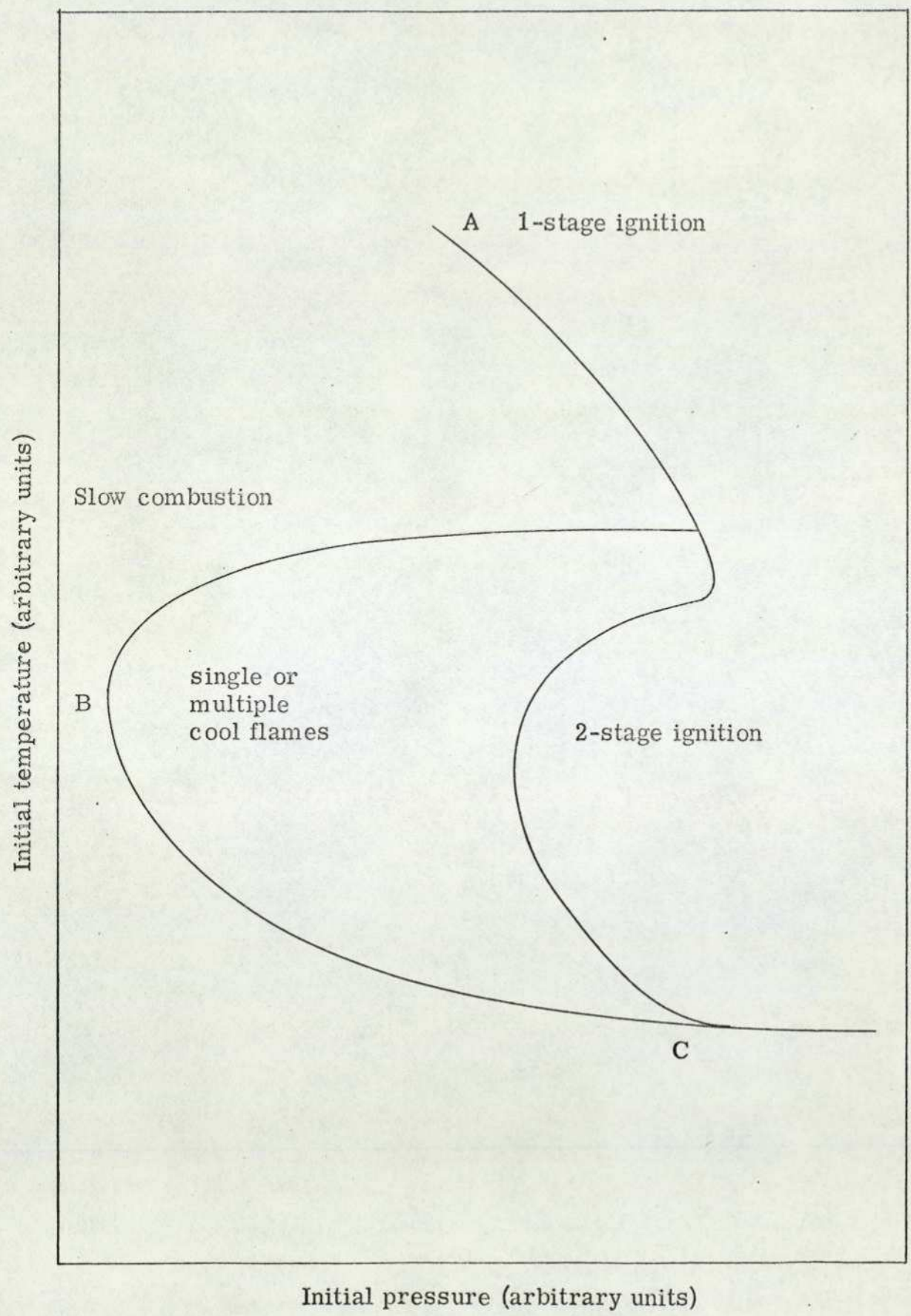
It is well understood that the oxidation of hydrocarbons takes place by a complex chain-branching reaction involving a multiplicity of chain carriers. The variation with initial temperature and pressure of the reaction rate in hydrocarbon oxidation leads to the complex pressure-temperature ignition profile shown in figure 1.1.

The initial conditions of temperature and pressure under which the various types of combustion behaviour are observed may be considerably altered both by influencing the kinetics of reactions which lead to the formation of branching agents (typically mono- and dihydroperoxides and peracids in hydrocarbon oxidation), and by causing a change, relative to normal oxidation, in concentration of the more important chain propagating species such as hydroxyl, alkylperoxy and hydroperoxy radicals.

Limits of flammability and spontaneous ignition temperatures of hydrocarbons in air or oxygen may be modified considerably by the addition of chemical catalysts and by changes in the size, shape or nature of the containing vessel. Each of these methods will be considered individually.

Figure 1.1

A simplified ignition profile showing regions of different
types of combustion phenomenon



1.4.2 The nature of the vessel surface

In metal reaction vessels, the spontaneous ignition pressure of n-heptane-air mixtures at 505°C have been found to be considerably higher than those in vitreous vessels of a corresponding size and shape.²⁵ Furthermore, the limiting ignition pressure was found to be different for the same vessel, depending on whether the surface of the vessel was rough or smooth. This latter effect has also been observed with several other hydrocarbon-air mixtures reacting in different metal vessels.¹³

The effects on the combustion reactions of hydrocarbons of coating a vitreous reaction vessel with alkali halides has been studied by several investigators. Whereas propane and n-heptane oxidation have been found to be unaffected by a KCl surface,^{26, 27} the cool flames of cyclohexane were inhibited.²⁸ The multiplicity of n-butane cool flames has been shown to be reduced in the presence of MnCl₂, NiCl₂, CuCl₂, PbCl₂, KCl and KI surfaces.²⁸

Surface coatings of PbO have been found to be very effective in inhibiting cool flames.^{27, 28, 29} In all these cases, the inhibition has been ascribed to an increase in the rate of heterogeneous destruction by the PbO surface of the species responsible for chain branching.

Studies made of the slow oxidation of methane in PbO-coated, heat-treated, HF-treated and aged silica reaction vessels indicated that the various surfaces differentially destroyed important chain carriers, which were probably HO₂ and H₂O₂.³⁰ Recent work has

shown that the large effect which some surfaces have on the gaseous combustion of hydrocarbon fuels may be correlated with the efficiency of the surface in destroying HO_2 and H_2O_2 .^{31, 32} Three categories of surface were thus defined; the first is inefficient in the destruction of both HO_2 and H_2O_2 (eg. silicic acid, boric acid, phosphoric acid, germanium dioxide and titanium dioxide), the second destroys HO_2 by a diffusion-controlled process (eg. metallic oxides, and probably hydroxides, and salts in general), and third destroys both HO_2 and H_2O_2 by diffusion-controlled processes (eg. silver coated surface and oxidised lead foil).

1.4.3 The extent of the vessel surface

The surface to volume ratio (S/V) of a reaction vessel is a characteristic often used to correlate the variation with size and shape of the vessel of the spontaneous ignition temperature of a particular compound. Discrepancies in the reported values of spontaneous ignition temperature of a given compound are due frequently to differences in S/V ratios of the vessels employed by various investigators. It has been shown, however, that by using results obtained in several different studies a linear relationship holds for the variation with S/V ratio of the spontaneous ignition temperatures of benzene, toluene, isooctane, n-heptane and hexadecane.¹⁰ A similar relationship has been shown to exist for aviation and jet fuels.^{18, 23}

Detailed studies of the combustion reactions of ten hydrocarbons in a number of different quartz reaction vessels have shown that the main effects of increasing S/V ratio are that: (a) reactions are inhibited in the earliest stages, but promoted in the subsequent stages; (b) ignition is strongly inhibited; (c) the tendency for ignition to occur with explosive violence decreases.³³ It is suggested that inhibition in the early stages of reaction is due to chemisorption of OH and HO₂ radicals on the reaction vessel surface. This continues until all the active sites have been hydroxylated through chemisorption; promotion then results as a result of hydrogen bonding between surface hydroxyl groups and RO₂ radicals, leading to the decomposition of RO₂ radicals to more reactive RO radicals. The striking inhibition of ignition is thought to be due mainly to the destruction of hydrogen atoms on both active and hydroxylated sites. The decrease in explosive tendency of ignition is attributed to: (a) an increase in the rate of termination processes taking place at the surface; (b) a greater loss of heat to the surface; and (c) the availability of smaller amounts of unconsumed reactants at the instant of ignition.

In a more recent investigation, the spontaneous ignition of kerosene was measured as a function of S/V ratio which was varied by changing the number of steel inserts in a steel reaction vessel.³⁴ Although, at 250°C, there is a discontinuity in the slope of this function, the results are believed to indicate that the risk of spontaneous ignition in, for example, an aircraft fuel tank would be reduced by inserting a metal honeycomb in order to increase the

S/V ratio. More recently, it has been shown that this conclusion is not necessarily correct.³⁵ The explanation for this is connected with the existence in hydrocarbon oxidation of a region of negative temperature coefficient in the rate of heat release curve. This region gives rise to an inflection in the curve corresponding to the discontinuity which was observed during the kerosene investigation. For a given initial temperature, the S/V ratio of the reaction vessel may be increased, until a theoretical steady-state temperature is attained near the point of inflection on the rate of heat release curve. In practice however, by the time that this steady-state temperature has been attained, the radical concentration is far in excess of its equilibrium value, and two-stage ignition occurs.

It was further suggested³⁵ that an ignition region such as the one described above, exists at higher values of the S/V ratio than that at which the discontinuity appeared in the kerosene investigation.

Studies have been made of the ignitability of n-heptane-air mixtures in a wide variety of packed and unpacked vitreous reaction vessels.^{25, 36} The variation with S/V ratio of the limiting ignition pressure was shown to be represented by a straight line which for unpacked vessels passed through the origin. However, the values of the limiting ignition pressure for packed vessels were found to be considerably lower than would be expected simply on the basis of the S/V ratio.

In an attempt to correlate the results for packed vessels with those for unpacked vessels, calculations were made of the average distance of a molecule from the surface.^{25, 36} It was shown that the limiting pressure for ignition varied almost linearly with the reciprocal of this average distance for all the vessels, thus providing a far better means of correlation than the S/V ratio.

1.4.4 The effects of incorporating a second fuel component (fuel blending)

A hydrocarbon fuel normally consists of a mixture of hydrocarbons, each of which has its own ignition tendency.

A useful indication of the fire hazard of a fuel may be given by its flash point. Since flash points are generally inversely proportional to volatility, it might be expected that the flash point of a hydrocarbon fuel will be similar to that of its most volatile component. This is likely to be the case if the volatile component is present in the mixture in concentrations high enough to permit the release of vapour sufficient to form a flammable mixture. The addition of a very volatile liquid to a liquid of low volatility has a disproportionately large effect in lowering the flash point of the mixture. For example, the flash point of gas oil may be lowered from 69°C to ca. 3°C by the addition of as little as 3% motor gasoline. Thus, the flash point of a fuel mixture may be suitably adjusted by careful fuel blending.

Measurements have been made of the spontaneous ignition temperature of n-dodecane containing 5 mole % of various additives.¹³

It was shown that although benzene, toluene and the xylenes in particular have a negligible effect on the spontaneous ignition temperature of n-dodecane, hexamethylbenzene raises this temperature from 232 to 246°C.

Recent studies have shown that the ignition tendencies of binary mixtures of hydrocarbons are, in general, influenced far more by the more readily ignitable component.³⁷ Moreover, studies made close to the lowest ignition temperature of the components have revealed that the ignition behaviour of the mixture is controlled largely by the preflame combustion reactions. In some cases, for example, with mixtures of alkanes and alkenes, the preflame activity is increased by a strong interaction between the components. When this occurs, the ignition tendency of the mixture is greatly increased, and is indeed sometimes greater than that of the more readily ignitable component. The ignition tendency of the mixture whose components display similar preflame and ignition behaviour has been shown to be similar to that of its components. In general, the ignition tendency of mixtures, with the exception of those in which preflame interaction occurs, has been found to be intermediate between those of the components, and proportional to their relative concentrations.

Similar studies have been made at 750°C where it can be shown that the ignitability of the mixture is influenced to a greater extent by the more readily ignitable component than is observed at temperatures close to the minimum ignition temperature. Some

oxidative degradation of alkanes is known to take place at 750°C , resulting in the formation of alkenes.³⁷ On account of this, mixtures such as those of an alkane and an aromatic hydrocarbon exhibit enhanced preflame activity resulting in the mixture being more readily ignitable than either of its components.

Detailed studies of the spontaneous ignition of mixtures of n-heptane and 1-heptene in oxygen have shown that below ca. 300°C , where 1-heptene is considerably less reactive than n-heptane, the alkene is not involved in the cool flame process leading to ignition, and that the ignitability of the mixture is controlled effectively by the concentration of the alkane.³⁸ In fact, partial replacement of the alkane by the alkene retards the cool flame stage of oxidation more effectively than does replacement of the alkane by an inert gas. Above 300°C , however, 1-heptene was found to be at least as ignitable as n-heptane and the alkene appears to contribute to the process leading to ignition. Under all conditions investigated, both hydrocarbons are consumed during ignition.

This dual inhibiting and promoting role of alkenes has also been observed in studies of the effects of several alkenes on the two-stage ignition of cyclohexane and n-heptane in a vertical flow reactor.³⁹

1.4.5 The influence of gaseous additives on the ignition and explosion tendencies of hydrocarbon-air mixtures

1.4.5.1 Inert gases

The addition to a flammable gas mixture of increasing amounts of a chemically inert substance causes the limits of flammability of the mixture to approach, and ultimately to meet. Examples of such inert substances, listed in decreasing order of effectiveness, are carbon dioxide, helium, nitrogen and argon. Helium, on account of its high thermal conductivity has an extinction capacity which increases more markedly with decreasing vessel dimensions than does that of other gases.⁴⁰

From curves constructed to show the effect of an inert diluent on the limits of a flammable gas in air, it is easy to deduce both the maximum and minimum percentages of oxygen necessary to support inflammation, and the minimum percentage of inert diluent which must be mixed with a combustible gas to prevent flame propagation. A graphical method has been devised for the deduction of such conclusions.⁴¹

Inert gases are used extensively during cleaning, loading and discharging operations in the cargo tanks of crude oil carriers. Since it is not essential that pure nitrogen or carbon dioxide be used as the inerting medium, then usually scrubbed flue gas is taken from oil-fired boilers and its composition is considered adequate to meet the limiting oxygen figure. The composition by volume of a flue gas after reasonably efficient combustion and scrubbing is approxi-

mately:

Carbon dioxide	12.0 - 14.5 %
Oxygen	2.5 - 4.5 %
Sulphur dioxide	0.02 - 0.03 %
Nitrogen	About 77 %
Remainder	Water vapour and solids.

Pure carbon dioxide or nitrogen, supplied from refrigerated bottles, is sometimes used as an inerting medium in special circumstances, such as on liquefied petroleum gas and liquid methane carriers.

Recent studies of the high temperature spontaneous ignition of n-heptane-oxygen mixtures, have shown that additions of nitrogen or helium to these mixtures have a promoting influence on ignition.^{25, 36} However, for a molar nitrogen: oxygen ratio of greater than 6.5, the limiting ignition pressure varies but little. This promoting influence on ignition by the addition of inert gases has been found to be less pronounced in larger reaction vessels (up to 2 l).

For a given hydrocarbon, the pressure range within which the limiting profiles of cool flames and two-stage ignitions lie, is much greater for oxidation of the hydrocarbon in air than in oxygen. Nevertheless, the cool flames of hydrocarbons in air and in oxygen are essentially similar phenomena.¹¹

The addition of chemically reactive substances

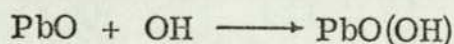
1.4.5.2 Metal alkyls

The occurrence of 'knock' in a spark-ignition engine limits both the power output and the economy of the engine. In a recent

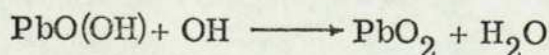
investigation 'knock' has been shown to arise from spontaneous ignition in the last part of the unburnt charge rather than as a result of flame acceleration.⁴²

The tremendously effective anti-knock properties of tetraethyl lead were discovered in ca. 1918, and its use as an anti-knock in the spark-ignition engine has continued to the present day. As a result of a series of very detailed studies, Walsh and his co-workers⁴³⁻⁴⁷ have concluded that tetraethyl lead exerts its anti-knock influence on the second stage of two-stage ignition by forming a 'fog' of solid particles of lead monoxide, the surface of which is particularly effective in destroying hydrogen peroxide. Many of the observations made during these experiments were confirmed under engine conditions.

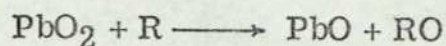
Another important line of work undertaken by Norrish et al.⁴⁸⁻⁵² has thrown some doubt on the conclusion that a fog of solid particles is involved. This work suggested that tetraethyl lead increases the delay period for the growth of hydroxyl radical concentrations, and it was therefore proposed that, even under engine conditions, tetraethyl lead acts as an anti-knock via a homogeneous mechanism involving gaseous lead atoms. This suggested mechanism was later modified and the following alternative mechanism was proposed:⁵²



followed by



and by the reduction of PbO_2 back to PbO via



Walsh et al. have questioned the relevance of this mechanism on the grounds that the results were obtained from experiments which were not representative of engine conditions.

Recent studies have shown that the addition of diethyl mercury, tetraethyl lead, tetraethyl tin and tetramethyl germane to n-heptane-oxygen mixture have a negligible effect on cool flame phenomena.⁵³

1.4.5.3 Halogen compounds

Halogen compounds inhibit reactions taking place in many oxygen-supported flames, and bromine compounds are especially effective in this respect.

The flammability limits of several hydrocarbon-air mixtures have been shown to be narrowed, and ultimately to meet, on addition of increasing amounts of methyl bromide.^{54, 55} Mixed organo-halogen compounds and carbon tetrachloride have also been found to be effective in narrowing flammability limits. For example, the addition of as little as 0.5% bromochloromethane to n-hexane-air mixtures reduced the upper flammability limit from 6.7 to 5.0%.⁵⁶ Furthermore, n-hexane-air mixtures are rendered non-flammable by the addition of 6.35% bromochloromethane or 13.0% dichlorodifluoromethane.^{54, 56}

Flame speeds in methane-air mixtures are reduced by the

addition of dibromodifluoromethane or trifluorobromomethane, and it has been shown that, as in other studies,⁵⁵ the effectiveness of these additives is essentially the same as that of an equivalent amount of bromine which is chemically incorporated into the additive.⁵⁷

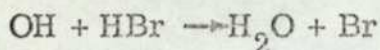
Thus, it was suggested that the chemically bound bromine in the additive is released by decomposition or oxidation before it can act effectively as an inhibitor. The inhibiting effect of trifluorobromomethane was however found to be greater than the equivalent amount of bromine, and it was concluded that, in this case, the CF_3 radical contributes in some way towards inhibition. The mechanism by which inhibition takes place was thought to involve the removal by a hydrogen halide of the chain-propagating radicals, viz:



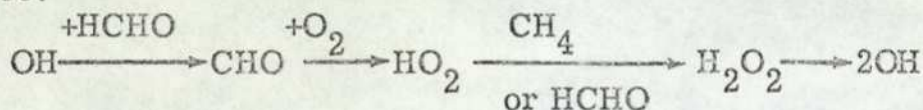
where R represents H or O atoms or OH or CH_3 radicals.

Studies have also been made of the effects of hydrogen bromide and several bromomethanes on the slow oxidation and spontaneous ignition of various hydrocarbons, formaldehyde, acetaldehyde, isopropyl alcohol and diethyl ether.⁵⁸ The results of these studies show that whereas hydrogen bromide exerts a marked, usually promoting, influence on the slow oxidation and spontaneous ignition of all the fuels studied, the bromomethanes have a well-defined effect as additives only when oxidation of the fuel takes place above ca. 250°C . Furthermore, when the organic bromine compounds do exert an appreciable influence on combustion, their effect is qualitatively similar to that of hydrogen bromide.

On account of this, it was suggested that the bromomethanes themselves do not appreciably affect the slow combustion or spontaneous ignition of the fuels studied, and that it is only their oxidation or pyrolysis products, presumably bromine or hydrogen bromide, which exert a well-defined influence. In this study, it was found that methane and formaldehyde were the only fuels, certain stages of the oxidation of which were retarded by hydrogen bromide. Retardation was thought to result from a reduction as a result of the reaction:



in the number of OH radicals which take part in the branching sequence:



It was suggested that this scheme bears a close chemical relation to the reactions by which bromine compounds exert a retarding influence on oxygen-supported flames. In agreement with this are the results of studies made elsewhere, which have been discussed earlier.⁵⁷

Both saturated and unsaturated halogen compounds have been shown to promote cool flames and two-stage ignition in cyclohexane and n-heptane.³⁹

1.4.5.4 Nitrogen compounds

In 1918, Kettering, Midgley and Boyd discovered, more by accident than design, that aniline and its derivatives were effective 'anti-knocks'. The effectiveness relative to benzene of benzene derivatives as 'anti-knocks' can indeed be correlated with the expected activating and de-activating effects of the side chains on the electron density of the benzene ring.⁵⁹ Studies of the 'anti-knock' action of aromatic amines have shown that all the anilines in which both hydrogen atoms of the $-NH_2$ group are replaced by alkyl groups have no effect on the tendency of a fuel to 'knock'.⁶⁰ Conversely, tertiary aromatic amines were found to be more effective inhibitors of non-engine combustion than were less highly N-substituted amines.⁶¹

Aliphatic amines also possess exceptional inhibiting properties. Studies of the inhibition of the slow gaseous oxidation of acetaldehyde by aliphatic amines have shown that, as with aromatic amines, the secondary and tertiary bases are considerably more effective than the primary amines.⁶² Furthermore, with primary and tertiary amines, the induction periods have been shown to be directly proportional to the pressure of the inhibitor, whereas with secondary amines, the induction periods are proportional to the square of the inhibitor pressure.

Two alternative explanations were proposed to account for the inhibiting influence of the amines. One involved homogeneous stabilization of acetyl radicals, and the other involved suppression

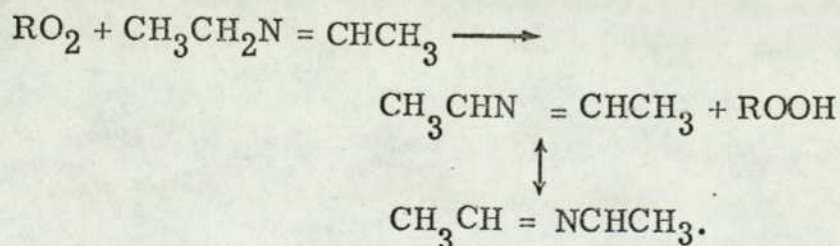
of chain initiation at the walls.

Similar studies have been made of the influence of aliphatic amines on the explosive oxidation of acetaldehyde.⁶³ In these studies, it was shown that, generally speaking, the inhibiting power of the amines decreased in the order secondary, tertiary, primary, and that in all the systems studied, the length of the induction period preceding explosion was directly proportional to the pressure of the inhibitor.

Recently, a detailed investigation has been made of the influence of both aromatic and aliphatic amines on the spontaneous ignition of mixtures of n-heptane + air.⁶⁴ It has been shown that the addition of small quantities of primary and secondary amines reduced considerably the ignitability of n-heptane-air mixtures, the most effective additive being dimethylamine. The inhibiting role of the primary amines was thought to be twofold. Firstly, a condensation reaction with acetaldehyde competes with the oxidation of the aldehyde, the latter reaction being responsible for the formation of the branching agent, viz:



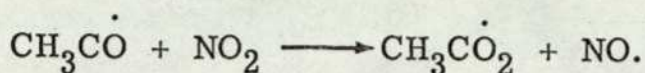
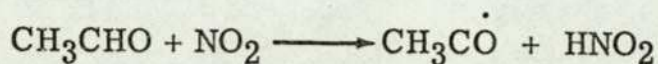
Secondly, a subsequent hydrogen abstraction from the imine leads to a resonance-stabilised radical which is unable to propagate effectively the reaction chain, viz:



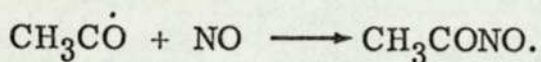
Tertiary amines were however found to have little influence on the induction period preceding a cool flame, and also to promote two-stage ignition. This latter effect was thought to be the result of the rapid oxidation of tertiary amines in the cool flame itself. Thus, at the temperatures attained in the cool flame (greater than 250°C) the oxidation products of triethylamine will include large amounts of acetaldehyde, resulting in a corresponding increase in the rate of subsequent chain-branching. Similarly, primary and secondary amines have been found to retard both cool flames and two-stage ignitions in cyclohexane and n-heptane, whereas trimethylamine exerts a marked promoting effect.³⁹

Oxides of nitrogen have also been reported to have a dual (promoting and inhibiting) effect on gaseous oxidation reactions. The addition of nitrogen dioxide to mixtures of diethyl ether has been shown to raise the limiting pressure necessary for cool flame propagation, and at the same time to lower the limiting pressure for two-stage ignition.⁶⁵ A point is reached where the two limits merge, and a further increase in the concentration of the additive raises the limiting pressure for two-stage ignition. It was concluded, therefore, that nitrogen dioxide inhibits reactions leading to the formation of a cool flame, but during the propagation of a cool flame it promotes reactions which are responsible for the occurrence of two-stage, hot ignition. This effect was explained by assuming that at low temperatures, a molecule of nitrogen dioxide acts as a free radical and tends to combine with other free radicals to form a relatively stable complex, $(\text{NO}_2) \text{R}$.

However, the inhibiting effect of nitrogen dioxide on the oxidation of acetaldehyde has been ascribed to the reaction between acetaldehyde and nitrogen dioxide to form nitric oxide:⁶⁶



The nitric oxide then combines with the acetyl radical, normally the chain initiator, to form the stable compound CH_3CONO :



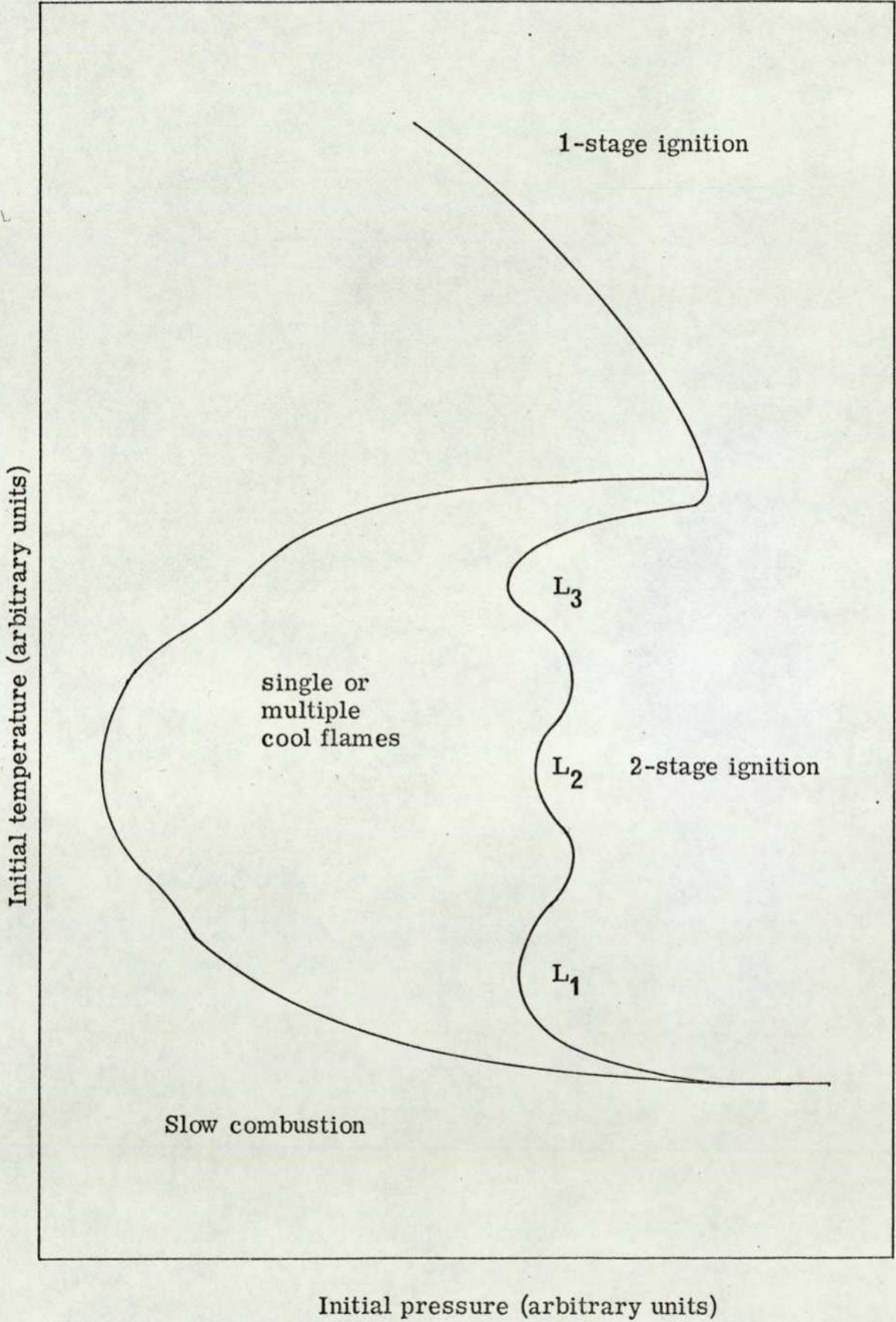
Although the suggested mechanisms for inhibition described above involve either nitrogen dioxide or nitric oxide as the inhibiting species, the ignition limits of methane + oxygen mixtures have been shown to be affected equally by either additive present in low concentration.^{67, 68}

1.5 Phenomena observed in hydrocarbon combustion

The several types of non-isothermal combustion phenomena have been described earlier (Section 1.4.1) and a simplified ignition profile giving the variation with the initial temperature and pressure of these types of combustion behaviour is shown in figure 1.1. In practice, however, the complex variation with initial temperature and pressure of the rate of hydrocarbon oxidation leads to the appearance of fine structure, or 'lobes', on the two-stage ignition limit. With low molecular weight hydrocarbons, these lobes are usually reflected on the spontaneous ignition limit profile (figure 1.2). These lobes have been associated with changes in the mechanism of cool flame propagation, and have been assigned L_1 , L_2 and L_3 mechanisms respectively with increasing temperature.⁶⁹ In particular, these mechanisms were thought to involve the variation with temperature of the ease of different modes of alkylperoxy radical isomerisation. The molecular structure of the hydrocarbon is thought to influence the appearance of the lobes. A recent theory accounts for this effect, and an additional lobe found for the oxidation of 2-methylpentane has been designated L_0 .⁷⁰

The propagation of a cool flame through a fuel-oxidant mixture occurs after a finite induction period, τ_1 , following the introduction of the reactants into the reaction vessel. For a given hydrocarbon, the induction period varies with initial temperature, T_0 , and pressure, P_0 , and at a constant temperature, the variation with P_0 of τ_1 follows the relationship:

Figure 1.2
A typical ignition diagram for a
hydrocarbon-oxygen mixture



$$\tau_1 = k P_o^{-n} + C$$

where k , n and C are constants. This equation has been shown to hold both at low and high pressures in the oxidation of 2-methylpentane, *n*-heptane and isooctane.⁷¹⁻⁷³ Values of n have been calculated from the logarithmic variation of τ_1 with P_o , and these values have been shown to vary with initial temperature in such a way that they reflect the lobes of the two-stage ignition profile.^{71, 73} The values of n lie in the range 0.3 to 3.0 for the above hydrocarbons, and it has been suggested that these values represent the effective order of reaction.⁷³

At constant pressure, an Arrhenius relationship holds between τ_1 and initial temperature, and from the variation with reciprocal temperature of τ_1 , the effective activation energy, E_{eff} , of the reaction has been calculated.⁷³ It has been shown that a linear relationship holds between the octane number of a hydrocarbon and the effective activation energy pertaining to the low temperature region of the ignition profile.⁷⁴

In a recent study of the oxidation of *n*-pentane, plots of $1/\tau_1$ vs $1/T_o$ exhibited distinct changes in slope, and therefore to changes in effective activation energy, at temperatures corresponding to a changeover from a region of multiple cool flames to a one cool-flame region. However, the large number of reactions co-existing in hydrocarbon oxidation precluded any correlation of these activation energies with any particular chemical process.⁷⁵ The variation of τ_1 with $1/T_o$ has also been reported to be non-

linear for the oxidation of n-heptane and isooctane at high pressures.⁷³

The induction period for two-stage ignition, τ_{ig} , is taken as the time between the pressure maximum for the cool flame and the pressure maximum corresponding to the second stage hot ignition.

At high pressures, for isooctane, the variation of τ_{ig} with P_o follows a similar power law relationship as was shown to hold for τ_1 ,⁷³

viz:

$$\tau_{ig} = K P_o^{-n_{ig}} + C$$

In this relationship, the values of n_{ig} fluctuated with increase in temperature, but the maximum and minimum values did not correspond either with the lobes on the two-stage ignition profile, or with the values of n associated with τ_1 . Thus it was proposed that a better kinetic characteristic of the preflame process of ignition would be a parameter such as the rate of pressure rise in the cool flame.

Indeed, it has recently been shown⁷⁶ that the cool flame in two-stage ignition has a controlling influence on the second stage. Consequently, the variation of τ_{ig} with the total pressure change accompanying the cool flame, ΔP_1 , has shown to follow a power relationship of the form:

$$\tau_{ig} = B \Delta P_1^{-m}$$

1.6 The chemical mechanism of hydrocarbon oxidation

1.6.1 Introduction

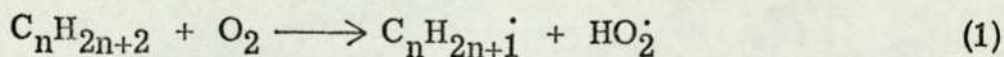
It is generally agreed that the gaseous oxidation of hydrocarbons proceeds via a complicated chain mechanism involving degenerate branching.⁷⁷

Known phenomena such as the negative temperature coefficient of reaction rate and the occurrence of single and multiple cool flames, indicate that the mechanism changes substantially with temperature.

The following sections are intended to outline only the salient features of the mechanism of hydrocarbon oxidation. For convenience, separate sections are included on the probable chain initiation, chain propagation, chain branching and chain termination steps believed to be involved in the gaseous oxidation of alkanes.

1.6.2 Chain initiation

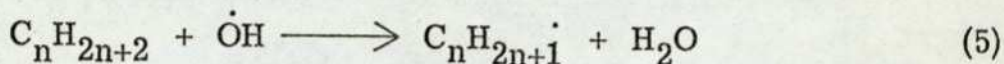
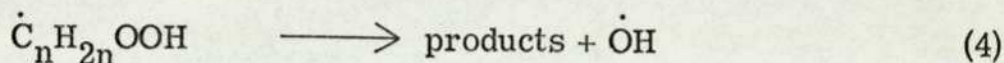
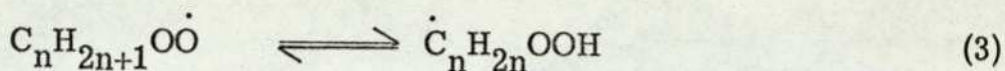
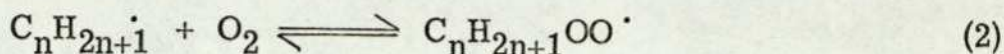
Chain initiation (reaction (1)) involves the abstraction of a hydrogen atom from the alkane by molecular oxygen,⁷⁸ viz:



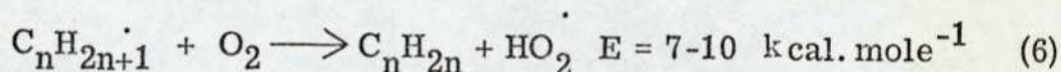
Since the activation energy for this reaction is estimated to be 45 to 50 kcal.mole⁻¹, the reaction proceeds relatively slowly and selectively. The ease with which the C - H bond is broken decreases in the order tertiary > secondary > primary.

1.6.3 Chain propagation

A simplified scheme for chain propagation is given below:



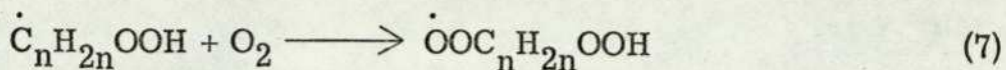
Reaction (2) is believed to be important at low temperatures (300°C), and requires virtually no activation energy.⁷⁹ At higher temperatures ($>400^{\circ}\text{C}$) however, reaction (6):



may compete effectively with reaction (2), the initial collision complex $C_nH_{2n+1}O_2$ breaking down almost immediately to give an HO_2 radical and an alkene.

Reaction (3) represents the isomerisation of an alkylperoxy radical, this process involving usually the internal abstraction of a hydrogen atom and the formation of an O - H bond incorporating the outer oxygen atom of the peroxy group.

The alkylhydroperoxy radical formed in reaction (3) may then decompose by reaction (4) and give rise to ketones, aldehydes or O-heterocycles (depending on the molecular structure of the radical) together with an OH radical. Reaction (7):

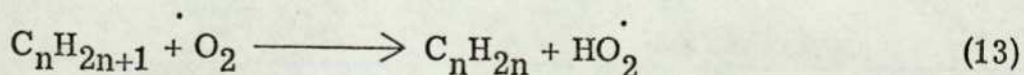
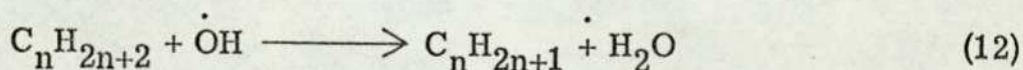
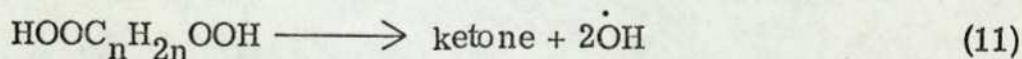
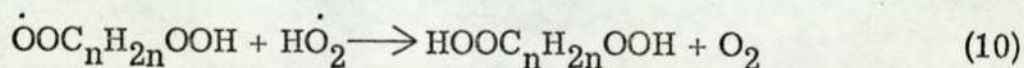
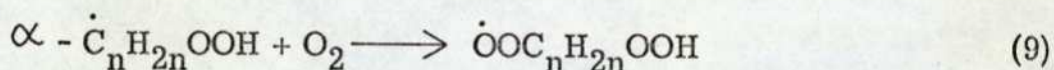
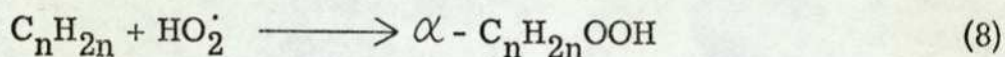


involving addition of oxygen to the alkylhydroperoxy radical, may however compete with reaction (4); this is particularly likely to occur with α -alkylhydroperoxy radicals.⁸⁰

The abstraction of a hydrogen atom from the alkane by an OH radical (reaction (5)), which completes the linear chain, requires a low activation energy ($E = 1-2 \text{ kcal. mole}^{-1}$).⁸¹

Reactions (3) and (4) in this primary chain cycle have been shown to account for the formation of numerous products resulting from the gaseous oxidation of a wide variety of hydrocarbons.^{80, 82-87}

Reactions (8) to (13):

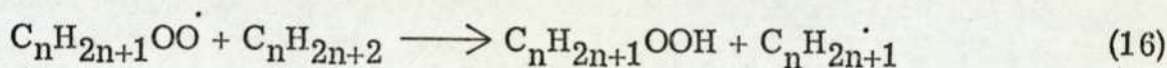


have been proposed as an alternative chain cycle.⁸⁸ This involves the addition of HO_2 radicals to alkenes (both of which are formed in

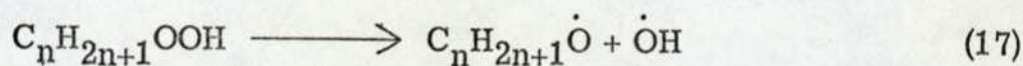
reaction (6)) to give α -hydroperoxyalkyl radicals, which is believed to be an important chain-propagating reaction of the HO_2 radical in the temperature range 300 to 400°C.⁸⁸

1.6.4 Degenerate chain-branching

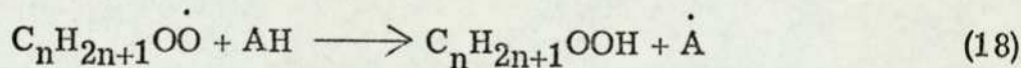
Degenerate chain branching accounts for the autocatalytic nature of hydrocarbon oxidation. In the oxidation of alkanes, such reactions have frequently been postulated to involve the thermal decomposition of peroxides. Monohydro peroxides may be formed by reaction (16):



in competition with reaction (3), and may then decompose by reaction (17):

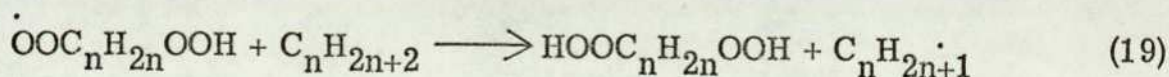


to give an alkoxy radical and a hydroxyl radical. The activation energy of this reaction is at least 35 kcal. mole⁻¹. When there are sufficiently labile hydrogen atoms present (eg. in aldehydes), reaction (18):

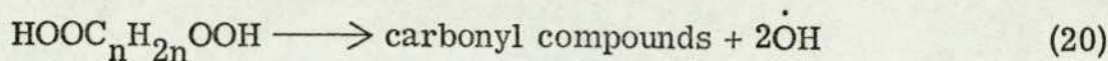


may be more important than reaction (16).

Dihydroperoxyalkyl radicals may be formed by reaction (19):

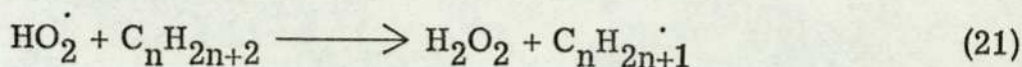


or by a reaction similar to (18), occurring in competition with reaction (10). Dihydroperoxides may decompose in reaction (20):

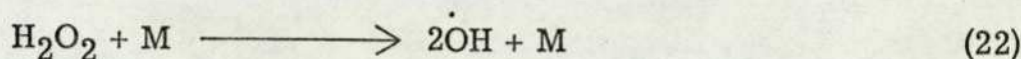


by homolysis of both O - O bonds, giving carbonyl compounds and two OH radicals.

Hydrogen peroxide may be formed in reaction (21):



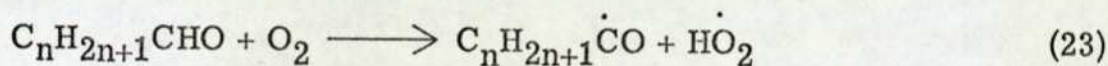
and subsequently decomposed in reaction (22):



with the aid of a second body to give two hydroxyl radicals.

Reaction (22) requires an activation energy of ca. 45 kcal. mole⁻¹,⁸⁹ and therefore probably becomes important at higher temperatures.

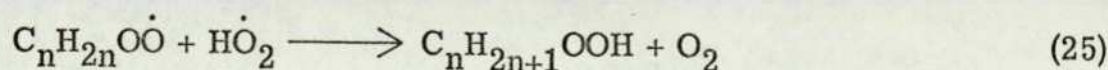
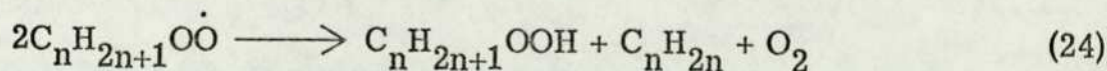
As the oxidation proceeds, chain branching may occur as a result of the abstraction by molecular oxygen of a labile hydrogen atom from an intermediate oxidation product, such as an aldehyde,^{90, 91}



As the temperature is raised, reaction (23) may well become more important than reaction (17).⁷⁰

1.6.5 Chain termination

Termination of radical chains may occur both by homogeneous radical-radical reactions (24) - (26):



or by the destruction of chain propagating species at the walls.

When the difference between the kinetic coefficient of chain-branching and chain-termination (the net branching factor, ϕ) is zero, the overall reaction rate will be in a critical "pseudo" steady state. When ϕ attains a small positive value, the overall rate of reaction increases exponentially, liberating heat which tends further to accelerate the reaction often ultimately resulting in a chain-thermal ignition. This sequence gives rise, in the lower temperature region of the ignition profile, to a cool flame, and in the high temperature region to a single-stage ignition.

1.6.6 The variation with temperature of the mechanism of hydrocarbon oxidation

Lobes occurring on the two-stage ignition profile of alkanes have been designated L_1 to L_3 with increase in temperature⁶⁹. The existence of lobes is probably associated with changes in the mechanism of oxidation, and their appearance is thought to be influenced to a considerable extent by the chemical structure of the alkane⁷⁹. Two principal theories have been proposed to account for the lobes, one of which is based on changes with temperature in the nature of the chain-propagating reactions⁸⁰ and the other on changes in the nature of the chain-branching reactions.

Alkylperoxy radical isomerization theory

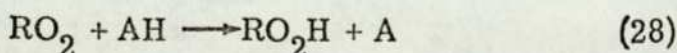
On the basis of reaction rate data, Fish proposed⁸⁰ that the predominant mode of alkylperoxy radical isomerization varied with temperature, and that there was a correlation between each lobe

in the two-stage ignition profile and a particular mode of isomerization. Thus, thermodynamic considerations of alkylperoxy radical isomerization (reaction 3) and of hydroperoxy alkyl radical decomposition (reaction 4) suggest that 1:6 H-atom transfer should predominate at low temperatures and therefore be responsible for lobe L_1 , and that 1:5 and 1:4 (together with 1:n where n is greater than 6) H-atom transfer should be responsible for lobes L_2 and L_3 respectively.

On the assumption that the molecular structure of an alkane influences the ease with which a particular H-atom transfer can take place, Fish used his theory to predict the number of lobes which should exist for various alkanes. There was for many systems good agreement between the predicted number of lobes and the number observed experimentally, although it was later shown⁹² that the predictions were not always correct.

Changes in the nature of the chain-branching reactions

Lucquin proposed⁷⁰ that the degenerate chain-branching agent changes between lobes L_1 and L_2 , and that two other lobes L_0 (lowest temperature lobe) and L_3 are special cases of L_1 and L_2 respectively. Lobe L_1 was shown to be associated with reactions (27) and (28)



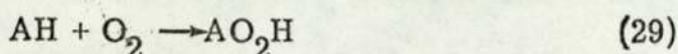
↓
degenerate
branching.

where AH is a compound, such as an aldehyde, which contains a

hydrogen atom more readily abstracted than those in the parent alkane.

Lobe L_0 is found only for alkanes containing a weak tertiary C-H bond, or may be induced with other alkanes by the addition of hydrogen bromide. The L_0 mechanism is thought to be associated with reactions similar to (27) and (28), but where an alkane containing a tertiary C-H bond replaces AH in reaction (27).

The L_2 mechanism is believed to involve reactions (27) and (29)



↓
degenerate
branching

in which AH is probably an aldehyde. The magnitude of lobe L_2 is sensitive to the partial pressure of oxygen, and does not favour cool-flame multiplicity for the alkanes studied (propane, butane, pentane isomers, 2-methyl pentane).

Lobe L_3 is thought to be associated with reactions analogous to (27) and (29), where AH is formaldehyde.

1.7 Thermal ignition theory

1.7.1 Introduction

It was shown in the previous Section that the spontaneous ignition of an alkane-oxidant mixture can occur when the net branching factor attains a small positive value. It is, however, also possible to predict spontaneous ignition temperature limits on the basis of purely thermal considerations of the combustion processes.

As heat is generated by an exothermic reaction, so too is it dissipated from the reaction zone by conductive, convective and radiative heat transfer, and hence lost to the surroundings. When the ambient temperature of the reacting medium is such that the rates of heat generation and heat loss are equal, a critical steady state will result. Steady states are also obtained at lower ambient temperatures, but they are not critical. The critical steady state will be characterised by a maximum temperature rise above ambient in the reacting medium. If the ambient temperature is raised, the rate of heat generation will exceed the rate of heat loss and the rate of reaction will, due to self-heating, increase exponentially resulting in ignition.

This concept was first observed by van't Hoff⁹³ in 1884, and the first mathematical representation of the critical conditions was formulated by Semenov some forty years later.⁹⁴

1.7.2 Thermal ignition theory according to Semenov

This treatment neglects reactant consumption, so that the rate of heat release, q_1 , from an n^{th} order reaction of exothermicity, Q cal. /unit mass, will be given by:

$$q_1 = QV\rho A \exp(-E/RT)C_0^n \quad (1.7.1)$$

where V is the volume, ρ the density and C_0 the initial concentration of the reactants, which have self-heated to a uniform temperature, T . Other symbols have their usual significance.

The temperature of the surroundings, T_0 , is assumed to be uniform over its surface area, S , and the rate of loss of heat, q_2 , from the reactants to the surroundings is given by:

$$q_2 = \chi (T - T_0) S \quad (1.7.2)$$

where χ (cal. sec^{-1} unit area $^{-1}$) is the heat transfer coefficient.

Figure 1.3 shows three conditions for q_1 and two conditions for q_2 as functions of the temperature. Curves a, b and c represent heat release rates corresponding to different initial concentrations of reactant, and heat loss lines I and II correspond to reaction vessels of different surface area.

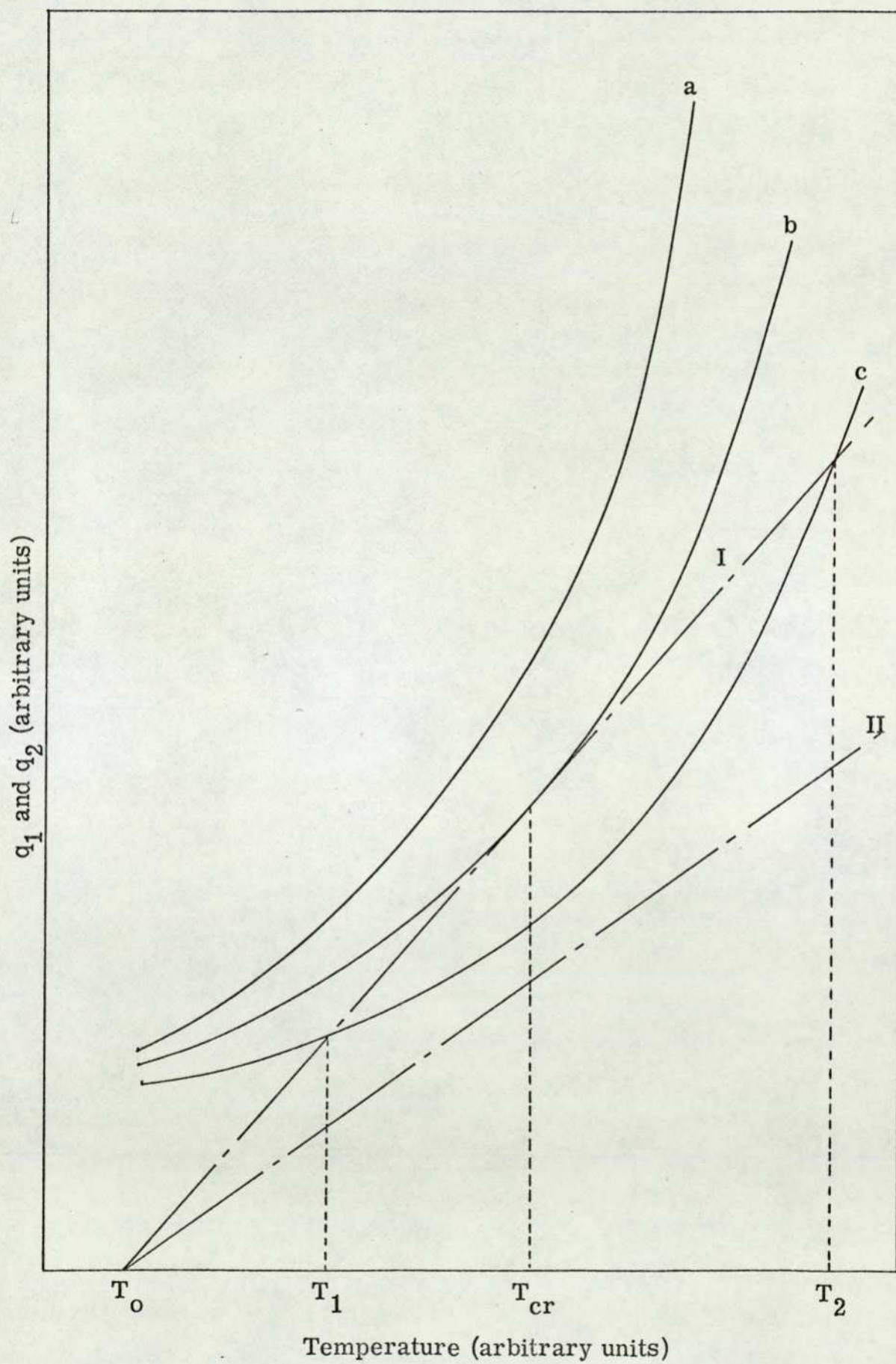
For a steady or stationary state to be possible, q_2 must intersect q_1 , and ignition would clearly always result if heat were lost according to line II. There are, however, three possible consequences of heat being lost according to line I; these are

(i) Stationary state

Heat is generated according to curve c, and causes the reactant to self-heat to a temperature, T_1 , which is a stable

Figure 1.3

The variation with temperature of heat release
and heat loss rates



temperature corresponding to a stationary state. If under these conditions the reactant temperature rises above T_1 , it will soon cool again to this temperature.

The temperature, T_2 , at which 'c' and I intersect again, is not stable since, if the temperature rises, ignition will result, or if the temperature falls, the system will cool to T_1 .

(ii) Explosive state

Heat generated according to curve 'a' will be greater than the heat lost by line I at all temperatures. Thus, a stationary state is not possible and ignition will always result.

(iii) The critical state

If heat is generated according to curve b, the reactants will self-heat to a critical temperature, T_{cr} , where the curve 'b' and line I are tangential. If this critical stationary state were perturbed, causing the temperature to rise fractionally, ignition would occur. The maximum pre-ignition temperature rise under these conditions is therefore $T_{cr} - T_0$.

At the point of tangency,

$$q_1 = q_2 \quad (1.7.3)$$

$$\text{and} \quad \frac{dq_1}{dT} = \frac{dq_2}{dT} \quad (1.7.4)$$

By expressing equations (1.7.3) and (1.7.4) in terms of equations (1.7.1) and (1.7.2), and eliminating S between them, the critical

temperature rise will be given as:

$$T_{cr} - T_o = \Delta T_{cr} = RT_{cr}^2/E$$

or
$$\frac{RT_{cr}^2}{E} - T_{cr} + T_o = 0$$

and therefore,

$$T_{cr} = \frac{1 \pm (1 - 4RT_o/E)^{\frac{1}{2}}}{2R/E} \quad (1.7.5)$$

Examination of equation (1.7.5) reveals that an explosion is possible only when $0 < T_o \leq E/4R$. If solutions with the positive sign of the terms under the square root are considered, values of T_{cr} will lie in the range $E/2R \leq T_{cr} < E/R$. Clearly, the maximum value for T_{cr} will be very high (15.0×10^3 °K for $E = 30$ kcal. mole⁻¹), and at these very high temperatures no stationary state is possible and explosion always occurs. Therefore, it is only necessary to consider the solutions with the negative sign of the terms under the square root and these are best obtained in a general form by expanding $(1 - 4RT_o/E)^{\frac{1}{2}}$ of equation (1.7.5) into a binomial series, viz:

$$T_{cr} = \frac{1 - (1 - 4RT_o/E)^{\frac{1}{2}}}{2R/E} = \frac{2(RT_o/E) + 2(RT_o/E)^2 + 4(RT_o/E)^3 + \dots}{2R/E}$$

For $RT_o/E < 0.05$, terms of the series greater than $2(RT_o/E)^2$ may be neglected, thus introducing only a 0.05% error in the measured value of T_{cr} . Thus, for a given reaction, the maximum critical temperature, T_{cr} , for a stationary solution may be calculated from

the ambient temperature by:

$$T_{cr} \simeq T_o + RT_o^2/E \quad (1.7.6)$$

or
$$\Delta T_{cr} \approx RT_o^2/E \quad (1.7.7)$$

At the critical stationary state condition, equation (1.7.4) gives:

$$\frac{E}{RT_{cr}^2} QV\rho A \exp(-E/RT_c) C_o^n = XS \quad (1.7.8)$$

By making use of the result in equation (1.7.7) and of the approximation:

$$\frac{1}{T_{cr}} = \frac{1}{T_o + \Delta T_{cr}} = \frac{1}{T_o} \left(1 - \frac{\Delta T_{cr}}{T_o} + \dots\right)$$

Semenov has obtained a relation between the critical pressure, P_{cr} , of the gas and the temperature, T_o , which is given as:

$$\frac{EQV\rho A \exp(-E/RT_o)}{R} \frac{P_{cr}^n}{T_o^{n+2}} = XS \quad (1.7.9)$$

which may be rearranged to give:

$$\ln \left[P_{cr}^n / T_o^{n+2} \right] = (E/RT_o) + \text{constant} \quad (1.7.10)$$

where the constant = $\ln(RXS/EQVA\rho e)$. Thus, the variation with reciprocal temperature of $\ln(P_{cr}^n/T_o^{n+2})$ should be a straight line of slope E/R . Whilst this relationship has been shown to hold at high temperatures and low pressures for many gaseous explosions, in some cases the plots are found to curve at high pressures. This curvature was observed, for example, with azomethane and was

thought to be due to the variation with temperature of the activation energy of the pre-explosion process.⁹⁵

Semenov, in setting the heat transfer to the walls as:

$$q_2 = \chi (T - T_0) S$$

assumed that the heat is transferred by convection. However, Semenov's assumption that the gaseous reactant temperature is uniform throughout the vessel and that all the resistance to heat transfer occurs at the wall of the vessel, does not represent the physical conditions existing in the reactants. At pressures less than atmospheric and for small pre-explosion temperature rises, the heat transfer process is very nearly that of conduction.

Consequently, there will be a spatial temperature distribution across the reactant. Frank-Kamenetskii⁹⁶ was the first to introduce into the theory of thermal self-ignition, heat transfer by conduction rather than convection.

1.7.3 Thermal explosion theory as derived by Frank-Kamenetskii

Frank-Kamenetskii made use of the stationary form of the equation of heat conductance with continuously distributed sources of heat, viz:

$$\lambda \nabla^2 T + \dot{q} = 0 \quad (1.7.11)$$

where the dependence on temperature, T , of the thermal conductivity,

λ , has been neglected.⁹⁶ In this equation, ∇^2 is the Laplace operator and $\dot{q}$ is the rate of heat release which, for a chemical reaction obeying the Arrhenius Law, is given by:

$$\dot{q} = QA \exp(-E/RT) C_o^n \quad (1.7.12)$$

The solution resulting from the integration of equation (1.7.11) under the boundary condition:

$$T = T_o$$

at the wall of the vessel, gives the stationary temperature distribution in the reacting mixture, and the condition under which such a stationary solution becomes impossible is in fact the critical condition for ignition. On account of the Arrhenius term, equation (1.7.11) cannot be integrated as it stands, and Frank-Kamenetskii introduced an exponential approximation for this term given as:

$$\exp(-E/RT) \simeq \exp(-E/RT_o) \exp(E(T-T_o)/RT_o^2) \quad ^{96}$$

Equation 1.7.11 now becomes:

$$\nabla^2 T = \frac{QA}{\lambda} \exp(-E/RT_o) C_o^n \exp(E(T-T_o)/RT_o^2) \quad (1.7.13)$$

and in order to simplify the integration, Frank-Kamenetskii defined two dimensionless parameters.⁹⁶ Firstly, he introduced a dimensionless temperature, θ , where:

$$\theta = E(T - T_o) / RT_o^2$$

and secondly, since the theory is applicable to geometrics where the conduction process depends on only one space coordinate, x , the Laplace operator was made dimensionless by introducing the variable:

$$z = x / r$$

in which r is the characteristic dimension of the vessel. Equation (1.7.13) now becomes:

$$\nabla_z^2 \theta = -\delta \exp \theta \quad (1.7.14)$$

where δ is a dimensionless rate of heat release given by:

$$\delta = \frac{Q}{\lambda} \frac{E}{RT_0^2} r^2 A \exp(-E/RT_0) C_0^n \quad (1.7.15)$$

In equation 1.7.14, the condition under which a stationary temperature distribution just ceases to be possible, i.e., the critical condition of ignition, is of the form:

$$\delta = \text{constant} = \delta_{cr}$$

Using the boundary condition that:

$$\theta = 0 \text{ when } z = 1$$

Frank-Kamenetskii solved equation (1.7.14) analytically for the case of self-ignition in a plane-parallel vessel, and showed that:

$$\delta_{cr} = 0.88$$

with a corresponding maximum pre-explosion temperature rise of:

$$\Delta T_{cr} = 1.2 \frac{RT_0^2}{E} \quad 96$$

Similarly, using the boundary conditions that:

$$\theta = 0 \text{ when } z = 1,$$

$$\text{and } d\theta/dz = 0 \text{ when } z = 0,$$

Frank-Kamenetskii solved equation 1.7.15 by numerical analysis for both an infinitely long cylindrical vessel and a spherical vessel, and showed that δ_{cr} has values of 2.00 and 3.32 respectively.⁹⁷

The corresponding maximum pre-explosion temperature rise in a cylindrical vessel was found to be:

$$\Delta T_{cr} = 1.37 \frac{RT_0^2}{E}$$

and in a spherical vessel, to be :

$$\Delta T_{cr} = 1.60 \frac{RT_o^2}{E}$$

These values for δ_{cr} and ΔT_{cr} have been confirmed by Chambre, who obtained solutions to equation 1.7.15 in terms of known functions.⁹⁸

Frank-Kamenetskii has tested the theory in terms of existing kinetic and explosion limit data obtained for the decomposition of azomethane, ethyl azide, and methyl nitrate, and for the oxidation of hydrogen sulphide. These tests have shown that, for the compounds concerned, the calculated explosion limits over a wide temperature range are within 2% of the observed values.^{96, 99} However, for azomethane and ethyl azide, the variation with $1/T_o$ of $\ln(P_o/T_o^3)$, which was used to calculate the activation energy, showed curvature at low temperatures. It has recently been shown that the effects of convection may be responsible for these curved plots on account of the Rayleigh number of the gas exceeding a critical value of 600.¹⁰⁰

In recent experiments on the thermal explosion of diethyl peroxide, measurements were made of the pre-explosive temperature-time histories, and the temperature-position profiles close to the critical conditions were established.^{101, 102} These results provide the most detailed confirmation to date of the conductive theory of thermal explosions.

1.7.4 Ignition caused by heated bodies

The critical condition for thermal self-ignition in gases for a plane-parallel slab, an infinite cylinder and a sphere have been considered above, where in each case the reactant was symmetrically heated. It is of practical importance however to find solutions which represent the critical condition for thermal self-ignition in an asymmetrically heated reactant, such as the case of ignition caused by a heated body.

Semenov has used conductive thermal ignition theory to calculate the ignition conditions for a gas contained between two parallel walls, one of which is maintained at a higher temperature than the other.⁹⁴ The ignition conditions have also been calculated for a gas filling an annular space between a hot (inner) and cold (outer) sphere, and for a gas in contact with a heated wire passing along the axis of a cold cylinder.⁹⁴ In each case, it was shown that ignition could be assumed to take place within a thin layer of reactant in contact with the hot surface, and that outside this layer a constant temperature gradient existed.

The critical condition for ignition for each of the systems outlined is given below, where T_i is the ignition temperature of the heated surface, and T_o is the temperature of the cold surface.

- (i) Parallel walled reactor with a distance, d , between the walls.

$$d = \left[\frac{\lambda E (T_i - T_o)^2}{2QW_i R T_i^2} \right]^{1/2}$$

where W_i = reaction rate at T_i .

- (ii) Small heated sphere of radius, r .

$$r = \left[\frac{\lambda E (T_i - T_o)^2}{2QW_i R T_i^2} \right]^{1/2}$$

- (iii) Hot wire of radius, r_2 , passing along the axis of a cylinder of radius, r_1 .

$$r_2 \ln \frac{r_1}{r_2} = \left[\frac{\lambda E (T_i - T_o)^2}{2QW_i R T_i^2} \right]^{1/2}$$

In this case, Semenov has shown that the conductive theory is applicable only if the radius of the wire is not greater than 1 mm.

Clearly, the critical condition for ignition is similar in each of the cases considered, the only difference being in the characteristic dimension of the particular geometry.

The conductive thermal ignition theory of Frank-Kamenetskii has been further developed to solve some steady state problems involving asymmetrically heated reactants. An approximate solution for the critical asymmetric heating of a reacting medium contained in a parallel plate vessel was obtained by Bowes and Thomas and was shown to be valid over a wide range of conditions.¹⁰³ The critical ignition parameter, δ_{cr} , as defined by Frank-Kamenetskii, was obtained as a function of two dimensionless parameters which were θ_o and α . The dimensionless temperature, θ_o , was defined as:

$$\theta_o = E (T_o - T_i) / R T_i^2$$

and the dimensionless heat transfer coefficient, α , was defined as:

$$\alpha = X r / \lambda$$

where X = heat transfer coefficient at the reacting medium/wall interface.

r = half-thickness of reacting medium.

λ = thermal conductivity of reacting medium.

The vessel walls may be considered to be perfect heat conductors if $\alpha = \infty$, and perfect insulators if $\alpha = 0$. The wide range of conditions under which δ_{cr} was calculated was obtained by varying the value of α between 0 and infinity.

Thomas and Bowes also calculated the critical conditions for ignition in a reacting medium in the form of a cylindrical annulus, in which the inner face is maintained at a constant high temperature.¹⁰⁴ For practical purposes, the value of α is large, so that the surface temperature of the reactant, T_s , is almost that of the environmental temperature, T_0 . A new critical ignition parameter, δ_{cr}^* was expressed conventionally in terms of the half-thickness of the annulus, and given by:

$$\delta_{cr}^* = \delta_{cr} (r_2 - r_1)^2 / 4$$

where r_1 = radius of the inner face,

r_2 = radius of the outer surface.

Furthermore, it was shown that:

$$\delta_{cr}^* = \left(|\theta_s| + 1.4 \right)^2 / 8$$

where

$$\theta_s = E (T_s - T_i) / RT_i^2$$

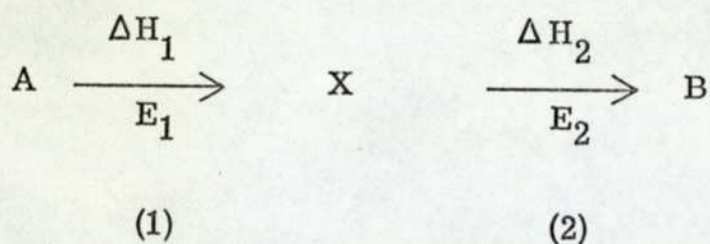
This result is the same as the expression which was obtained for a reactant in the form of a plane-parallel slab with the hot face in contact with a perfect insulator, with $a \gg 1$ and $|\theta_s| > 5$.

Thus, a thin cylindrical annulus tends to behave like a plane slab.

1.8 Unified chain-thermal theory of ignition

It is well known that the ignition of an alkane in oxygen occurs as a result of interdependent chain branching and exothermic processes, and that thermal explosion takes place only when the rate of reaction and hence of heat liberation is high enough for chain autoacceleration.

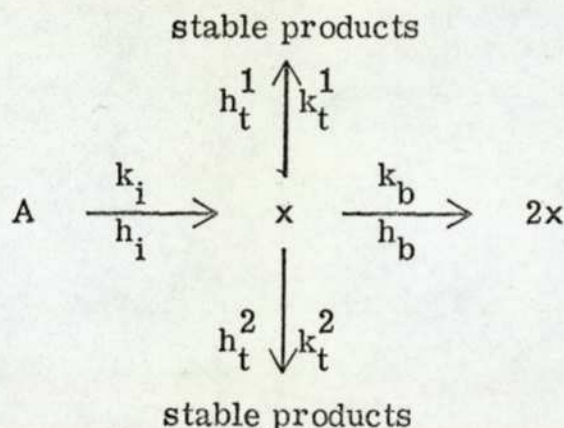
A simple chain-thermal scheme has been proposed by Salnikov to explain the existence of oscillatory cool-flame behaviour during hydrocarbon oxidation.¹⁰⁵ In this scheme, two consecutive reactions involving the formation and destruction of an important chain carrier, X, are considered:



where $|\Delta\text{H}_2| > |\Delta\text{H}_1|$ and $\text{E}_2 > \text{E}_1$. The concentration of X increases as a result of reaction (1), the rate of which accelerates as a result of self-heating. As the temperature rises, reaction (2) becomes important, and at a sufficiently high temperature, X is consumed faster than it is produced. The rapid consumption of X causes a decrease in the rate of reaction (2), and consequently the temperature falls, thereby restoring the initial conditions of temperature for which reaction (1) is more important than reaction (2). Theoretically, this cycle may be repeated until the reactant concentration is reduced to such an extent that A can no longer be

formed. This simple model devised by Salnikov, failed however to provide a formalism enabling a quantitative calculation to be made. Furthermore, the model could not account for other characteristics of hydrocarbon combustion, such as negative temperature coefficient of reaction rate and "lobes" on two-stage ignition profiles.

Recently, Gray and Yang have devised a mathematical model involving a chain-thermal scheme which assumes that the oxidation of a hydrocarbon is dominated by an autocatalytically produced chain-carrier, x .^{106, 107} The reaction scheme is outlined below



where k and h are the rate constants and enthalpy changes respectively for the reactions, and the subscripts i , t and b indicate whether the reaction is a chain-initiating, chain-terminating or chain-branching step. Activation energies for the reactions are expected to increase in magnitude according to $E_t^1 < E_b < E_t^2$.

The model is based on the variation with time of the concentration of the chain carrier, x , (kinetic equation) and of the

temperature, T (energy equation). The solutions of these equations were obtained in the so-called T - x phase plane and were observed as trajectories which could be related to explosion and cool-flame oscillation limits.

Using a single set of assumed rate constants, it has been shown that two-stage ignition limits, cool flame oscillation limits, oscillation period and amplitude, lobes and the negative temperature coefficient effect can all be calculated and are found to be in good agreement with experimental observations.

Gray and Yang^{108, 109} have generalised this chain-thermal theory to any number of reaction intermediates. By properly defining a 'rate of heat release' curve, thermal diagrams have been used so that the critical condition for non-oscillatory, steady states may be reducible to a tangency condition (ie. $q_1 = q_2$ and $dq_1/dT = dq_2/dT$ as in Section 1.7.2).¹⁰⁸ The thermal diagrams can also explain the existence of cool flame oscillations, a negative temperature coefficient region and lobes on the ignition profile boundaries.¹⁰⁹

Recently, a detailed model of the non-isothermal oxidation of acetaldehyde has been devised which, unlike the model of Gray and Yang, takes into account the consumption of reactants.¹¹⁰ The model has been found to give a realistic simulation of single and multiple cool flames with their limits, amplitudes and induction periods; it also accounts satisfactorily for two-stage ignition, of the negative temperature coefficient for the maximum rate of slow combustion.

1.9 The Present Work

It was shown in Section 1.3 that the spontaneous ignition of organic compounds and in particular of hydrocarbons accounts for a large proportion of the accidents taking place in the petroleum and chemical industries. Naval diesel fuels are readily ignitable materials, and serious fire and explosion risks occur when these substances make contact with hot surfaces. n-Decane is a major constituent of Naval fuels and is reported to be a very easily ignitable hydrocarbon. Hitherto, the non-isothermal combustion of this compound has not been studied in any depth and the details of its spontaneous ignition profile have not been reported. In the present work, emphasis has been placed on establishing the way in which the spontaneous ignition temperature limits in a large spherical reaction vessel vary with n-decane-air ratio.

The ignitability of alkanes increases with increasing molecular weight and with decreasing branching of the carbon chain. By measuring under the same experimental conditions as those used for n-decane the spontaneous ignition-temperature limits for several other alkanes, it is possible to identify a characteristic parameter which is quantitatively related to the ignitability of the alkane.

The ignitability of a pure hydrocarbon may be altered by fuel blending as described in Section 1.4.4. For lower molecular weight hydrocarbons (less than C_7), the ignitability of a binary fuel mixture has been shown to be influenced to a greater extent by the more easily ignitable component. Studies of the non-isothermal

combustion of binary fuel-air mixtures containing different proportions of n-decane and 2, 2, 5-trimethylhexane have shown to what extent higher molecular weight alkanes conform to this general pattern of behaviour. Furthermore, an attempt has been made to discover a characteristic parameter which is quantitatively related to both the composition and the ignitability of the fuel mixture.

It was shown in Section 1.7.3 that the conductive theory of thermal ignitions has been confirmed by a number of workers using gas-phase decomposition reactions in which degenerate chain-branching reactions are absent. The validity of application of thermal ignition theory to gaseous explosions has been shown to be limited by the effects of convection. The application of thermal ignition theory to the oxidation of alkanes has however been little investigated. The extent to which thermal ignition theory may be applied to n-decane combustion may be assessed indirectly as described in Section 1.7.2. using spontaneous-ignition temperature limit data. Temperature measurements in reacting n-decane-air mixtures at the spontaneous ignition boundary enable direct tests of thermal ignition theory to be made. Maximum stable temperature rises in the centre of the vessel have therefore been measured and compared with calculated temperature rises (Section 1.7.3). The effects of convection have been determined from both direct and indirect tests of thermal ignition theory. The value of the Rayleigh number of the gas mixture above which convective heat transfer becomes significant may be compared with reported literature values (Section 1.7.3).

Problems involving asymmetrically heated reactants have been tackled using the conductive theory of thermal ignition (Section 1.7.4). Measurements of the conditions required to cause spontaneous ignition of n-decane-air mixtures in contact with a hot glass tube contained in a cooler spherical vessel have helped to establish the factors affecting ignition in asymmetrically heated gaseous reactants in which the effects of convection are significant.

SECTION 2

EXPERIMENTAL

SECTION 2.

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2.1. THE APPARATUS

2.1.1. The vacuum system.

The vacuum apparatus was constructed from Pyrex glass and is shown schematically in figure 2.1.

The section of the line bounded by taps T1, T3 and T4 was constructed from 8 mm. i.d. tubing. Permanent gases were introduced into the apparatus through T1, dried by passage through a column of Linde 5A molecular sieve and silica gel and then condensed and fractionated between traps TR1 and TR2 which were cooled by liquid nitrogen. A mercury manometer, M1, was used both for calibration purposes and as a pressure safety valve during fractionation of gases.

Permanent gases were subsequently stored in 5 litre vessels, S1 and S2, and liquid alkanes were kept in 50 cm³ flasks, F1 and F2, which were attached to the line by cylindrical joints sealed with Viton rubber 'O'-rings. Heated premix vessels, PM1 and PM2, of 3 and 5 litre volume respectively, were encased in metal boxes as a protection against possible explosion resulting from a flash-back from the reaction vessel. In order to reduce the risk of such a flash-back, a flame-trap, FT, filled with 2 mm. diam. glass beads, was incorporated into the line between the premix vessels and the reaction vessel.

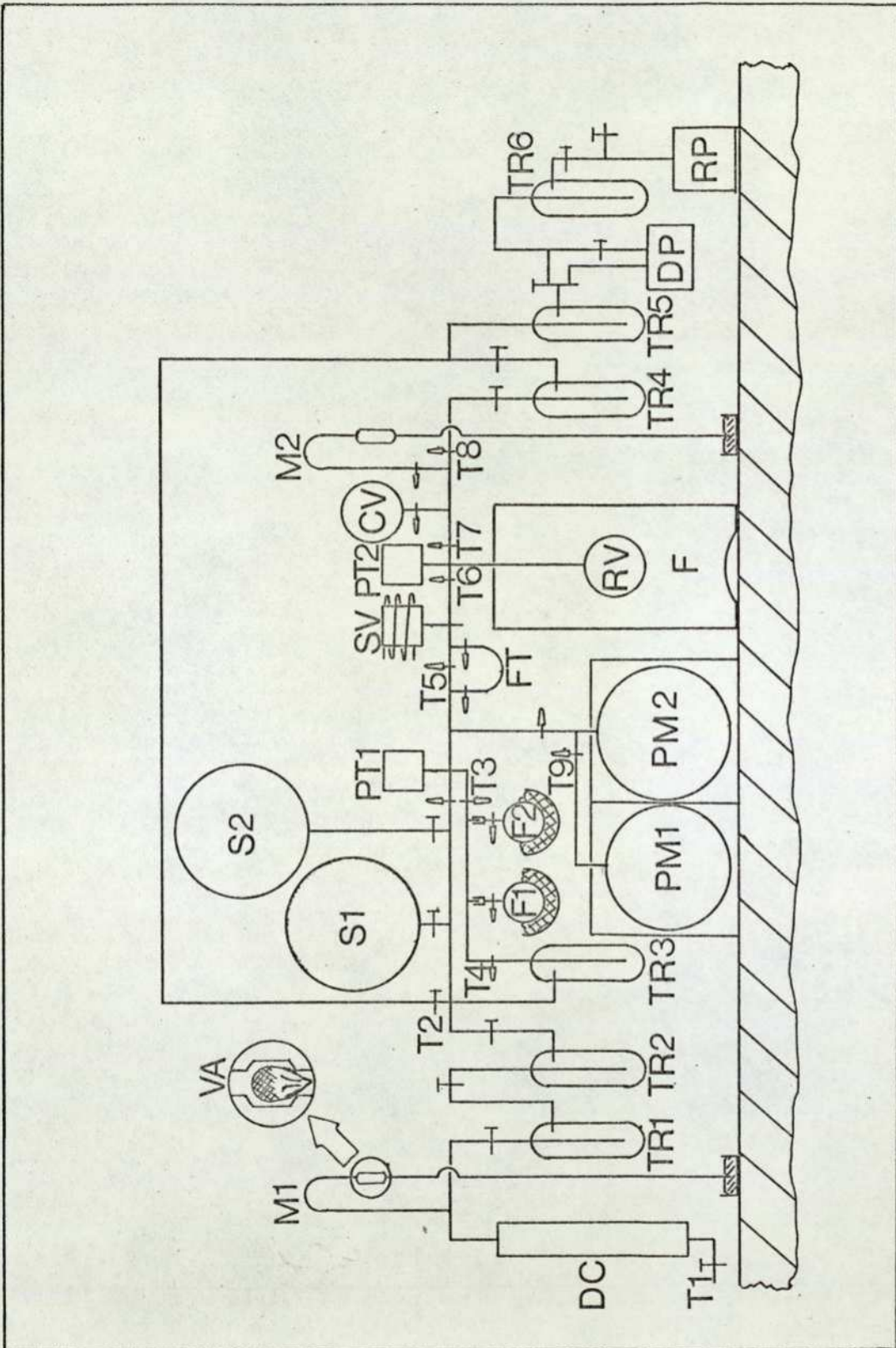
The reaction section of the apparatus, bounded by taps T5 and T8, was constructed from 6 mm. i.d. tubing, and here attempts were made to reduce the dead space to a minimum.

Key to figure 2.1.

CV	=	500 cm ³ volume calibration vessel.
DC	=	drying column containing Linde 5A molecular sieve and silica gel.
DP	=	mercury diffusion pump.
F	=	vertical tube furnace.
F1 and F2	=	50 cm ³ volume, alkane storage vessels.
FT	=	flame trap packed with 0.2 cm. diam. glass beads.
M1 and M2	=	mercury manometers.
PM1 and PM2	=	heated premix vessels.
PT1 and PT2	=	pressure transducers.
RP	=	rotary pump.
RV	=	550 cm ³ volume reaction vessel.
S1 and S2	=	permanent gas storage vessels.
SV	=	solenoid-operated valve.
T1 to T9	=	taps: $\top$ ground glass stop cocks. $\uparrow$ Rotaflow greaseless taps.
VA	=	ground glass manometer valves.

Figure 2.1

A line diagram of the vacuum apparatus.



The introduction of reactants to the reaction vessel was controlled by a solenoid-operated valve actuated by a time-variable electronic circuit (Section 2.1.3.). Reactions were carried out in a 550 cm³ spherical reaction vessel which was washed with fuming nitric acid, rinsed with distilled water and baked in air at 450°C for 24 hours prior to use. The neck of the reaction vessel was sealed by a pressure transducer, and a constant volume was obtained by closing taps T6 and T7. A calibration vessel of 500 cm³ volume, CV1, and a mercury manometer, M2, were also attached to the line adjacent to this reaction section. Small ground-glass valves, VA, were incorporated into both manometers M1 and M2 to prevent mercury being carried over into the apparatus in the event of a sudden reduction of pressure in the apparatus. These valves allowed gas to pass freely in either direction, but provided an immediate seal when subjected to the upward force of a mercury thread. A liquid nitrogen trap, TR4, prevented combustion products from condensing in the 30 mm. i.d. by-pass line, bounded by T2 and TR5.

The pumping section, bounded by TR5 and RP, was constructed from 8 mm. i.d. tubing. A vacuum of 10^{-4} torr was easily attained by means of a single-stage mercury diffusion pump, DP, backed by an Edwards Speedivac (type ES35) rotary oil pump. Liquid nitrogen-cooled traps, TR5 and TR6, protected the diffusion pump from contamination by combustion products and also prevented mercury vapour diffusing into the line or the rotary pump.

Rotaflow taps with PTFE keys were used in the parts

of the apparatus where the line was heated. Ground-glass stop-cocks, greased with Kel-F90 high vacuum grease, were used in other parts of the apparatus.

Experiments designed to simulate the ignition tendency of an alkane-air mixture in the vicinity of a hot pipe, were carried out in 550 cm³ spherical reaction vessels containing heated glass tubes passing through the centre (figure 2.2.). The heaters were made by cementing electrical resistance windings onto hollow glass formers, through the centre of which passed a fine chromel-alumel thermocouple. The thermocouple junction was placed at the centre and adjacent to the outer surface of the glass former in such a way that it made good contact with the glass tube passing through the centre of the reaction vessel. The cement layer on the outside of the glass former was ca. 0.2 cm. thick and helped to provide an even temperature distribution along the length of the tube. The temperature variation along the surface of the tube was measured using a chromel-alumel thermocouple, and was shown to be less than 1.5° K over 95% of the tube length. The power supplied to the heaters was varied by means of a Variac variable transformer.

2.1.2. Furnace and line heating.

The temperature distribution of the vertical tube furnace was measured using a chromel-alumel thermocouple which had been calibrated against a standard platinum-rhodium thermocouple. The results of these measurements, which were taken at two temperatures,

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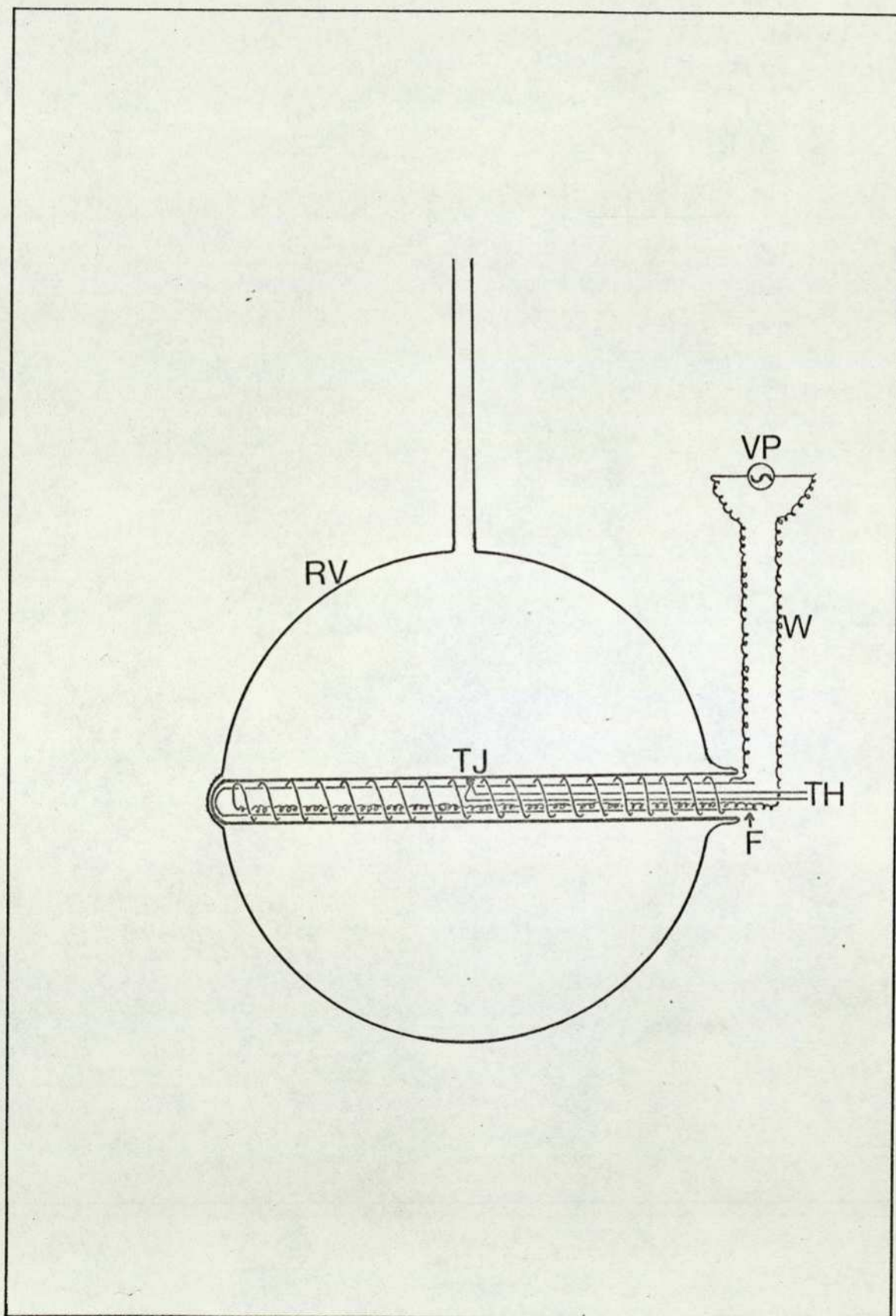
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Key to figure 2.2.

F	=	glass former.
RV	=	550 cm ³ volume reaction vessel.
TH	=	40 s.w.g. chromel-alumel thermocouple leads.
TJ	=	thermocouple junction.
VP	=	Variac variable power supply.
W	=	'Brightray C' heating wire.

Figure 2.2

Reaction vessel containing a heated glass tube.



are given in figures 2.3(a) and (b), and show that a stable temperature region ($\pm 1^{\circ}\text{K}$) exists over an 11 cm. length of the furnace tube. In this region, the temperature variation across a 12 cm. diameter of the furnace tube was less than 1.9°K (figure 2.3. (c)). The reaction vessel was therefore placed in this reasonably constant temperature region, with the junction of the thermocouple adjacent to the vessel.

The temperature of the furnace could be controlled to within $\pm 0.5^{\circ}\text{K}$, and at temperatures up to 873°K , by using an A.E.I. type RT3/R Mk 2 proportional temperature controller and power regulator, with temperature feedback from a 10-ohm platinum resistance thermometer placed near the reaction vessel.

The glass line between T4 and T9, and that between FT and T8 was maintained at ca. 390°K by means of heating tape, and the manometer, M2, was heated separately to ca. 350°K by nichrome wire. The premix vessels were independently maintained at a temperature of ca. 390°K by means of 3 in. heating tape, and were covered with glass-fibre lagging. Chromel-alumel thermocouples were placed at several points along the surface of both vessels, and measurements confirmed that there were no hot-spots and that the temperature was uniform.

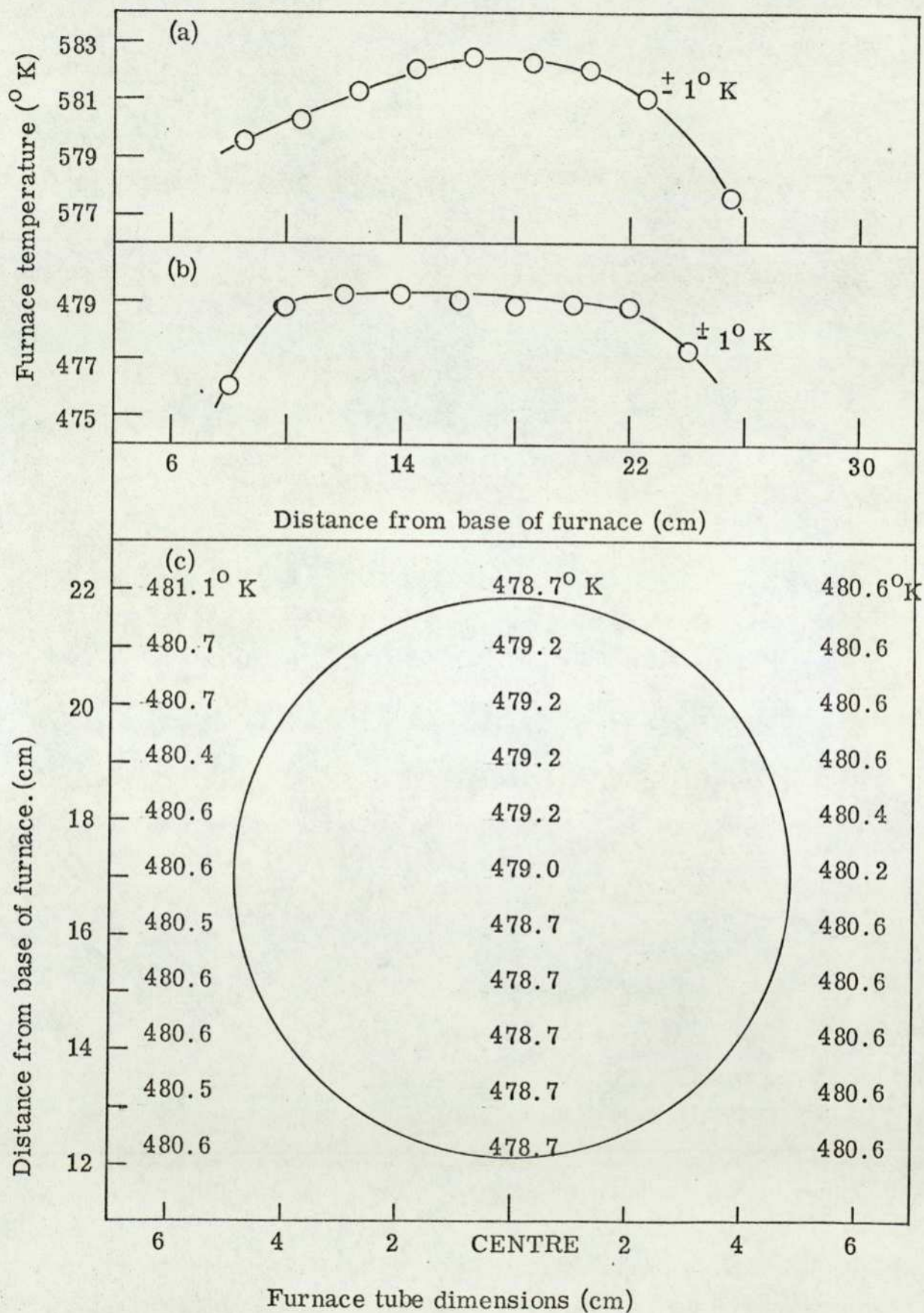
The alkane storage vessels, F1 and F2, were heated by isomantles connected to Sunvic energy regulators.

2.1.3. Solenoid valve and timing circuit.

The solenoid valve is shown diagrammatically in figure 2.4. The valve seal was made by compressing a viton rubber 'O'-ring,

Figure 2.3.

Temperature distribution and profiles in the vertical tube furnace.



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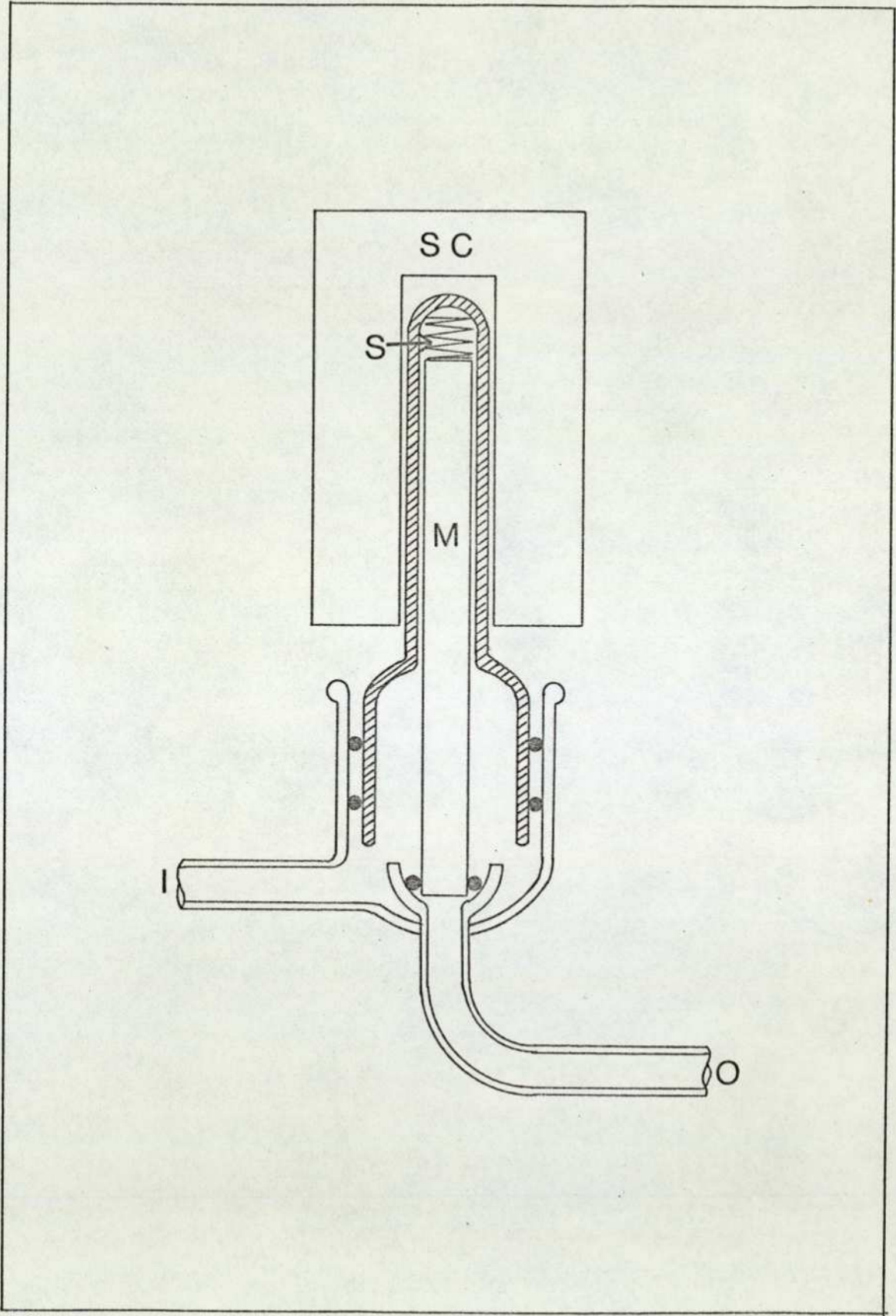
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Key to figure 2.4.

I	=	gas inlet.
M	=	iron rod.
O	=	gas outlet.
S	=	spring.
SC	=	240 V a.c. solenoid coil.
●	=	viton rubber 'O' rings.

Figure 2.4.

The Solenoid valve.



attached to a metal rod, into a glass cup. When the solenoid coil was activated, a magnetic field was induced which lifted the metal rod from the glass cup and permitted gas to flow through the valve. When the solenoid coil was isolated from the voltage supply, the metal rod returned quickly under the combined forces of gravity and the spring to the glass cup, thus renewing the seal.

The length of time for which the 250 volt, a.c. solenoid coil was active was controlled by an electronic circuit (figure 2.5). With the microswitch, MS, in position 1, the capacitor C1 became charged. When MS was in position 2, C1 discharged in a time determined by the resistances of DS1 and DS2 and of VR1. The capacitor discharge current was amplified by a transistor circuit involving TR1 and TR2, and hence enabled the relay to operate. The contacts on the relay closed the circuit between the mains voltage and the solenoid coil, which then operated the valve. This arrangement enabled the valve to be operated for time intervals from 0.1 sec. to several sec.

2.1.4. Temperature and pressure measurements.

Temperature changes accompanying combustion reactions were measured at any chosen position on the vertical diameter of reaction vessel by means of a very fine platinum-rhodium thermocouple supported on an adjustable capillary glass probe (figure 2.6). The thermocouple junction was made by butt-welding 0.0025 cm. diam. wire in a Spembley Electronic Products, argon-arc welder, and the resulting thermocouple bead was less than 0.005 cm. in diameter.

TABLE 1

1. Total number of cases	100	100
2. Number of cases with symptoms	85	85
3. Number of cases with signs	70	70
4. Number of cases with both symptoms and signs	55	55
5. Number of cases with neither symptoms nor signs	15	15
6. Number of cases with symptoms only	30	30
7. Number of cases with signs only	15	15
8. Number of cases with both symptoms and signs only	10	10
9. Number of cases with neither symptoms nor signs only	5	5
10. Number of cases with symptoms and signs only	5	5
11. Number of cases with symptoms and signs only	5	5
12. Number of cases with symptoms and signs only	5	5
13. Number of cases with symptoms and signs only	5	5
14. Number of cases with symptoms and signs only	5	5
15. Number of cases with symptoms and signs only	5	5
16. Number of cases with symptoms and signs only	5	5
17. Number of cases with symptoms and signs only	5	5
18. Number of cases with symptoms and signs only	5	5
19. Number of cases with symptoms and signs only	5	5
20. Number of cases with symptoms and signs only	5	5

Key to figure 2.5.

C1	=	100 μ F electrolytic capacitor.
D1	=	oA 81
DS1	=	decade switch, 0.1 to 1.0 Kr.
DS2	=	decade switch, 1.0 to 10.0 Kr.
MS	=	two-way microswitch.
R1	=	1 K Ω
R2	=	10 K Ω
R3	=	10 K Ω .
R4	=	27 K Ω .
RL	=	1 K Ω relay.
S1	=	Single way on/off switch.
S2	=	Single way range switch.
TR1	=	OC 200
TR2	=	OC 72
VR1	=	5 K Ω potentiometer, gain control.

Figure 2.5.

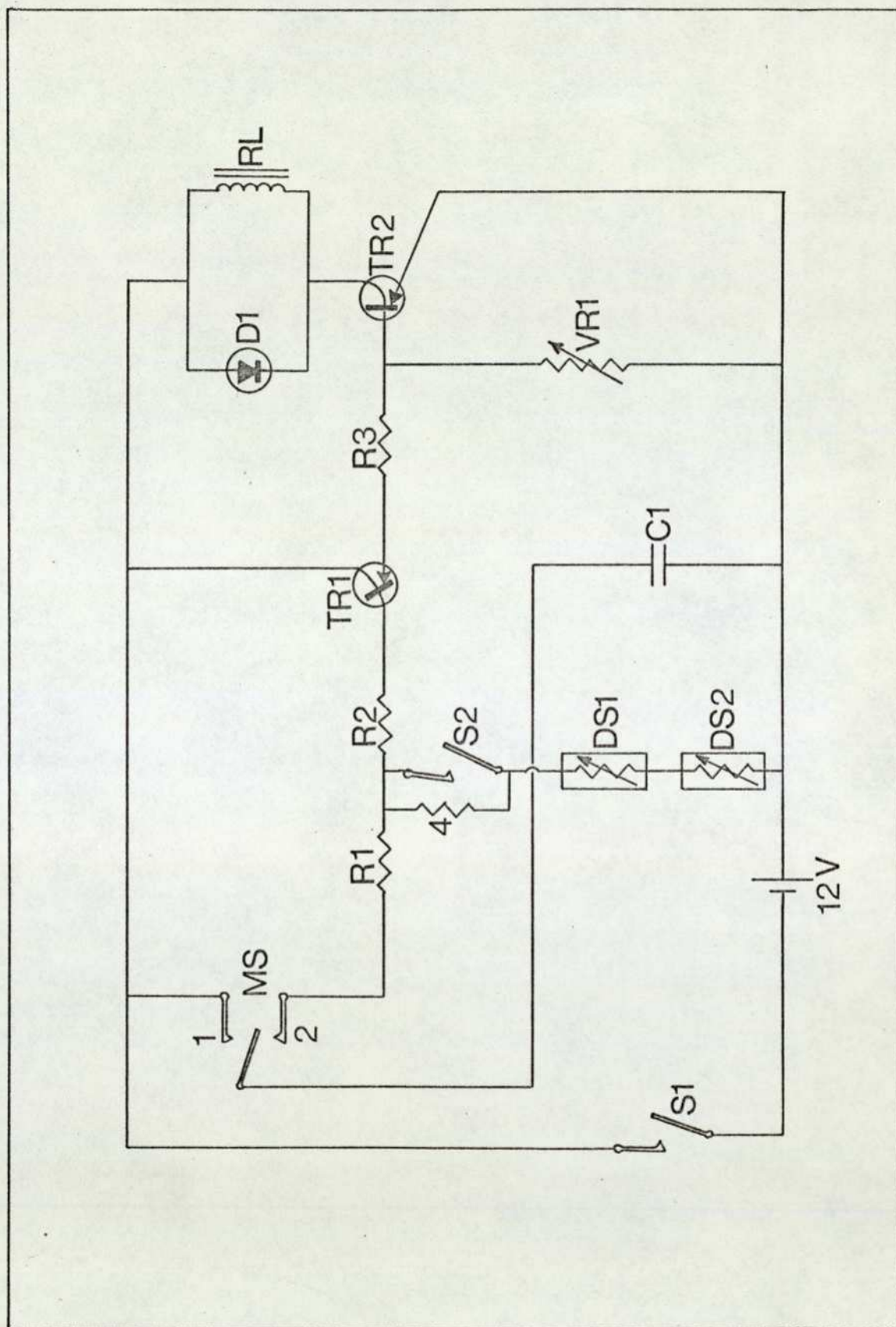
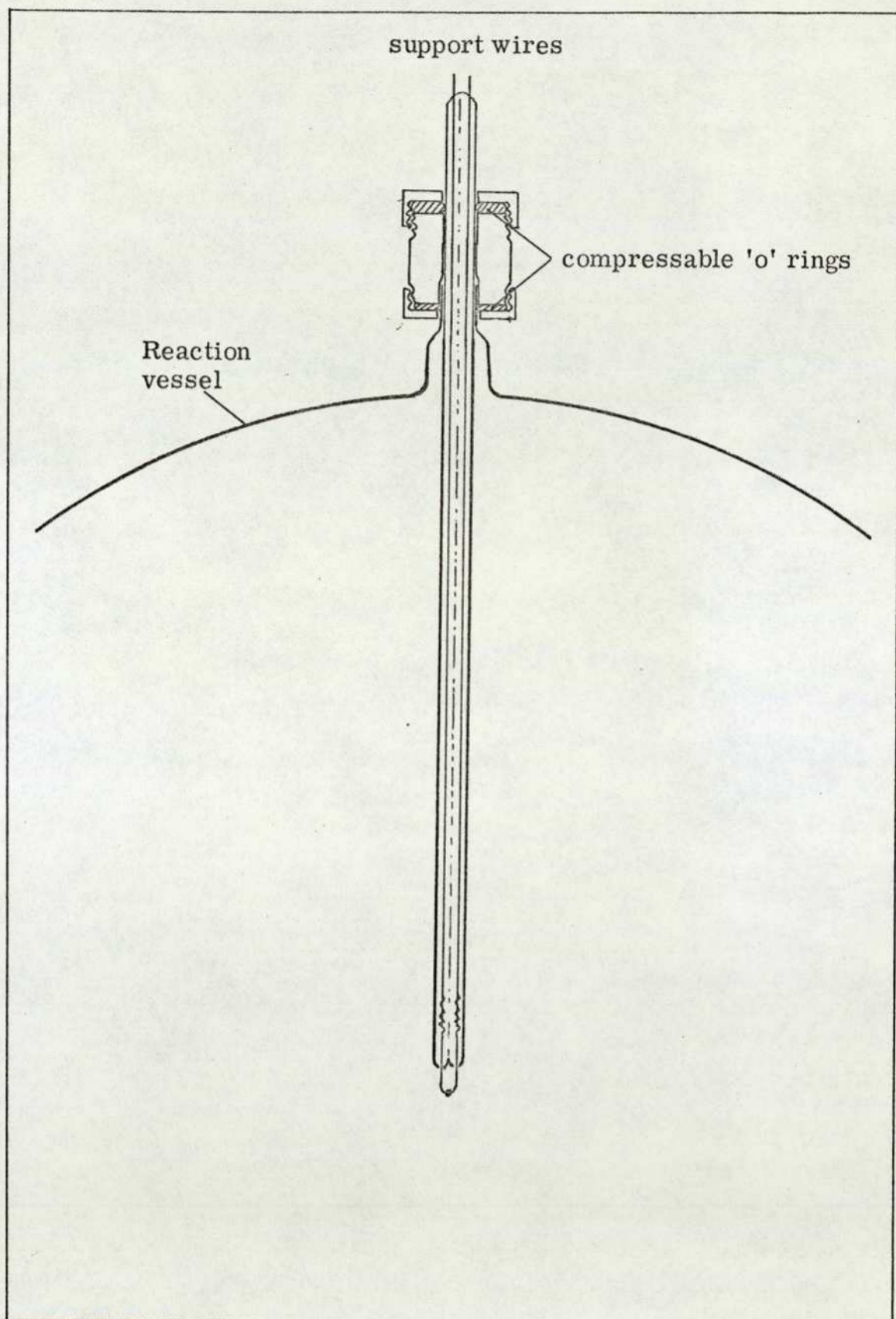
Solenoid valve timing circuit.

Figure 2.6.

The micro-thermocouple.



The thermocouple was flame-welded onto 0.025 cm. diam. support wires, and the wires were then sealed into fine capillary glass tubing. Finally, Kaskan's method¹¹¹ was used to deposit a thin layer of silica onto the exposed thermocouple wire and thus prevent catalysis of the combustion reactions. A similar thermocouple was maintained at a constant temperature of 0°C and was used as a reference.

Pressure changes accompanying combustion reactions were followed using a Bell and Howell type 4-366 general purpose transducer, giving a 0-40 mv output over a 0-50 psi pressure range. In this instrument, pressure changes unbalanced a controlled strain in an excited Wheatstone's bridge of strain gauge windings, in which all four arms were activated (figure 2.7). The transducer was electrically excited by a stabilised 10 v d.c. potential from a Bell and Howell type 3-142 transformer. The incorporation of a zero-balance circuit, involving resistors R1 to R3, and potentiometer, VR1, facilitated fine adjustment of the transducer output.

2.1.5. Amplification and recording equipment.

Output signals from the thermocouple and pressure transducer were amplified by means of National Semiconductor, type LM 201, operational amplifiers, used as inverting d.c. amplifiers with a balancing circuit (figure 2.8). The gain of the amplifier was determined by the ratio of the feedback resistance, R2, to the input resistance, R1. By selecting, with S1, appropriate resistances for R2, gains in the range 2 to 95 could be obtained.

Key to figure 2.7.

R1 = 3.9 K Ω

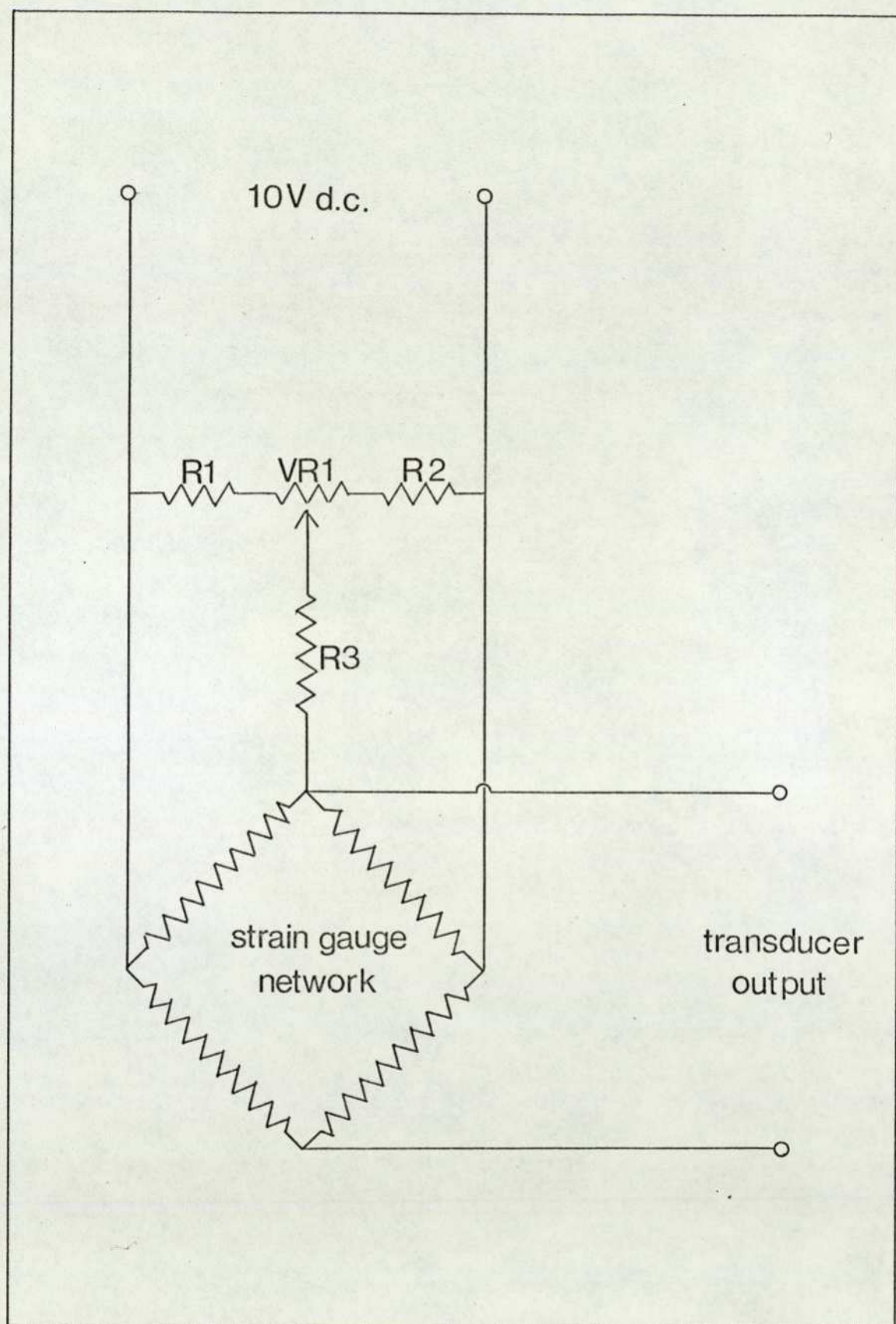
R2 = 3.9 K Ω

R3 = 68 K Ω

VR1 = 5 K Ω mult iturn, helical potentiometer.

Figure 2.7.

The pressure transducer and zero-balance circuit.

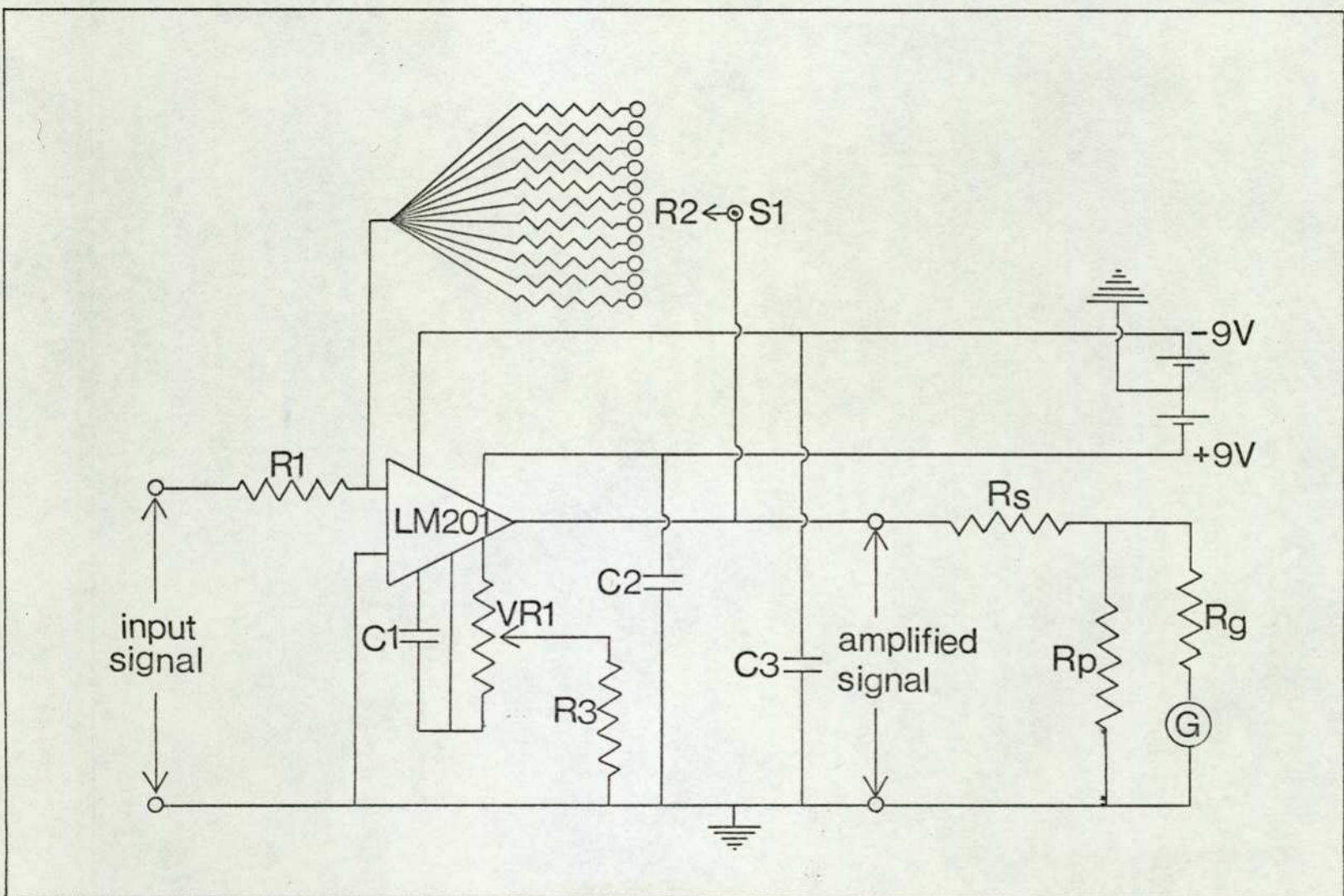


Key to figure 2.8.

C1	=	30 pF
C2	=	0.22 μ F
C3	=	0.22 μ F
Ⓒ	=	Honewell BB 130 A galvanometer.
LM 201	=	National Semiconductor operational amplifier.
R1	=	10 K Ω
R2	=	20 to 200 K Ω
R3	=	5.6 M Ω
R _g	=	75 Ω
R _p	=	2.5 K Ω
R _s	=	278 Ω
VR1	=	5 M Ω

Figure 2.8.

Inverting d.c. amplifier and galvanometer damping circuits.



The amplifier was intrinsically balanced by adjusting the potentiometer, VR1.

The amplified signals were suitably damped with series, R_s , and parallel, R_p , resistances, and were transmitted to Honeywell BB 130A sub-minature galvanometers which were placed in the magnetic assembly of a Honeywell 1706 visicorder. In this instrument, a light beam from a mercury vapour lamp, is focussed onto the galvanometer mirror. The reflected beam strikes light-sensitive paper which is drawn through the recorder at a selected speed. The resistances of R_s and R_p were calculated to provide a damping ratio of 0.64 to the output from the amplifier, which is the optimum value for a fast, but accurate response.

It was not only essential that the values of R_s and R_p should be correct, but also that the galvanometer was physically capable of responding to the rise-time of the cool flame. The maximum rise time for cool flames in these studies was shown to correspond to a frequency of 70 Hz. Since a BB 130 A galvanometer has a flat frequency response of 0-80 Hz, it was concluded that it would faithfully reproduce cool flames. This conclusion was supported by the good agreement between the measurements made using a BB 130 A galvanometer, and those made using a BB 500 galvanometer which has a much greater flat frequency response.

2.1.6. Calibration of the volume of the reaction vessel and line.

The volume of the reaction vessel and line between taps T6 and T8 was found by weighing the amount of 'Analar' acetone required to fill the space at 295⁰ K.

2.2. Reactants.

Oxygen (99.6% pure) and 'white spot' nitrogen (at least 99.98% pure) were obtained from cylinders supplied by the British Oxygen Company, and were purified as described in section 2.3.1.

n-Decane was kindly supplied by the British Petroleum Company Limited and was shown by gas chromatography to have a purity greater than 99.8%. Isooctane was provided by the Esso Petroleum Company Limited, and was shown by gas chromatography to be at least 99.6% pure. 2,2,5 - trimethylhexane was supplied by Phillips Petroleum Company and was shown by gas chromatography to be at least 99.6% pure, the only impurity being 2,2,4 - trimethylhexane. 2 methylheptane, 2,4 - dimethylheptane, 2,5 - dimethylhexane and 2,2,3 - trimethylbutane were obtained from Ralph N. Emanuel Limited, and were shown by gas chromatography to have a purity greater than 99%.

The alkanes listed above were used without further purification, but were degassed before use, as described in Section 2.3.1.

2.3. General procedure.

2.3.1. Introduction of reactants into the apparatus.

Gaseous oxygen was taken from a cylinder, passed through a drying column and condensed in trap, TR1, which was cooled by liquid nitrogen. When sufficient liquid oxygen had been collected, a middle fraction was vaporised into storage vessel, S1, considerable head and tail fractions being rejected.

Gaseous, 'white-spot' nitrogen, taken direct from a cylinder, was allowed to flow slowly into storage vessel, S2, after passing through a drying column, and traps, TR1 and TR2, which were immersed in liquid nitrogen.

Liquid alkanes were stored in an atmosphere of nitrogen to prevent oxidation on standing. The alkanes were transferred by syringes to flasks F1 and F2, and were degassed by successive freeze-thaw operations, carried out under vacuum until bubbles of gas ceased to leave the liquid.

2.3.2. Preparation of reactant mixtures.

Gaseous reactant mixtures were prepared on a partial pressure basis, the component with the lowest required partial pressure being admitted first to the premix vessels, PM1 and PM2. In these mixtures, the ratio of oxygen to nitrogen was 1:4, (i.e. almost the same as in air). During reactant mixture preparation, pressure measurements were made with a 0-25 psia, Bell and Howell type 4-366 general purpose transducer, PT1, which was calibrated with dry nitrogen and shown to have a linear response. The output from the transducer was measured with a Croydon Type P3, Precision Potentiometer, which is accurate to 0.0025 mv., corresponding to a pressure of 0.01 kPa.

Prepared reactant mixtures were allowed to stand for 10 minutes, after which time such mixtures in heated vessels are believed to be homogeneous¹¹². Periodic gas chromatographic analysis was carried out on reactant mixtures which had been stored in the premix vessels for longer than 5 hours. A portion of the

reactant mixture was condensed in trap TR3, and a 1 μ l sample of the condensate was injected onto a 2-metre stainless steel column, packed with 10% silicone grease supported on 72-85 mesh celite and maintained at 160°C. Nitrogen was used as a carrier gas and the eluted components of the mixture were identified by a flame-ionisation detector. Analyses carried out in this way confirmed that less than 0.2% of the n-decane had reacted in the premix vessel.

2.3.3. Conditioning of the reaction vessel.

A 1:10 n-decane-air mixture was prepared in PM1 and PM2 at a total pressure of 100 kPa. With tap T7 closed, a fraction of the mixture was admitted to the reaction vessel, and as soon as the operation of the solenoid valve was complete, tap T6 was closed. In this way, ca. 50 cool-flame and two-stage ignition reactions were carried out, and as a result a reproducible surface was obtained in the reaction vessel. The results were considered to be reproducible when the induction period preceding a cool-flame varied by less than 5% for consecutive reactions carried out under the same initial conditions of temperature and pressure. Between these consecutive runs, the reaction vessel was pumped out for a period of 6 minutes, after which time additional pumping had a negligible effect on the induction period.

2.3.4. Calculation of Kinetic parameters from pressure-time records

Since the output signal from the pressure transducer PT2 was not always amplified at the same gain, it was necessary to make a

separate calibration of the transducer for each run. This calibration was performed when the combustion reactions were complete, by opening T7 with T8 closed, and measuring the pressure on the manometer M2. The measured pressure corresponded to a deflection, P_m , on the pressure-time record shown in figure 2.9(a), from which a calibration factor of pressure/unit deflection was calculated.

The induction period of the first cool flame, (τ_1 in figure 2.9(a)), was taken as the time elapsing between the introduction of the reactants into the reaction vessel and the attainment of the maximum value of the pressure rise of the cool flame, ΔP_1 . The induction periods of the ignition effect pulse, τ_{ie} , and those preceding the second cool flame, τ_2 , and ignition, τ_{ig} , (figures 2.9(b) and 2.9(c) respectively) were similarly taken as the time elapsing between τ_1 and the appropriate pressure pulse.

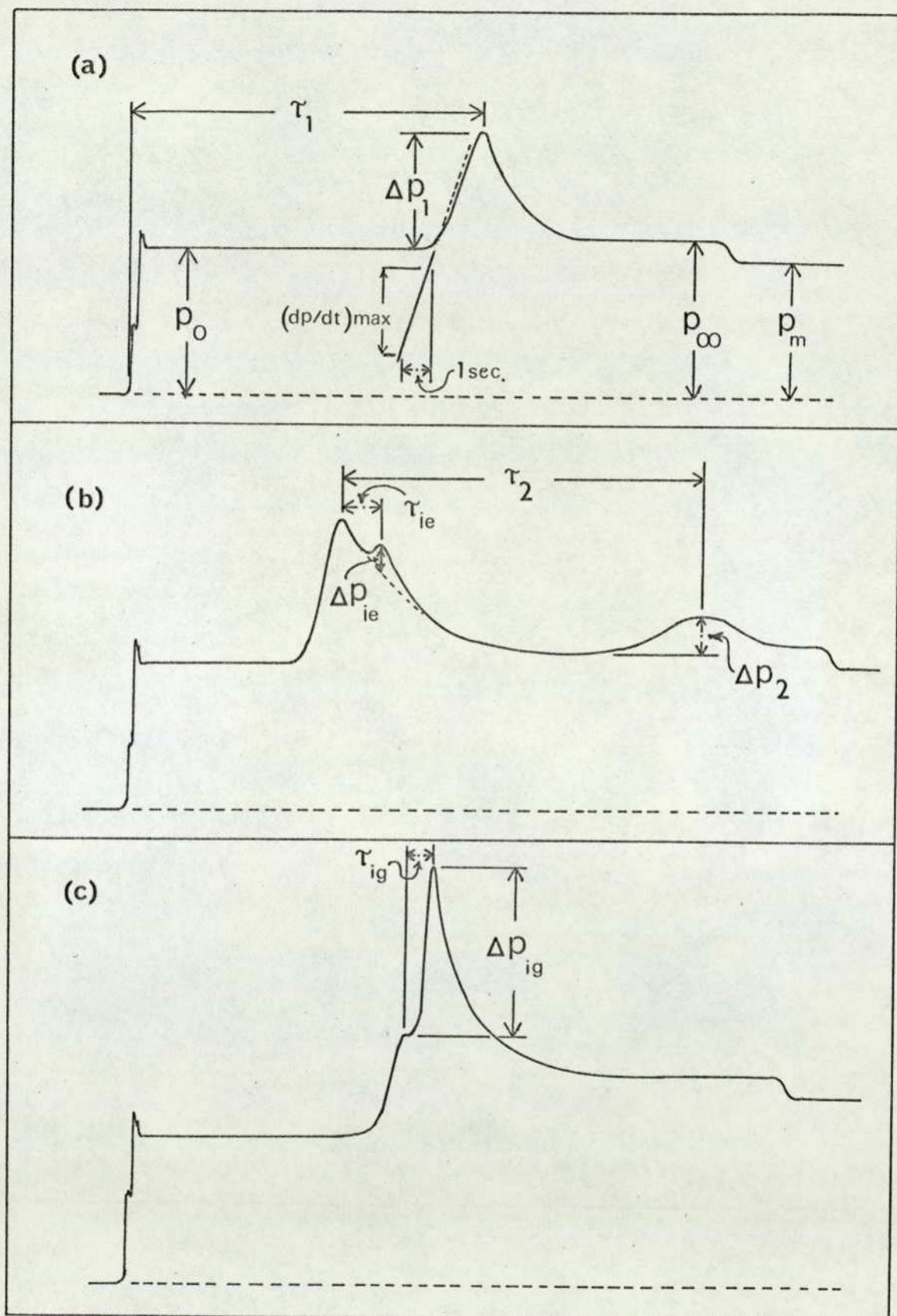
The maximum rate of pressure rise, $(dP/dt)_{max.}$ of the cool flame was calculated from the slope of a line constructed tangentially to the maximum rate of rise of the pressure trace.

In figure 2.9(a), P_o and P_{∞} represent the initial and final gas pressures in the reaction vessel, and ΔP_1 represents the maximum pressure rise of the cool flame. Figures 2.9(b) and (c) show the methods used to calculate the maximum pressure rise accompanying the ignition effect pulse, ΔP_{ie} , the second cool flame, ΔP_2 , and hot ignition, ΔP_{ig} .

Similar kinetic parameters were calculated from temperature - time traces which were the result of measurements, made with the micro-thermocouple, of temperature changes

Figure 2.9.

Kinetic measurements from pressure-time traces.



accompanying combustion reactions. A thermocouple calibration factor of temperature change per unit galvanometer deflection was calculated for each amplifier gain. These calibrations were carried out using measurements of the deflection which corresponded to a temperature change from 273° K up to the reaction vessel temperature.

2.4. Computer programming.

Computer programmes were coded in Fortran four language, and were run on an I.C.L. 1905 digital computer.

SECTION 3

RESULTS

SECTION 3

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3.1 The combustion of pure alkanes in air and oxygen

3.1.1 Phenomena resulting from the observation of pressure changes

3.1.1.1.(a) Ignition profiles of n-decane-air mixtures

The initial conditions of temperature and pressure under which 1:10 and 1:17.5 n-decane-air mixtures undergo non-isothermal oxidation are shown in figure 3.1. On account of the shortness of the induction periods preceding a cool flame or two-stage ignition (ca. 0.3 sec.), certain regions of the ignition profile could not be completely constructed.

Figure 3.1 shows that, for both mixtures and at initial pressures, P_0 , greater than 3kPa, there is a large single cool flame region having a smooth boundary and extending from 485° to 650°K. At low initial temperatures, T_0 , (up to ca. 510°K) the passage of a cool flame is accompanied by a large and sharp pressure rise as shown in figure 3.2a. Above 510°K, the pressure rise accompanying the cool flame decreases with increasing temperature (figure 3.2b). A pressure pulse, henceforth referred to as an 'ignition effect', which occurs as a 'shoulder' on the first cool flame, is observed throughout the cool-flame region, but more particularly at temperatures about ca. 510°K (figures 3.2c and d). The ignition effect increases in magnitude as the two-stage ignition boundary is approached isothermally, eventually becoming the pressure pulse representing hot ignition (figure 3.2e).

At initial pressures greater than ca. 40kPa, two-stage ignition is observed. The two-stage ignition profile exhibits two distinct low-pressure lobes occurring at temperatures of ca. 510°K and 560°K, and these have been designated A and B

Figure 3.1

Ignition profiles for 1:10 and 1:17.5 n-decane-air mixtures

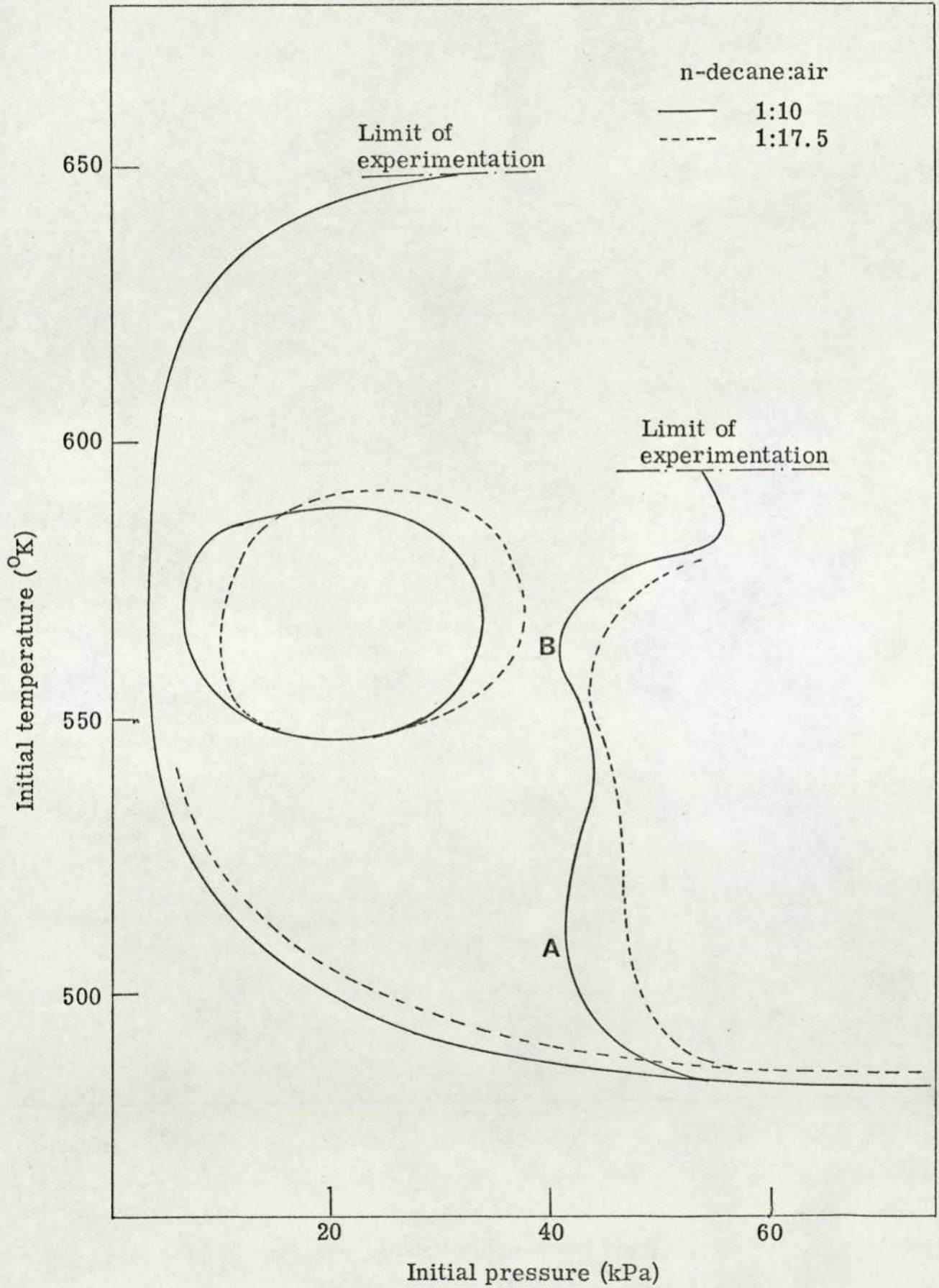
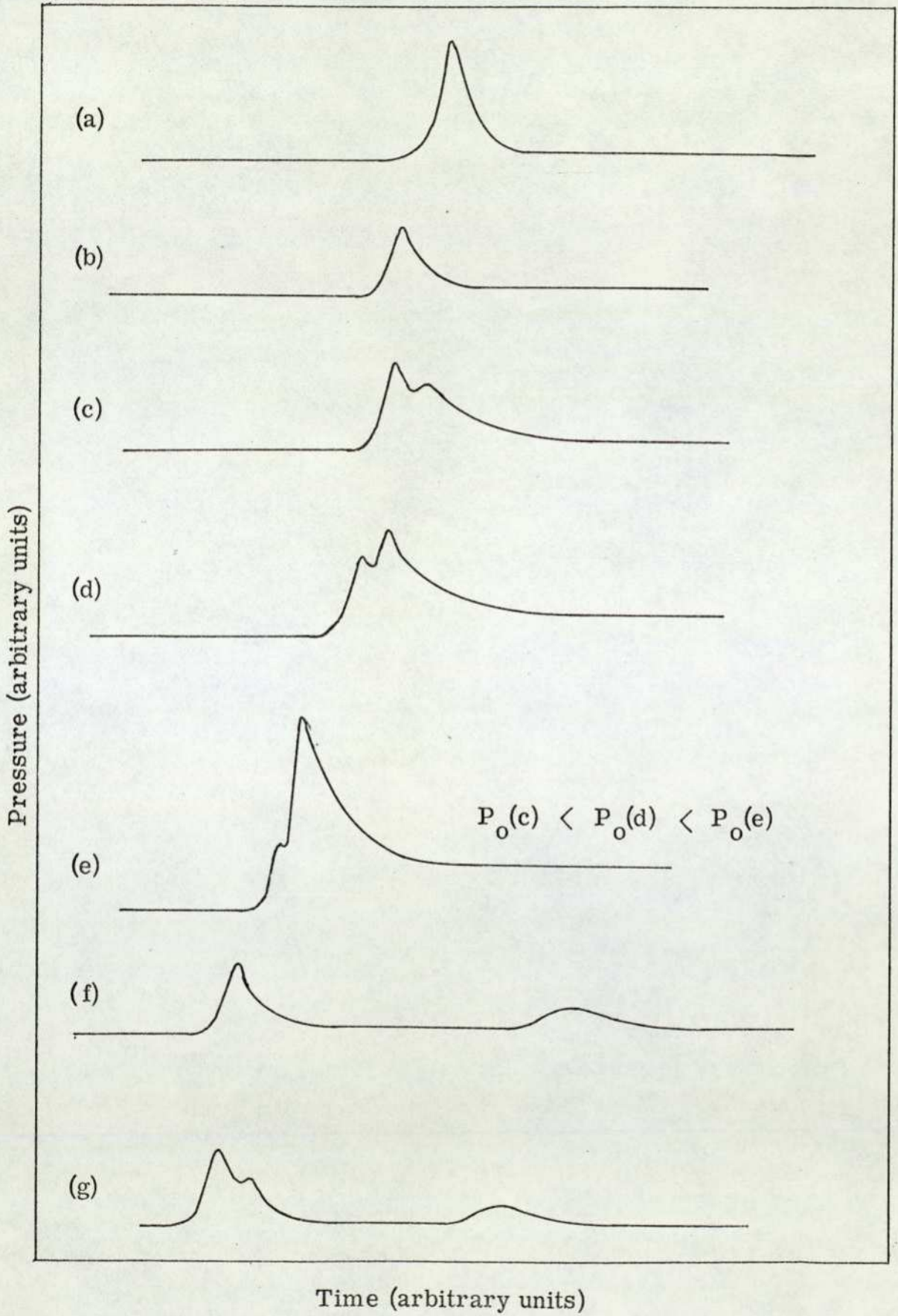


Figure 3.2
Pressure-time traces of non-isothermal
combustion phenomena



respectively.

Within the single cool-flame region, there is a region in which two cool flames may propagate consecutively, and the centre of this region corresponds with a temperature of ca. 570°K . The second cool flame possesses completely different characteristics from the first, and is accompanied by a small pressure pulse (figure 3.2f). The ignition effect has also been observed in the two cool-flame region, and a typical pressure-time record of this is shown in figure 3.2g.

The effect on the ignition profile of increasing the ratio of air to n-decane has been to raise the limiting temperatures and pressures necessary for propagation of cool flames and two-stage ignition. Furthermore, lobe A is less pronounced for the 1:17.5 n-decane-air mixture than for the 1:15 mixture, whereas lobe B is larger and extends to a lower temperature.

The variation with mixture composition of the minimum temperature required for two-stage ignition at an initial pressure of 60kPa is shown in figure 3.3.a. From this, it is clear that, as the mixture becomes more fuel-rich, the limiting temperature decreases markedly and tends to a minimum at 487.5°K .

The boundaries separating slow combustion from both cool flames and two-stage ignition have also been determined for 1:7.5, 1:15, 1:20 and 1:25 n-decane-air mixtures in the temperature range 480 to 570°K . Figure 3.4 shows these boundaries together with that determined for the 1:10 n-decane-air mixture. Clearly, as the

Figure 3.3

Variation with mixture composition of the minimum
temperature required for two-stage ignition

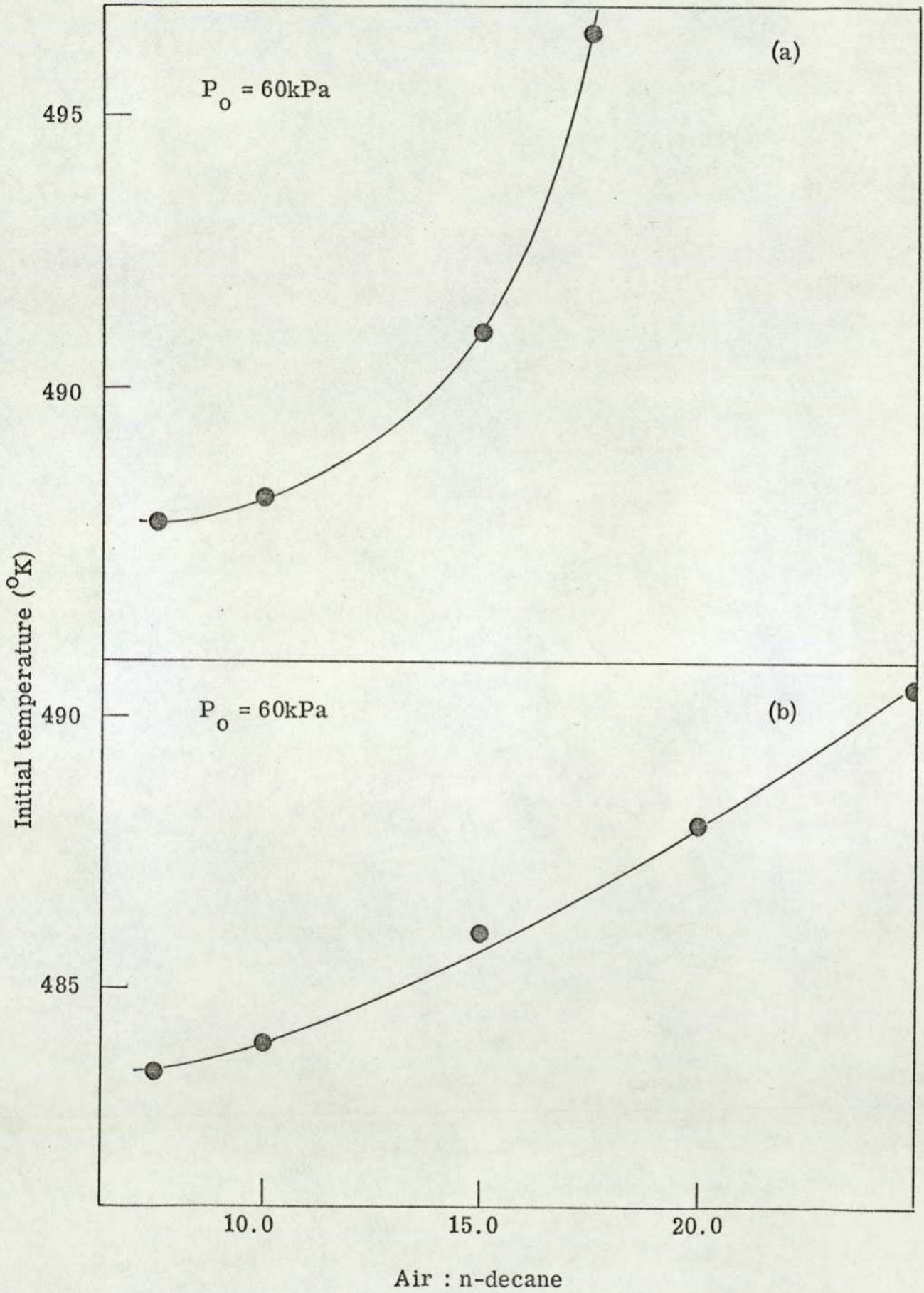
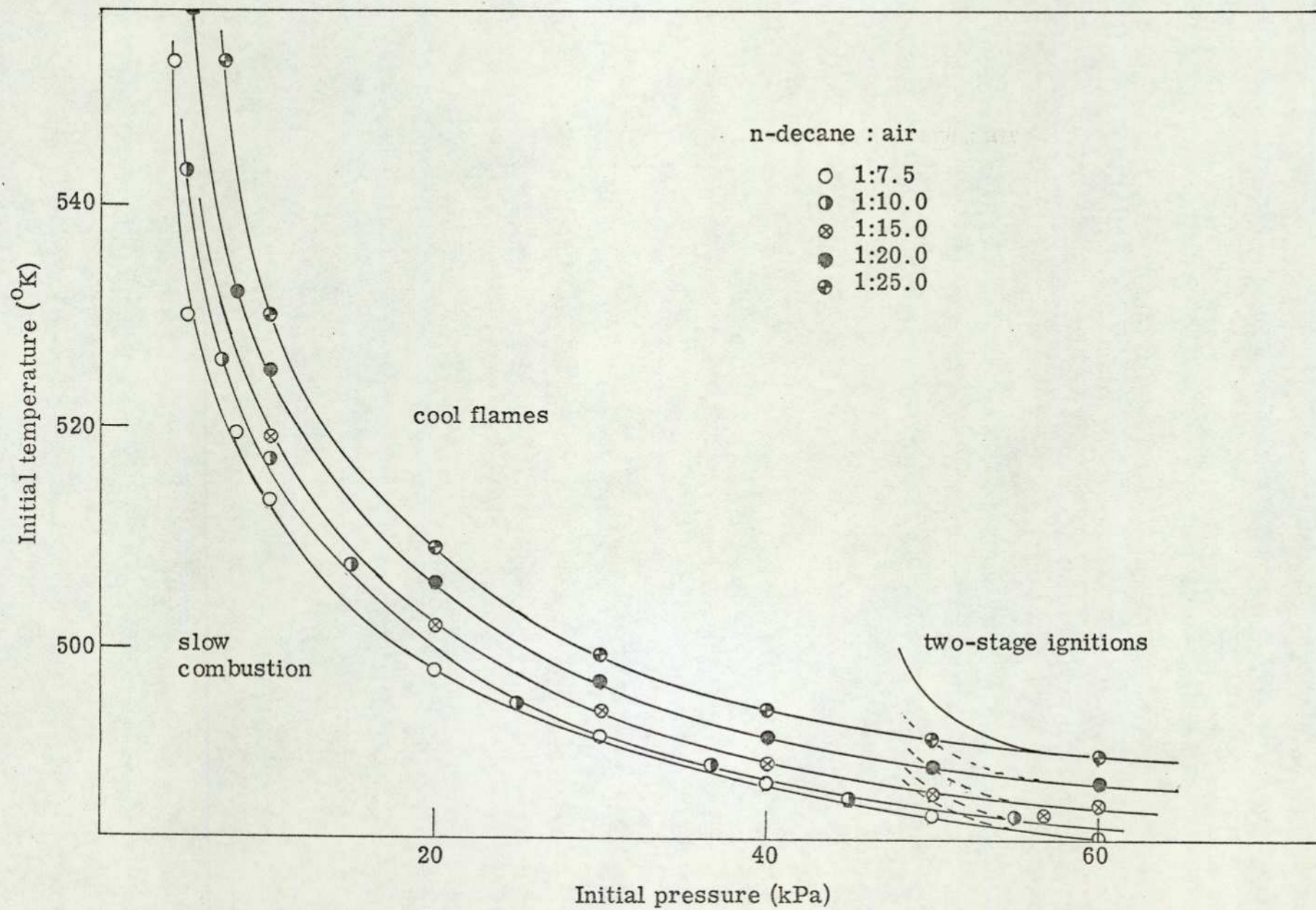


Figure 3.4

Slow-combustion/cool-flame boundaries for several
n-decane-air mixtures



ratio of air to n-decane is increased, the limiting temperature and pressure necessary for the propagation of a cool flame or two-stage ignition are increased.

Using the results shown in figure 3.4, the variation with mixture composition of the limiting temperature required for two-stage ignition at 60kPa is shown in figure 3.3.b. Although it is clear that the limiting temperature decreases and tends to a minimum as the fuel mixture becomes more fuel-rich, the variation with mixture composition of this temperature is much less marked than was found for the preliminary results shown in figure 3.3.a. This discrepancy may be accounted for by the fact that the two sets of results were obtained from experiments carried out in different reaction vessels (although these were of the same size and shape).

3.1.1.1. (b) Ignition profiles of other alkane-air mixtures

The boundaries separating slow combustion from both cool flames and two-stage ignition in 1:15 alkane-air mixtures have been determined in the temperature range 490 to 600^oK for 2-methylheptane (figure 3.5), 2,4-dimethylpentane and 2,5-dimethylhexane (figure 3.6) and isooctane (figure 3.7). A similar boundary has been determined for a 1:3 2,2,3-trimethylbutane-oxygen mixture (figure 3.7); no cool flames were observed in mixtures with air at pressures below ca. 100kPa. Figures 3.6 and 3.7 represent pairs of alkanes of different molecular weight but similar molecular structure. It is apparent from figures 3.5, 3.6 and 3.7 that the limiting conditions

Figure 3.5
Slow-combustion/cool-flame boundary for
a 1:15 2-methylheptane:air mixture

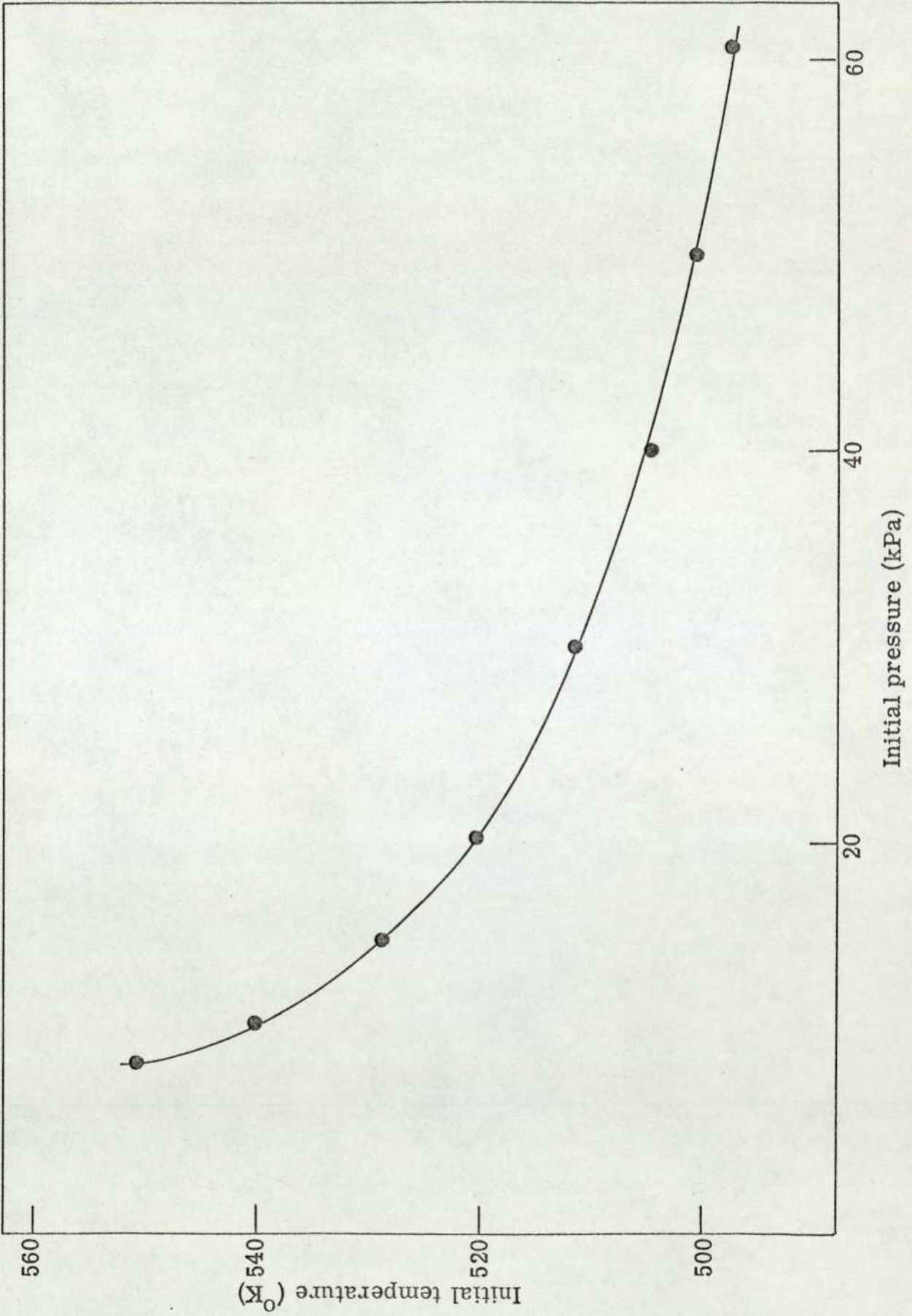


Figure 3.6

Slow-combustion/cool-flame boundaries for 1:15

2,4-dimethylpentane: air and 2,5-dimethylhexane: air mixtures

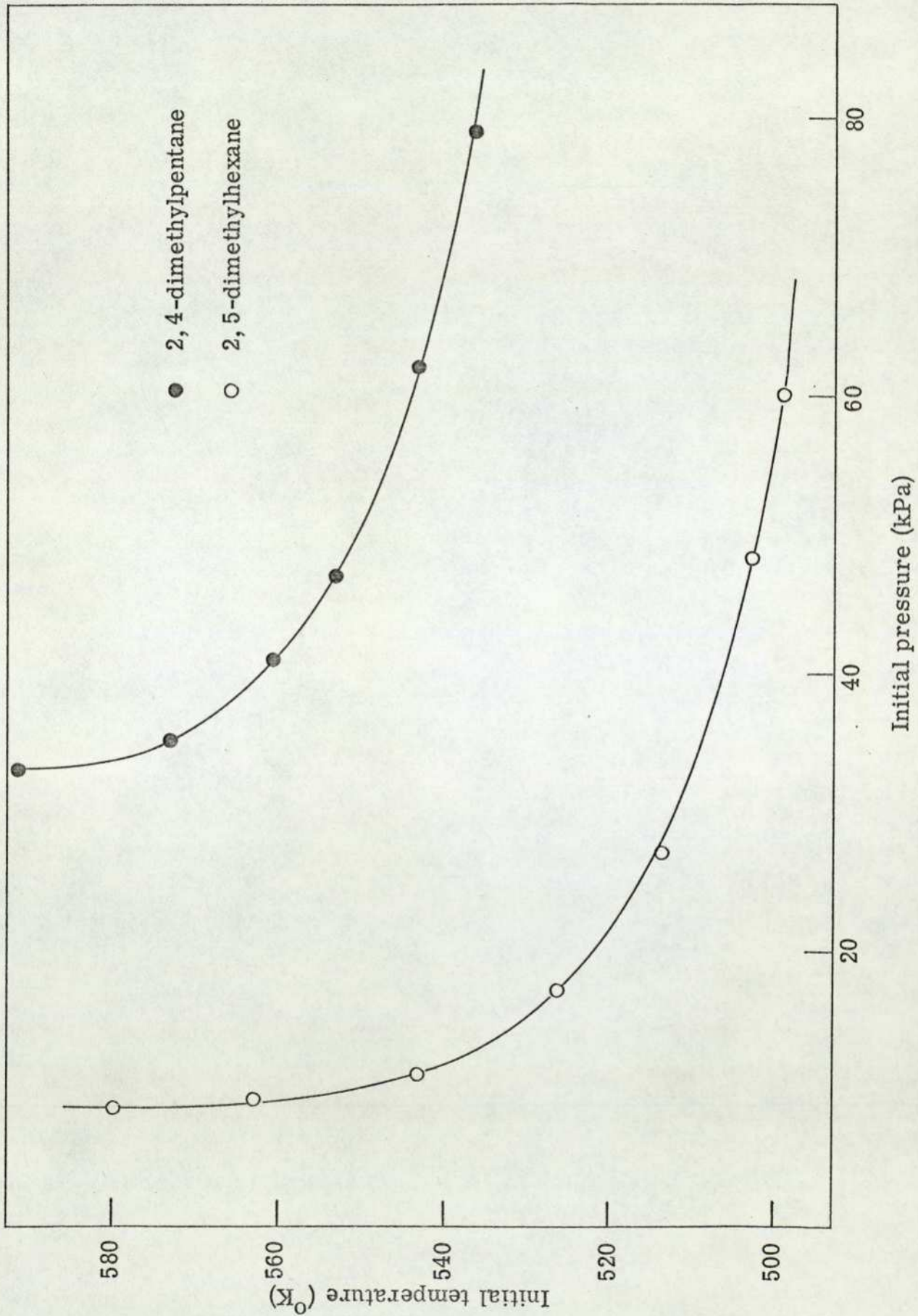
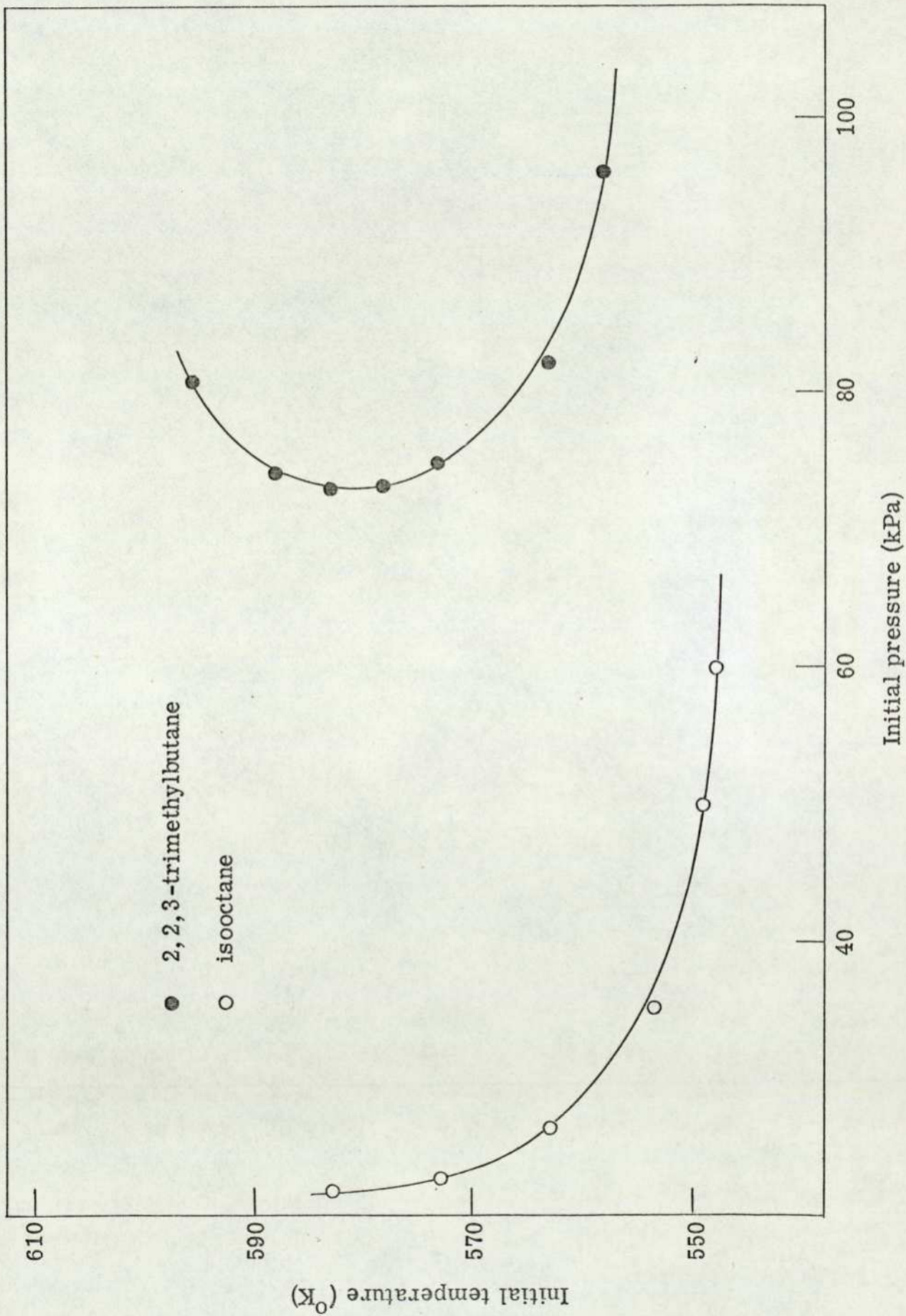


Figure 3.7

Slow-combustion/cool-flame boundaries for a 1:15
isooctane: air mixture and a 1:3 2,2,3-trimethylbutane: oxygen
mixture



of temperature and pressure required for cool flames and two-stage ignition increase with the degree of branching for alkanes having the same molecular weight, but decrease with increasing molecular weight of alkanes having a similar molecular structure.

3.1.1.2 The maximum pressure rise accompanying cool flames

Figure 3.8 shows the variation with initial pressure, P_0 , of the maximum transient pressure rise accompanying the first cool flame, ΔP_1 , for 1:10 n-decane-air mixtures. A relationship of the form

$$\Delta P_1 = A P_0^m \quad (3.1)$$

has been shown to hold for these mixtures, and figure 3.9 shows the variation with $\log P_0$ of $\log \Delta P_1$. In the temperature range 493 to 530°K, the value of the constant, A , in equation (3.1) shows a dependence on temperature, whereas m is more or less temperature independent and has values varying between 1.23 and 1.46.

Figure 3.10 shows the variation with initial temperature, T_0 , of ΔP_1 for 1:10 n-decane-air mixtures at a pressure of 35kPa. Although ΔP_1 decreases steadily as T_0 increases, the curve shows a distinct point of inflection corresponding to a temperature of ca. 530°K.

The variation with T_0 and P_0 of the locus of a constant value for ΔP_1 of 9kPa is shown in figure 3.11. Clearly, the shape of the locus between 490 and 560°K resembles that of the two-stage ignition profile shown in figure 3.1. Furthermore, the two pressure

Figure 3.8
Variation of ΔP_1 with P_0 for a 1:10
n-decane-air mixture

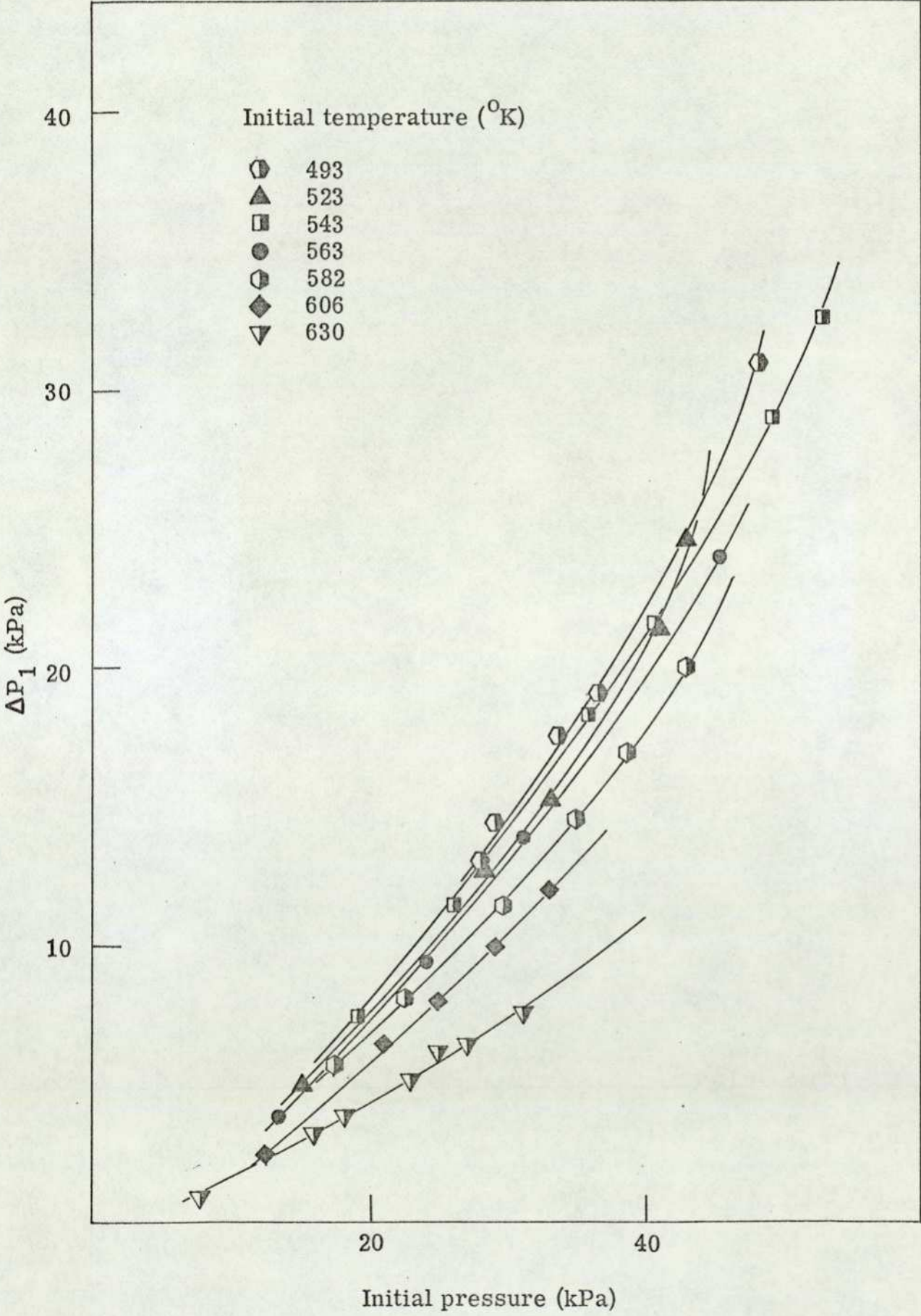


Figure 3.9

Variation of $\log_{10} \frac{\Delta P_1}{P_0}$ with $\log_{10} P_0$ for a 1:15
n-decane-air mixture

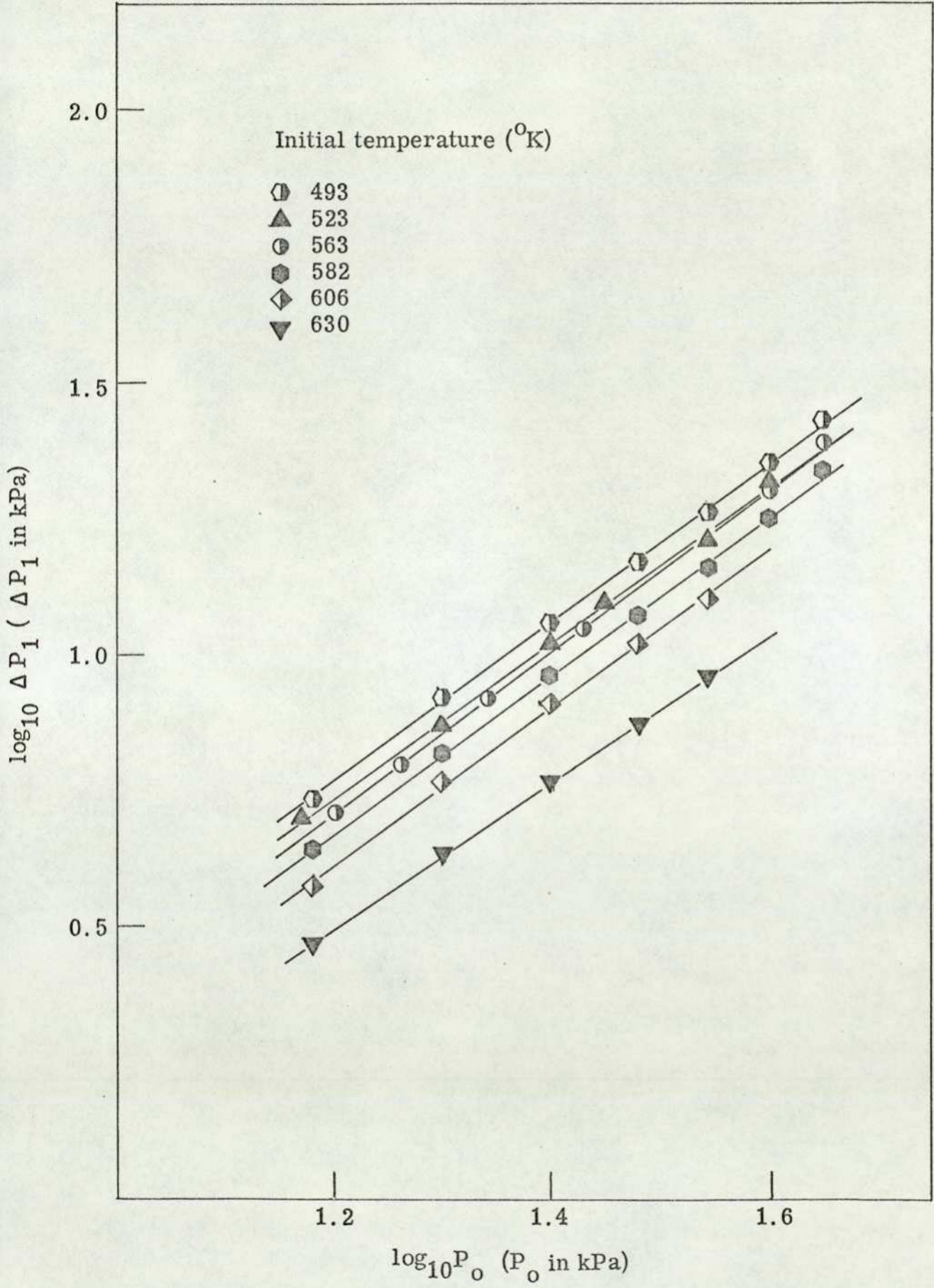


Figure 3.10

Variation of ΔP_1 with T_o for a 1:15 n-decane-air
mixture at an initial pressure of 35kPa

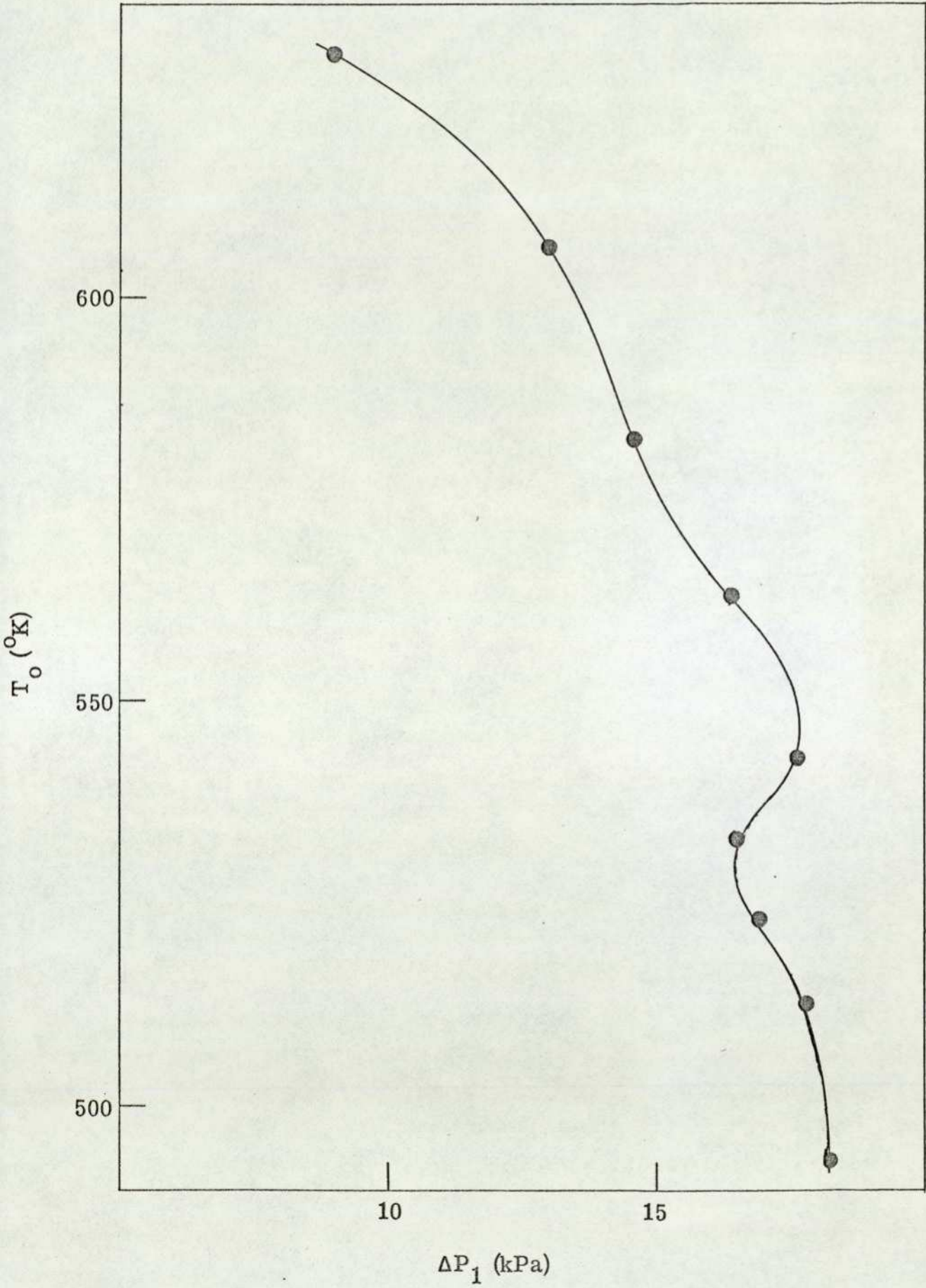
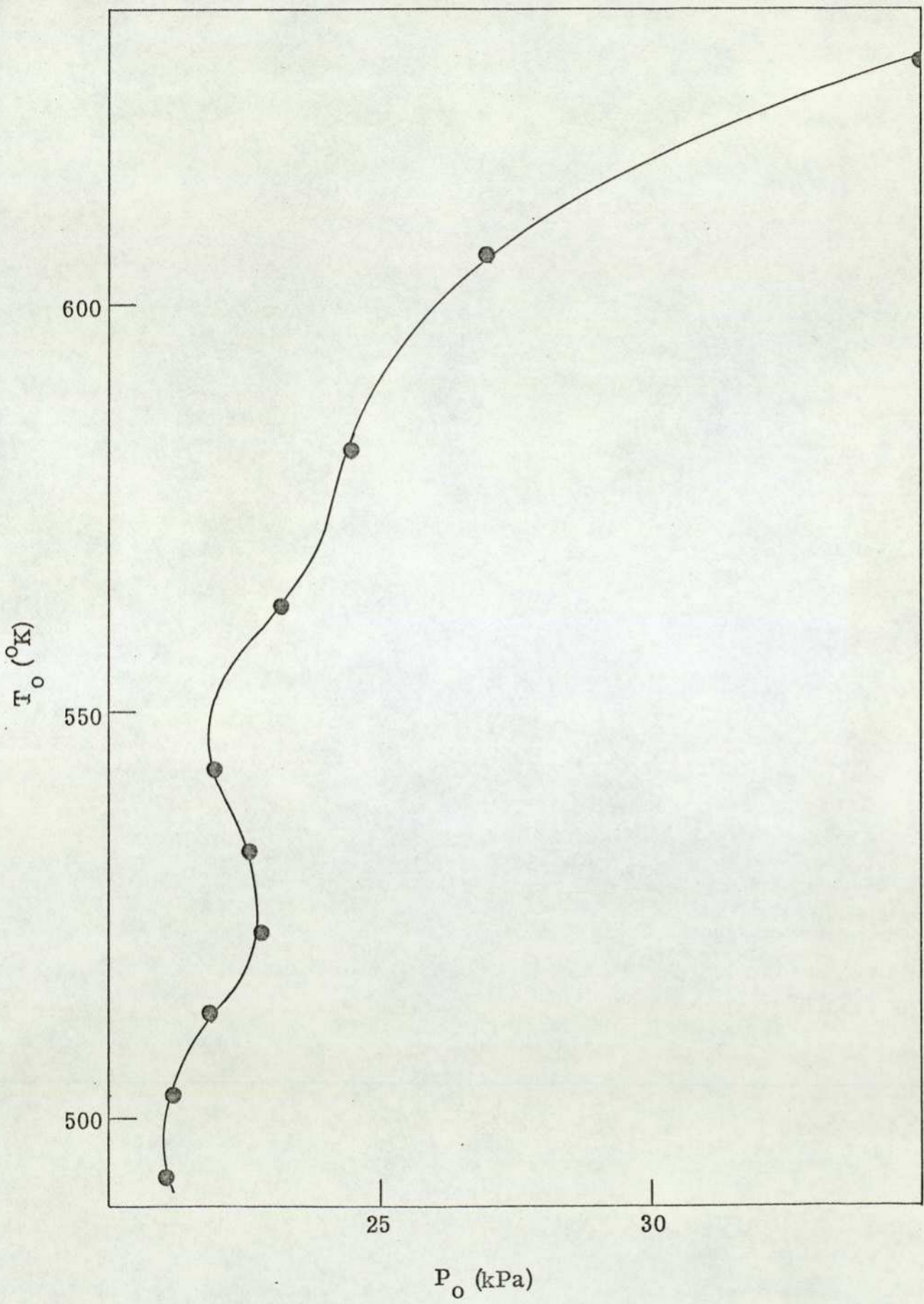


Figure 3.11

Variation with T_o and P_o of the locus of a constant
value for ΔP_1 of 9kPa. n-decane:air = 1:10



minima in the locus correspond with the temperatures at which the lobes A and B are observed.

3.1.1.3 The rate of pressure rise during cool flame propagation

An indication of the maximum, overall rate of oxidation occurring during cool flame propagation is given by the maximum rate of pressure rise of the cool-flame, $(dp/dt)_{\max}$. Figure 3.12 shows the complex variation with initial pressure of $(dp/dt)_{\max}$ for 1:15 n-decane-air mixtures at a constant temperature. Loci of constant $(dp/dt)_{\max}$ exhibit pressure maxima and minima (figure 3.13) at temperatures which correspond with the positions of the lobes on the two-stage ignition profile.

The variation with reactant mixture composition of $(dp/dt)_{\max}$ at a constant pressure of 30kPa is shown in figure 3.14 for several temperatures. From this, it is clear that, below a temperature of 523°K, $(dp/dt)_{\max}$ increases only very slightly with increasing air-n-decane ratio. At temperatures above 523°K, however, $(dp/dt)_{\max}$ increases markedly when the air-n-decane ratio is changed from 7.5 to 10.0, and then decreases gradually with further increase in the ratio of air to n-decane. This effect is most noticeable at temperatures of 543 and 563°K.

3.1.1.4 Induction periods preceding the first cool flame, τ_1

Figure 3.15 shows the variation with initial pressure, P_o , of the induction period, τ_1 , preceding the first cool flame in 1:15

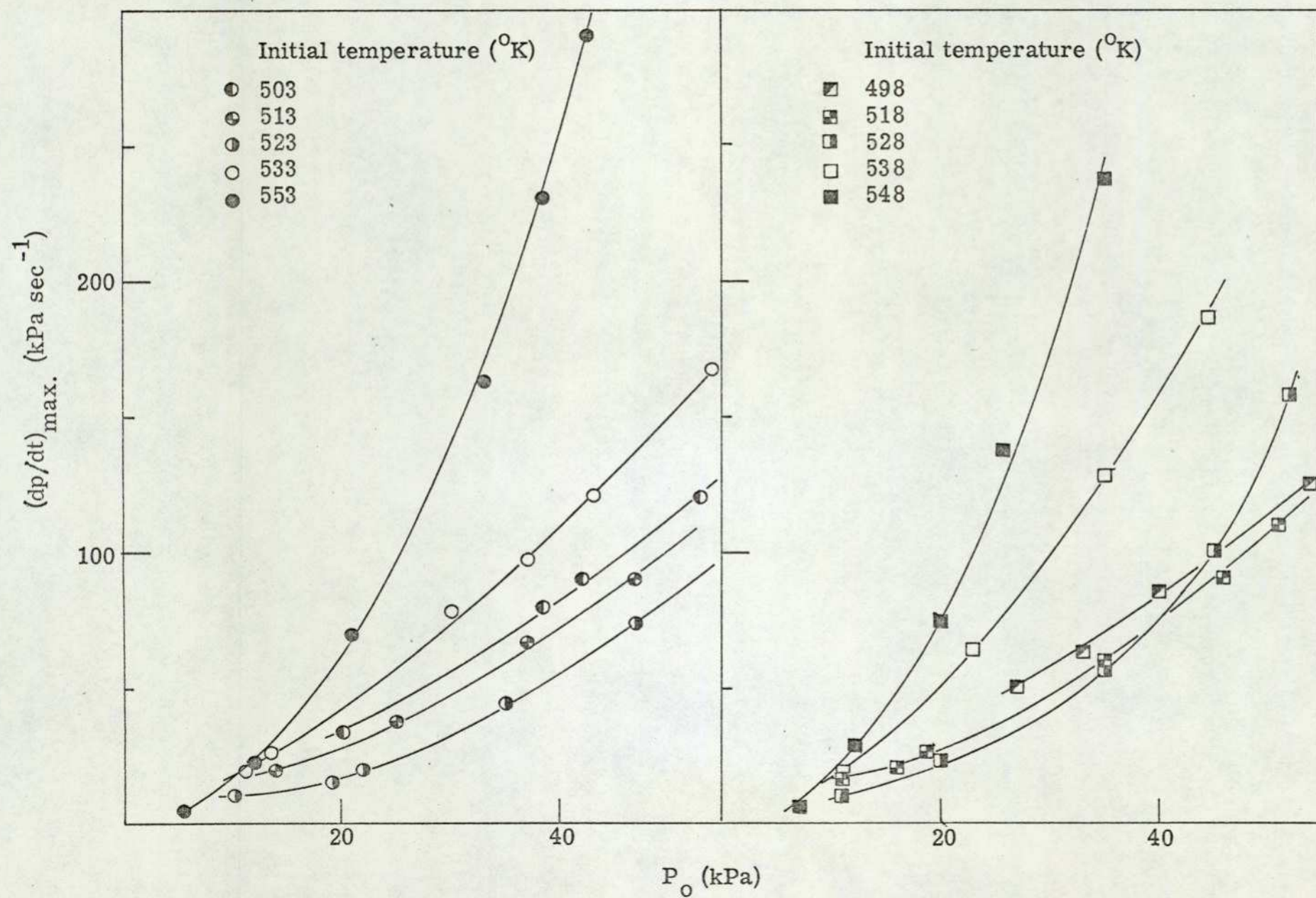


Figure 3.12
 Variation of $(dp/dt)_{\max}$ with P_0 for 1:15 n-decane-air mixture

Figure 3.13
Loci of constant $(dp/dt)_{\max.}$ for a
1:15 n-decane-air mixture

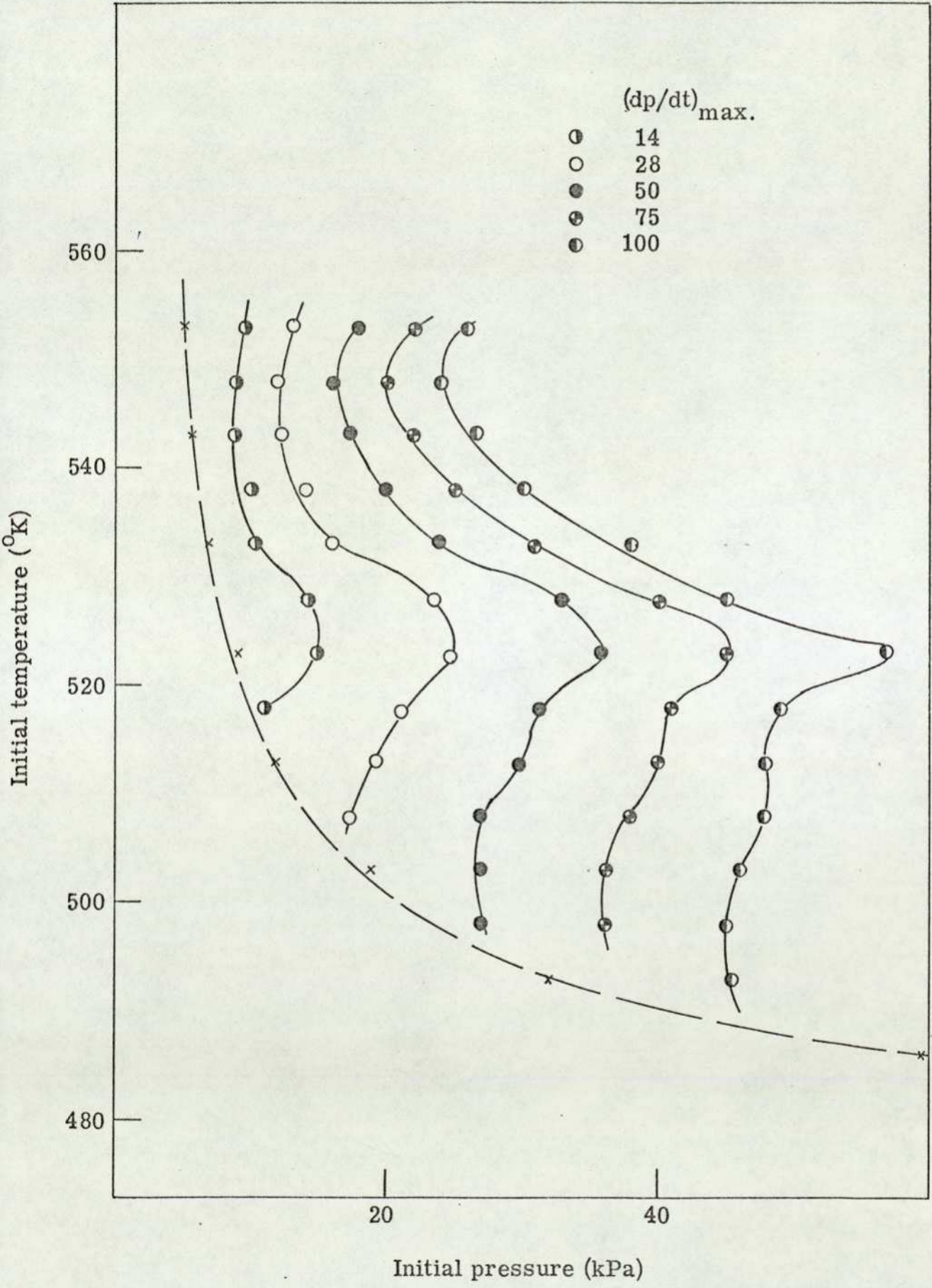


Figure 3.14

Variation of $(dp/dt)_{\max.}$ with mixture composition at several initial temperatures. Initial pressure = 30kPa

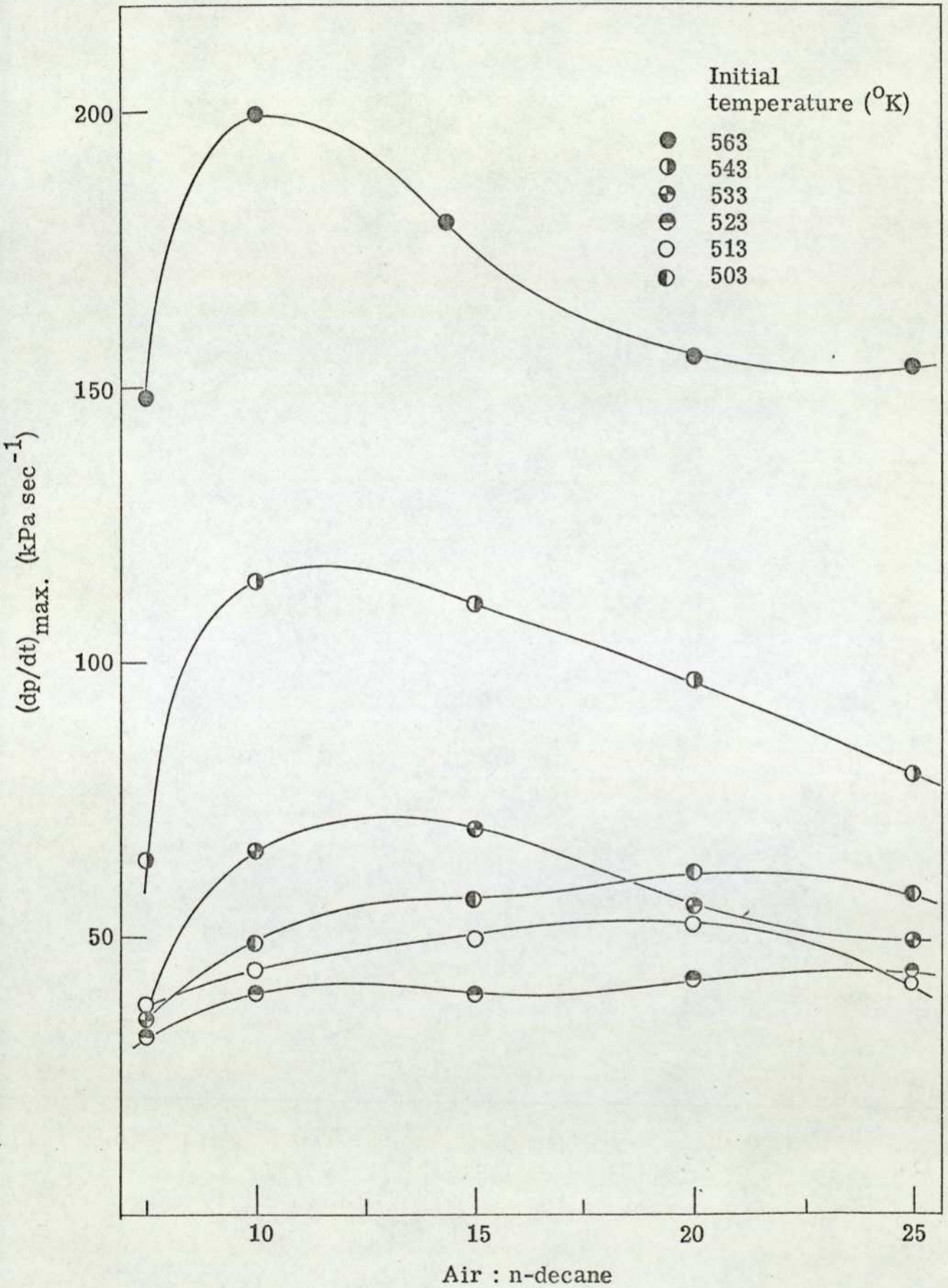
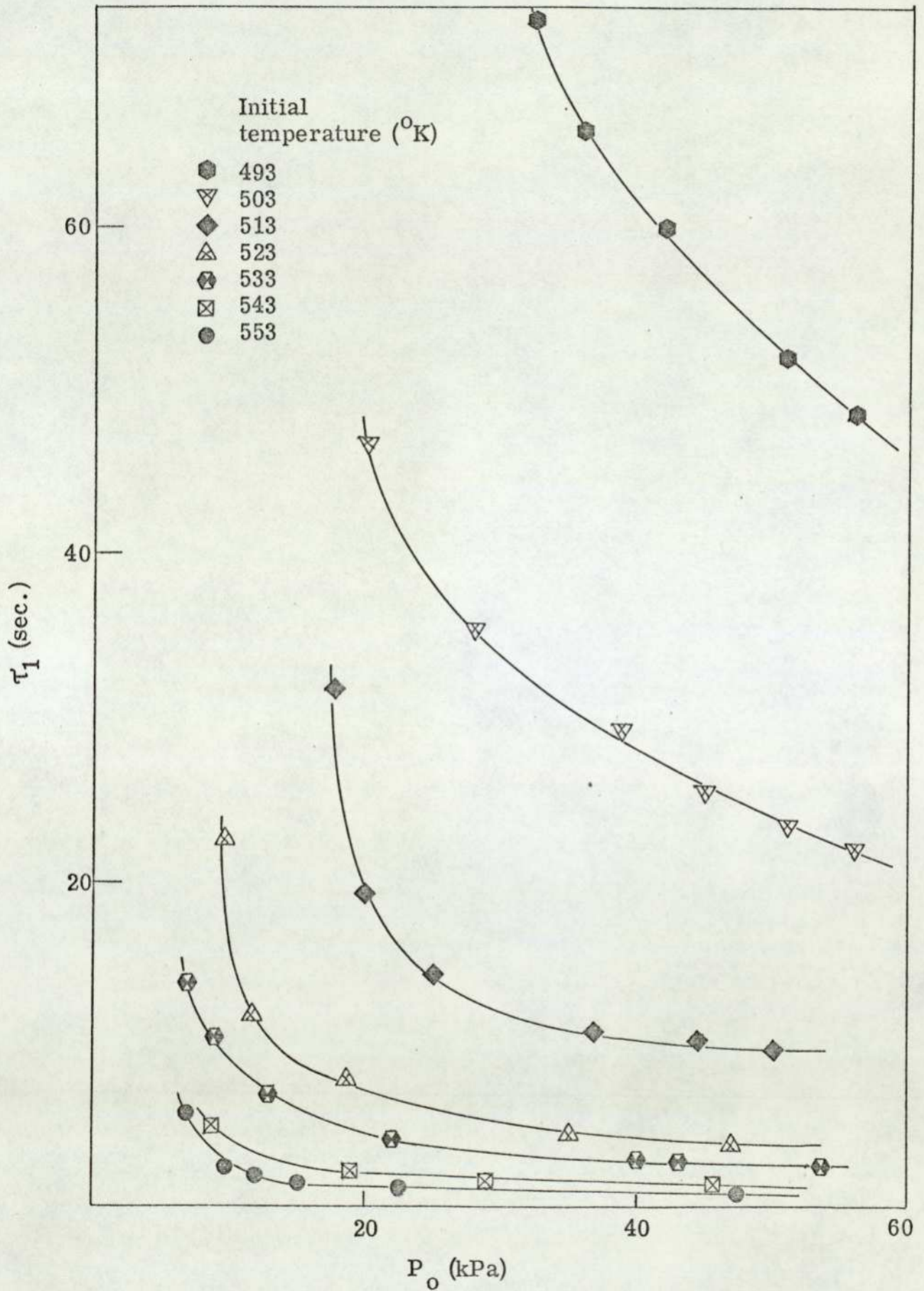


Figure 3.15

Variation of τ_1 with T_0 and P_0 in 1:15 n-decane-air mixtures



n-decane air mixtures under conditions of constant temperature. Similar curves have been obtained for 1:7.5, 1:10, 1:20 and 1:25 n-decane-air mixtures and these are shown in figures 3.16.a, b, c and d respectively.

Below ca. 525°K, τ_1 is lengthened as the ratio of air to n-decane is increased at a constant total pressure of 25kPa. Above this temperature, but under otherwise similar conditions, τ_1 becomes smaller. These effects are shown in figure 3.17.

At all temperatures, the relationship

$$\tau_1 = kP_o^{-n} + C \quad (3.2)$$

has been shown to hold for the n-decane-air mixtures studied. However, although previous workers have assumed that the value of C is negligible compared with τ_1 , it has recently been shown^{113, 114} that this assumption is incorrect, and that the value of C has a significant effect on the absolute values of n and k. Using a previous computer programme¹¹³, values for C, n and k have been calculated for all the n-decane-air mixtures at several initial temperatures, and these values are given in Table 3.1. This computer programme was designed to vary the value of C for given sets of P_o and τ_1 values until the coefficient of correlation in the relationship

$$\log (\tau_1 - C) = \log k - n \log P_o \quad (3.3)$$

was at its maximum value.

Key to Figure 3.16

n-decane : air

- (a) 1:7.5
- (b) 1:10.0
- (c) 1:20.0
- (d) 1:25.0

Legends

Temperature ($^{\circ}\text{K}$)

- 493
- ▼ 503
- ◆ 513
- ▲ 523
- ⬢ 533
- 543
- 563

Figure 3.16

Variation of τ_1 with T_o and P_o for several n-decane-air mixtures

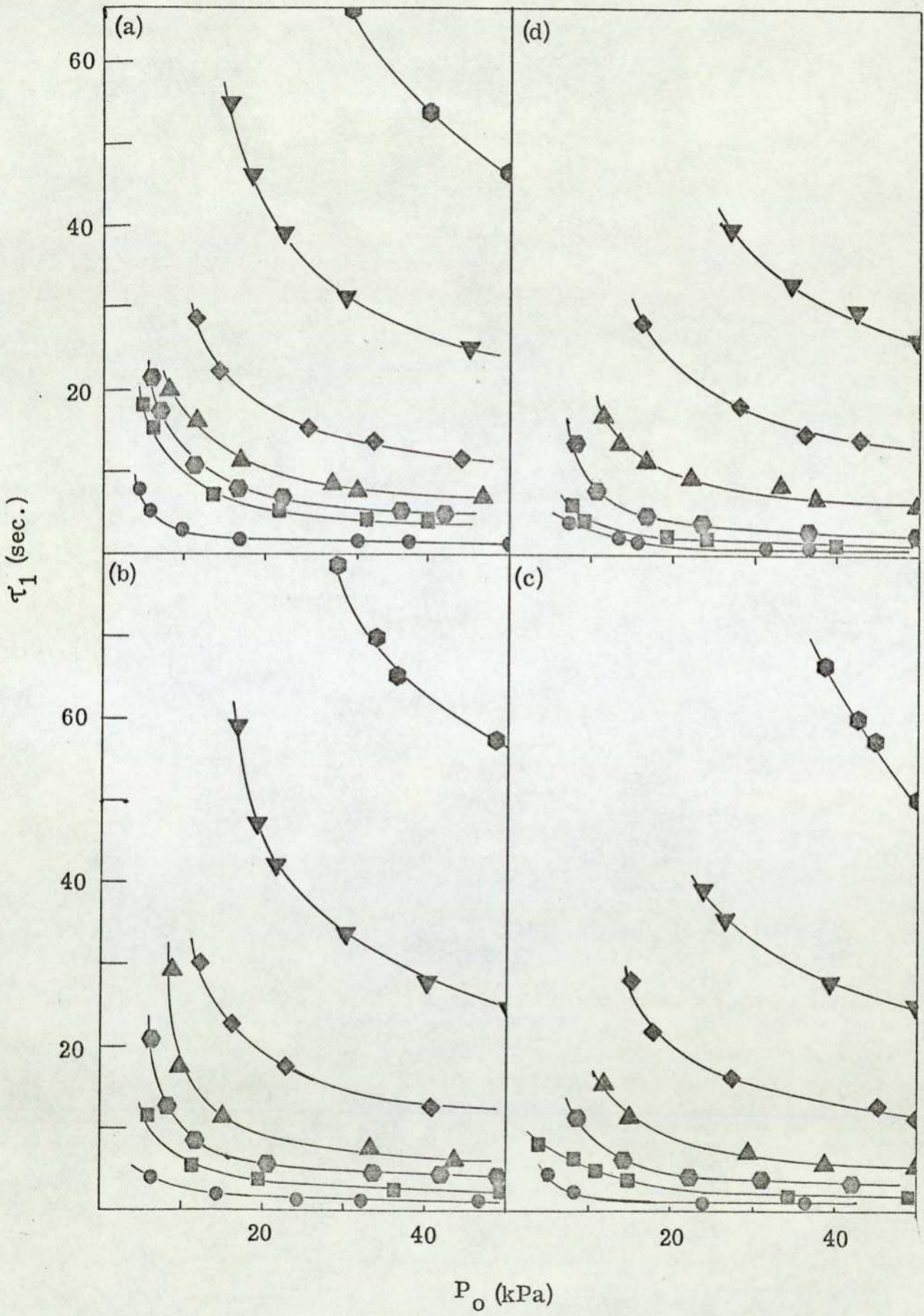


Figure 3.17
Variation of τ_1 with n-decane-air mixture
composition at 25kPa

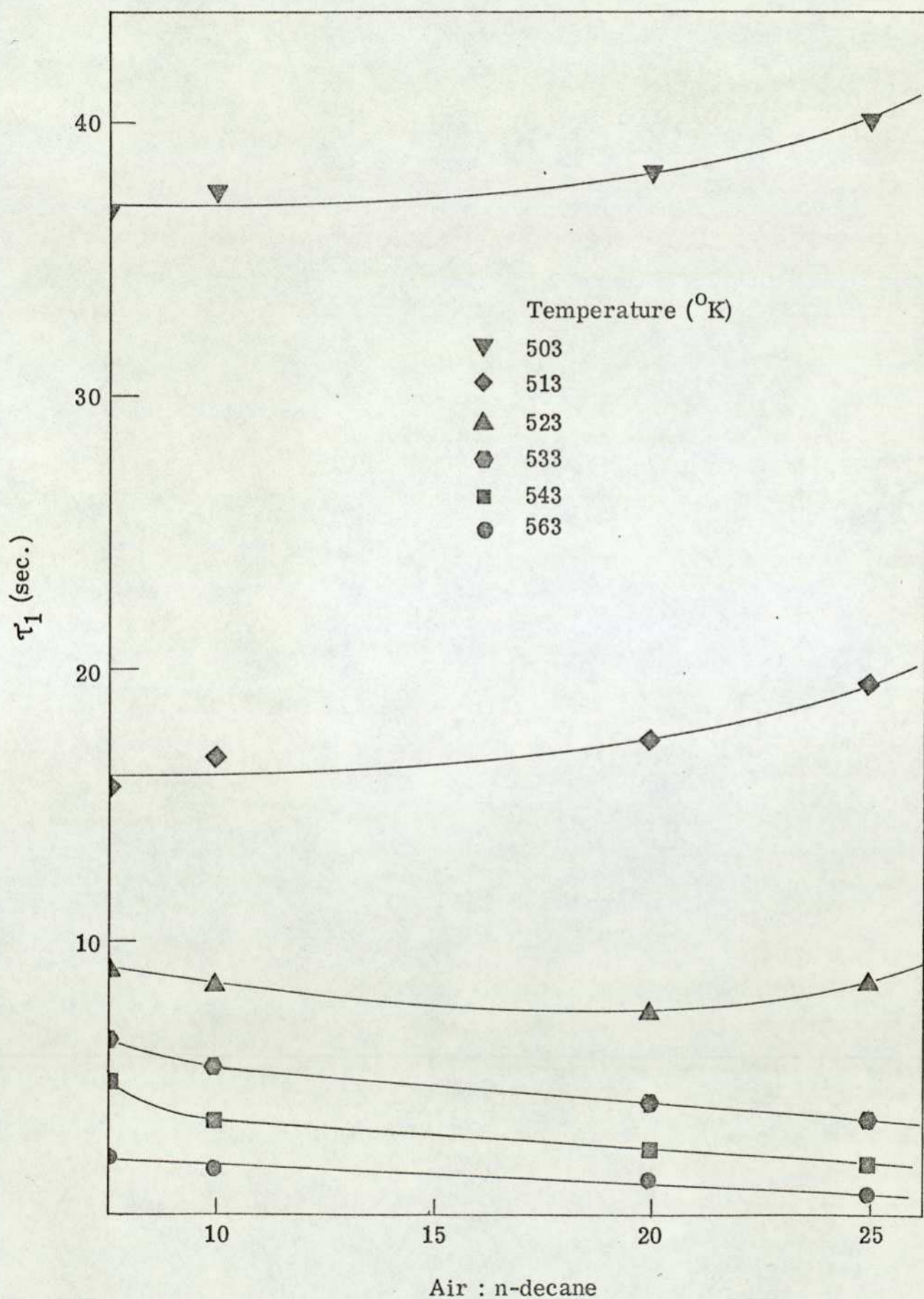


Table 3.1

Values of k , n and C for n -decane-air mixtures

Temp. ($^{\circ}\text{K}$)	493	503	513	523	533	543	553	563
Air/ n -decane = 7.5								
k	2400	2266	158	196		94		28.8
n	1.16	1.50	0.85	1.16		1.12		1.14
c	21.39	17.47	5.03	4.62		2.39		1.05
Air/ n -decane = 10.0								
k	2186	3666	330	143	215	64		24
n	1.14	1.60	1.11	1.07	1.43	1.15		1.08
c	29.43	17.83	7.36	3.76	3.10	1.55		0.75
Air/ n -decane = 15.0								
k	840	380	765	360	211	77	46	
n	0.72	0.71	1.32	1.35	1.49	1.35	1.37	
c			4.96	2.12	1.26	0.78	0.59	
Air/ n ;decane = 20.0								
k	936	979	683	104	112	63		
n	0.73	1.13	1.29	0.90	1.23	1.21		
c		11.8	6.52	2.04	1.99	1.08		
Air/ n -decane = 25.0								
k		400	410	122	97	81	40	
n		0.72	1.12	0.96	1.19	1.41	1.29	
c		2.38	7.89	3.09	1.52	1.08	0.66	

At an initial temperature of 523°K , the variation with $\log P_0$ of τ_1 for the 1:15 n-decane-air mixture is markedly curved, whereas the variation with $\log P_0$ of $\log(\tau_1 - C)$ is linear as shown in figure 3.18. Similar results have been found for the other n-decane-air mixtures studied and at all temperatures investigated.

The variation with reciprocal temperature of the values of $\log C$ is linear, as shown in figure 3.19, although there is an abrupt change in slope in the temperature range 514 to 527°K .

The calculated values of n and k vary with temperature in such a way that they reflect the shape of the two-stage ignition profile. These variations are shown for a 1:10 n-decane-air mixture in figures 3.20 and 3.21, which give plots of n versus T_0 and of $\log k$ versus $\log T_0$ respectively.

The variation of τ_1 with $1/T_0$ for 1:15 n-decane-air mixtures at several initial pressures is shown in figure 3.22. At initial pressures greater than 30kPa , these linear relationships show two changes of slope, the break points corresponding to temperatures of ca. 510°K and 533°K . From the slopes, the overall activation energy has been calculated to be 40 kcal.mole^{-1} at temperatures below 510°K , $46.8\text{ kcal.mole}^{-1}$ in the temperature range 510 to 533°K and 33 kcal.mole^{-1} at temperatures above 533°K . At initial pressures less than ca. 30kPa , there is only one change in slope and this corresponds to a value for T_0 of 533°K . In this case, the overall activation energies are 46 kcal.mole^{-1} and 28 kcal.mole^{-1} at temperatures above and below 533°K respectively.

Figure 3.18
Logarithmic relationship between initial
pressure and (a) τ_1 , (b) $(\tau_1 - C)$

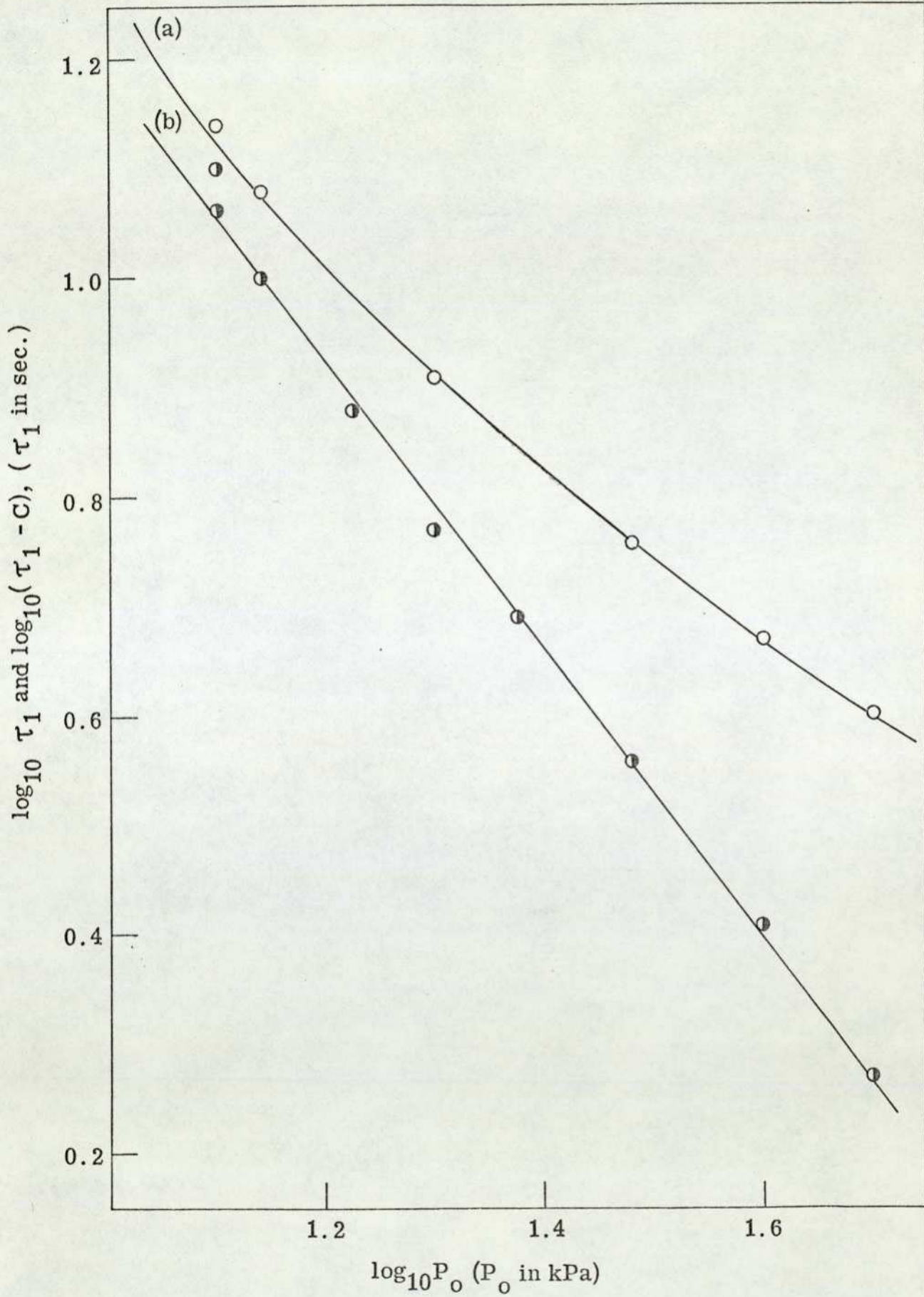


Figure 3.19

Variation of $\log_{10} C$ with reciprocal of T_o for several
n-decane-air mixtures

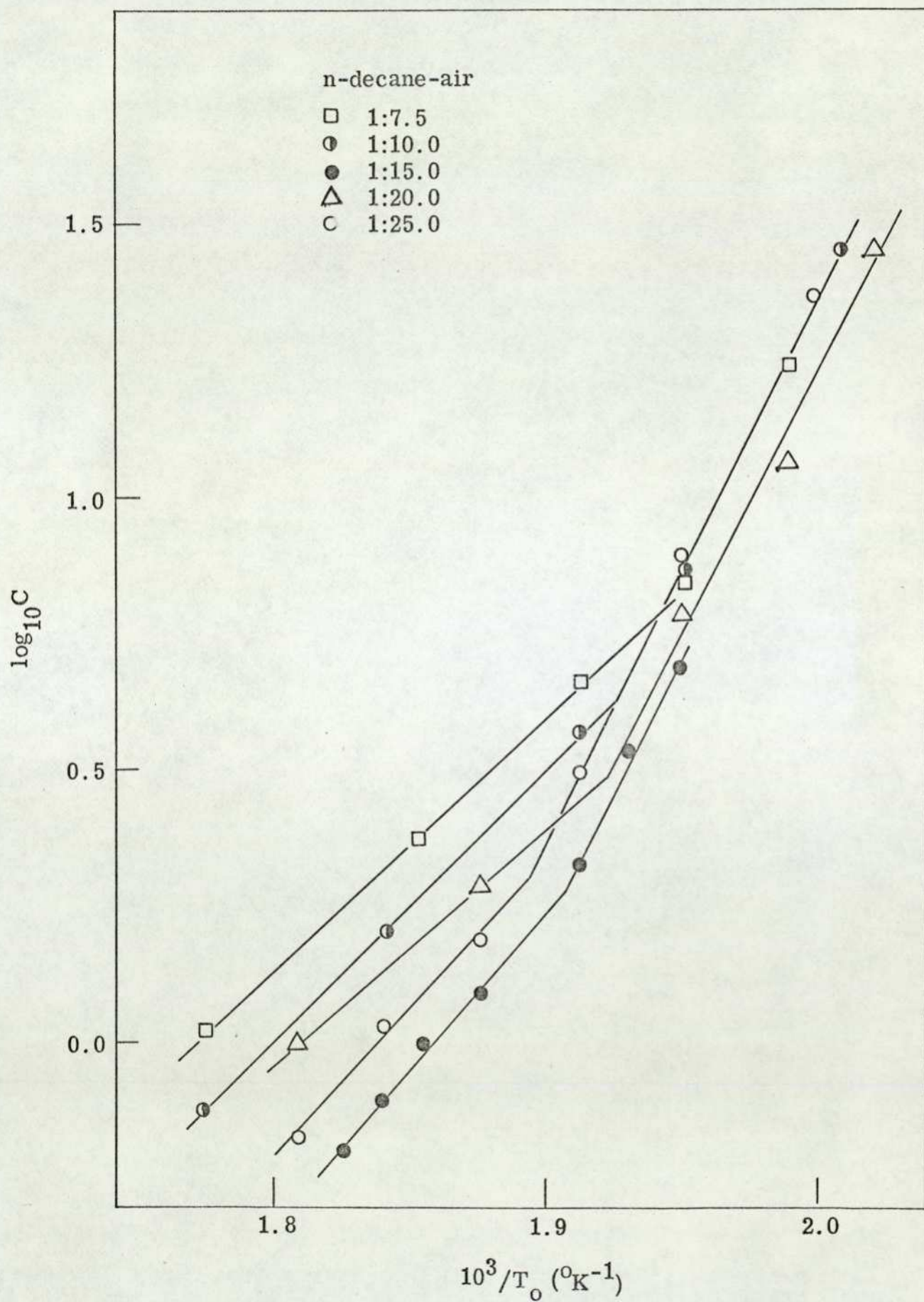


Figure 3.20
Variation of n with T_o for a 1:10
 n -decane : air mixture

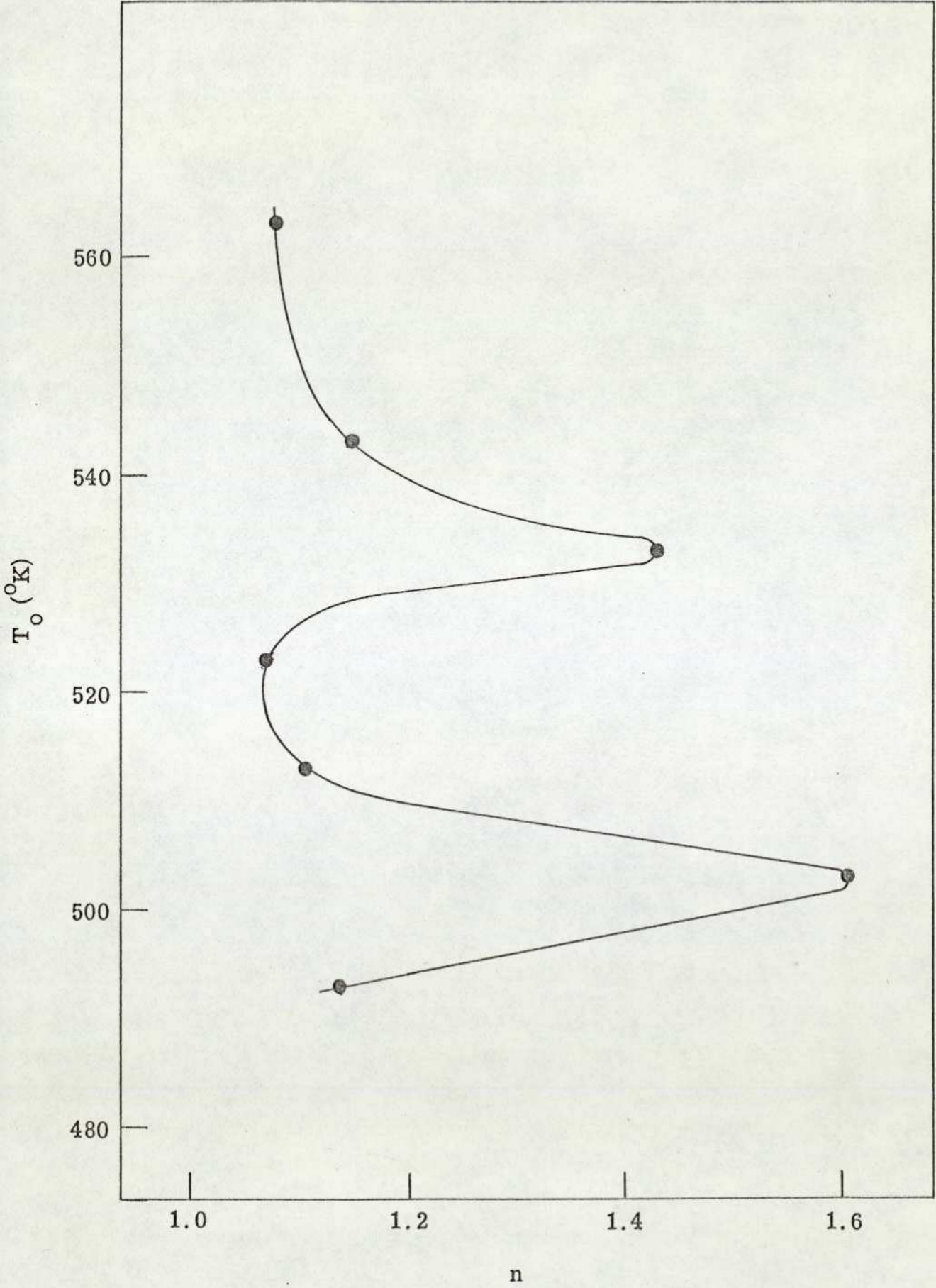


Figure 3.21
Logarithmic relationship between k and T_o

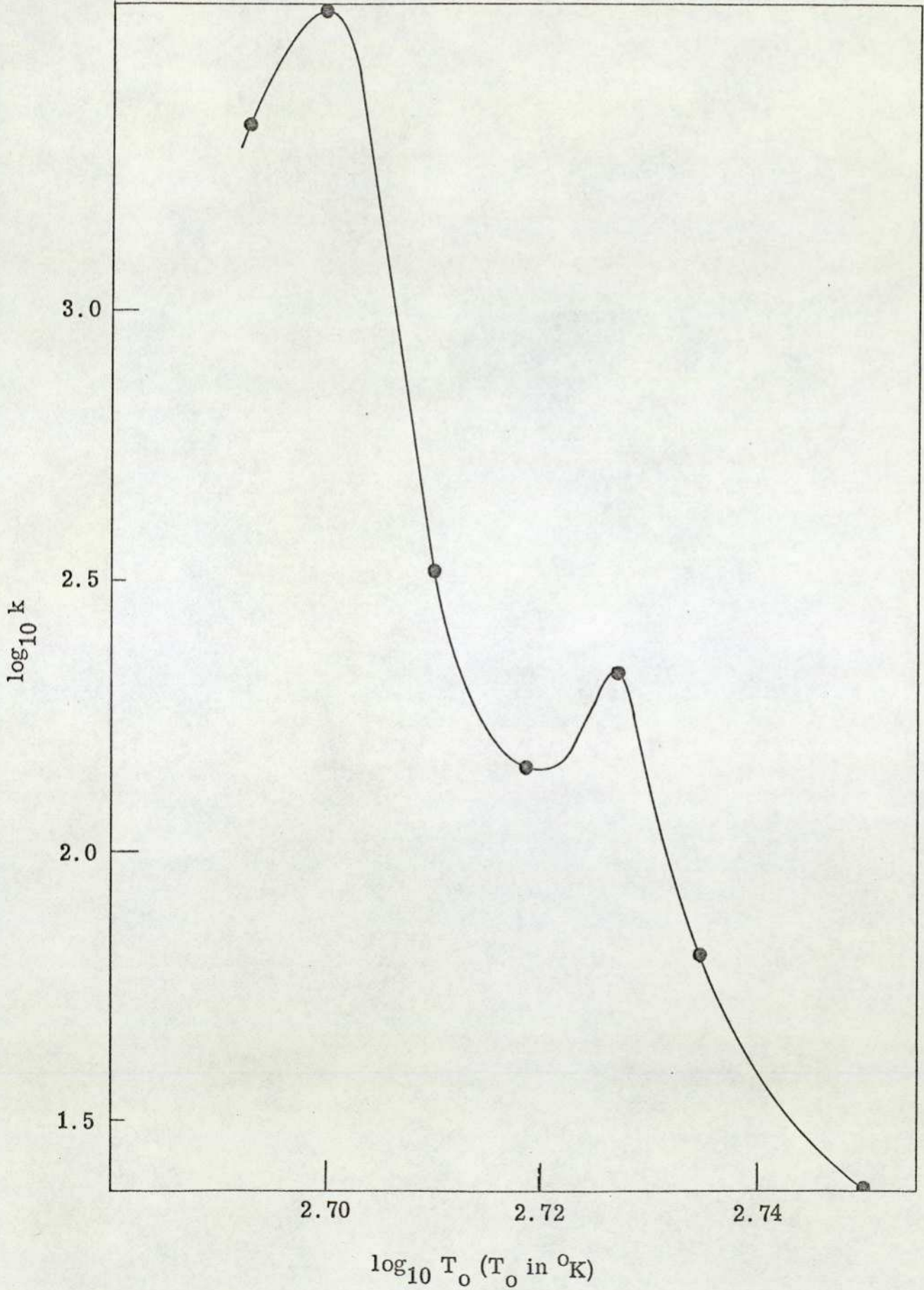


Figure 3.22

Variation of $\log_{10} \tau_1$ with reciprocal of T_0 for 1:15
n-decane : air mixtures at several initial pressures

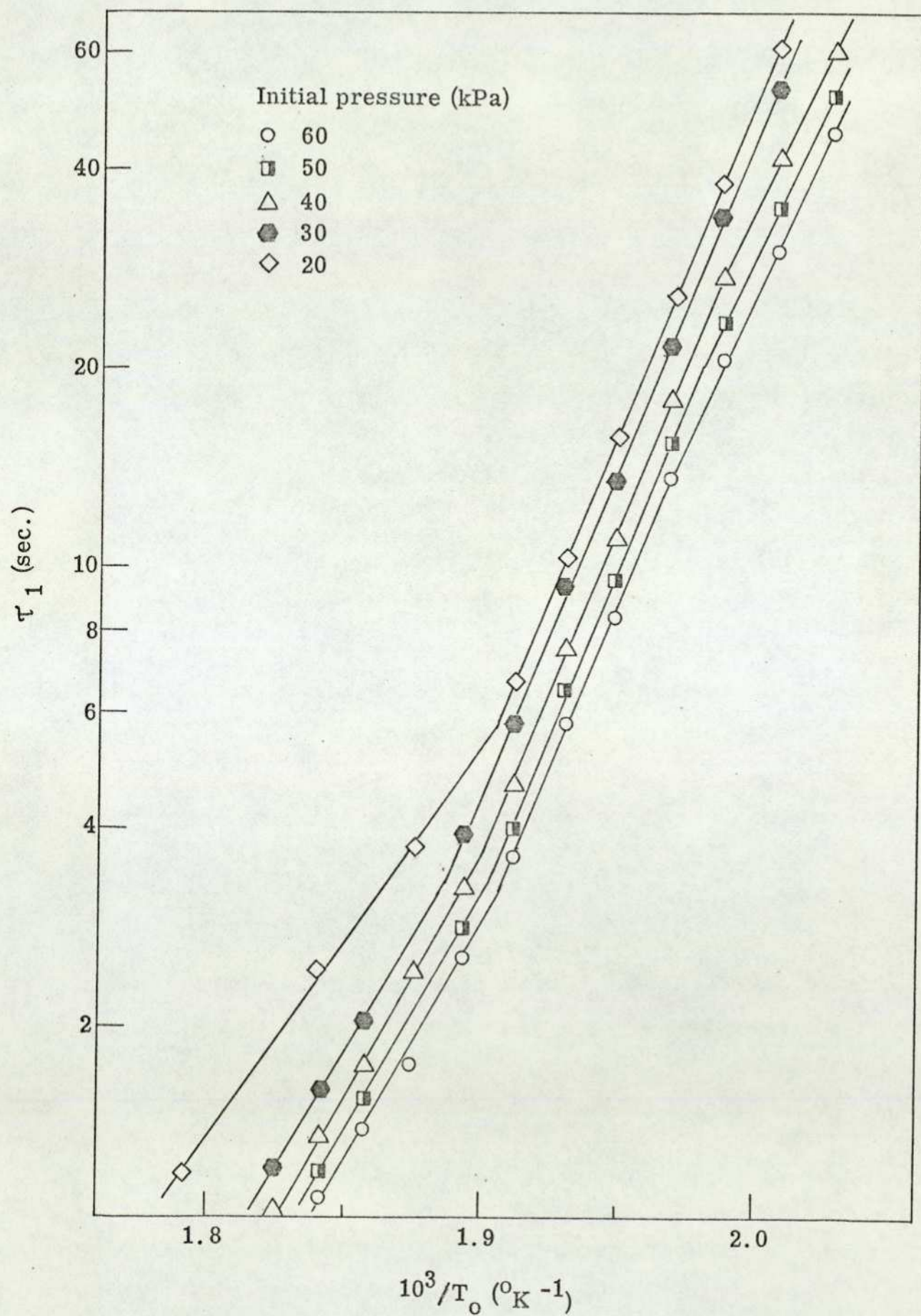


Figure 3.23 shows the way in which $\log \tau_1$ varies with $1/T_0$ for several n-decane-air mixtures at a pressure of 20kPa. It can be seen that at temperatures below 533°K the slopes of the lines are independent of mixture composition and the overall activation energy is ca. 42.5 k cal.mole⁻¹. At temperatures above 533°K however, the slope of the lines changes markedly with mixture composition, and the overall activation energy varies from 20 k cal.mole⁻¹ for a 1:7.5 n-decane-air mixture to 43 k cal.mole⁻¹ for a 1:25 n-decane-air mixture.

3.1.1.5 Induction periods preceding the second cool flame, τ_2

Figure 3.24 shows the way in which the induction period preceding the second cool flame, τ_2 , varies with initial pressure, P_0 , for 1:10 and 1:15 n-decane-air mixtures at an initial temperature of 563°K. As P_0 is increased along this isotherm, the value of τ_2 tends sharply to a minimum near the low pressure limit, below which only single cool flames are observed; it then rises gradually until the high pressure limit is attained, above which two successive cool flames can no longer propagate.

3.1.1.6 Induction periods preceding the ignition effect, τ_{ie} , and the second stage of two-stage ignition, τ_{ig}

A pressure pulse referred to earlier (Section 3.1.1.(a)) as an 'ignition effect' occurs as a shoulder on the first cool flame and increases in magnitude as the two-stage ignition profile is

Figure 3.23

Variation of $\log_{10} \tau_1$ with reciprocal of T_0 for several
n-decane-air mixtures at an initial pressure of 20kPa

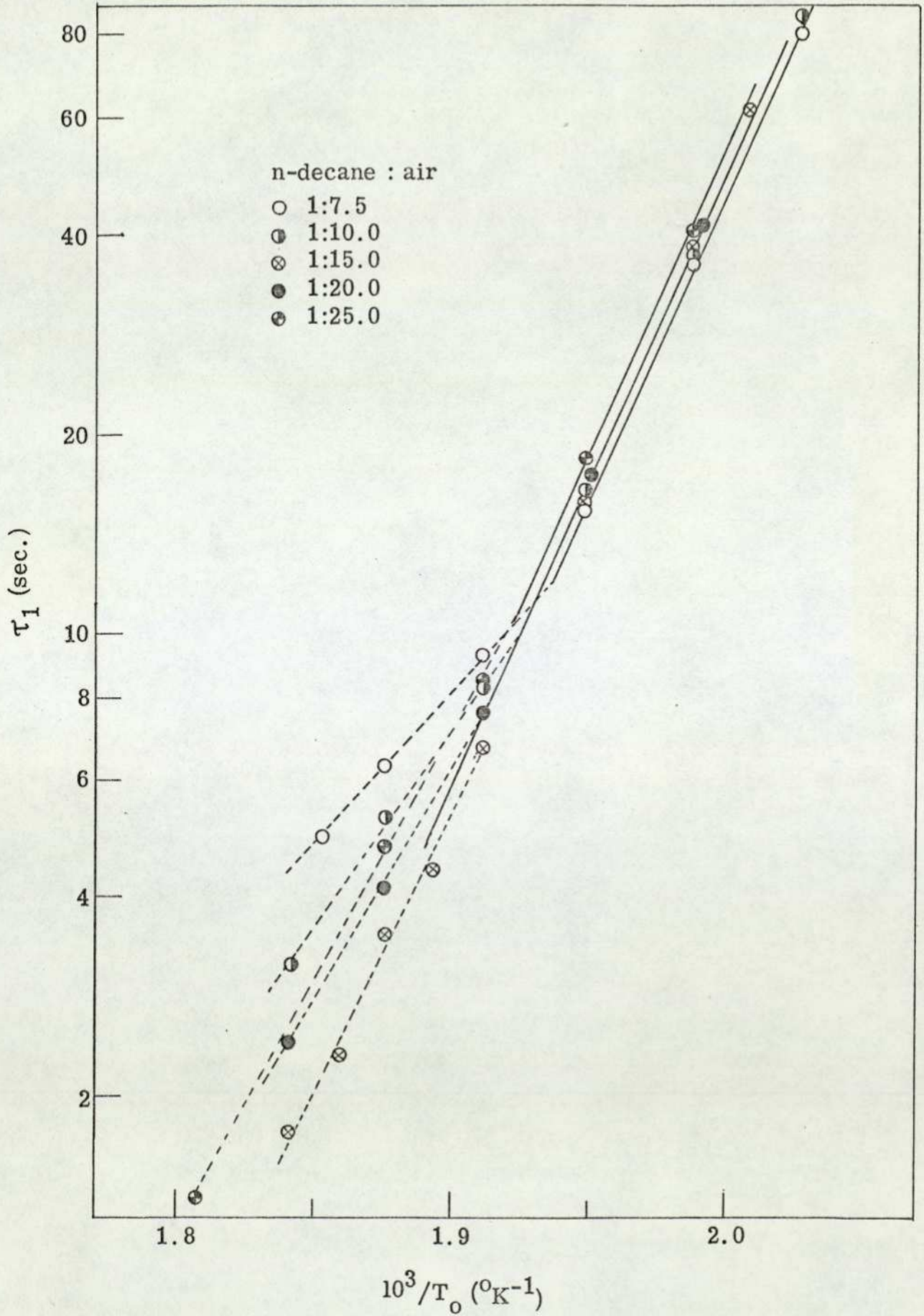
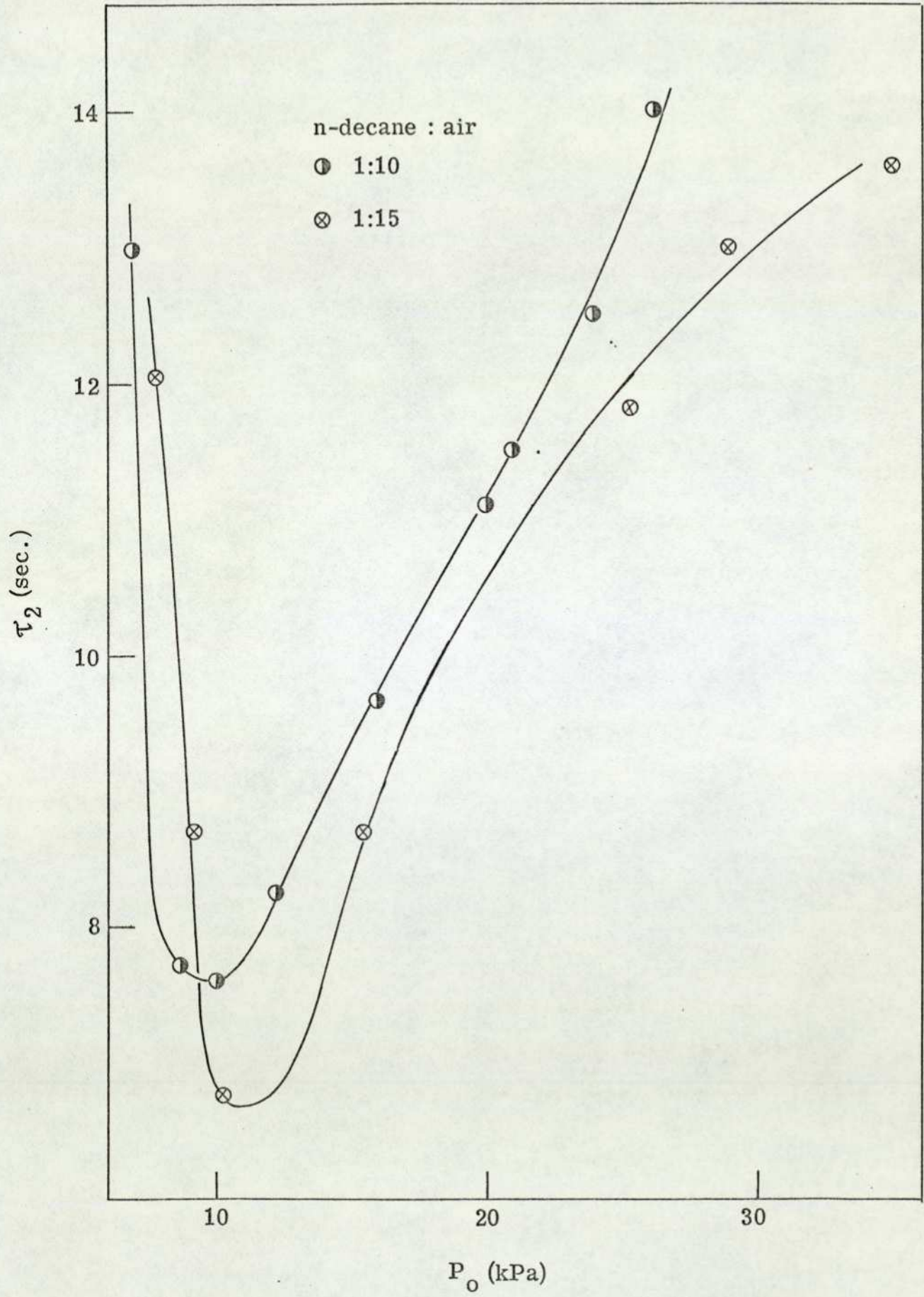


Figure 3.24
Variation of τ_2 with P_o at 563°K



approached isothermally, eventually becoming the pressure pulse representing hot ignition. At 563⁰K the ignition effect first becomes noticeable at a pressure of ca. 10kPa, and the variation with P_o of

τ_{ie} for a 1:10 n-decane-air mixture is shown in figure 3.25.

Clearly τ_{ie} varies very little with P_o up to ca. 30kPa; thereafter

τ_{ie} becomes τ_{ig} and decreases at first sharply and then more gradually with further increase in P_o .

In recent studies carried out under engine conditions⁷⁶ of the high pressure ignition of 2-methylpentane, a relationship of the form

$$\tau_{ig} = B \Delta P_1^{-m} \quad (3.4)$$

is shown to hold, the constants B and m being independent of temperature. Figures 3.26 shows the variation with $\log \Delta P_1$ of $\log \tau_{ig}$ for 1:15 n-decane-air mixtures at several initial temperatures. The straight line shown in this figure is the result of a least-squares regression analysis of the data, and gives a value for m of 2.10. The positions of the data points on either side of this line indicate that the value of m is independent of temperature, whilst that of B shows a small temperature dependence.

Figure 3.25
Variation of τ_{ie} with P_o at 563°K.
n-decane : air = 1:10.0

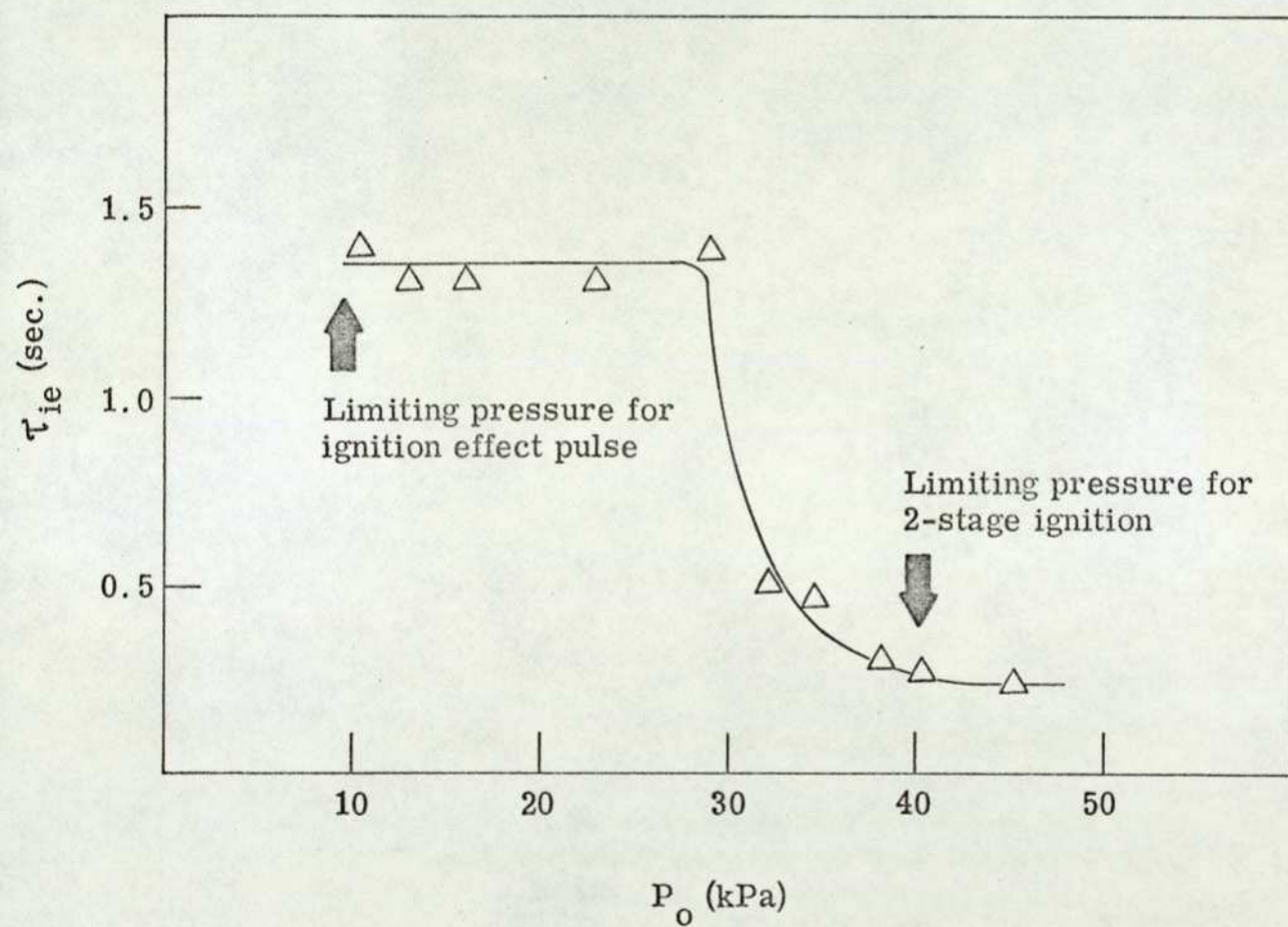
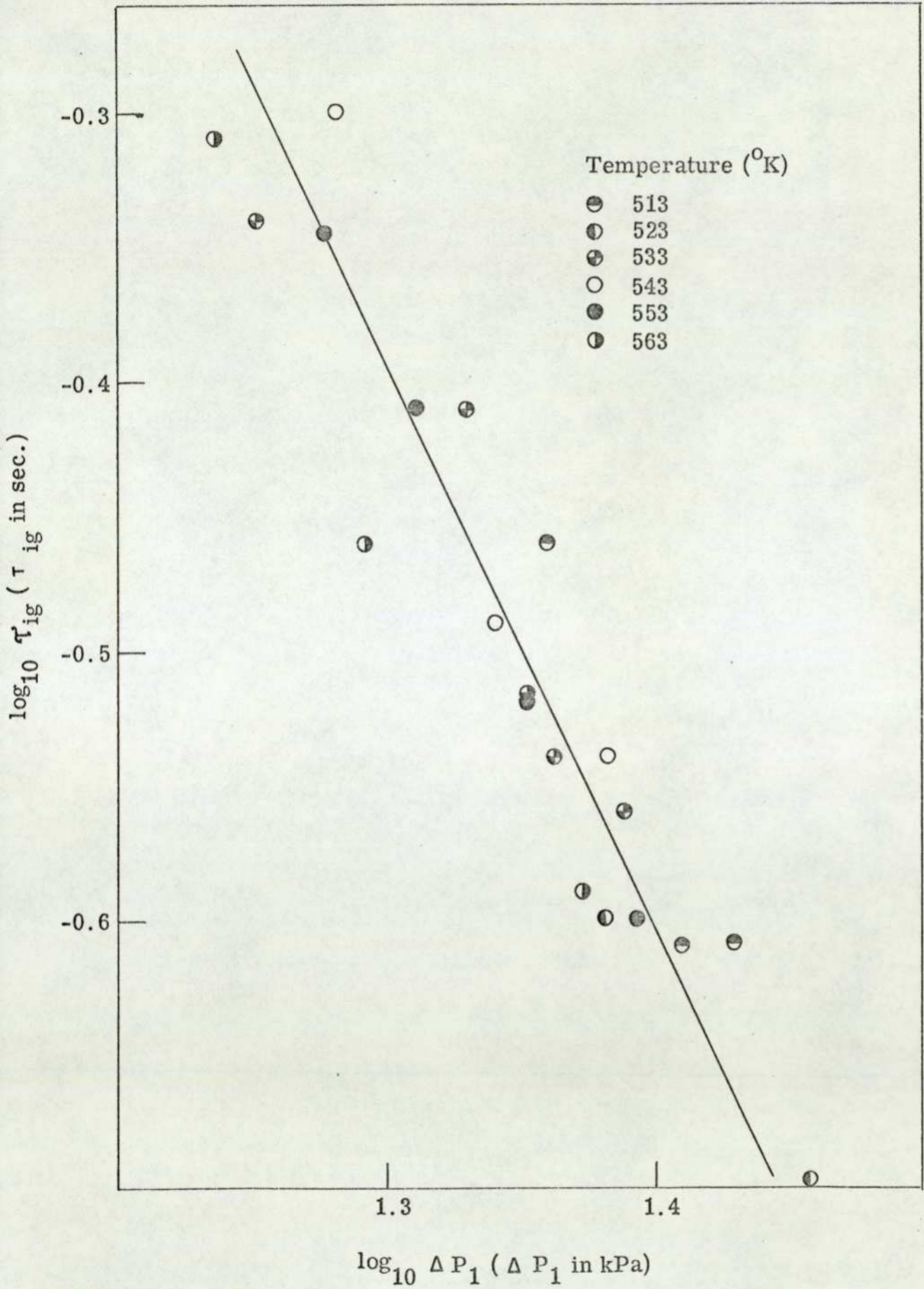


Figure 3.26

Logarithmic relationship between τ_{ig} and ΔP_1 .

n-decane : air = 1:15.0



3.1.2 Temperature measurements

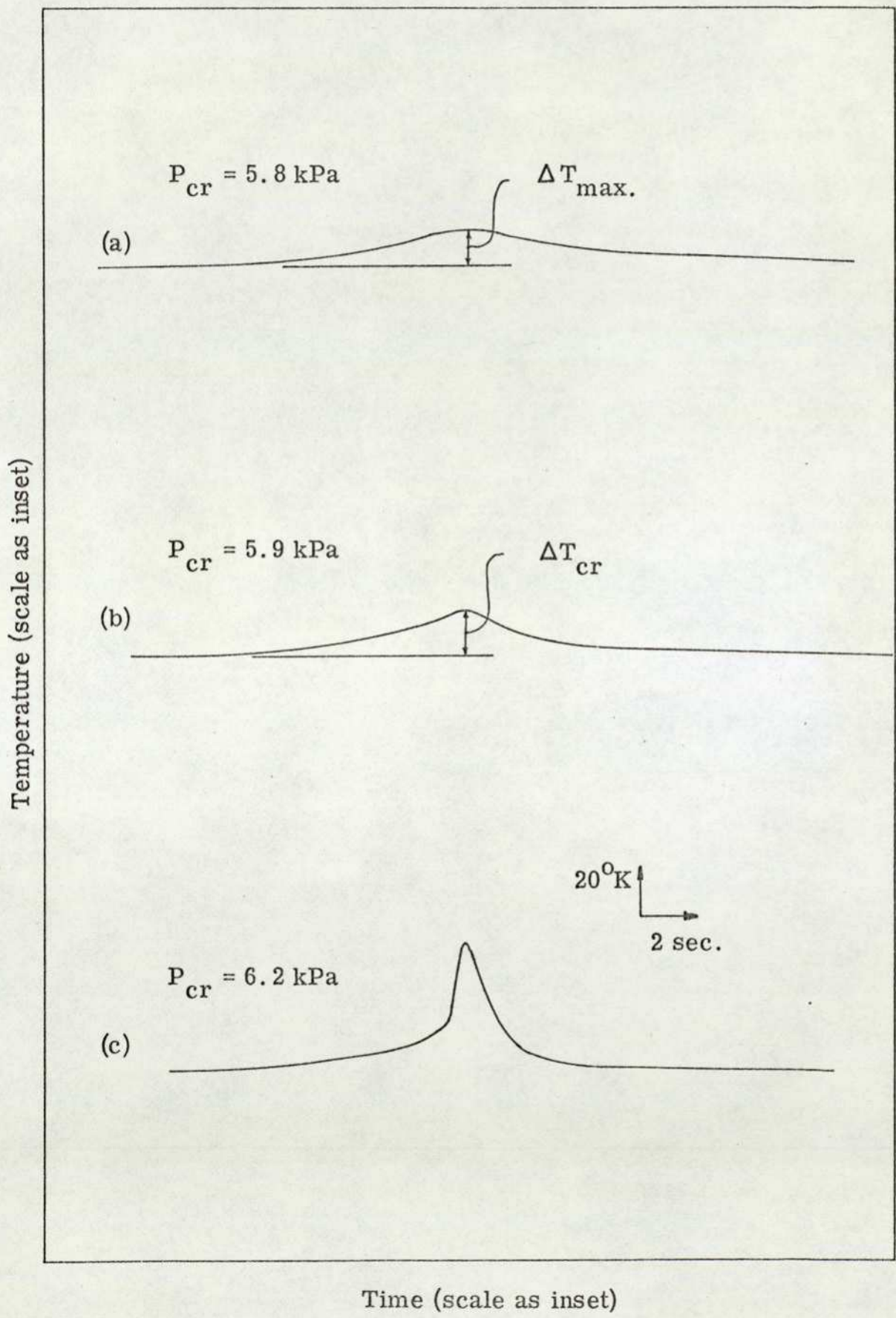
Temperature measurements have been made of the combustion reactions taking place in 1:15 n-decane-air mixtures at pressures close to the boundary separating slow combustion from cool flames. Figures 3.27.a, b and c show the variation with time of the temperature at the centre of the reacting gas mixture which was initially at a temperature of 543°K. The maximum temperature rise, $\Delta T_{\text{max.}}$, attained during slow combustion (figure 3.27.a) increases as the initial pressure is increased isothermally up to the slow combustion/cool flame boundary. At the critical pressure, P_{cr} , corresponding to the slow combustion/cool flame boundary, the value for $\Delta T_{\text{max.}}$ is the largest possible one in the absence of a cool flame and is denoted as ΔT_{cr} (figure 3.27.b). However, at pressures greater than P_{cr} , the temperature-time trace (figure 3.27.c) shows the usual type of self-heating on top of which is superimposed a large transient temperature pulse representing the passage of a cool flame. Traces similar to those shown in figures 3.27.a, b and c were observed at several other temperatures. In all cases, the slow-combustion reactions preceding a cool flame were almost isothermal for nearly the whole of the induction period, giving a maximum temperature rise of ca. 3°K up to ca. 0.5 sec. before the passage of the cool flame.

Under supercritical conditions, traces similar to the one shown in figure 3.27.c were obtained, although the value of $\Delta T_{\text{max.}}$ was not consistent for the same initial conditions, and was sometimes greater and sometimes smaller than ΔT_{cr} .

Figure 3.27

Temperature-time traces of combustion reactions at the
slow combustion/cool-flame boundary.

$T_0 = 543^{\circ}\text{K}$

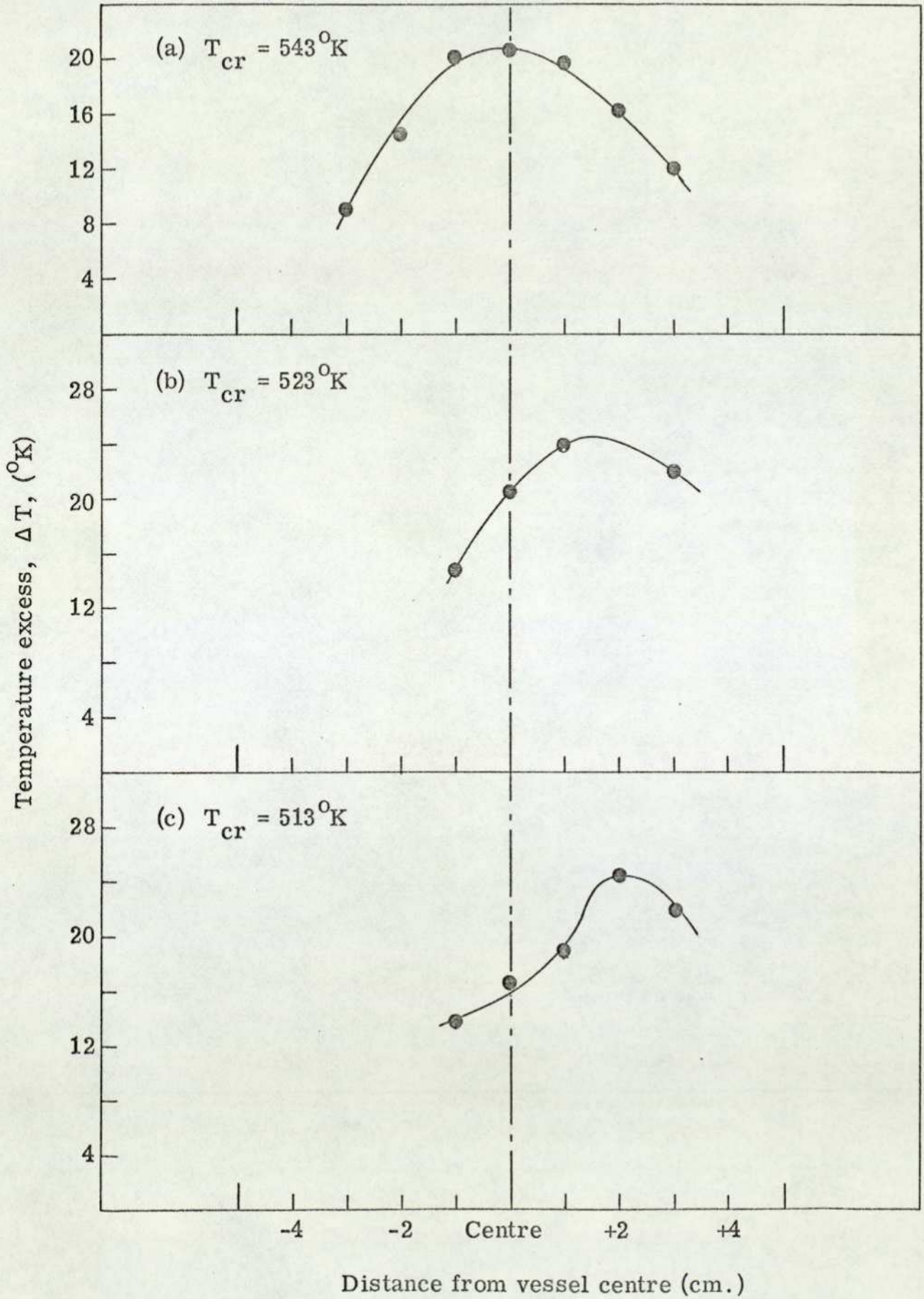


Temperature profiles have been measured along the vertical diameter of the reaction vessel for reactions taking place at the slow combustion/cool flame boundary and at initial temperatures of 543°K , 523°K and 513°K ; these are shown in figures 3.28.a, b and c respectively. At an initial temperature of 543°K , the temperature profile appears to be parabolic and is symmetrical about the centre of the reaction vessel, showing a maximum temperature rise of 20.8°K . At initial temperatures of 523°K and 513°K , the temperature profile is asymmetric, and the maximum temperature rise in the gases occurs some distance above the centre of the vessel.

Figure 3.28

Temperature profiles across the vertical diameter of the reaction vessel at the critical condition for cool flames.

n-decane : air = 1:15.0



3.2 The combustion in air of fuel mixtures containing n-decane and 2, 2, 5-trimethylhexane

3.2.1 Reactant mixture composition

In these studies an overall fuel-air ratio of 1:15 was used, whilst the relative amounts of n-decane and 2, 2, 5-trimethylhexane in the fuel were varied.

3.2.2 Phenomena resulting from the observation of pressure changes

3.2.2.1 Ignition profiles

Figure 3.29 shows the effect on the boundary separating slow combustion from both cool flames and two-stage ignition of the composition of the fuel. The presence of up to 10 mole % of 2, 2, 5-trimethylhexane in the fuel has little effect on the position of the boundary. However, the more n-decane is replaced by the nonane isomer, the more marked is the increase in the limiting conditions of temperature and pressure required for a cool flame or two-stage ignition. This effect is better shown in figure 3.30; this indicates the variation with mole % of 2, 2, 5-trimethylhexane of the limiting temperature required to cause spontaneous ignition in the gas mixture, when this is at an initial pressure of 60kPa.

Figure 3.31 shows an ignition profile for a fuel containing 50 mole % each of n-decane and 2, 2, 5-trimethylhexane and for a

Figure 3.29
Spontaneous ignition temperature limits for
1:15 fuel : air mixtures

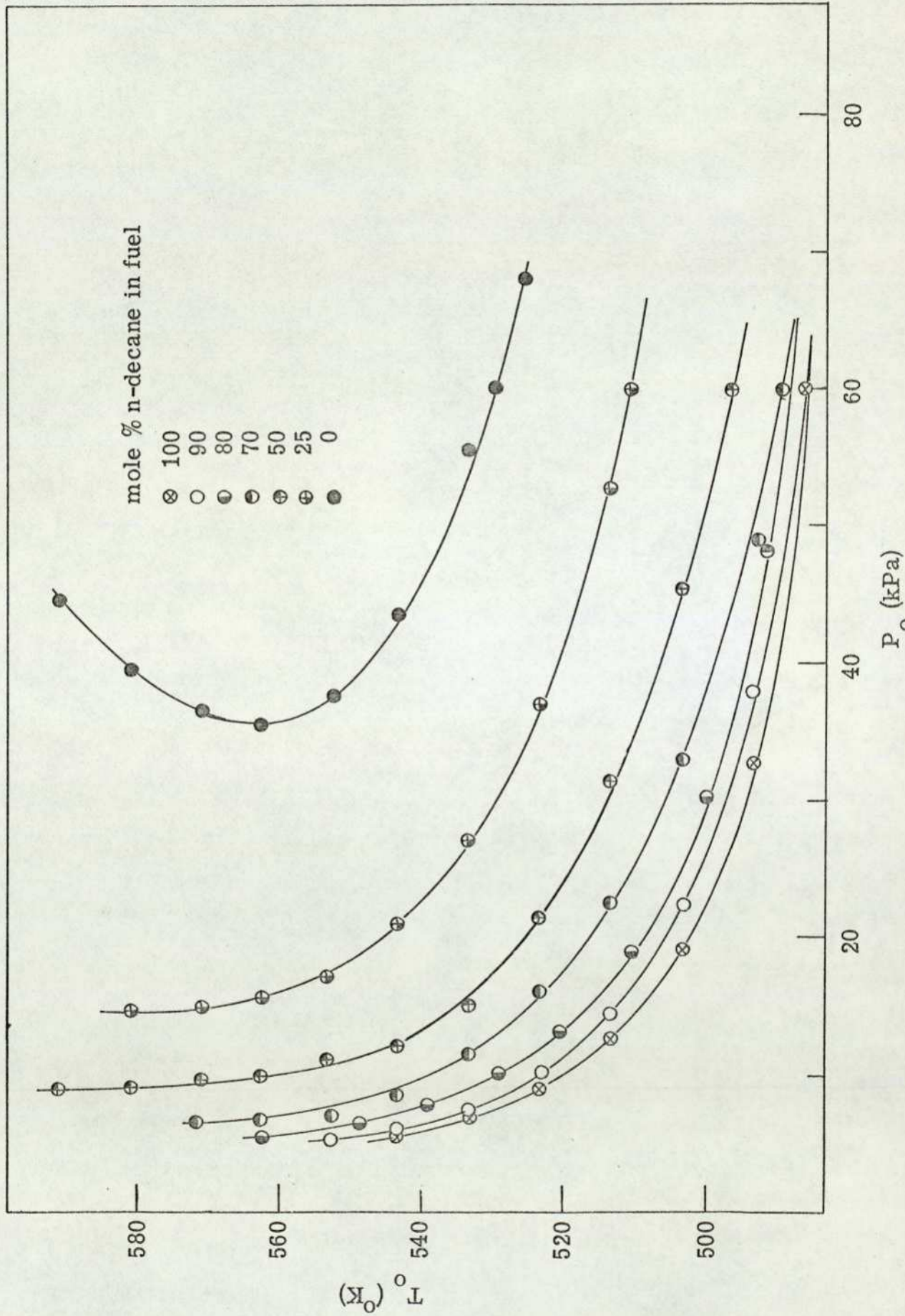


Figure 3.30

Variation with fuel composition of minimum temperature
for spontaneous ignition. Fuel : air = 1:15.0, $P_o = 60\text{kPa}$

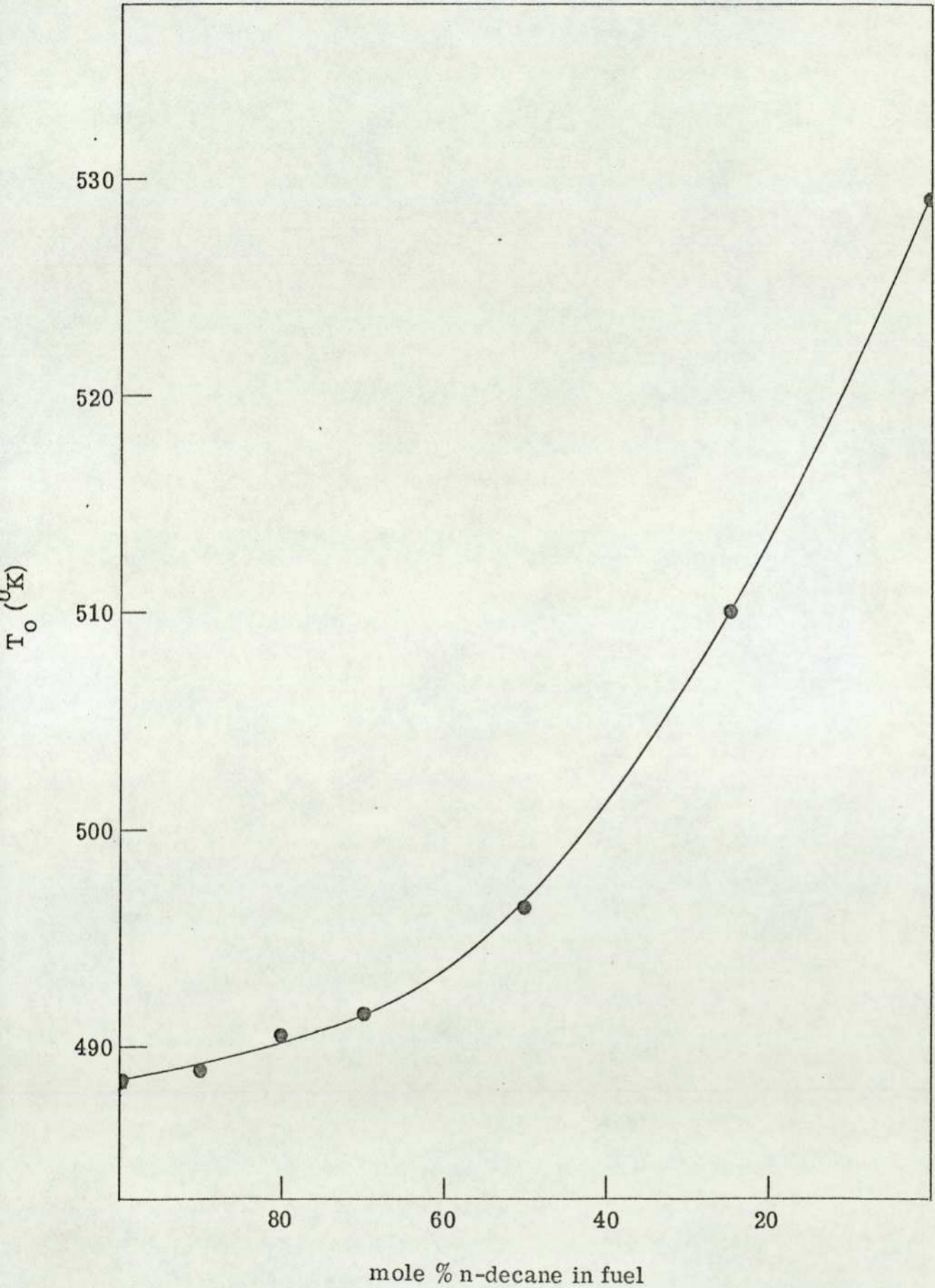
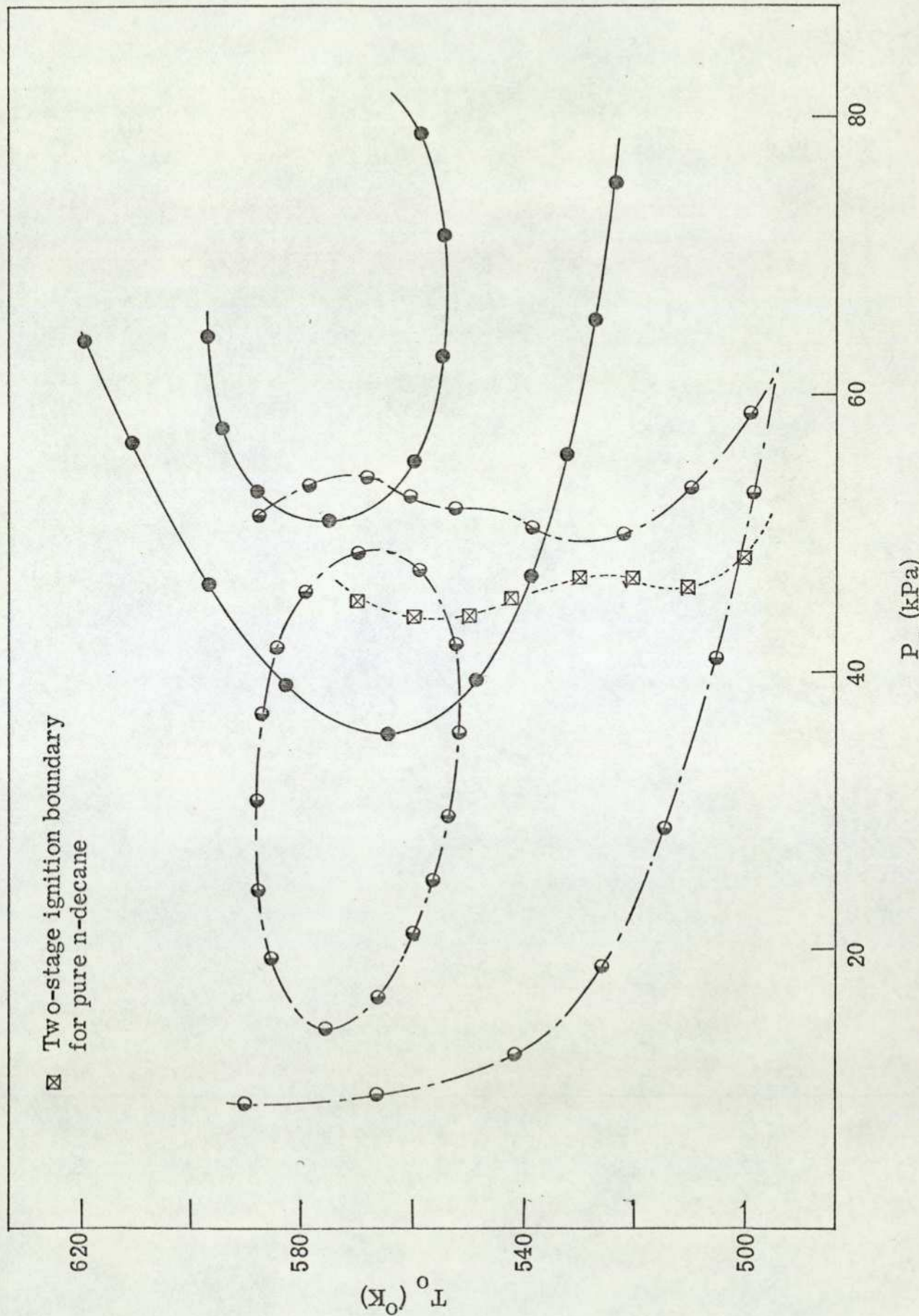


Figure 3.31

Ignition profiles for 1:15 fuel air mixtures containing
(a) 50 mole % n-decane and 50 mole % 2, 2, 5-trimethylhexane, ($\circ$),
and (b) pure 2, 2, 5-trimethylhexane, ($\bullet$)



1:15 pure 2, 2, 5-trimethylhexane-air mixture, the latter of which is incomplete owing to the restricted pressure range over which the measurements could be made. Clearly, the single cool-flame region in the pure 2, 2, 5-trimethylhexane-air mixtures extends over a smaller temperature range than has been found for pure n-decane-air mixtures (figure 3.1).

A region of two cool flames has been observed during the combustion of 2, 2, 5-trimethylhexane, and the pressure/temperature boundary enclosing this region is similar in size and shape to the boundary enclosing the two-cool flame region with n-decane. Furthermore, the position in the pressure/temperature diagram of the two cool-flame region is almost independent of the fuel composition; the centre of this region corresponds to a temperature of ca. 565°K for mixtures containing both the two pure hydrocarbons and equal proportions of the two components.

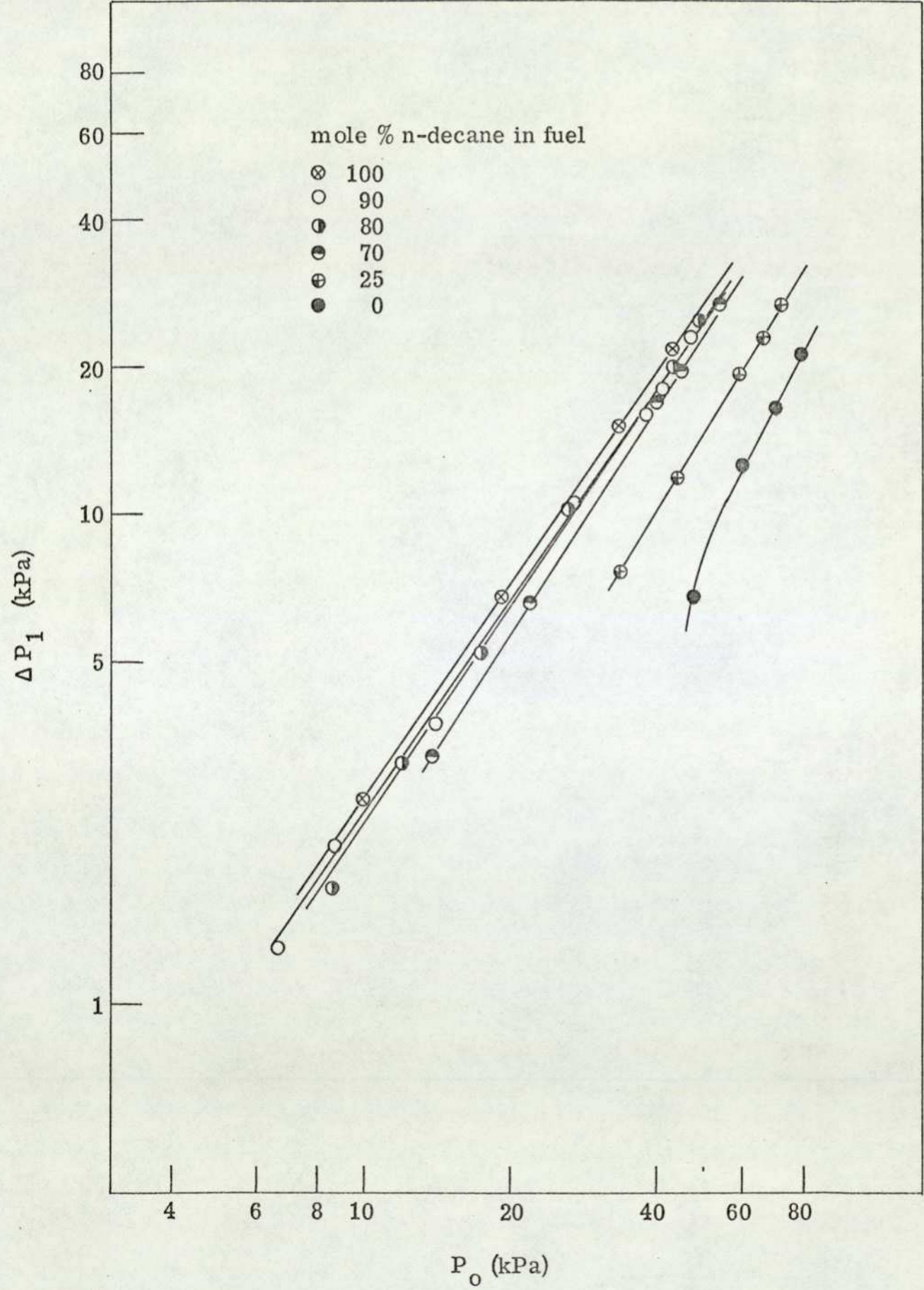
Figure 3.31 also shows the effect on the two-stage ignition profile of replacing 50 mole % of the n-decane in a 1:15 fuel-air mixture by 2, 2, 5-trimethylhexane. Clearly, the presence of the branched alkane in the fuel broadens considerably lobe A relative to that found with n-decane only, whereas lobe B is markedly depressed.

3.2.2.2 The maximum pressure rise accompanying the first, ΔP_1 , and second, ΔP_2 , cool flames

Equation (3.1) has also been shown to hold for the 1:15 fuel-air mixtures studied. Figure 3.32 shows the variation with

Figure 3.32

Logarithmic relationships between ΔP_1 and P_o
for several fuel compositions. Fuel : air = 1:15.0



$\log P_0$ of $\log \Delta P_1$ for these mixtures at an initial temperature of 543°K , and it is clear that both the constants A and m in equation (3.1) are dependent on the concentration of the branched alkane. The value of m has been shown to lie between 1.66 and 1.90 for mixtures containing pure n-decane and pure 2,2,5-trimethylhexane respectively.

Figure 3.33 shows the variation with P_0 and T_0 of the loci of a constant value for ΔP_1 of 9kPa for fuels containing 50 and 20 mole % 2,2,5-trimethylhexane, and for a fuel containing pure n-decane. Clearly the fluctuating nature of the loci is markedly accentuated by the presence of 50 mole % 2,2,5-trimethylhexane, which gives rise to two well-defined maxima in ΔP_1 . Furthermore, these maxima occur at higher temperatures than those occurring for pure n-decane, which are less well-defined.

The variation of ΔP_2 with P_0 at 563°K is shown in figure 3.34 for pure n-decane, and for fuels containing 20 mole % and 75 mole % 2,2,5-trimethylhexane.

3.2.2.3 The rate of pressure rise during cool-flame propagation

Figure 3.35 shows the variation with fuel composition of the locus of a constant value (50kPa/sec) for the maximum rate of pressure rise, $(dp/dt)_{\max}$. The locus representing a mixture containing pure n-decane displays two pressure minima at temperatures of 503°K and 550°K . The pressure minimum corresponding to the lower temperature becomes more pronounced and moves progressively to a higher temperature and pressure as the concentration of

Figure 3.33

Variation with T_o and P_o of the locus of $\Delta P_1 = 9\text{kPa}$ for
several 1:15 fuel : air mixtures

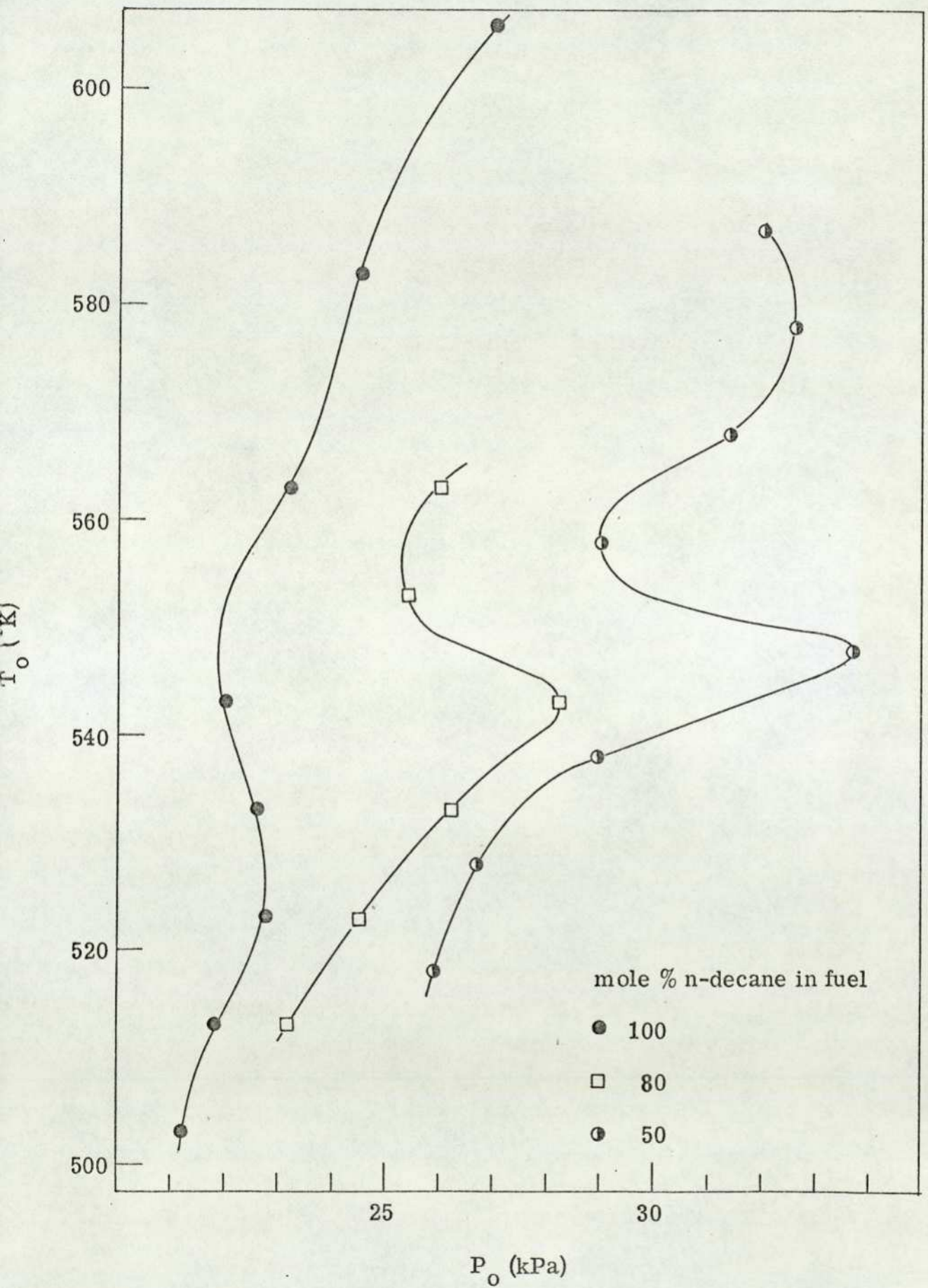


Figure 3.34
Variation of ΔP_2 with P_0 for several
1:15 fuel : air mixtures

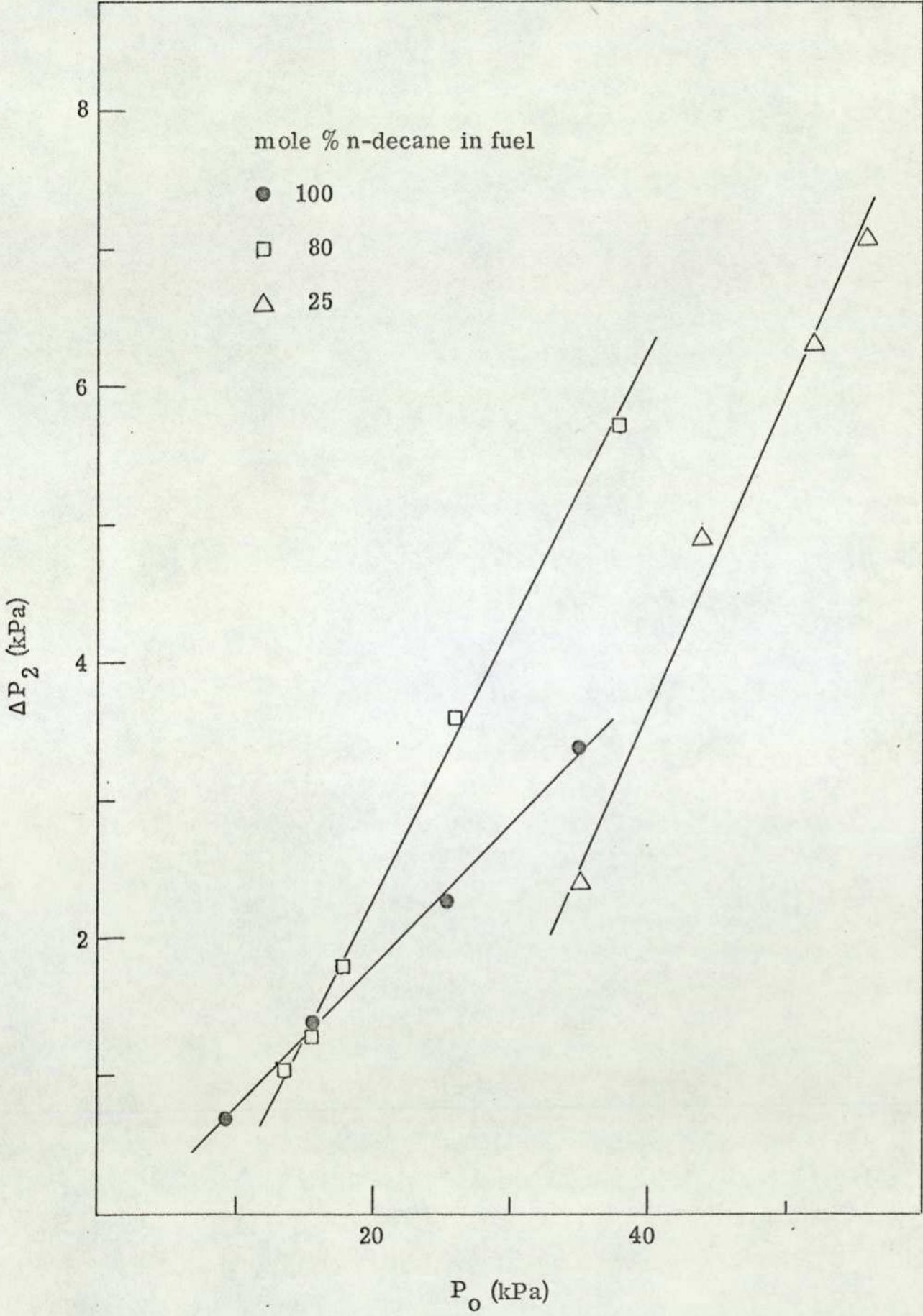
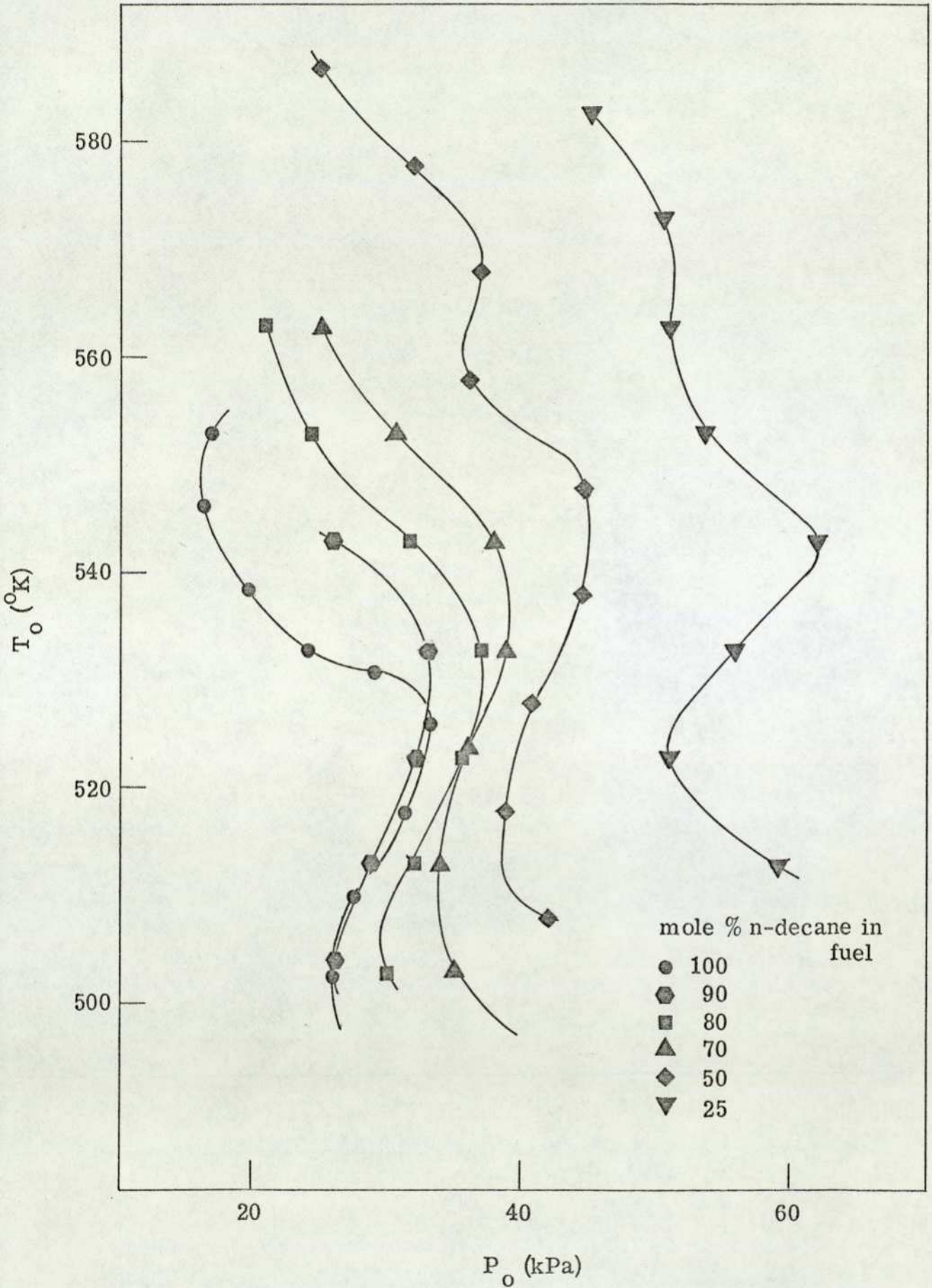


Figure 3.35

Variation with T_o and P_o of the locus of
 $(dp/dt)_{\max.} = 50 \text{ kPa sec}^{-1}$ for several 1:15 fuel : air mixtures



2, 2, 5-trimethylhexane in the fuel is increased. Whilst similar changes are observed in the minimum corresponding to the higher temperature, the general appearance of the curve is unaltered by a change in fuel composition.

3.2.2.4 Induction periods preceding the first cool flame, τ_1

The variation of τ_1 with initial pressure at several initial temperatures for fuel mixtures containing 10, 30, 75 and 100% mole 2, 2, 5-trimethylhexane is shown in figures 3.36. a, b, c and d respectively. From these curves, it is clear that, as the proportion of 2, 2, 5-trimethylhexane in the fuel mixture increases, τ_1 becomes more pressure dependent, and for a given temperature and pressure τ_1 increases. The latter effect is better illustrated in figure 3.37, which gives the variation of τ_1 with initial pressure for several fuel compositions at a temperature of 543°K. Figure 3.38 shows the way in which τ_1 varies with fuel composition in a reactant mixture maintained initially at a temperature of 553°K and a pressure of 50kPa. Clearly, the presence of the nonane isomer in the fuel increases τ_1 relative to the value for a fuel consisting of pure n-decane. This increase in τ_1 is very marked when the fuel contains more than 30 mole % of 2, 2, 5-trimethylhexane.

Values of k, n and C in the equation

$$\tau_1 = k P_o^{-n} + C$$

have been calculated, using the computer programme described earlier, for fuel mixtures containing 10, 30, 50, 75 and 100% mole 2, 2, 5-trimethyl-

Figure 3.36

Variation of τ_1 with P_o and T_o for 1:15 fuel : air mixture containing (a) 90 mole %, (b) 70 mole % and (c) 25 mole % n-decane and (d) pure 2,2,5-trimethylhexane

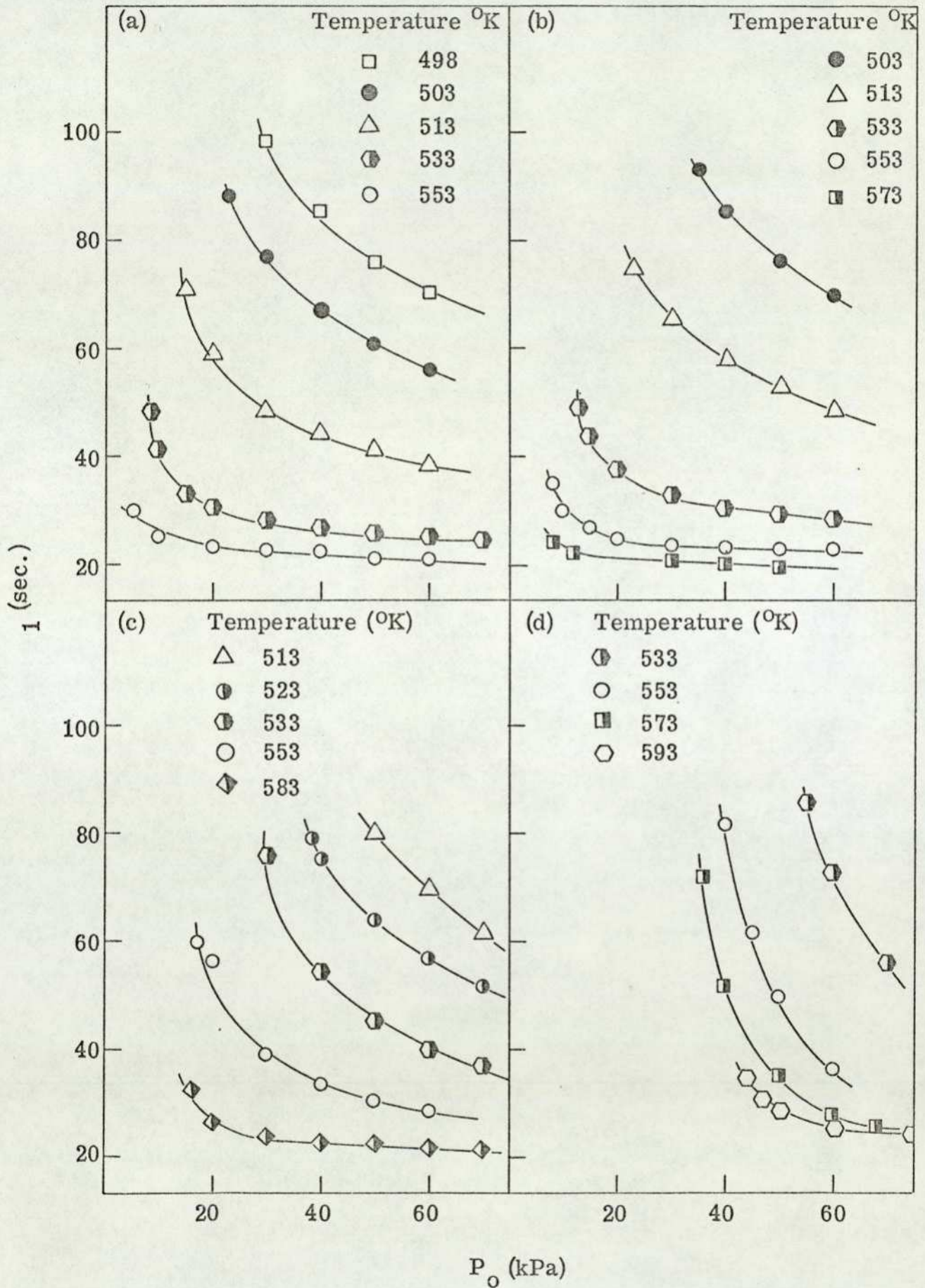


Figure 3.37

Variation of τ_1 with P_o and fuel composition.
 $T_o = 543^\circ\text{K}$

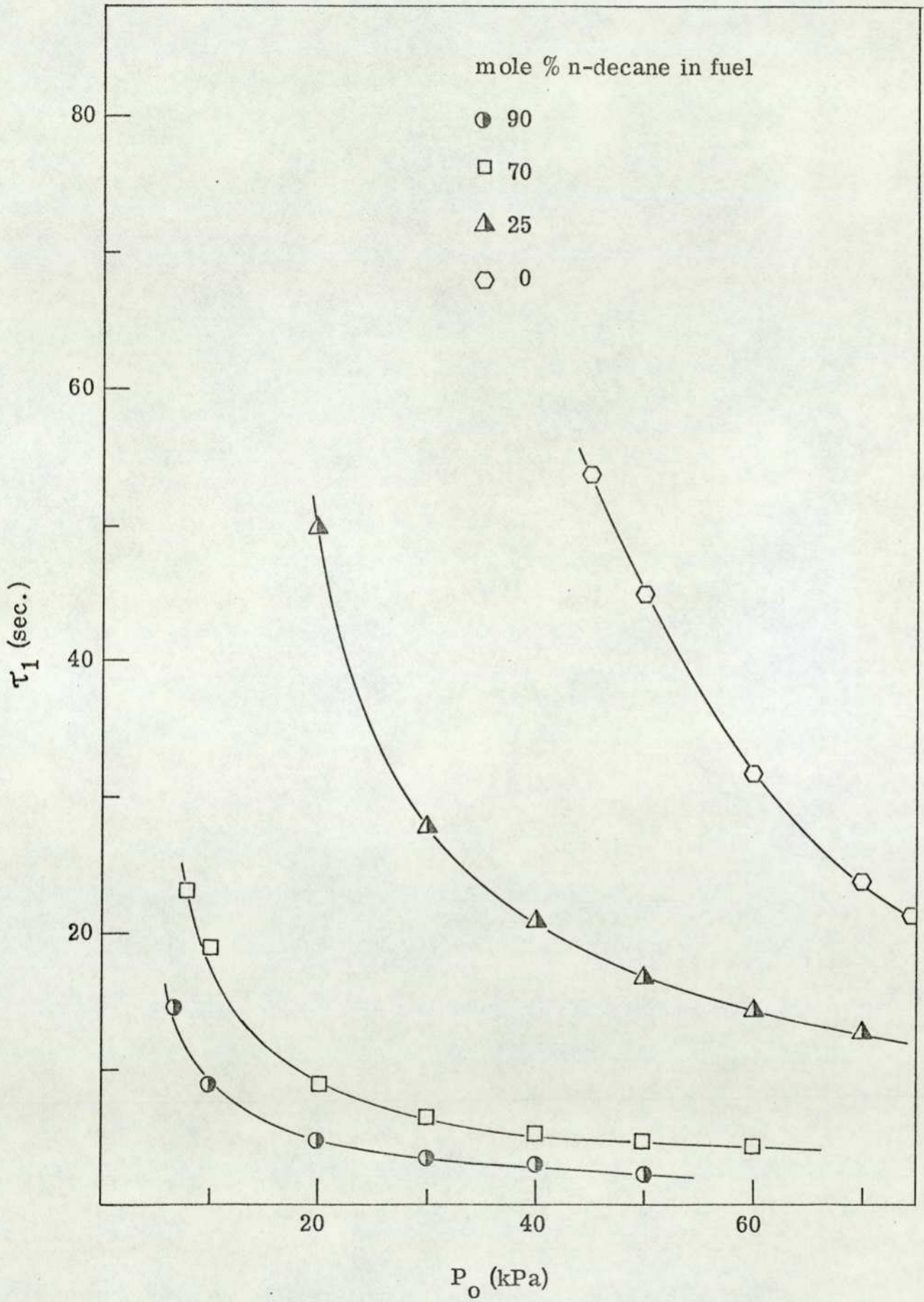
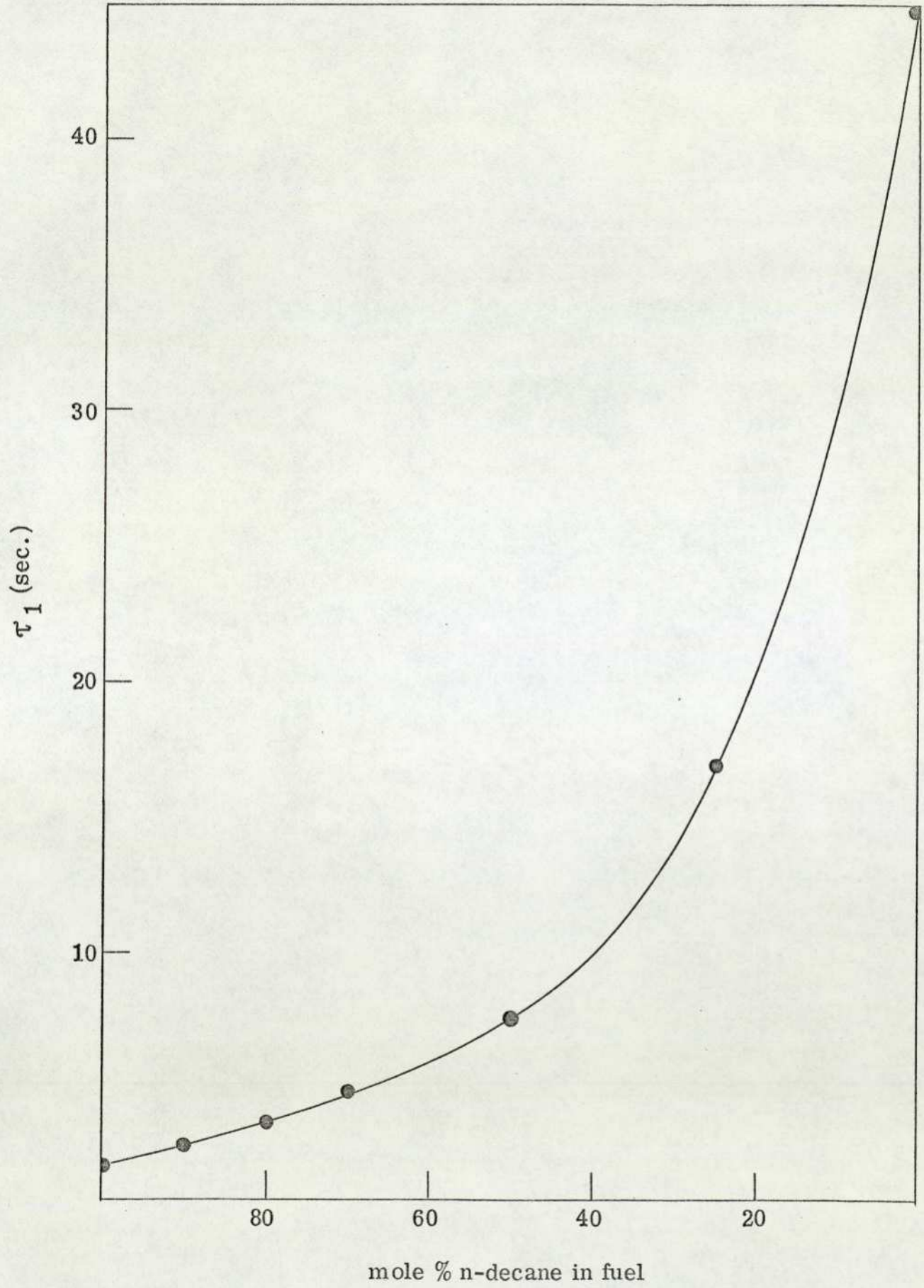


Figure 3.38
Variation of τ_1 with fuel composition.
 $\underline{P}_O = 50 \text{ kPa}, \underline{T}_O = 553^\circ \text{K}$



hexane. These values are given in Table 3.2.

The variation of n with T_o for some of the fuel mixtures studied is shown in figure 3.39, from which it can be seen that the values of n for each mixture oscillate as the temperature increases. Furthermore, the amplitude of these oscillations increases with the proportion of 2,2,5-trimethylhexane in the fuel. Similar behaviour is observed with the plots of $\log_{10} k$ against $\log_{10} T_o$ which are shown in figure 3.40. The variation of $\log_{10} C$ with $1/T_o$ for several fuel compositions is shown in figure 3.41; as the concentration of 2,2,5-trimethylhexane in the fuel is increased, the appearance of the plot changes from two intersecting straight lines to curves with a point of inflection.

Figure 3.42 shows plots of $\log_{10} \tau_1$ and $\log_{10}(\tau_1 - C)$ against $\log_{10} P_o$ for a fuel containing 10 mole % 2,2,5-trimethylhexane at 533°K and for the pure nonane isomer at 593°K. Clearly, the plots for $\log_{10} \tau_1$ are markedly curved whilst those for $\log_{10}(\tau_1 - C)$ are straight lines. Similar results were found for the other fuel mixtures studied, but the inclusion of these in figure 3.42 would have led to confusion.

The variation with $1/T_o$ of τ_1 for several fuel compositions, and at a total reactant pressure of 50kPa, is shown in figure 3.43. It can be seen that the plots vary with fuel composition in a complex manner. Plots representing all the fuel compositions are a series of straight lines which, except for the mixture containing pure 2,2,5-trimethylhexane, change slope twice.

Table 3.2

Values of k, n and C for several fuel compositions

Temp. (°K)	Mole % 2, 2, 5-trimethylhexane in the fuel								
	10			30			50		
	$k \times 10^{-3}$	n	C	$k \times 10^{-3}$	n	C	$k \times 10^{-3}$	n	C
493	10.6	0.7	0.0	-	-	-	-	-	-
498	12.0	0.6	14.1	-	-	-	-	-	-
503	5.1	0.6	0.0	7.1	0.6	0.0	-	-	-
513	9.1	1.1	10.7	4.4	0.7	0.0	-	-	-
518	-	-	-	-	-	-	11.0	0.9	2.5
523	7.9	1.4	5.5	1.9	1.5	11.8	-	-	-
528	-	-	-	-	-	-	13.0	1.2	5.2
533	2.4	1.1	2.9	6.9	1.3	5.9	-	-	-
538	-	-	-	-	-	-	30.0	1.6	4.5
543	1.4	1.3	1.8	8.7	1.7	4.0	-	-	-
548	-	-	-	-	-	-	15.0	1.6	3.2
553	-	-	-	2.6	1.5	1.8	-	-	-
558	-	-	-	-	-	-	6.8	1.5	1.9
563	-	-	-	1.4	1.4	1.1	-	-	-
568	-	-	-	-	-	-	9.2	1.8	1.3
573	-	-	-	5.9	1.4	0.7	-	-	-
578	-	-	-	-	-	-	5.4	1.8	0.9
587	-	-	-	-	-	-	2.2	1.8	0.8

Table 3.2 continued

Temp (°K)	75 mole % 2, 2, 5-trimethyl- hexane in fuel			Pure 2, 2, 5-trimethylhexane		
	k	n	C	k	n	C
513	2.8×10^8	3.5	31.9	-	-	-
523	8.1×10^3	7.5	0.0	-	-	-
528	-	-	-	5.1×10^6	2.2	0.0
533	2.2×10^5	1.8	7.2	2.4×10^8	3.2	11.6
543	5.4×10^4	1.6	7.8	1.2×10^6	2.0	2.7
553	1.1×10^5	1.9	4.8	1.0×10^8	3.3	-
563	2.1×10^5	2.3	3.7	6.9×10^5	-	0.0
573	-	-	-	2.2×10^8	3.8	3.7
583	4.4×10^4	2.2	1.3	-	-	-
593	-	-	-	4.0×10^9	4.6	3.5

Figure 3.39
Variation of n with T_o and fuel composition

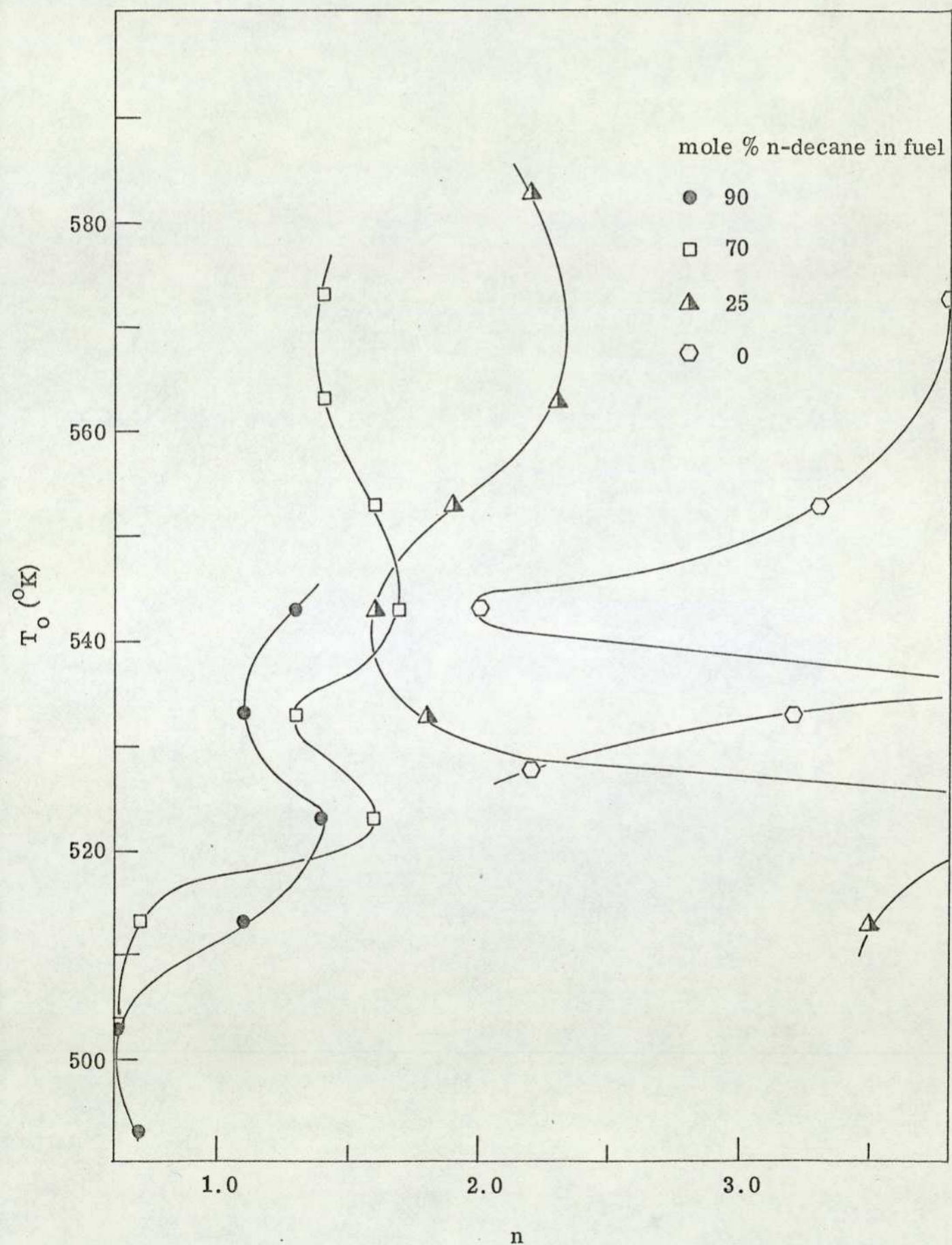


Figure 3.40
Logarithmic relationship between k and T_o for
several fuel compositions

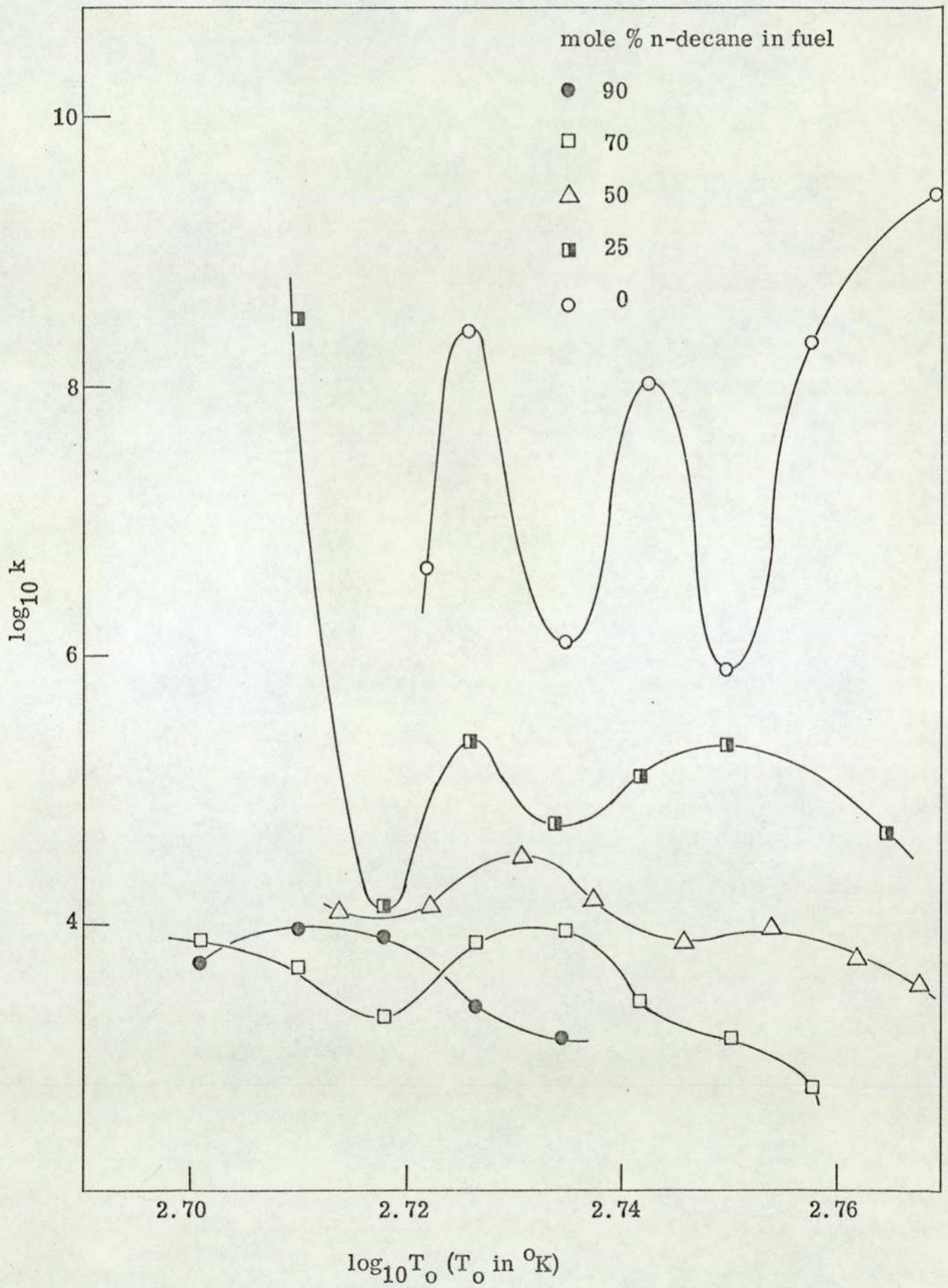


Figure 3.41
Variation of $\log_{10} C$ with reciprocal of T_o
and fuel composition

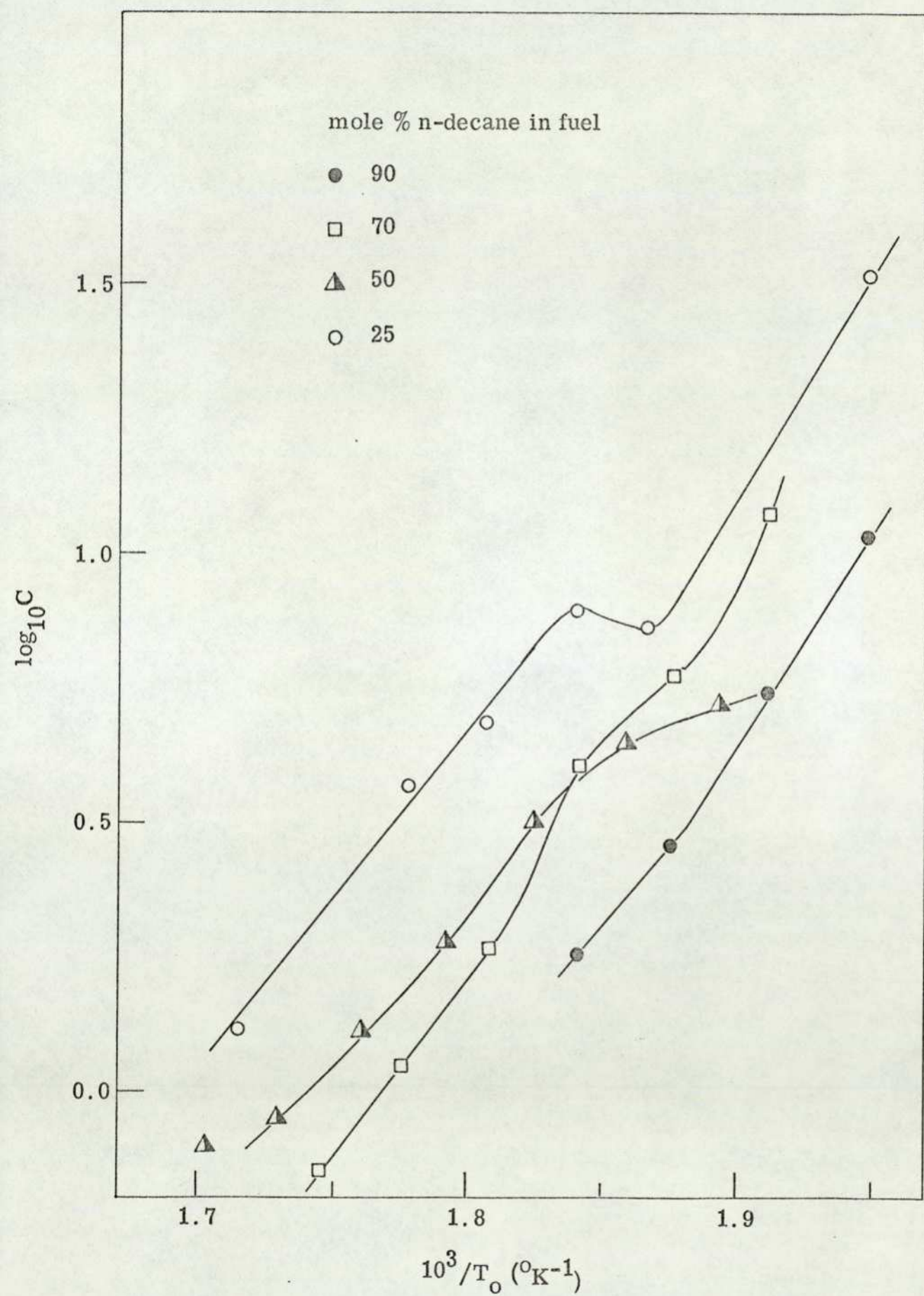


Figure 3.42

Logarithmic variation of P_o with τ_1 and $(\tau_1 - C)$ for fuels
containing (a) 10 mole % 2,2,5-trimethylhexane and
(b) pure 2,2,5-trimethylhexane

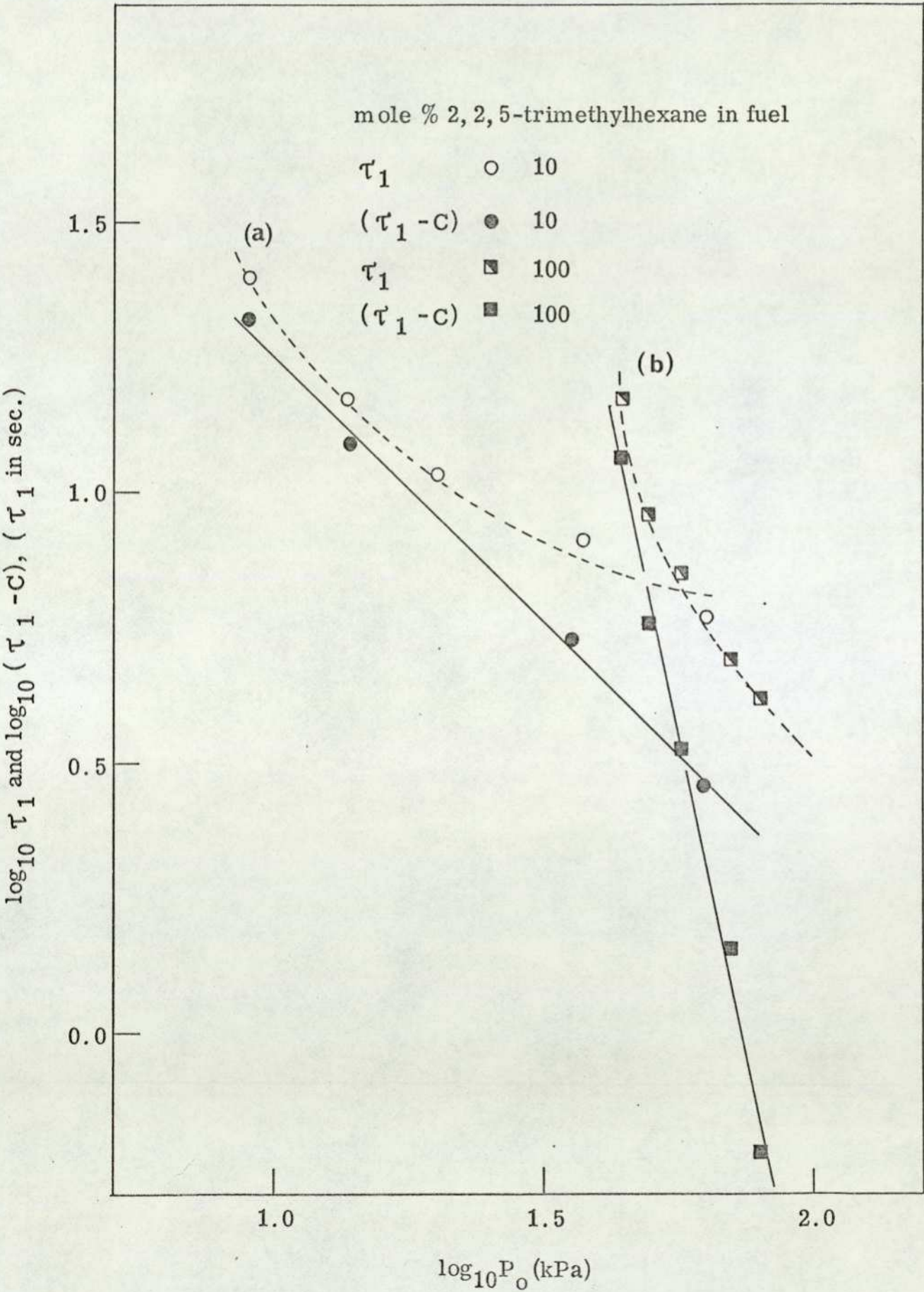
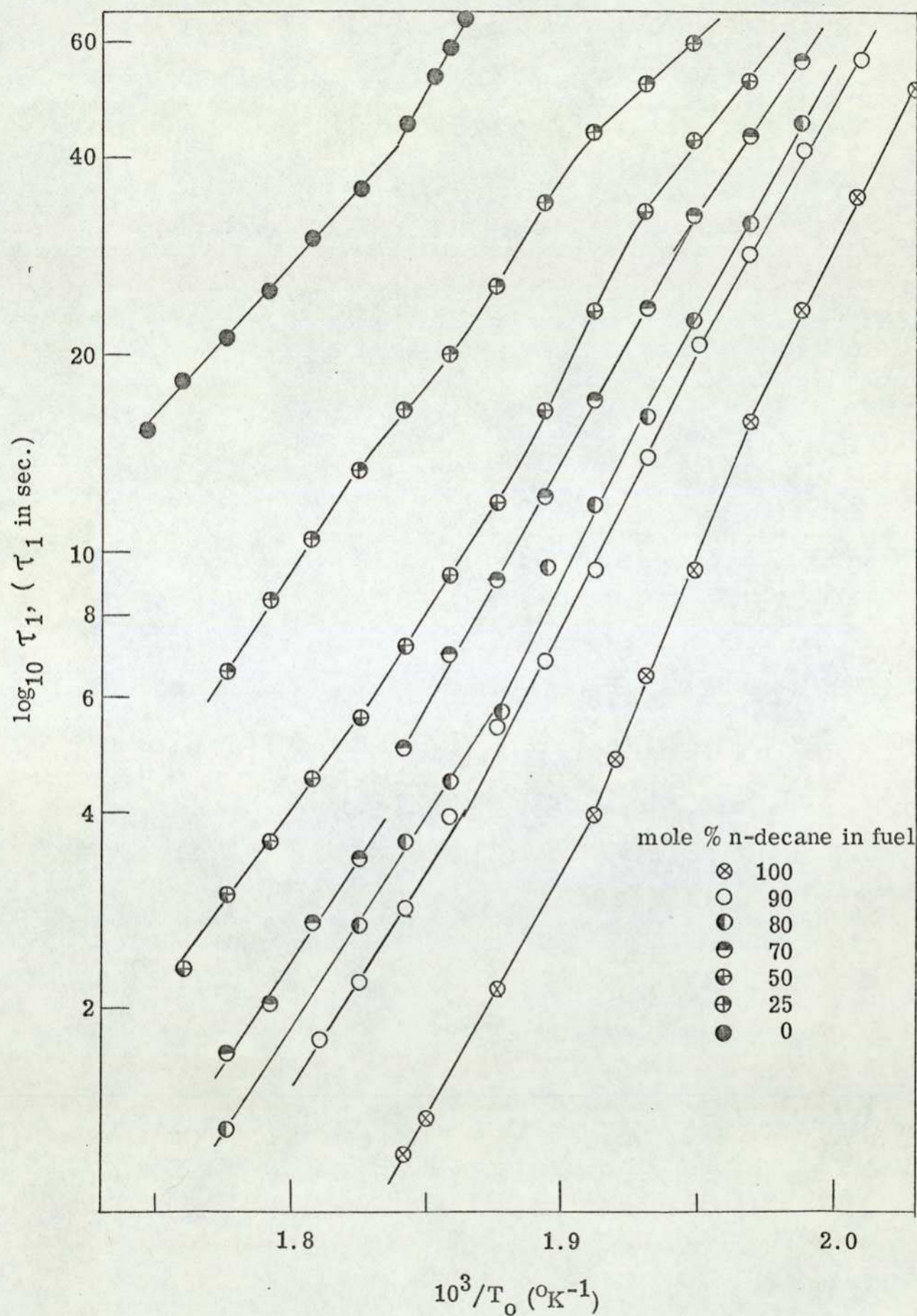


Figure 3.43

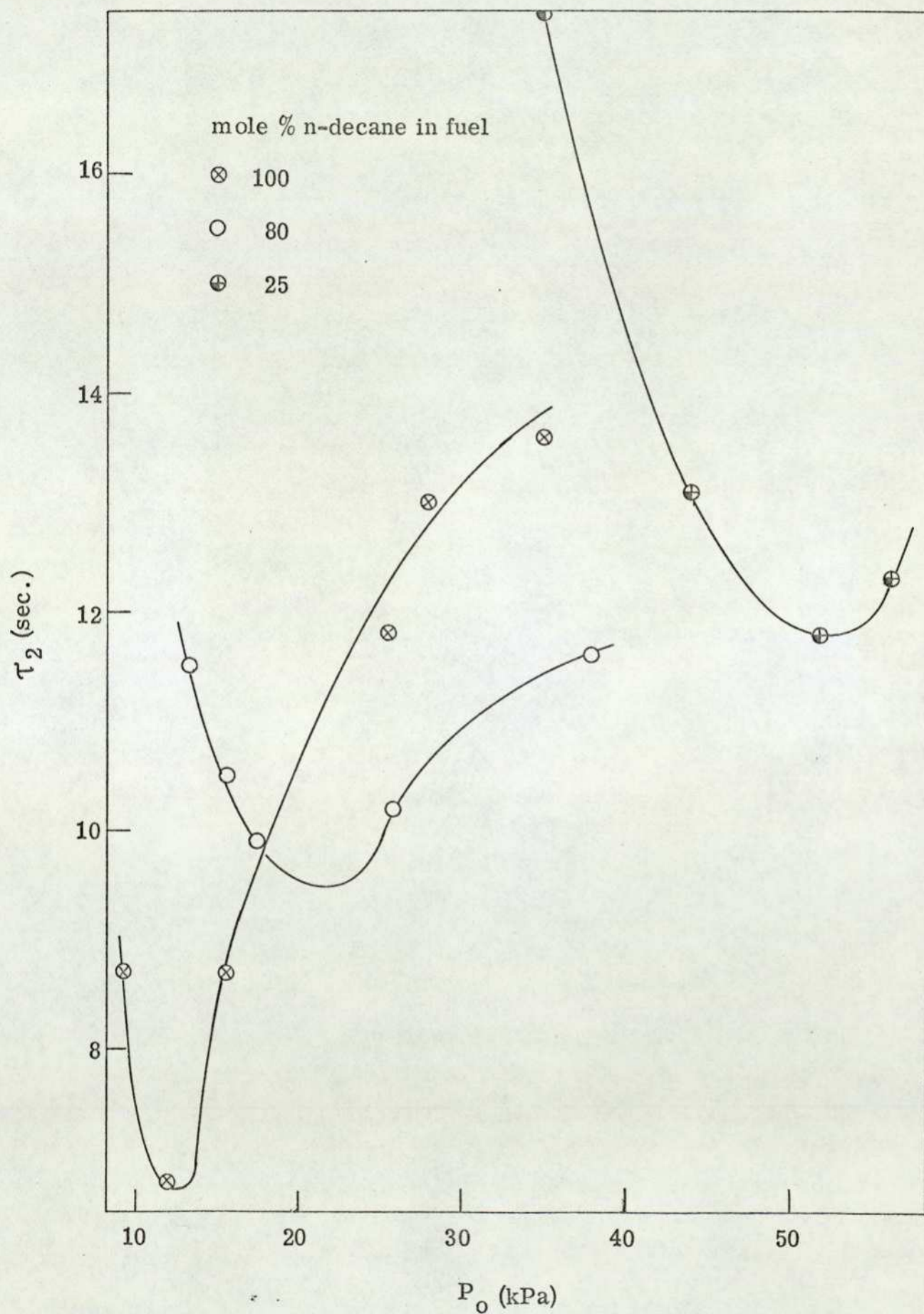
Variation of $\log_{10} \tau_1$ with reciprocal of T_o
and fuel composition. $P_o = 50\text{kPa}$



3.2.2.5 Induction periods preceding the second cool flame, τ_2

The variation with initial pressure, P_0 , of τ_2 at a temperature of 563°K is shown for three fuel compositions in figure 3.44. The curves are similar to those obtained for pure n-decane-air mixtures (figure 3.24), but, as the proportion of branched alkane in the fuel is increased, the minimum value for τ_2 becomes greater, and the position of this minimum is moved to higher pressures.

Figure 3.44
Variation of τ_2 with P_o for several fuel
compositions. $T_o = 563^\circ\text{K}$



3.3 Spontaneous ignition in asymmetrically heated n-decane-air mixtures

3.3.1 Ignition temperature limits

Studies have been made of the ignition limits in 1:15 n-decane-air mixtures, at an initial pressure of ca. 55kPa, in the vicinity of four heated Pyrex glass tubes of different diameter. The criterion for ignition was that the pressure rise during the reaction was greater than 5kPa. The lowest temperature of the tube, T_i , required to cause spontaneous ignition of the mixture, was determined for each tube for a series of vessel temperatures, T_o , between 357 and 493°K.

The variation of T_i with T_o for each tube is shown in figure 3.45. Clearly, for the 2.4 cm. diam. tube, as the value of T_o increases towards the spontaneous ignition temperature limit for n-decane in an empty spherical vessel, T_i decreases markedly.

The variation of T_i with tube diameter, d , for values of T_o between 423°K and 453°K, is shown in figure 3.46, from which it can be seen that, for each vessel temperature, T_i decreases with increasing tube diameter.

3.3.2 Pressure changes accompanying cool flames and two- stage ignitions

No detailed measurements were made of the maximum pressure rise accompanying cool flames, ΔP_1 , and two-stage

Figure 3.45

Variation of T_i with T_o for several different
diameter tubes. $P_o = 55\text{kPa}$, vessel diam. = 10 cm

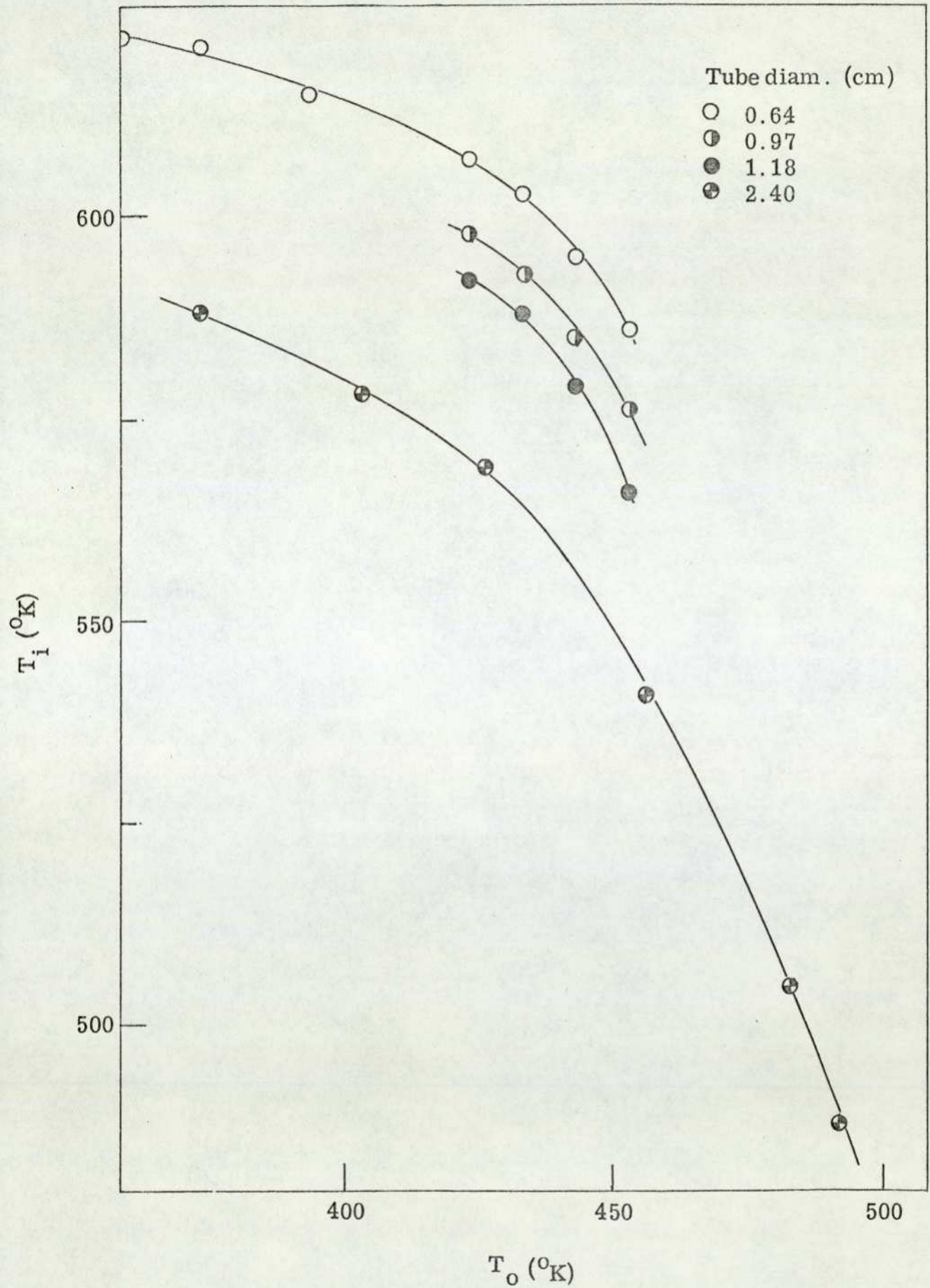
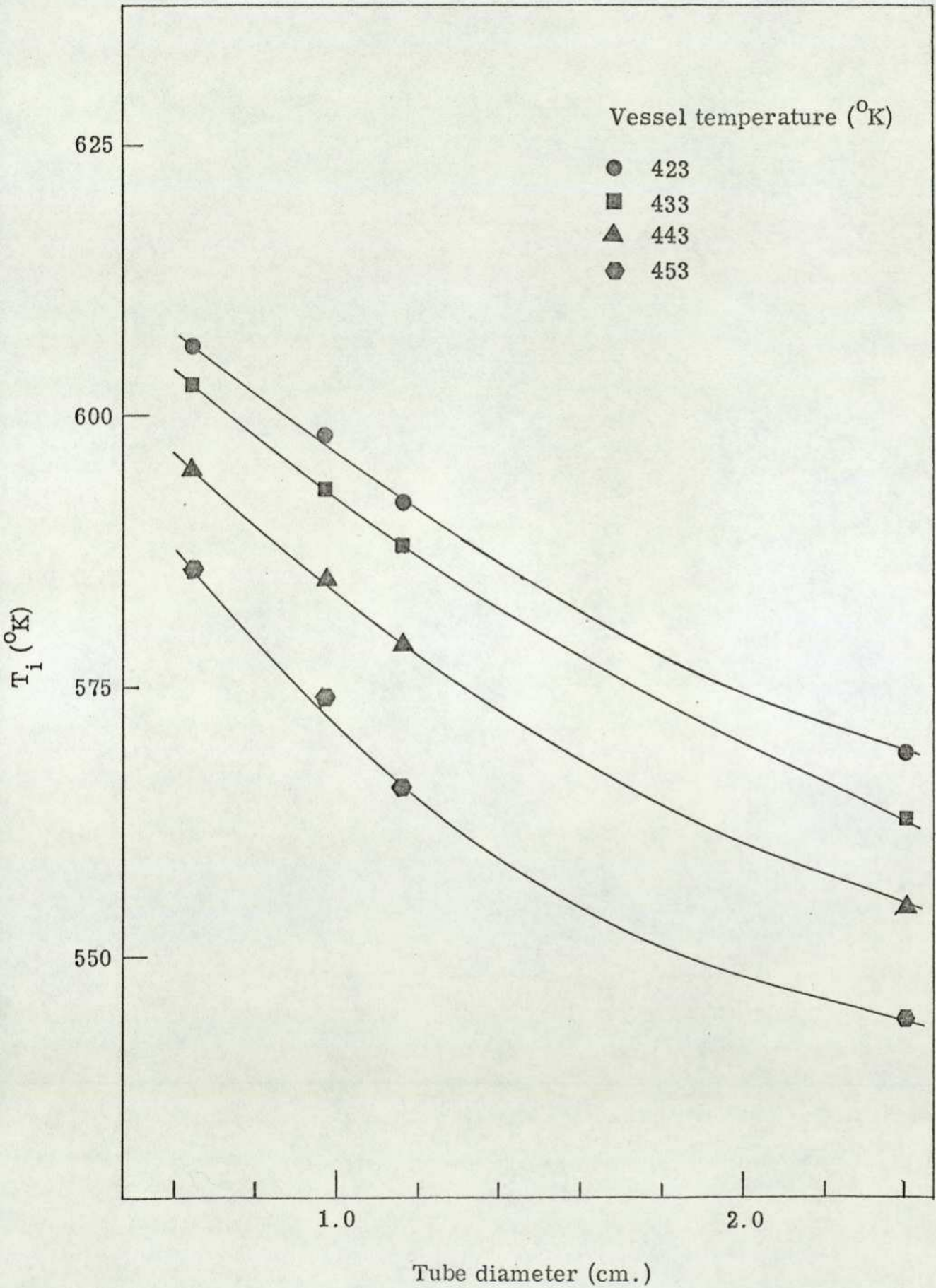


Figure 3.46

Variation of T_i with tube diameter and vessel temperature

$P_o = 55\text{kPa}$



ignitions, ΔP_{ig} , but in all cases the values of these parameters were smaller than those measured in an empty spherical vessel.

The variation with tube temperature, T_p , of the maximum rate of pressure rise in the cool flame, $(dp/dt)_{max.}$, for a 2.4 cm. diam. tube and a vessel temperature of 455°K is shown in figure 3.47. Clearly, $(dp/dt)_{max.}$ decreases markedly as T_p increases above ca. 553°K .

The variation of $(dp/dt)_{max.}$ with T_o at the critical condition for ignition ($T_p = T_i$) is shown in figure 3.48, from which it is clear that a relationship of the form

$$(dp/dt)_{max.} = \text{constant } T_o^n$$

applies.

3.3.3 Ignition delay, τ_{ig}

The variation with tube temperature of the induction period preceding the first stage of two-stage ignition, τ_{ig} , is shown in figure 3.49 for a 2.4 cm. diam. tube and vessel temperatures of 373°K and 453°K .

Table 3.3 gives some values of τ_{ig} at the critical condition for ignition for tubes of different diameter and at several vessel temperatures between 403°K and 453°K .

Figure 3.47

Variation of $(dp/dt)_{\max.}$ with T_i

$T_o = 456^{\circ}\text{K}$; tube diam. = 1.2 cm

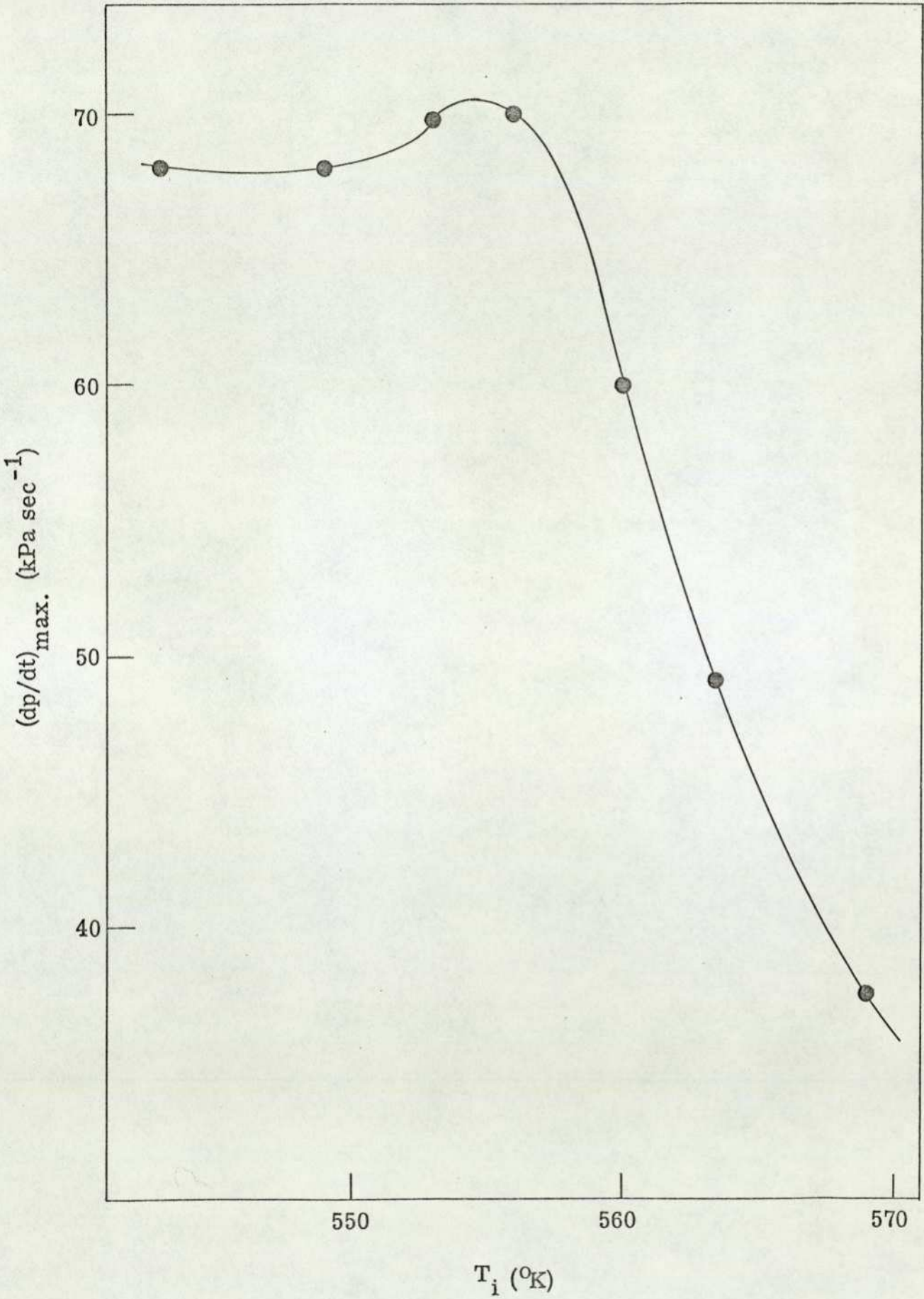


Figure 3.48

Variation of $(dp/dt)_{\max.}$ with vessel temperature.

$T_p = T_i$, tube diameter = 2.4 cm

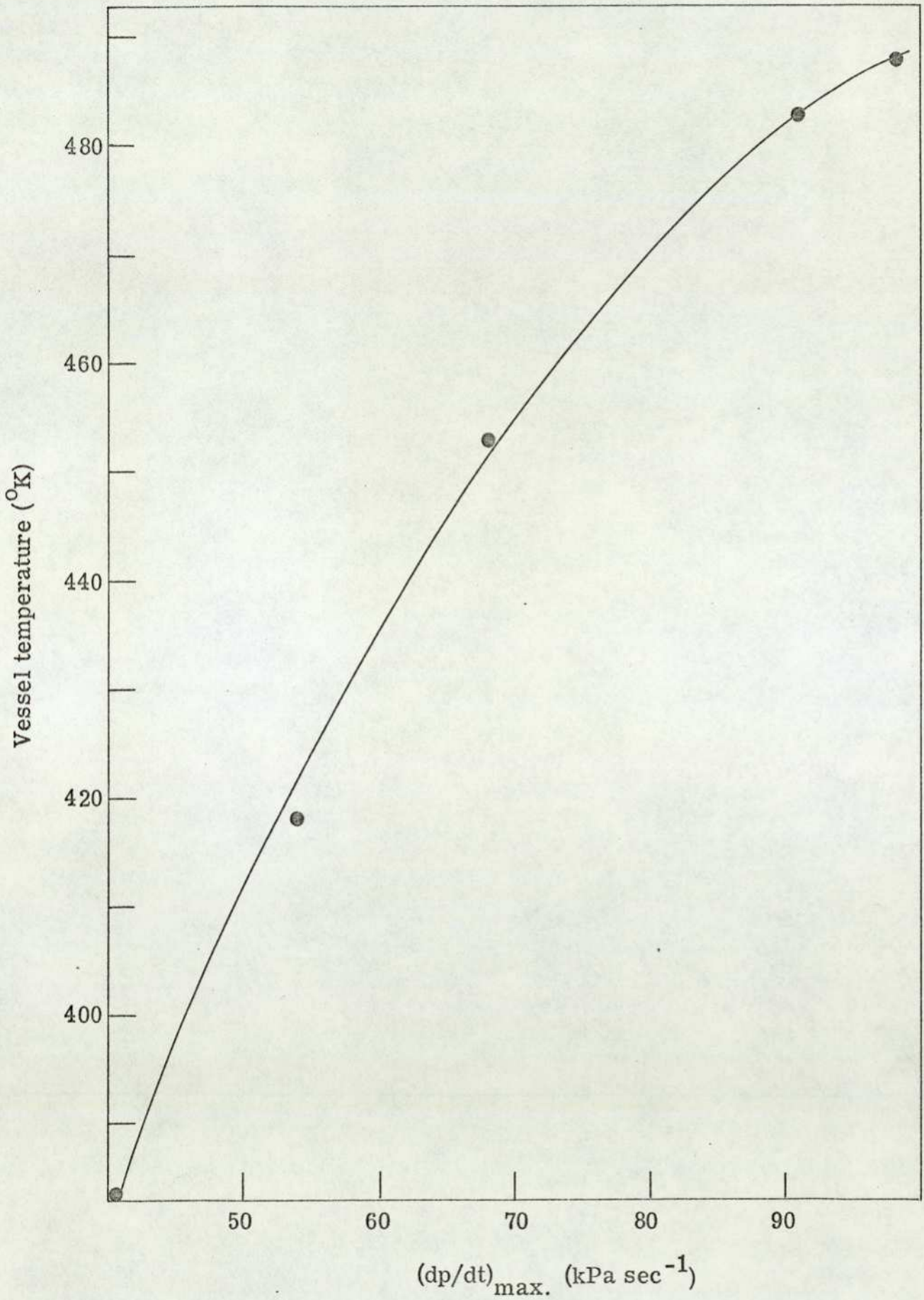


Figure 3.49
Variation of τ_{ig} with T_p .
Tube diameter = 2.4 cm

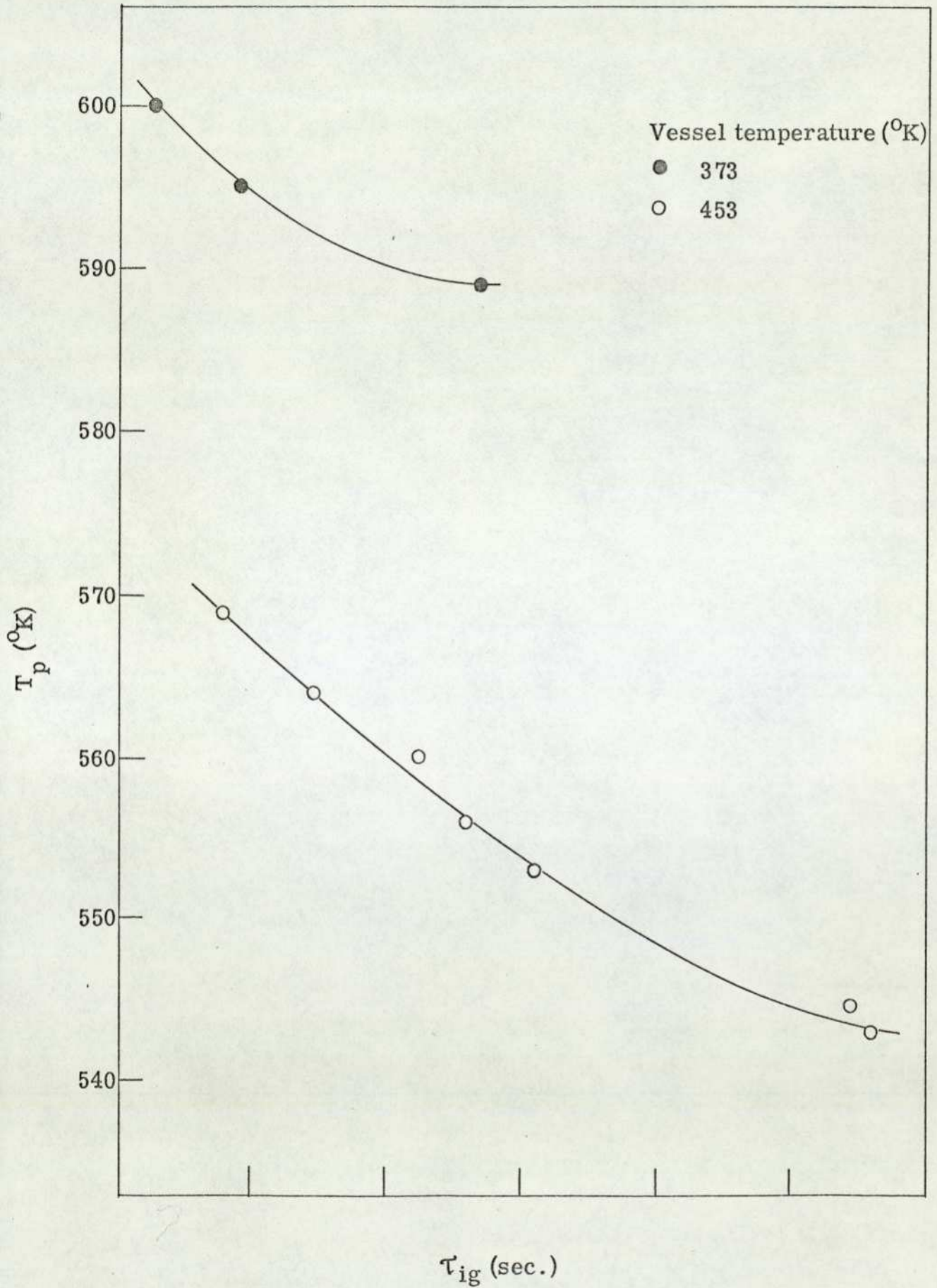


Table 3.3

Values of τ_{ig} for each tube and several
vessel temperatures

Tube diam., d. (cm.)	$T_o(^{\circ}\text{K})$	$\tau_{ig}(\text{secs.})$
0.64	423	
	433	33.4
	443	48.3
	453	60.0
0.97	443	52.0
	453	65.0
1.18	423	44.0
	433	51.2
	443	59.6
	453	70.0
2.40	403	30.0
	423	35.6
	453	59.0

SECTION 4

DISCUSSION

SECTION 4

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SECTION 4

4.1 Physical characteristics of the combustion of pure alkanes

4.1.1 Ignition profiles

4.1.1.1 n-Decane-air mixtures

Studies of the influence of molecular structure on the oxidisability of alkanes have shown that the ease of oxidation increases rapidly with the length of the uninterrupted carbon chain⁷⁸. In particular the maximum rate of pressure rise (a criterion of the ease of oxidation) during the slow combustion of n-decane at low temperatures (ca. 455°K) has been shown to be approximately a thousand times greater than that for n-pentane under similar initial conditions⁷⁸. Thus, the relatively low spontaneous ignition temperature limit of 483°K measured for a 1:7.5 n-decane-air mixture at an initial pressure of 60kPa is not a surprising value, and is in good agreement with a value of 475°K measured at atmospheric pressure (101kPa)¹¹⁵.

The two-stage ignition profiles exhibited two 'Lobes' which have been designated A and B respectively with increase in temperature. On account of the shortness of the induction period (ca. 0.2 sec.) preceding two-stage ignition it has not been possible to complete the ignition profile above ca. 590°K and thereby ascertain whether or

not other lobes exist. For the same reason, previous attempts¹¹⁶ at measuring autoignition temperatures of n-decane-air mixtures were abandoned. Two-stage ignition profiles have, however, been completely measured for other reasonably long-chain n-alkanes (n-hexane^{11, 117}, n-heptane^{64, 116} and n-octane¹¹⁶) and these also exhibit two Lobes which are similar in appearance to those observed for n-decane.

Since n-decane does not contain a tertiary C-H bond, it is probably correct to assign to Lobe A an L_1 mechanism on the basis of Lucquin's theory⁷⁰ (Section 1.6.6). Without analytical evidence, it is not a simple matter to identify Lobe B with an L_1 or L_2 mechanism although a preponderance of the evidence presented below favours its association with the latter mechanism.

According to Lucquin⁷⁰, the assignment of the L_2 mechanism to Lobe B implies that between Lobe A (L_1) and Lobe B a change takes place in the nature of the degenerate chain-branching agent. Such a change should be reflected in the kinetic parameters characteristic of the combustion reactions, and indeed this is found to be the case. Thus the variations with reciprocal temperature of both τ_1 and C in figures 3.19 and 3.22 show marked changes at ca. 520°K, and so too do the locus of constant $(dp/dt)_{\max}$ in figure 3.13 and the locus of constant ΔP_1 in figure 3.10. Similarly, both n and k in the equation

$$\tau_1 = kP_o^{-n} + C$$

(figures 3.20 and 3.21 respectively) pass through distinct minima at ca. 520°K as the temperature is varied.

Lucquin observed⁷⁰ that the L_2 mechanism is favoured by a high oxygen concentration so that the induction period preceding the first cool flame, τ_1 , decreases with increasing partial pressure of oxygen. Figure 3.1 shows that, as the oxygen content of the reactant mixture is increased, Lobe B extends over a larger temperature range. Furthermore, in the temperature range defined by Lobe B, τ_1 decreases with increasing air-n-decane ratio (figure 3.17) whilst in the temperature region defined by Lobe A, τ_1 shows a slight increase which, according to Lucquin, is characteristic of an L_1 mechanism.

The two-cool-flame region lies in the ignition profile within the temperature range defined by Lobe B (L_2). This is not considered in Lucquin's studies⁷⁰ which have shown that it is the L_1 mechanism which usually favours cool-flame periodicity. However, recent studies of the combustion of n-heptane⁶⁴ have shown that there is cool-flame periodicity in regions of the ignition profile associated with all but the lowest temperature Lobe, which extends from ca. 500 to 530°K . There is therefore possibly a difference between the multiple cool-flame regions exhibited by normal alkanes of carbon number greater than six and those exhibited by the less reactive lower molecular weight alkanes studied by Lucquin⁷⁰.

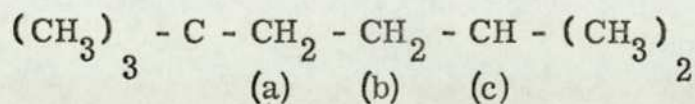
From the foregoing discussion, it seems likely that Lobes A and B are associated with L_1 and L_2 mechanisms respectively.

This conclusion agrees with the recent assignment⁶⁴ of L_1 and L_2 mechanisms to Lobes occurring at ca. 510°K and 560°K respectively on the two-stage ignition profile for n-heptane.

4.1.1.2 Other alkane-air mixtures

The variation with molecular structure of the ease of oxidation of a hydrocarbon has been shown to be a function of the number of methyl groups in the molecule; such groups apparently exert a specific stabilizing effect on the molecule as a whole¹¹⁸. Cullis and Hinshelwood¹²⁰ attributed to the methyl group a stabilizing effect of unity at an adjacent carbon atom, and then assumed that this stabilizing effect decreased by one third on each carbon atom successively further removed from the methyl group. Thus it is possible to calculate a combined stability factor, S , for oxidation taking place at all the carbon atoms in the molecule (neglecting methyl groups), the lowest overall value of which is characteristic of the ignitability of the hydrocarbon and therefore offers a means of comparing the relative ignitabilities of different hydrocarbons.

In the example given below, values of S have been calculated for attack at the different carbon atoms in 2, 2, 5-trimethylhexane.



For attack at carbon atom (a)

$$S = 3 (1 \times 1/3) + 2 (1 \times 1/3 \times 1/3) = 1.22$$

for attack at carbon atom (b)

$$S = 3 (1 \times 1/3 \times 1/3) + 2 (1 \times 1/3) = 1.0$$

while for attack at carbon atom (c)

$$S = 3 (1 \times 1/3 \times 1/3 \times 1/3) + 2 \times 1 = 2.11$$

Thus, the minimum stability factor of $S = 1.0$ is taken for this alkane. Characteristic stability factors have been calculated in a similar way for several other alkanes of different molecular structure, and these are given in Table 4.1 together with the corresponding spontaneous ignition temperatures measured at a pressure of 60 kPA (Section 3.1.1.1 (b)). It is clear from Table 4.1 that, as the value of S increases, so too does the spontaneous ignition temperature, although the relationship does not appear to be quantitative.

Table 4.1 also shows that, with all alkanes except 2,2,3-trimethylbutane, a CH_2 group is associated with the lowest value of S . The significance of this result is not certain, but it has been proposed¹¹⁹ that initial attack by oxygen at a CH_2 group leads subsequently to the formation of a peroxy compound which is relatively little affected by the stabilizing influence of methyl groups and may therefore be an important chain-branching agent, contributing considerably to the overall oxidation rate. On the other hand, whilst initial oxidation of the fuel molecule may occur most frequently at a CH group, such attack contributes little to the overall oxidation rate since the chain-branching which follows is relatively unimportant.

It has been suggested that the ease of the low temperature oxidation of an alkane is governed to a large extent by the stability

Table 4.1
Calculated values of minimum stability factors
for several alkanes

Alkane	Molecular structure	Minimum stability factor (S)	S.I.I. at 60kPa(°K)
2-methylheptane	$(\text{CH}_3)_2 \text{CH CH}_2 \overset{*}{\text{CH}}_2 \text{CH}_2 \text{CH}_3$	0.55	497
2,5-dimethylhexane	$(\text{CH}_3)_2 \text{CH} \overset{*}{\text{CH}}_2 \text{CH}_2 \text{CH} (\text{CH}_3)_2$	0.90	499
2,2,5-trimethylhexane	$(\text{CH}_3)_3 \text{C CH}_2 \overset{*}{\text{CH}}_2 \text{CH} (\text{CH}_3)_2$	1.00	529
2,4-dimethylpentane	$(\text{CH}_3)_3 \text{CH} \overset{*}{\text{CH}}_2 \text{CH} (\text{CH}_3)_2$	1.33	544
2,2,4-trimethylpentane	$(\text{CH}_3)_3 \text{C} \overset{*}{\text{CH}}_2 \text{CH}_2 (\text{CH}_3)_2$	1.66	548
2,2,3-trimethylbutane	$(\text{CH}_3)_3 \text{C} \overset{*}{\text{CH}} (\text{CH}_3)_2$	3.00	/

* Carbon atom for which S is a minimum.

/ No cool flames or two-stage ignitions observed at 60kPa pressure.

of the peroxides derived from it, and Hinshelwood proposed¹²⁰ that the apparent increased stability of a peroxy-linkage when adjacent to methyl groups was due to strengthening of the O-O bond as a result of the electron-donating ability of the methyl group.

Salooja¹²¹ investigated the combustion processes leading to ignition of isomeric hexanes and showed that the cool-flame activity of these hydrocarbons is related to the number of CH₂ groups in the molecule. Thus, 2,2-dimethylbutane shows low cool flame activity whilst n-hexane shows much more. The presence of tertiary hydrogen atoms in the hydrocarbon molecule was shown to have a strong influence on its ignition tendency¹²¹. Hence, the ignitability of 2,3-dimethylbutane was found to be higher, but the overall oxidisability was shown to be lower than that for 2,2-dimethylbutane.

4.1.2 Pressure changes accompanying cool flame combustion

The maximum pressure rise accompanying the passage of a cool flame, ΔP_{cf} , in a reaction vessel of constant volume results from both a temperature rise due to the exothermicity of the reaction and a simultaneous increase in the number of molecules present.

Sokolik and Yantovskii¹²² have shown that a relationship of the form:

$$\frac{P_{cf}}{P_o} = C + AP_o$$

holds for the combustion of isooctane-air mixtures, where C and A are constants and P_{cf} is the maximum total pressure change attained as a result of the passage of the cool flame through the reactant

volume. The above equation was modified to give

$$\Delta P_{cf} = (C-1) P_o + A P_o^2$$

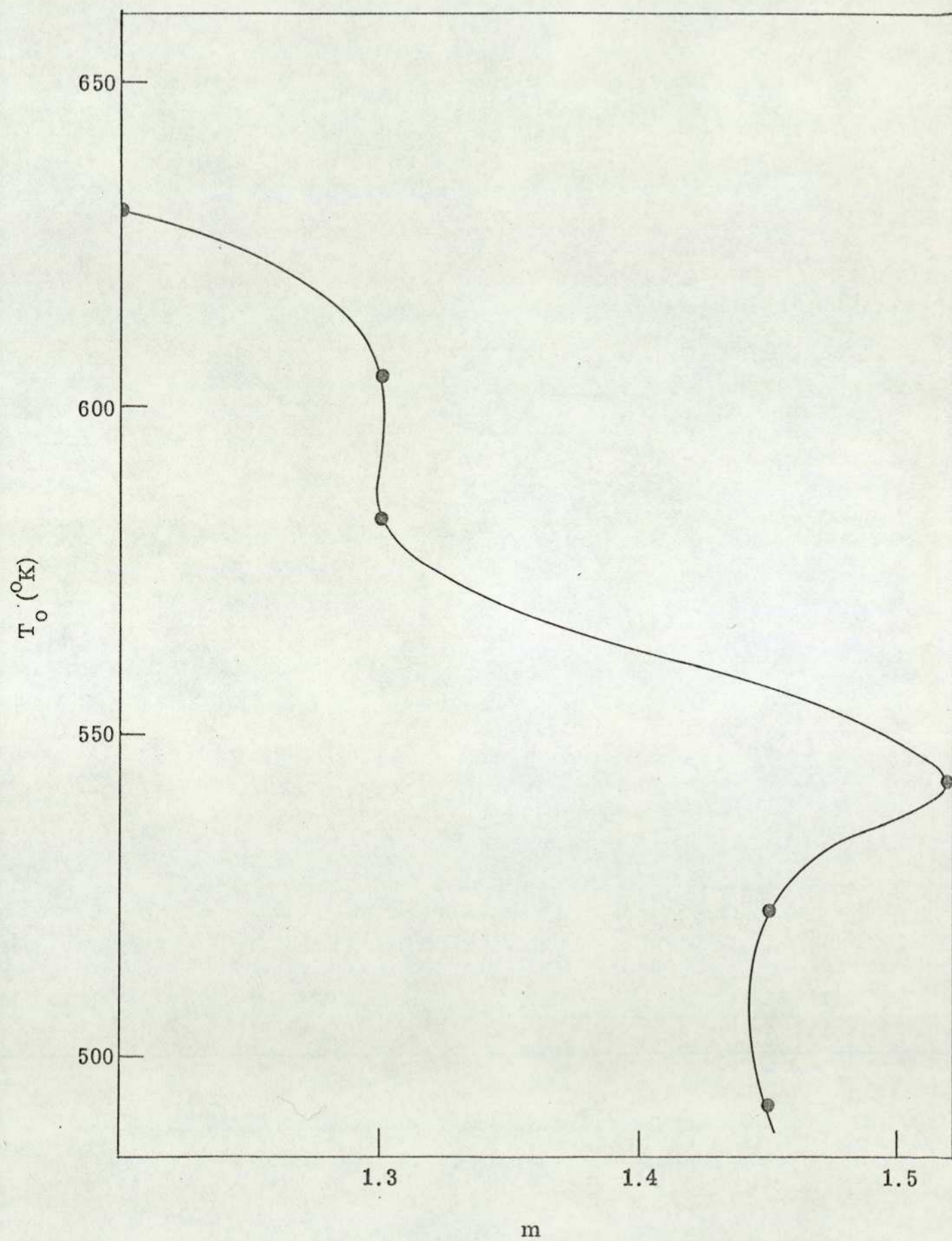
and this was approximated to an equation of the form

$$\Delta P_{cf} \simeq A P_o^m, \quad (4.1)$$

where m for most hydrocarbons lies between one and two.

Since the cool-flame process involves a spreading of the reaction zone throughout the mixture volume, ΔP_{cf} does not characterise the reaction kinetics. However, figure 4.1 shows that values of m in equation (4.1) vary with T_o in a complex manner for the first cool flame in a 1:10 n-decane-air mixture. Indeed, the variation with T_o of m is qualitatively similar in shape to the two-stage ignition profile. Thus, from equation (4.1), it is to be expected that the variation with T_o of ΔP_1 at constant pressure will follow the fluctuating values of m . This is shown to be the case in figure 3.10, from which it can also be seen that the two ΔP_1 maxima lie in temperature regions defined earlier in terms of L_1 and L_2 reaction mechanisms.

Similar results have been found for the high pressure oxidation of n-heptane and isooctane^{73, 74}. With these systems, ΔP_1 maxima were shown to be in low temperature and high temperature regions which were thought to be associated with chain-branching reactions involving peroxides and aldehydes respectively. Whilst ΔP_1 may not be directly related to the reaction kinetics of cool-flame combustion, the magnitude of this pressure change appears to be related to the ease with which two-stage ignition can occur. Thus

Figure 4.1Variation of m with T_o for a 1:10 n-decane-air mixture

at the temperatures where the locus of constant ΔP_1 reaches a maximum value, two-stage ignition takes place most easily.

Possible explanations for the dependence on the magnitude of ΔP_1 of the ease with which two-stage ignition takes place are given in Section 4.1.4.

The rate of pressure rise in cool flame combustion is proportional to the rate of heat liberation per unit volume and hence to the overall oxidation rate. The loci of constant $(dp/dt)_{\max.}$ shown in figure 3.13 reflect a change at ca. 520°K in the reaction kinetics, and the rate of reaction indeed decreases markedly between 510 and 520°K. This change is probably associated with the changing importance of chain-branching agents, or of reactions leading to them, which characterise L_2 and L_1 mechanisms above and below 520°K respectively.

At temperatures below ca. 520°K the effect on $(dp/dt)_{\max.}$ of increasing the air-n-decane ratio is quite small, as is shown in figure 3.14. A similar finding has been reported for the low temperature slow combustion of n-pentane⁷⁸. In these studies, it was shown that the results could be reproduced from purely theoretical considerations by using a kinetic scheme involving an alkylhydroperoxide as the degenerate chain-branching agent. This therefore favours the view that an L_1 mechanism is characteristic of the important chain-branching reactions in the temperature range defined by Lobe A.

4.1.3 Induction periods preceding the first cool flame, τ_1

A relationship of the form

$$\tau_1 = kP_o^{-n} + C \quad 4.2$$

where the values of k , n and C vary with temperature, has been shown to hold for the n -decane-air mixtures studied. It is clear from equation 4.2 that, as P_o is increased, τ_1 approaches the value of C which must be the shortest possible induction period at a given temperature. C must therefore be related to the net branching factor which will depend on the effectiveness of the chain-branching process. Arrhenius plots of $\log C$ against $1/T_o$ for several n -decane-air mixtures display two linear portions which intersect at a value for T_o of ca. 523°K (figure 3.19). This value corresponds to a temperature midway between Lobes A and B on the two-stage ignition profile. Thus, it appears that a change in the nature of the chain-branching agent takes place at ca. 523°K supporting the contention that different chain-branching processes are important in Lobes A and B. Similar results have been reported for the cool-flame combustion of isobutane¹¹³, where it was also shown that the values of C at a given temperature were independent of the nature of the surface of the reaction vessel.

k and n have been found to vary with temperature in such a way that they reflect the two-stage ignition profile. Similar results have been found with isobutane¹¹³, and it has therefore been proposed that these parameters are interdependent or both dependent upon a third variable. Yantovskii⁷³ has shown that the values of n for

n-heptane and isooctane vary with temperature in a similar manner, and has denoted n as the overall order of reaction. For a given temperature the values of k , n and C vary in a seemingly arbitrary manner with mixture composition.

A relationship of the form

$$\tau_1 = \text{constant} \exp(E/RT_0)$$

has been shown to hold for the combustion of n-heptane and isooctane at an initial pressure of 3 atmospheres⁷³, where E represents the overall activation energy of the pre-flame reactions. At these high pressures, it is likely that the value of τ_1 will be close to the corresponding value of C at a given temperature. Indeed, the slope of plots of $\log \tau_1$ against $1/T_0$ has been shown⁷³ to change sharply at a particular temperature, and two values for E can thus be calculated. The change in the value of E may well be connected with the effect of temperature on the nature of the preflame reactions. Similar results have been found for all the n-decane-air mixtures studied where the value of E changes sharply at ca. 523°K.

Clearly, E is not an absolute thermodynamic property of a specific reaction since, even during the pre-flame stage, the oxidation mechanism is complex. In the temperature range defined by Lobe A, a value for E of ca. 42.5 k cal.mole⁻¹ was calculated for all the n-decane-air mixtures studied, and was found to vary very little with pressure. Similar values for E have been reported for the cool-flame combustion of n-butane¹²³ (46 k cal.mole⁻¹), isobutane¹²⁴ (56 k cal.mole⁻¹) and n-pentane¹¹⁴ (49 k cal.mole⁻¹)

in the low-temperature regions of their corresponding ignition profiles. At higher initial temperatures, E varies between 28 and 33 k cal.mole⁻¹ for the 1:15 n-decane-air mixture, compared with the corresponding values of 25, 27, 20 and 31 k cal.mole⁻¹ reported for n-butane¹²³, isobutane¹²⁴, and n-pentane^{114, 125} respectively.

It was shown in Section 3.1.1.4 that E is almost independent of air-n-decane ratio in the temperature range defined by Lobe A. At higher temperatures, however, the value of E increases from 20 to 43 k cal.mole⁻¹ as the air-n-decane ratio is changed from 7.5 to 25.0. This increase results in a corresponding decrease with air-n-decane ratio of τ_1 at constant temperature; this trend becomes more pronounced as the temperature is raised and has been shown to be characteristic of the L_2 mechanism⁷⁰. Whilst E is thermodynamically imprecise, its magnitude may provide a useful means of comparing, under similar conditions, the relative ignition tendencies of hydrocarbons having a different molecular structure. In making such a comparison, the values of E for each hydrocarbon must relate to similar temperature regions of the ignition profiles, eg. those within the temperature range defined by the lowest temperature Lobe. Sokolik has shown⁷⁴ that the empirical equation

$$ON = 180 - 5E \quad 4.3$$

where ON is the octane number of the hydrocarbon, holds for hydrocarbons of different molecular structure. This equation was calculated from results obtained by several investigators studying high pressure combustion under both static and dynamic conditions.

Clearly, according to equation 4.3, E decreases as the octane number of the fuel increases. Oberdorfer¹²⁶ has, however, found the reverse to be the case and has shown that E for isomeric hexanes increases with the degree of branching in the molecule, and hence with the octane number. Values of E which have been measured for the cool-flame combustion of isobutane¹²⁴ ($56 \text{ k cal.mole}^{-1}$) and n -pentane¹¹⁴ ($49 \text{ k cal.mole}^{-1}$) also indicate that this parameter increases with decreasing ignition tendency of an alkane.

4.1.4 Induction periods preceding the second cool flame, τ_2 , the second stage of ignition, τ_{ig} , and the ignition effect pulse, τ_{ie}

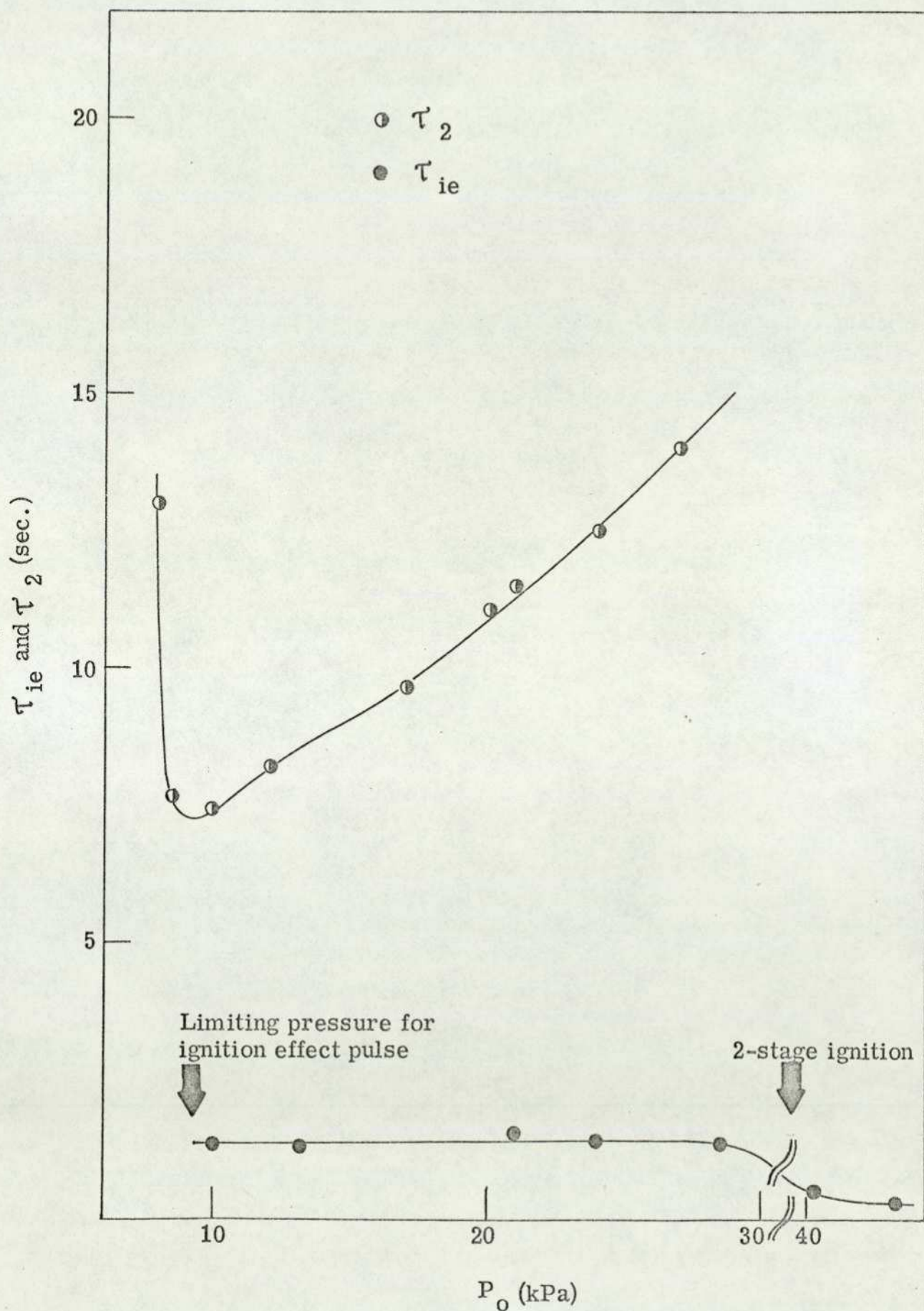
Many of the products of the first cool flame, eg. aldehydes, are known to be more easily oxidised than the parent hydrocarbons. It is to be expected therefore that the first cool flame will influence both the reactions leading to subsequent cool flames and the second stage of ignition. Indeed, for n -decane combustion, the dependence on ΔP_1 of the second stage of ignition has already been demonstrated (Section 4.1.2). Furthermore, for initial pressures up to ca. 60kPa, τ_{ig} for 1:15 n -decane-air mixtures has been shown (figure 3.26) to be related to the maximum pressure rise accompanying the first cool flame, ΔP_1 by an equation of the form

$$\tau_{ig} = 219.0 \Delta P_1^{-2.1}$$

Figure 4.2 shows the variation with pressure of both τ_{ig} and τ_2 at 560°K . It is interesting to observe that, when the ignition

Figure 4.2

Variation of τ_{ie} and τ_2 with P_o for a 1:10 n-decane:air mixture. $T_o = 565^\circ\text{K}$



effect pulse is first visible at ca. 10kPa, τ_2 suddenly increases and continues to increase with pressure until a limit is reached beyond which a second cool flame can no longer propagate. Thus the cause of the ignition effect pulse appears to have a delaying effect on the reactions giving rise to the second cool flame. This behaviour may be expected if similar chain-branching reactions are responsible for both the ignition effect and the second cool flame, or if products of the first cool flame, which play an important role in reactions leading to the second cool flame, are partially consumed in the ignition effect pulse. A pressure pulse occurring as a shoulder on the first cool flame has also been observed in the oxidation of n-butane¹²³ and n-pentane¹¹⁴. With n-butane¹²³, the ignition effect also influenced subsequent cool flames and became the pulse representing the second-stage, hot ignition at sufficiently high pressures. The change with time in the concentrations of products formed during the first cool flame did not show any trends characteristic of branching agents which could be responsible for hot ignition. Fish et.al.¹²⁷ in their studies of the combustion of 2-methylpentane concluded that products formed during the first cool flame acted as, or led as a result of further reaction to, degenerate chain-branching agents which are responsible for the second-stage, hot ignition. The identity of these agents was not established, although it was thought that they are compounds, such as aldehydes, with readily abstracted hydrogen atoms.

Recent studies of the two-stage ignition of n-butane-oxygen

mixtures¹²⁸ have shown that, at least for this alkane, hydrogen peroxide is probably the degenerate chain-branching agent responsible for the second stage of ignition. This result is in good agreement with the work carried out by Oberdorfer¹²⁶ on the cool-flame combustion of isomeric hexanes, in which it was shown that, immediately after the first cool flame, the hydrogen peroxide concentration rises sharply to a maximum and then decreases gradually.

4.1.5 Temperature changes in 1:15 n-decane-air mixtures

For a 1:15 n-decane-air mixture at an initial temperature of 543°K , the propagation of cool flames is just possible above a critical pressure, P_{cr} , of 5.9 kPa. Under these conditions, the temperature profile of the reacting gas mixture (measured along the vertical diameter of the reaction vessel) is approximately parabolic, and symmetrical about the centre of the vessel where a maximum stable temperature rise, ΔT_{cr} , of 21°K occurs (figure 3.28(a)). Such symmetry indicates that, during the reaction, heat loss through the gases to the vessel wall takes place purely by conduction. Under these conditions, Frank-Kamenetskii's equation⁹⁷

$$\Delta T_{\text{cr}} = 1.60RT_0^2/E \quad (4.4)$$

may be used, and this gives a value for E of $44.6 \text{ k cal.mole}^{-1}$.

The validity and accuracy of equation 4.4 have been tested and proven using systems with established kinetics^{eg.100,102}, and thus this value for E is probably correct. There is, however, a considerable difference between this value for E ($44.6 \text{ k cal.mole}^{-1}$) and the value of ca. $30 \text{ k cal.mole}^{-1}$ calculated at the same temperature from induction period data. Nevertheless, there is good agreement between the value of E calculated from induction period data below ca. 523°K ($42.5 \text{ k cal.mole}^{-1}$) and the value calculated from equation 4.4 above. It is possible that E changes very little with temperature, at least below 543°K , for reactions taking place under the critical conditions of temperature and pressure existing at the slow combustion/cool-flame boundary. Indeed, the absence of Lobes on the boundary

supports this, since the variation with temperature of E is thought to be responsible, in part, for the occurrence of Lobes on the two-stage ignition profile.

At 523°K and 9.1kPa , the maximum stable temperature rise in the reacting gases occurs at a point on the vertical diameter 1 cm. above the vessel centre, and the temperature profile is approximately parabolic and symmetrical about this point (figure 3.28(b)). Clearly, convective heat transfer in the gases becomes significant under these conditions, although not pronounced enough to distort the temperature profile.

At 513°K , P_{cr} for a cool flame is 12.8kPa and, under these conditions, convective heat transfer becomes important. At the critical condition, the symmetry of the temperature profile is lost and the maximum stable temperature rise occurs 2 cm. above the vessel centre (figure 3.28(c)).

When a value for E of $44.6\text{ k cal.mole}^{-1}$ is substituted into equation 4.4, the calculated maximum stable temperature rise at the vessel centre, ΔT_{cr} (calc.), is 19.5°K and 18.7°K for initial temperatures of 523°K and 513°K respectively. The corresponding observed values, ΔT_{cr} (obs.) are 20.0°K and 16.0°K . Thus, as the initial temperature is lowered and P_{cr} increases, convective heat transfer becomes increasingly important and the ratio ΔT_{cr} (calc.) / ΔT_{cr} (obs.) exceeds unity. These results are similar to those reported by Ashmore et.al.¹⁰⁰, who also showed that convective heat transfer in gases becomes significant when the

Rayleigh Number exceeds a value of 600, and that, when Ra is less than 600, the ratio $\Delta T_{cr} \text{ (calc.)} / \Delta T_{cr} \text{ (obs.)}$ is approximately unity.

The Rayleigh number, Ra, is defined by $Ra = g \alpha d^3 \Delta T \rho^2 C_p / \eta \lambda$, where g is the acceleration due to gravity, α is the coefficient of thermal expansion of the gas, d is the characteristic dimension of the vessel, in this case the vessel radius, ρ is the gas density, C_p is the heat capacity of the gas, η is the gas viscosity, λ is the gas thermal conductivity, and ΔT is the temperature excess of the gas over its surroundings. Some values of Ra have been calculated for 1:15 n-decane-air mixture under the three critical conditions discussed above, i.e. at 543°K, 523°K and 513°K, and these are given in Table 4.2 together with the corresponding values of $\Delta T_{cr} \text{ (calc.)} / \Delta T_{cr} \text{ (obs.)}$. In these calculations, ΔT was taken to be $\Delta T_{cr} \text{ (calc.)}$, λ and C_p for the gas mixtures were computed using Brokaw's rule¹²⁹ based on simple and reciprocal gas mixing and η for the gas mixtures was calculated using Wilke's estimation method¹³⁰. In these calculations, literature values calculated at the appropriate temperature of η ¹³⁸, C_p ¹³⁸ and λ ¹³⁹ were used for n-decane, oxygen and nitrogen.

Adopting Ashmore's criterion for Ra¹⁰⁰, Table 4.2 shows that convective heat transfer should just become significant at 523°K; this is in excellent agreement with the temperature at which the temperature profile in the reacting gases just ceases to be symmetrical about the vessel centre. These results therefore confirm that, when Ra exceeds a value of ca. 600, convective heat transfer becomes

Table 4.2

Values of $\Delta T_{cr}(\text{calc.}) / \Delta T_{cr}(\text{obs.})$ and
corresponding Rayleigh numbers

P_{cr} , (kPa)	T_{cr} , (°K)	$\Delta T_{cr}(\text{calc.})$	Ra
		$\Delta T_{cr}(\text{obs.})$	
5.9	543	1.0	243
9.1	523	0.98	616
12.8	513	1.15	1250

significant and equation 4.4 hence leads to inaccuracies in the value of E .

4.2 Physical characteristics of the combustion of fuel mixtures containing n-decane and 2, 2, 5-trimethylhexane

4.2.1 Ignition profiles

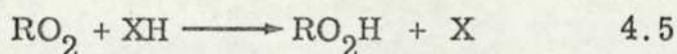
All fuel mixtures containing 10 mole % or more of 2, 2, 5-trimethylhexane are less readily ignitable than pure n-decane, and at a pressure of 60kPa the spontaneous ignition temperature of pure 2, 2, 5-trimethylhexane is 529°K compared with 486°K for pure n-decane. The difference in ignitability of these alkanes is in agreement with the difference in the values of their minimum stability factors, S , which are 1.00 and 0.05 respectively. As was shown earlier (Section 4.1.1.2) the relationship between S and the spontaneous ignition temperature of an alkane is only qualitative. Moreover, the relative magnitudes of S for different alkanes probably indicate the relative oxidisability rather than the ignitability of the alkanes. Thus a quantitative relationship may exist between S and the cool-flame induction period or the maximum rate of cool flame oxidation of different alkanes measured under the same experimental conditions.

At an initial pressure of 60kPa, the spontaneous ignition temperature of a fuel containing 30 mole % of 2, 2, 5-trimethylhexane is only 6°K greater than that for pure n-decane, indicating that the ignitability of the mixture is influenced more by n-decane than by the nonane isomer. This result is in agreement with the results of Salooja³⁷, who has shown that, generally speaking, the ignitability of a binary fuel mixture, whose components display similar pre-flame

reactivity, is influenced to a greater extent by the more readily ignitable component than by the less readily ignitable one.

A region of two-cool flames exists for all fuel mixtures and the size, shape and position in the ignition profile are almost independent of the mixture composition. It is possible, therefore, that similar types of products are formed in the first cool flame of both pure n-decane and 2,2,5-trimethylhexane, and that these products play an important role in reactions leading to the second cool flames of both alkanes.

The addition of 2,2,5-trimethylhexane to n-decane broadens considerably Lobe A (L_1) relative to that for pure n-decane, but causes Lobe B (L_2) to become very weak. This behaviour can be explained in terms of the expected effects of the nonane isomer on the L_1 and L_2 mechanisms⁷⁰. Thus, the L_1 mechanism is probably caused⁷⁰ by initial hydroperoxidation involving hydrogen donors, XH,



and 2,2,5-trimethylhexane, containing a relatively weak tertiary C-H bond, may fill the role of XH. At higher temperatures, where the L_2 mechanism is probably responsible for Lobe B, the intramolecular isomerisation and decomposition of RO_2 radicals is fast, and the bimolecular reaction 4.5 becomes relatively unimportant. In view of this, the presence of 2,2,5-trimethylhexane in the fuel will not enhance its pre-flame reactivity, and may even reduce it owing to the greater resistance to oxidation of the nonane isomer relative to n-decane.

4.2.2 Pressure changes accompanying cool flame combustion

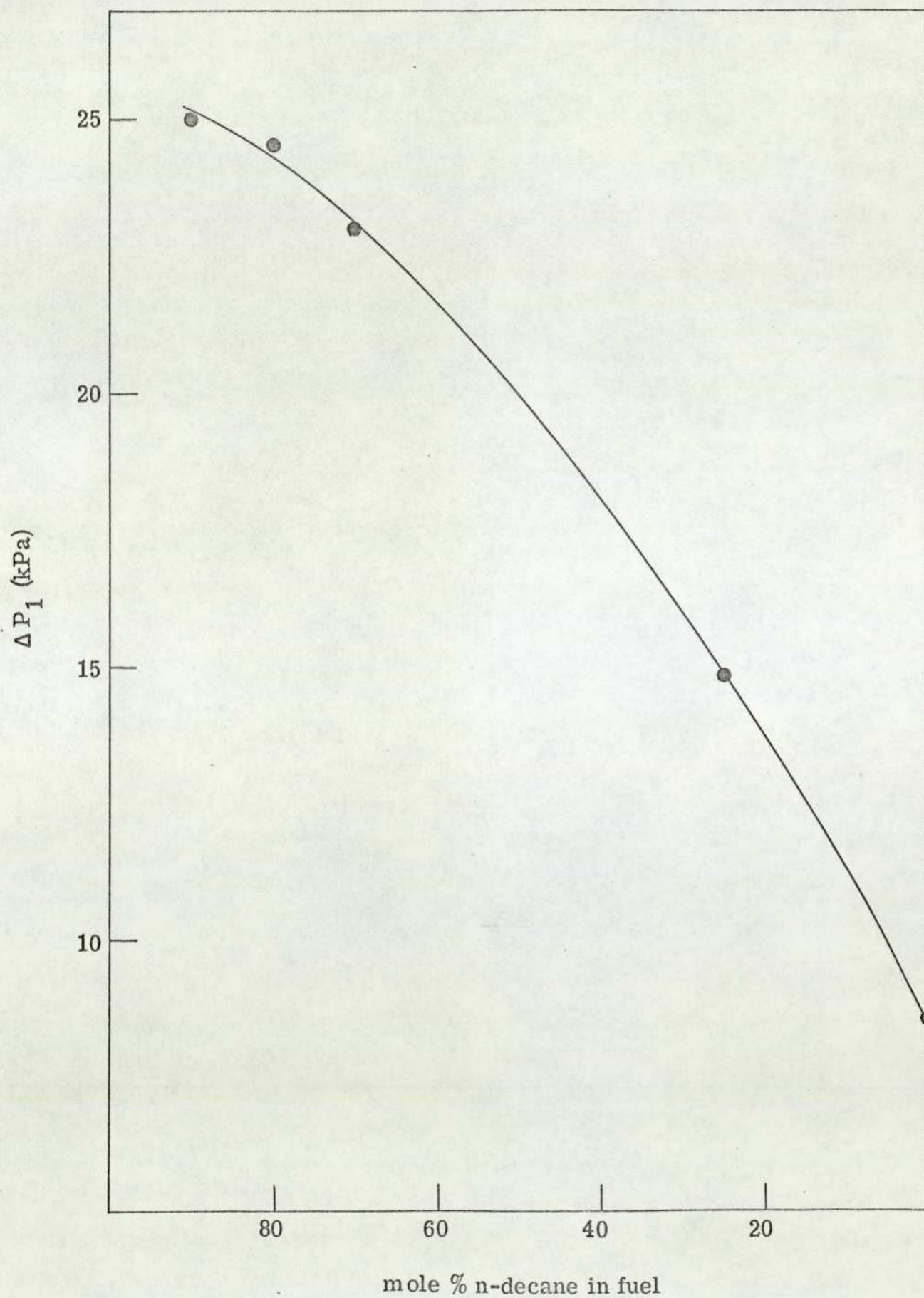
It has been shown (figure 3.32) that, as the concentration of 2,2,5-trimethylhexane in the fuel mixture is increased, the magnitude of the maximum pressure rise accompanying the first cool flame, ΔP_1 , becomes more dependent on the initial pressure, ie. m in equation 4.1

$$\Delta P_1 = A P_0^m \quad 4.1$$

increases. Thus, under the same initial conditions of temperature and pressure, ΔP_1 decreases with increasing 2,2,5-trimethylhexane concentration as shown in figure 4.3. This is probably due to the greater resistance to oxidation of the nonane isomer. These results are in general agreement with those reported by Caplan¹³¹, who studied the effects on precombustion reactions in a firing engine of varying the molecular structure of the fuel components.

It was shown in Sections 4.1.2 and 4.1.4 that the magnitude of ΔP_1 in n-decane-air mixtures influences the ease with which two-stage ignition occurs. Indeed, the variation with T_0 and P_0 of the locus of ΔP_1 was shown to reflect the shape of the two-stage ignition profile. Similar results were obtained for mixtures containing both 2,2,5-trimethylhexane and n-decane as shown in figure 3.33. This figure shows two interesting features. In the first place the low temperature pressure maximum, visible in each of the curves, increases markedly in amplitude and occurs at higher temperatures with increasing concentration of 2,2,5-trimethylhexane in the fuel. This maximum takes place at a temperature corresponding to a point mid-

Figure 4.3
Variation of ΔP_1 with fuel composition.
 $T_o = 543^{\circ}\text{K}$; $P_o = 50\text{kPa}$



way between Lobes A and B in the two-stage ignition profile, where a narrow region of negative temperature coefficient of reaction rate is thought to exist. Figure 3.33 indicates therefore, that such a region becomes more pronounced with increasing concentration of 2,2,5-trimethylhexane in the fuel.

The second interesting feature of figure 3.33 is that the pressure minimum corresponding to Lobe A (L_1) in the two-stage ignition profile extends over a larger temperature range, and that the minimum corresponding to Lobe B (L_2) extends over a smaller temperature range with increasing concentration of 2,2,5-trimethylhexane in the fuel. This behaviour is expected from the earlier discussion of the effects on Lobes A and B of increasing concentrations of 2,2,5-trimethylhexane in the fuel.

Similar conclusions may be drawn from the variation with T_o and P_o of the loci of constant $(dp/dt)_{max.}$ for several fuel compositions. These curves (figure 3.35) confirm the existence of a narrow region of negative temperature coefficient of reaction rate between Lobes A and B which becomes more marked with increasing concentration of 2,2,5-trimethylhexane in the fuel.

The pressure rise accompanying the passage of the second cool flame, ΔP_2 , has been found to be proportional to P_o (figure 3.34). A large proportion of the pressure rise denoted by ΔP_2 must be ascribed to the oxidation of primary fuel since only 10 mole % of the fuel at the most reacts in the first cool flame. Furthermore, some of the products of the first cool flame are probably more

resistant to oxidation than the fuel itself.

4.2.3 Induction periods preceding the first cool flame, τ_1

Equation 4.2

$$\tau_1 = kP_o^{-n} + C \quad 4.2$$

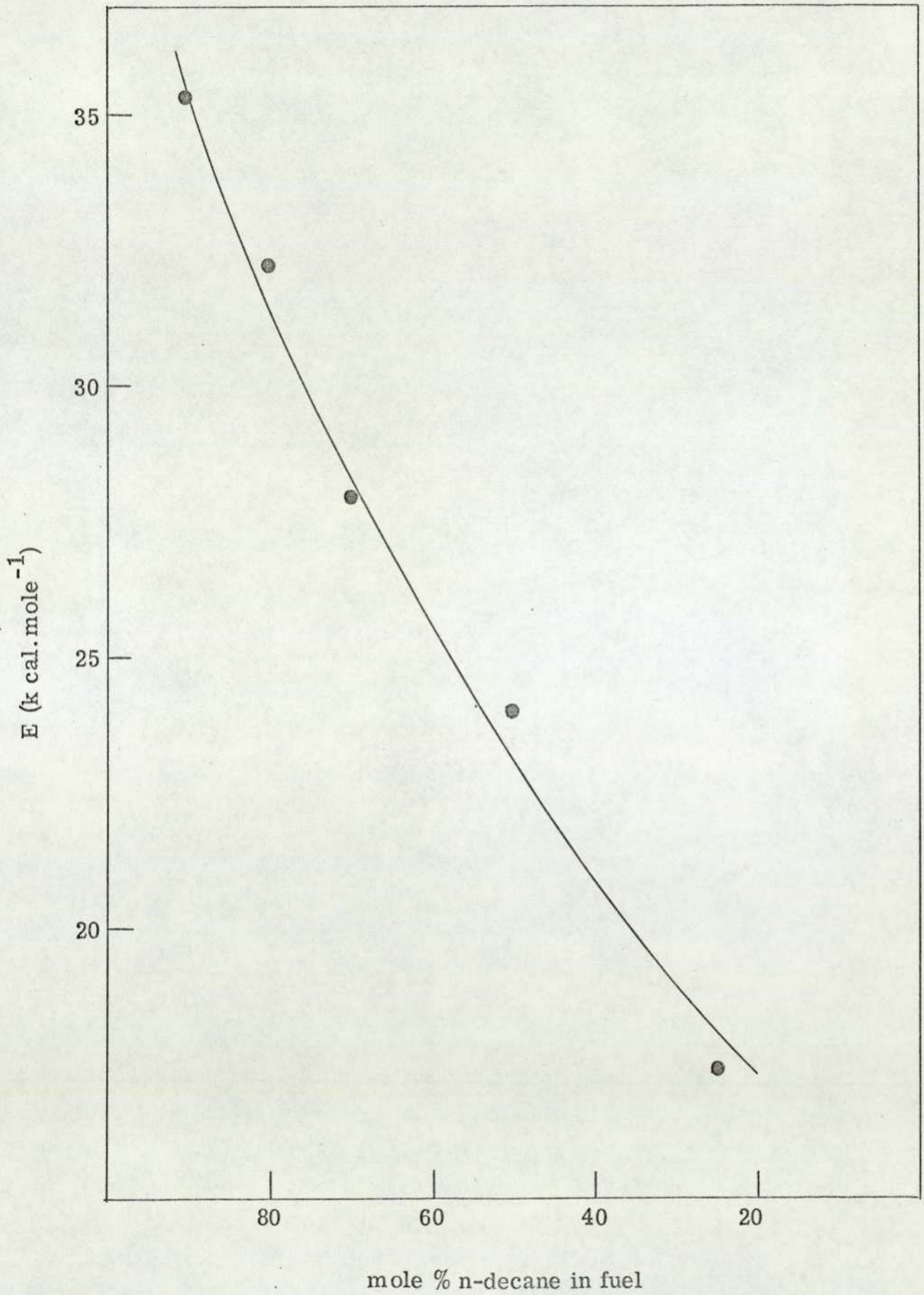
has been shown to hold for all the fuel-air mixtures studied, and the significance of the parameters k , n and C , was discussed in Section 4.1.3. The variation of $\log C$ with $1/T_o$ is complex, and changes from two intersecting straight lines for a fuel containing 10 mole % of 2,2,5-trimethylhexane to a series of curves with points of inflection for fuels containing more than 10 mole % of the nonane isomer. The temperature at which the two straight lines intersect, 533°K , corresponds to the temperature between Lobes A and B on the two-stage ignition profile. Hence, as with the combustion of pure n-decane, C is thought to be related to the nature of the chain-branching reactions, or of other reactions associated with them, which changes at ca. 533°K .

For the other fuel-air mixtures, the point of inflection occurs at a temperature of ca. 540°K , and becomes more pronounced with increasing concentration of 2,2,5-trimethylhexane. The non-uniformity of these curves reflects the complex nature of the chain-branching reactions which probably involve the interaction of the alkanes. At ca. 540°K , it would appear that there is a fundamentally important change in the nature of the chain-branching reactions which is independent of the composition of the fuel.

Values of k and n in equation 4.2 oscillate with temperature in such a way that they reflect the shape of the two-stage ignition profile. Thus, as with pure *n*-decane-air mixtures, k and n appear to be interrelated or to be both dependent on a third variable. Whilst there is no apparent relationship between values of k or n and fuel composition, at a given temperature the values increase in magnitude with an increase in the proportion of 2, 2, 5-trimethylhexane in the fuel.

The variations of $\log \tau_1$ with $1/T_0$ for the fuel-air mixtures show interesting trends. In the corresponding low-temperature region of the ignition profiles, the slope of the straight lines, ie. $E/2.303R$ is inversely proportional to the concentration of 2, 2, 5-trimethylhexane in the fuel in the range 10 to 75 mole %. The relationship between E and the fuel composition is shown in figure 4.4. It is apparent, therefore, that, if E is related to the chain-branching reactions or to other associated processes, then these reactions taking place during the oxidation of *n*-decane are made energetically more favourable by the presence of 2, 2, 5-trimethylhexane. The decrease in ignitability of fuel-air mixtures with increasing concentration of 2, 2, 5-trimethylhexane in the fuel is not, therefore, the result of a change in the value of E .

Another interesting feature of these plots in the low temperature region of the ignition profile is that, when extrapolated, they converge to a point corresponding to a temperature of 486°K , this being the minimum ignition temperature for pure *n*-decane at a

Figure 4.4Variation of E with fuel composition.Low temperature region of ignition profile

pressure of 50kPa.

In the high temperature region of the ignition profiles for fuels containing from 10 to 75 mole % 2,2,5-trimethylhexane the plots of $\log \tau_1$ against $1/T_0$ are complex, in some cases displaying a slight change of slope. The overall activation energy varies from ca. 20 to 30 k cal.mole⁻¹ and does not appear to be dependent on fuel composition.

For pure 2,2,5-trimethylhexane, the plot of $\log \tau_1$ against $1/T_0$ displays two straight lines of different slope which intersect at a temperature of ca. 545°K. From the slopes of the lines, E has been calculated to be 45.0 k cal.mole⁻¹ and 21 k cal.mole⁻¹ in the low and high temperature regions of the ignition profile respectively.

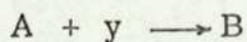
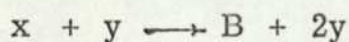
4.2.4 Induction periods preceding the second cool flame, τ_2

Under the same initial conditions of temperature and pressure, τ_2 increases with increasing concentration of 2,2,5-trimethylhexane in the fuel. Thus, the reactions leading to the second cool flame in n-decane-air mixtures are retarded by the addition of the nonane isomer. The variation of τ_2 with P_0 for fuel-air mixtures shows a minimum in τ_2 which is probably associated with the appearance of an ignition-effect pulse as a shoulder on the first cool flame as was observed for pure n-decane-air mixtures (Section 4.1.4). This is indeed the case for a fuel containing 20 mole % of 2,2,5-trimethylhexane for which the ignition effect pulse first becomes visible at a pressure of ca. 22 kPa. For the fuel containing 75 mole % of nonane isomer, the ignition effect pulse is very weak and the initial pressure at which

it first becomes visible is difficult to ascertain.

A further increase in P_0 above the pressure corresponding to the minimum in τ_2 results in a dramatic increase in τ_2 . This increase is possibly due to the further reaction in the ignition-effect pulse of products of the first cool flame, these products playing an important role in the reactions leading to the second cool flame.

These results, together with the fact that there is a marked difference in general appearance between the first and second cool flames, indicate that the periodic cool-flame phenomena in pure n-decane-air mixtures and fuel-air mixtures may be described by Frank-Kamenetskii's "two-product" theory¹³². This theory involved a reaction scheme of the type:



where both x and y are branching agents, A is the fuel and B is a non-reactive product. It has been shown¹³³ that even in a closed system, ie. where the concentration of A is limited, the concentrations of x and y may pass through successive maxima and minima provided that appropriate values are chosen for the reaction rate coefficients and the initial concentration of A .

4.3 Spontaneous ignition in asymmetrically heated n-decane-air mixtures

4.3.1 Ignition temperature limits

The minimum temperature of the glass tubes, T_i , required to cause spontaneous ignition in the gas mixture decreases as the vessel temperature, T_o , is increased. This decrease in T_i becomes dramatic as T_o approaches 488°K , the minimum spontaneous ignition temperature for n-decane in the empty vessel. However, when $T_o = 488^\circ\text{K}$, ignition does not occur until the temperature of the 2.4 cm diam. tube has been raised to 510°K . This is probably due to an increased surface volume ratio in this vessel compared with that of the empty vessel. Similar results were obtained by Macdonald¹³⁴ in studies of the ignition of aviation kerosene by hot pipes. It is expected that T_i for the vessels containing other tubes will lie between 488°K and 510°K when $T_o = 488^\circ\text{K}$.

A temperature difference of 2 or 3°K between the tube and sphere is sufficient to raise the Rayleigh number of the gas to about 1000, which indicates that convective heat transfer will be significant. Thus, in all the hot-tube-in-a-sphere studies, convection probably plays a major role in heat transfer.

The rate of loss of heat from the tube to the gas should follow a Newtonian Law, viz:

$$dq_1/dt = \chi S (T_p - T_m) \quad 4.6$$

where X = heat transfer coefficient, $\text{cal. sec.}^{-1} \text{cm.}^{-2}$

S = surface area of tube, cm.^2

T_p = tube temperature, $^{\circ}\text{K}$

$T_m = (T_p + T_o)/2$

Values of X were calculated from the Nussett number, Nu ,

where $Nu = X d / \lambda (T_p - T_m)$ 4.7

and d = diameter of tube,

for each tube at the critical condition for ignition, ($T_p = T_i$).

Appropriate Nussett numbers were obtained from a plot of $\log Nu$ against $\log Ra$ (Ra = Rayleigh number) prepared from the results of experimental studies of gases filling cylindrical annuli in which the inner cylinder is hotter than the outer cylinder¹³⁵. Rayleigh numbers were calculated as in Section 4.1.5, using d as the characteristic dimension of the system.

Some values of dq_1/dt for each tube at the critical condition for spontaneous ignition, are given in Table 4.3, and figure 4.5 shows the variation of dq_1/dt with T_o . From this figure it can be seen that, as T_o approaches 488°K , dq_1/dt becomes less dependent on tube diameter. However, as T_o is lowered, there is divergence in the values of dq_1/dt for each tube.

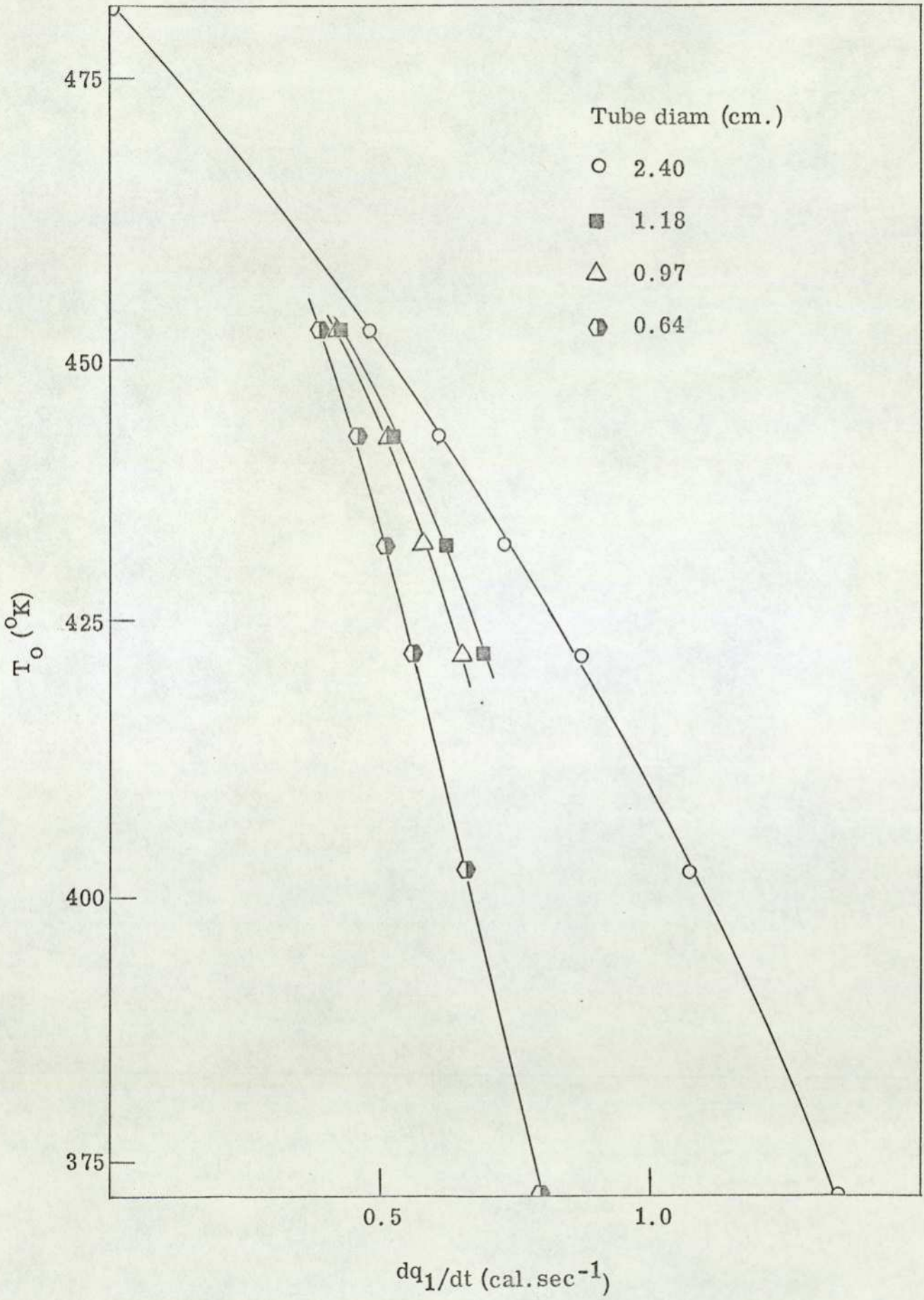
Some values for the total amount of heat supplied by the hot tube, Q_1 , during the induction period preceding ignition, τ_{ig} , have been calculated and these values are given in Table 4.3 (Q_1 = product of τ_{ig} and dq_1/dt). Clearly, the values of Q_1 for a given tube are almost independent of T_o and, with the exception of the 0.64 diam.

Table 4.3

Values of dq_1/dt and Q_1 for each tube at
the critical condition for spontaneous ignition

d (cm)	T_o (°K)	T_i (°K)	τ_{ig} (sec.)	dq_1/dt (cals.sec ⁻¹)	Q_1 (cals.)
0.64	433	603	33.4	0.51	17.0
	443	595	48.3	0.46	22.2
	453	586	60.0	0.39	23.4
0.97	443	585	52.0	0.52	27.0
	453	576	65.0	0.43	27.9
1.18	423	590	44.0	0.69	30.3
	433	588	51.2	0.62	31.7
	443	579	59.6	0.53	31.6
	453	566	70.0	0.43	30.1
2.4	373	590	27.0	1.35	36.4
	403	578	30.0	1.07	32.1
	423	568	35.6	0.87	31.0
	453	542	59.0	—	28.3

Figure 4.5
Variation of dq_1/dt with T_o for each tube at the
critical condition for ignition



tube, do not vary appreciably with tube diameter. Thus, it appears to be necessary to supply a critical amount of heat to the gas mixture before spontaneous ignition can occur. This critical amount of heat may be required to raise a volume element of the gas mixture to a temperature at which the rate of heat generated by the reaction, dq_r/dt , is greater than that lost by convection and conduction from the volume element, dq_c/dt . Once this condition is attained, the reaction process in the volume element can probably propagate independently of the hot tube and lead to spontaneous ignition throughout the gas mixture. Indeed, Macdonald¹³⁴ has provided good evidence that zones of recirculation are set up some way from a hot pipe in which, under favourable conditions, reaction continues to take place, leading eventually to spontaneous ignition.

4.3.2 Pressure changes accompanying two-stage ignition

Although a detailed study was not made of the overall pressure rise, ΔP , accompanying two-stage ignition in asymmetrically heated n-decane-air mixtures, values for ΔP were always lower than those measured at the same initial pressure in an empty spherical vessel. However, the ignition event was of a longer duration than in the empty vessel and the final overall pressure rise, ΔP_{∞} , was similar in both systems; viz. ca. 15kPa.

Values for the maximum rate of pressure rise preceding the first stage of two-stage ignition, $(dp/dt)_{\max.}$, were always smaller than values measured at an initial pressure of 55kPa in an empty spherical vessel. This is understandable since a major

contribution to $(dp/dt)_{\max.}$ is made by the rate of temperature rise in the gas which will be smaller in the hot-tube-in-a-sphere experiments owing to a greater rate of heat loss to the walls of the cooler spherical vessel.

At the critical condition for ignition, $(T_p = T_i)$, $(dp/dt)_{\max.}$ increases exponentially as T_o increases. Figure 4.6 shows a logarithmic plot of $(dp/dt)_{\max.}$ against T_o , which is indeed a straight line. From this line, the characteristic constants have been calculated and these give rise to a relationship of the form

$$(dp/dt)_{\max.} = 1.85 \times 10^{-7} T_o^{3.24}$$

The marked decrease in $(dp/dt)_{\max.}$ with increasing tube temperature above ca. 560°K (figure 3.47) highlights a large region of negative temperature coefficient of reaction rate. This is in good agreement with the position of the region of negative temperature coefficient reflected in the two-stage ignition profile above ca. 565°K (figure 3.1).

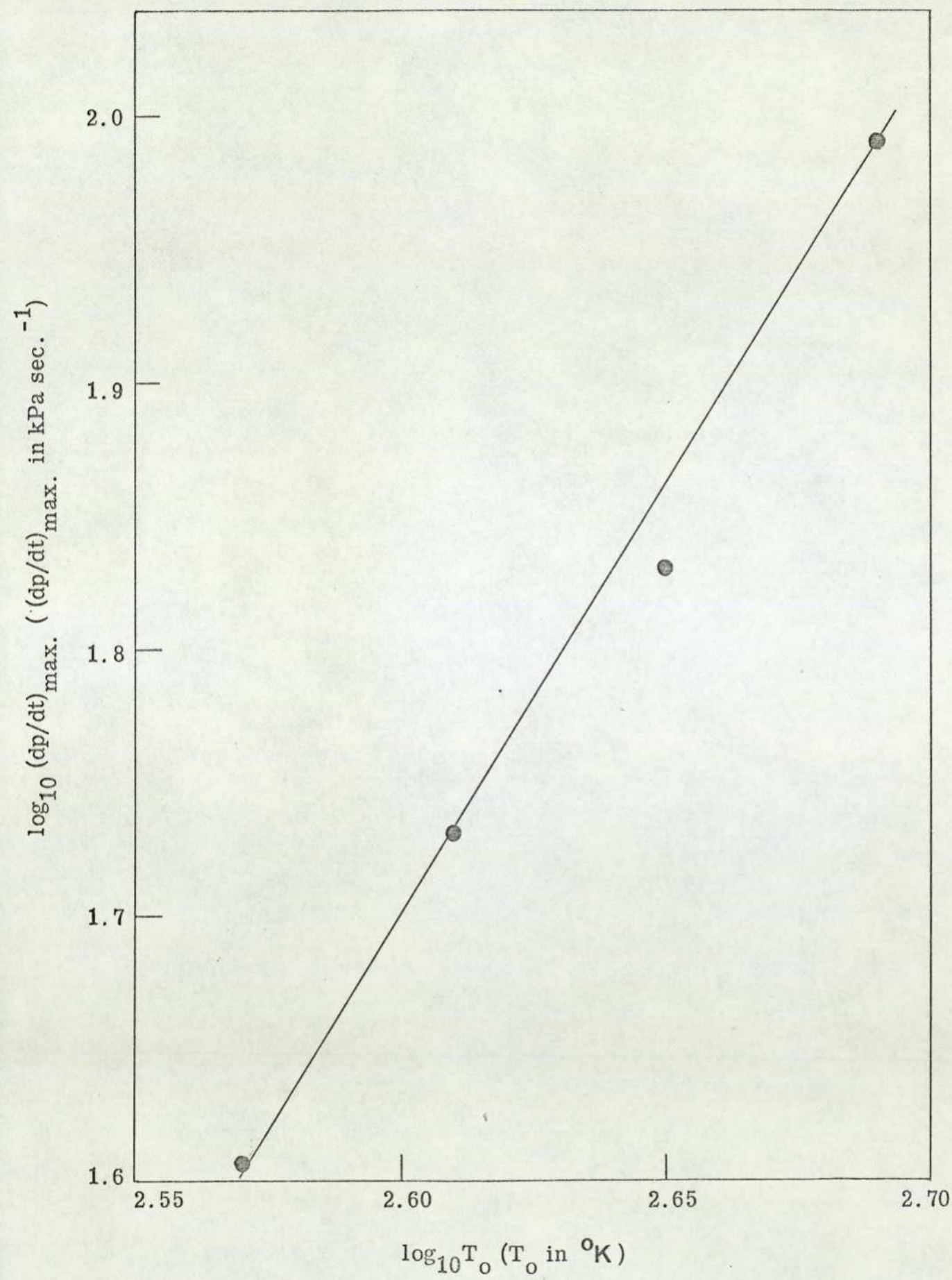
4.3.3 Induction periods preceding two-stage ignition, τ_{ig}

The induction periods preceding spontaneous ignition, τ_{ig} , in asymmetrically heated n-decane-air mixtures varied from ca. 3 to 70 seconds depending on the tube and sphere temperatures. Thus, the range of values for τ_{ig} were similar to those measured for spontaneous ignition in symmetrically heated n-decane-air mixtures in the temperature interval 480 to 570°K.

For a fixed sphere temperature, τ_{ig} is more dependent

Figure 4.6

Variation of $\log_{10} \left(\frac{dp}{dt} \right)_{\max.}$ with $\log_{10} T_o$ under conditions
 when $T_p = T_{ig}$. Tube diam. = 2.4 cm



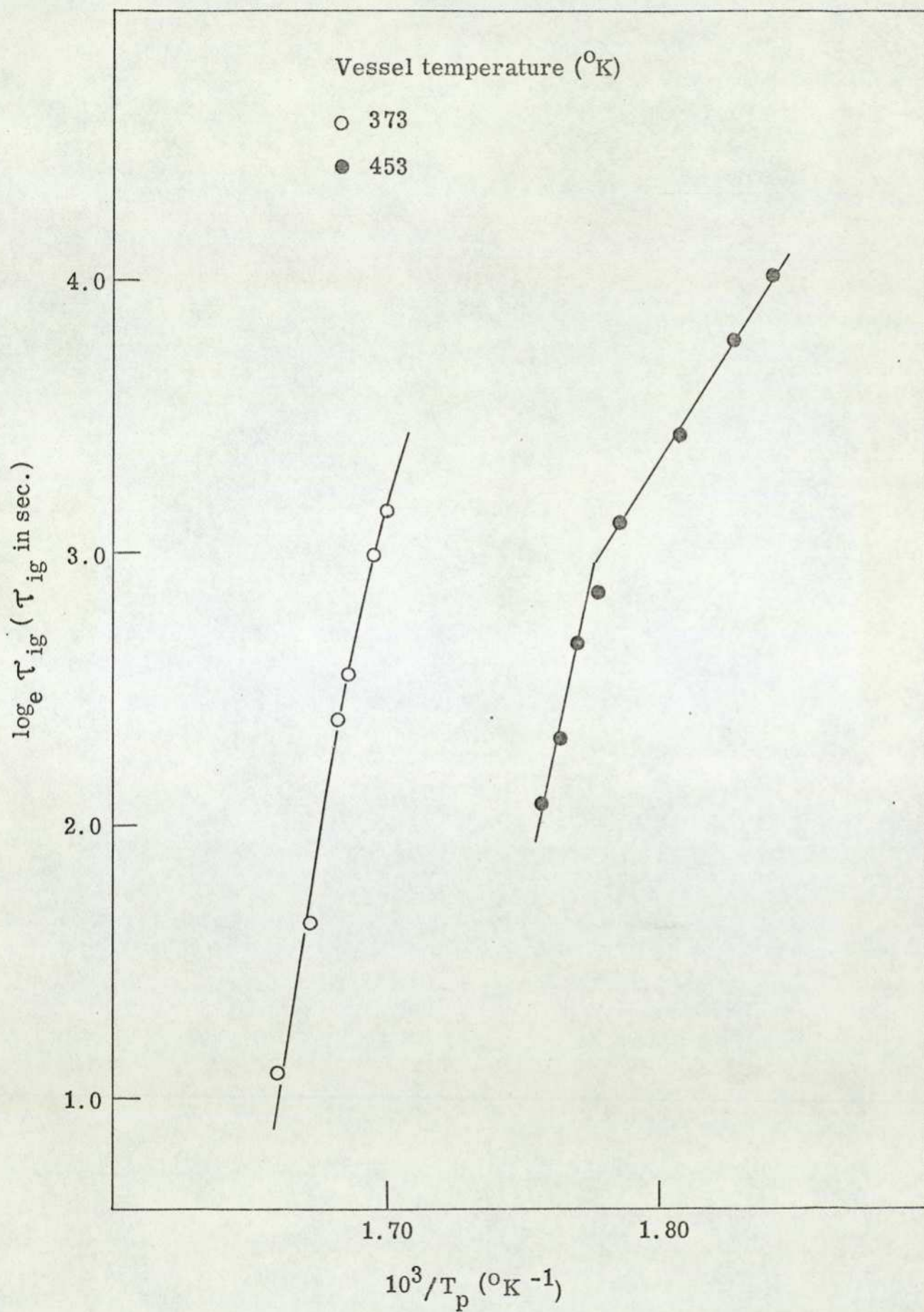
on T_p than it is on T_o in the empty spherical vessel. Thus, in the latter vessel, an increase in T_o of 30°K causes τ_{ig} to decrease by a factor of 10. However, in the hot-tube-in-a-sphere experiments, a similar decrease in τ_{ig} is brought about by an increase in T_p of only 10°K .

For the 2.4 cm. diam. tube, and sphere temperatures of 373 and 453°K , the variation with reciprocal tube temperature of $\ln \tau_{ig}$ is shown in figure 4.7. From this it can be seen that for a vessel temperature of 453°K there are two intersecting straight lines, the point of intersection corresponding to a temperature of 560°K . From these lines the overall activation energy of the reaction, E , above and below 560°K has been calculated to be $71.5 \text{ k cal.mole}^{-1}$ and $31.5 \text{ k cal.mole}^{-1}$ respectively. The value for E of $31.5 \text{ k cal.mole}^{-1}$ is in very good agreement with that of ca. $30 \text{ k cal.mole}^{-1}$ calculated from induction period measurements in an empty spherical vessel in the temperature range 525 to 560°K (Section 4.1.3). The change in value of E at 560°K may be associated with a second change in the nature of the chain-branching reactions (the first change occurring at a temperature of ca. 530°K , (see Section 4.1.3). The change at 560°K coincides with the appearance of a large negative temperature coefficient of reaction rate as indicated by the variation with tube temperature of $(dp/dt)_{\text{max}}$.

The variation of $\ln \tau_{ig}$ with $1/T_p$ for a vessel temperature of 373°K (figure 4.7) is slightly curved and indicates that E increases continuously with T_p in the temperature range 588 to 600°K .

Figure 4.7

The variation of $\log_e \tau_{ig}$ with reciprocal of T_p for
two vessel temperatures



The variation with temperature of the kinetic parameters (ie. τ_{ig} , $(dp/dt)_{max.}$) characteristic of the spontaneous ignition of n-decane-air mixtures caused by a hot tube of 2.4 cm.diam. is thus in good quantitative agreement with studies carried out in an empty spherical vessel. However, the absolute values of these kinetic parameters appear to be appreciably dependent on the method of study.

4.4 Application of thermal ignition theory to the cool-flame limits of n-decane-air mixtures

4.4.1 Validity of application of thermal ignition theory

The boundary separating slow combustion from both cool flames and two-stage ignition in the ignition profile of an alkane may be regarded as the locus of critical pairs of values of temperature and pressure which, when exceeded, result in an explosion. It is possible, therefore, that such a locus may be predicted from thermal ignition theory. In view of the fact that cool flames result from interdependent chain-branching and exothermic processes, they cannot be regarded simply as pure thermal explosions. The complexity of the overall kinetics of cool-flame reactions in n-decane-air mixtures has already been discussed.

Tests of the validity of application of thermal ignition theory, based on purely conductive heat transfer in the reacting gases, may be direct or indirect in their approach.

4.4.2 Indirect tests of thermal ignition theory

These tests may be carried out by rearranging into a suitable form the equation derived by Frank-Kamenetskii⁹⁶ which represents the dimensionless rate of heat release by the reaction at the critical condition, viz:

$$\delta_{cr} = \frac{Q_w r^2 E}{\lambda R T_o^2} \quad 4.8$$

= 3.32 for a spherical reaction vessel where w is the initial isothermal reaction rate

$$= A \exp(-E/RT_o) [RH]^a [O_2]^b \quad 4.8 (a)$$

The rearranged form of equation 4.8 is usually

$$\log_e \left(P_{cr}^n / T_{cr}^{n+2} \right) = E/RT_{cr} + \log_e \text{const.} \quad 4.9$$

where n is the overall order of reaction = $(a + b)$ in equation 4.8 (a) and P_{cr} , T_{cr} are pairs of values of pressure and temperature on the explosion boundary. Plots of $\log_e (P_{cr}^n / T_{cr}^{n+2})$ against $1/T_{cr}$ have been used to calculate E .⁹⁴ In view of the uncertainty in the value of n for cool-flame reactions in n -decane-air mixtures, similar plots used to calculate E for this alkane may be misleading. However, the value of E has been shown (Section 3.1.1.4) to be constant at ca. $42.5 \text{ k cal.mole}^{-1}$ for all the n -decane-air mixtures studied below a temperature of ca. 530°K . Equation 4.8 may therefore be rearranged differently so that a value for n can be calculated using the above value for E . If the ratio of oxygen to hydrocarbon is denoted by X , then

$$[O_2] = X [RH] \quad \text{mole.cm}^{-3} \quad 4.10$$

$$\text{and } [RH] + [O_2] = (X + 1) [RH] \quad \text{mole.cm}^{-3} \quad 4.11$$

Thus it follows that

$$[O_2]^b = X^b [RH]^b \quad 4.12$$

and therefore that

$$[\text{RH}]^a [\text{O}_2]^b = X^b [\text{RH}]^{a+b} \quad 4.13$$

Putting $[\text{M}] = [\text{RH}] + [\text{O}_2] \quad \text{mole cm}^{-3}$

and making the appropriate substitution in equation 4.11, it can be shown that

$$[\text{RH}]^a [\text{O}_2]^b = \frac{X^b [\text{M}]^{a+b}}{(X+1)^{a+b}} \quad 4.14$$

If X , Q , A , E and λ in equations 4.8 and 4.8 (a) are taken to be constant, and the substitution for $[\text{RH}]^a [\text{O}_2]^b$ (equation 4.14) is made in equation 4.8, it follows that

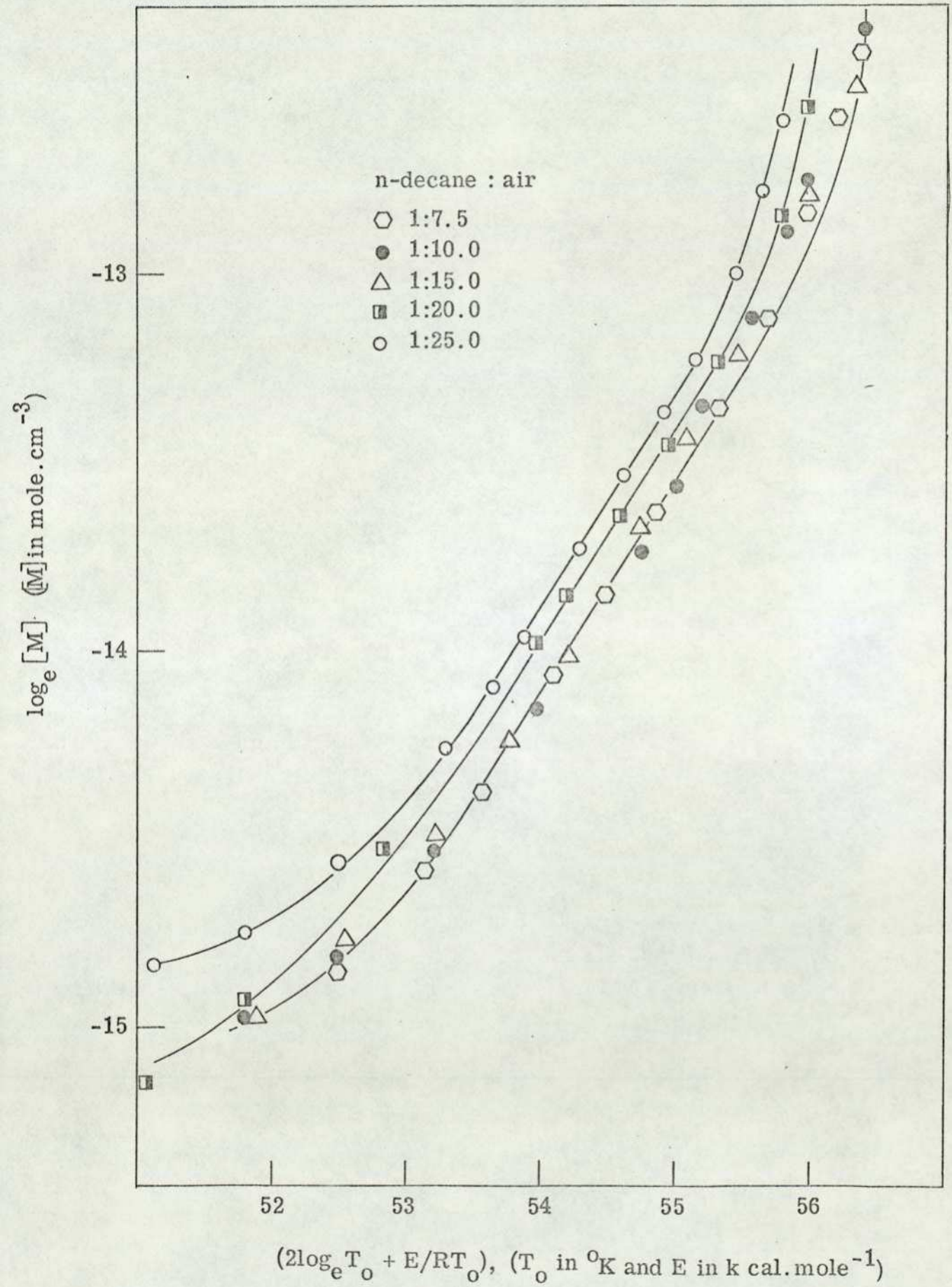
$$\log_e [\text{M}] = \frac{1}{(a+b)} (2 \log_e T_o + E/RT_o) + \log_e C \quad 4.15$$

where $C = \frac{3.32 R \lambda (X+1)^{a+b}}{Q r^2 A E} = \text{a constant.}$

The variation of $\log_e [\text{M}]$ with $(2 \log_e T_o + E/RT_o)$ for all the n-decane-air mixtures studied is shown in figure 4.8. From this figure, it can be seen that for each mixture composition, and for values of $\log_e [\text{M}]$ between -13.2 and -14.2, the plots display an almost linear portion from which a value for $(a+b)$ has been calculated to be 1.78. For values of $\log_e [\text{M}]$ less than ca. -14.2, which corresponds to a temperature of ca. 520°K, there is some departure from linearity of the plot. This may be due to a change in the value of E as a result of a change in the nature of the chain-branching reactions above ca. 520°K. Indeed, an increase in the value of E from 42.5 to 43.5 k cal.mole⁻¹ restores the linearity of

Figure 4.8

Variation of $\log_e [\bar{M}]$ with $(2\log_e T_0 + E/RT_0)$
for several n-decane-air mixtures



the plot for the lowest values of $\log_e [M]$ corresponding to a temperature of ca. 550°K .

The departure from linearity of the plots for values of $\log_e [M]$ greater than -13.2 is probably associated with a breakdown in equation 4.8 owing to the heat transfer being mainly convective rather than conductive. Indeed, the value for the Rayleigh number of the gas mixture corresponding to $\log_e [M] = -13.2$ is 5750 (ΔT in this calculation taken to be $1.60 RT_o^2/E$). This exceeds by almost a factor of 10 the critical value of 600 which has been shown to mark the onset of natural convection in a 1:15 n-decane-air mixture. Frank-Kamenetskii proposed¹³⁶ that the conductive theory of thermal explosions should break down when the Grashof number of the gas mixture exceeds a value of ca. 10^4 . (For self-heating gases, the Rayleigh number and Grashof number are interchangeable.)

The departure from linearity of the plot for high values of $\log_e [M]$ (low values of T_o) may also be associated with the fact that thermal control over the reaction has become insignificant. Indeed, induction periods preceding cool flames at low initial temperatures are too long (ca. 50 sec.) to reflect thermal control.

Equation 4.8 has also been rearranged to the form shown in equation 4.16

$$\log_e [O_2] = \frac{1}{b} (2 \log_e T_o + E/RT_o) + \log_e B \quad 4.16$$

where
$$B = \frac{\lambda R 3.32}{r^2 Q A [RH]^a} = \text{a constant.}$$

Figure 4.9 shows the variation of $\log_e [\text{O}_2]$ with $(2 \log_e T_0 + E/RT_0)$ for all the n-decane-air mixtures with a constant value for $[\text{RH}]$ of $5.54 \times 10^{-7} \text{ mole.cm}^{-3}$. From this figure, it can be seen that equation 4.16 holds, and the value of b has been calculated to be 0.91. Therefore, from figure 4.8, a is 0.87.

Since the initial temperature and concentration of the reacting gases may be measured accurately, the calculated values of a and b will be dependent on the precision with which E has been determined. It has been shown that a variation of $\pm 1.0 \text{ k cal.mole}^{-1}$ in the value of E will lead to a 15% variation in the value of $(a+b)$, although b remains unchanged.

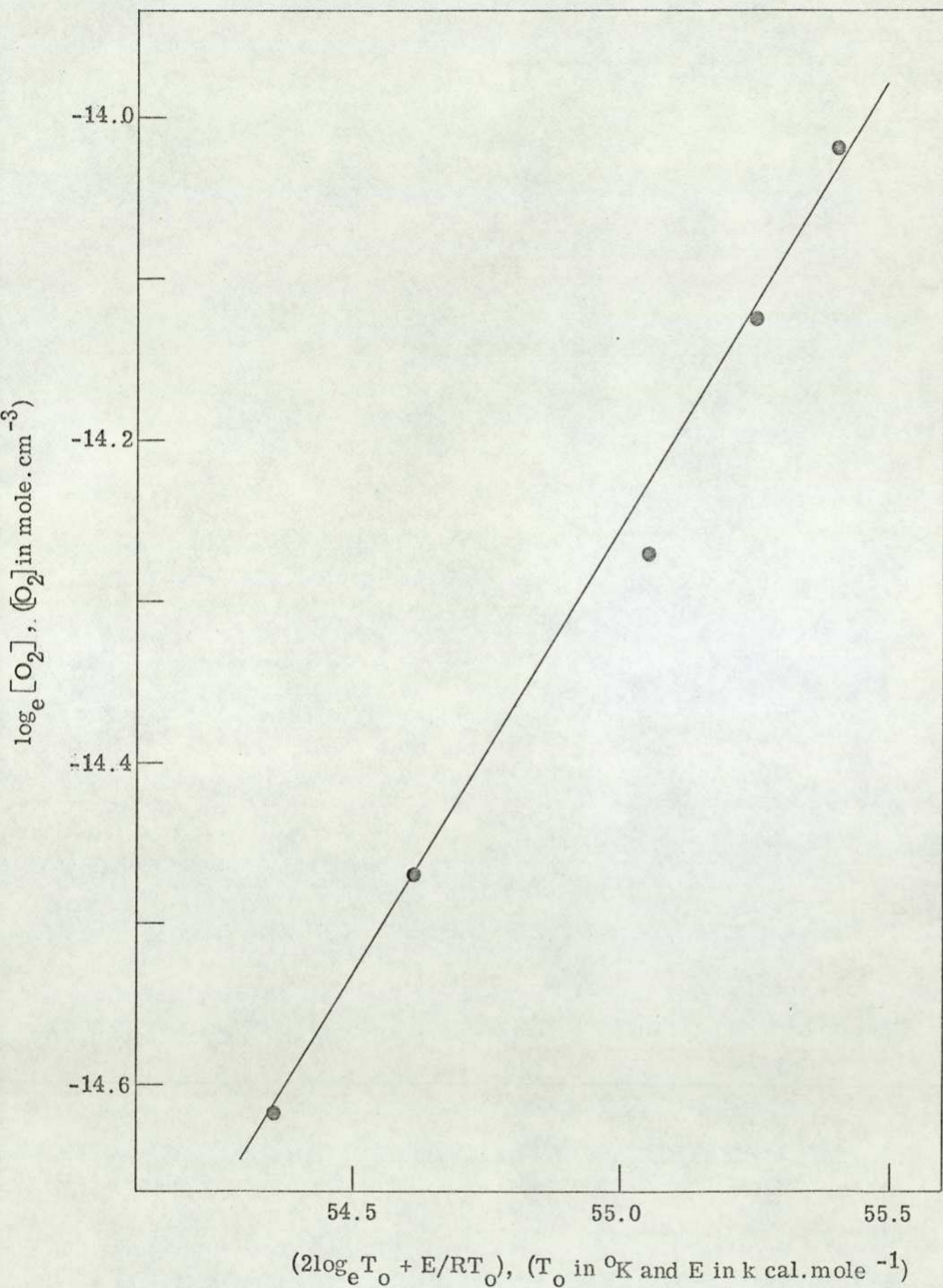
4.4.3 Direct tests of thermal ignition theory

Direct tests of thermal ignition theory may be made by direct temperature measurements in the reacting gases. Confirmation of the conductive theory of thermal ignition may be given by the presence of pre-ignition self-heating, the dependence of this self-heating on the position in the reactant relative to the vessel centre and the existence and size of a maximum stable temperature rise at the vessel centre.

Confirmation of the presence of pre-ignition self-heating in 1:15 n-decane-air mixtures has already been given in Section 4.1.5, where it was also shown that, under the initial conditions of temperature and pressure representing the slow-combustion/cool-flame boundary, purely conductive heat transfer in the reacting gases did

Figure 4.9

Variation of $\log_e [\text{O}_2]$ with $(2\log_e T_o + E/RT_o)$
for several n-decane-air mixtures



not occur below a temperature of 523°K . Furthermore, a maximum stable temperature rise of 21°K was shown to exist at the vessel centre. The temperature at other positions in the reactant decreased radially from the centre, and the tip of the resulting temperature profile was shown to approximate in shape to a parabola.

It is possible to estimate experimentally¹³⁷ the value of δ_{cr} in equation 4.8 from the measured shape of the critical temperature profile shown in figure 3.28 (a); ie. when $T_0 = 543^{\circ}\text{K}$. The parabola which best fits the centre portion of this profile is given in equation 4.17,

$$T - T_0 = 1.33 (r^2 - x^2) - 12.33 \quad (4.17)$$

In a spherical vessel, the stationary form of the equation of heat conductance with continuously distributed heat sources is given by equation 4.18,

$$-\frac{Q_w}{\lambda} = \frac{d^2T}{dx^2} + \frac{2}{x} \cdot \frac{dT}{dx} \quad 4.18$$

where x is the distance from the centre of the reactant, and other symbols have their usual significance. At the critical condition for ignition, the right-hand side of equation 4.18 may be evaluated using equation 4.17, viz:

$$\frac{dT}{dx} = -2.66x, \quad \frac{d^2T}{dx^2} = -2.66$$

Thus,

$$\left(\frac{Q_w}{\lambda}\right)_{\text{cr}} = 7.98 \text{ deg.cm}^{-2} \quad 4.19$$

corresponding to a temperature of 564°K at the centre of the reactant.

Since δ_{cr} in equation 4.8 is defined in terms of the vessel temperature, T_0 , it is necessary to make a correction to w using the Arrhenius law, where E is taken to be $44.64 \text{ k cal. mole}^{-1}$ and $T_0 = 543^{\circ}\text{K}$, and to λ . The corrected value for $(Qw/\lambda)_{\text{cr}}$ is $1.75 \text{ deg. cm}^{-2}$, whereupon

$$\delta_{\text{cr}} = 1.75 \frac{r^2 E}{RT_0^2}$$

$$= 3.35$$

in excellent agreement with Frank-Kamenetskii's theoretical value of 3.32. Thus, for a 1:15 n-decane-air mixture at an initial temperature of 543°K , the conductive theory of thermal ignition is applicable to the cool-flame limit. The extent of application of this theory to the slow combustion/cool-flame boundary in 1:15 n-decane-air mixtures has been tested by selecting pairs of values for P_{cr} and T_{cr} from figure 3.4, and calculating corresponding values of δ_{cr} . Appropriate corrections to w were made by using the Arrhenius law as above, and corrections for the change in concentration of reactants were made using the multiplication factor

$$[\text{RH}]^{0.87} [\text{O}_2]^{0.91} \text{ (i)} / [\text{RH}]^{0.87} [\text{O}_2]^{0.91} \text{ (ii)}$$

where $[\text{RH}]$ and $[\text{O}_2]$ are expressed in mole. cm^{-3} , subscripts (i) and (ii) correspond to P_{cr} under consideration and $P_{\text{cr}} = 5.9 \text{ kPa}$ respectively and 0.87 and 0.91 are the partial orders of reaction obtained from figures 4.8 and 4.9. Corrections were also made for

the variation with temperature of the thermal conductivity of the gas mixture.

The results of these calculations are given in Table 4.4, in which corresponding values of the Rayleigh number have also been included. From this table it can be seen that in the temperature range 543 to 523°K, it is necessary to alter the value of E by ca. 1.0 k cal.mole⁻¹ to achieve a value for δ_{cr} of 3.35. This is expected since it has already been calculated from figure 4.8 that a change in the value of E of 1.0 k cal.mole⁻¹ would restore linearity to the plot. Between 523°K and 498°K, δ_{cr} varies by less than 1% for E = 43.8 k cal.mole⁻¹. Thereafter, δ_{cr} increases as T_o decreases, possibly because convective heat transfer becomes important.

Frank Kamenetskii proposed¹³⁶ that above a Rayleigh number, Ra, of ca. 10^4 , δ_{cr} should be a function of Ra, and that this function should be the same for all gases. Figure 4.10 shows the variation of δ_{cr} with Ra for 1:15 n-decane-air mixtures. From this figure it can be seen that for values of Ra less than 4.0×10^3 , δ_{cr} is independent of Ra. However, for values of Ra greater than 4.0×10^3 , a linear relationship exists which is described by equation 4.20

$$\delta_{cr} = 1.0 \times 10^{-4} Ra + 2.96 \quad 4.20$$

The linearity of this relationship is understandable since, in the low temperature region of the ignition profile where P_{cr} increases markedly for only a small decrease in T_o , both δ_{cr} and Ra are

Table 4.4

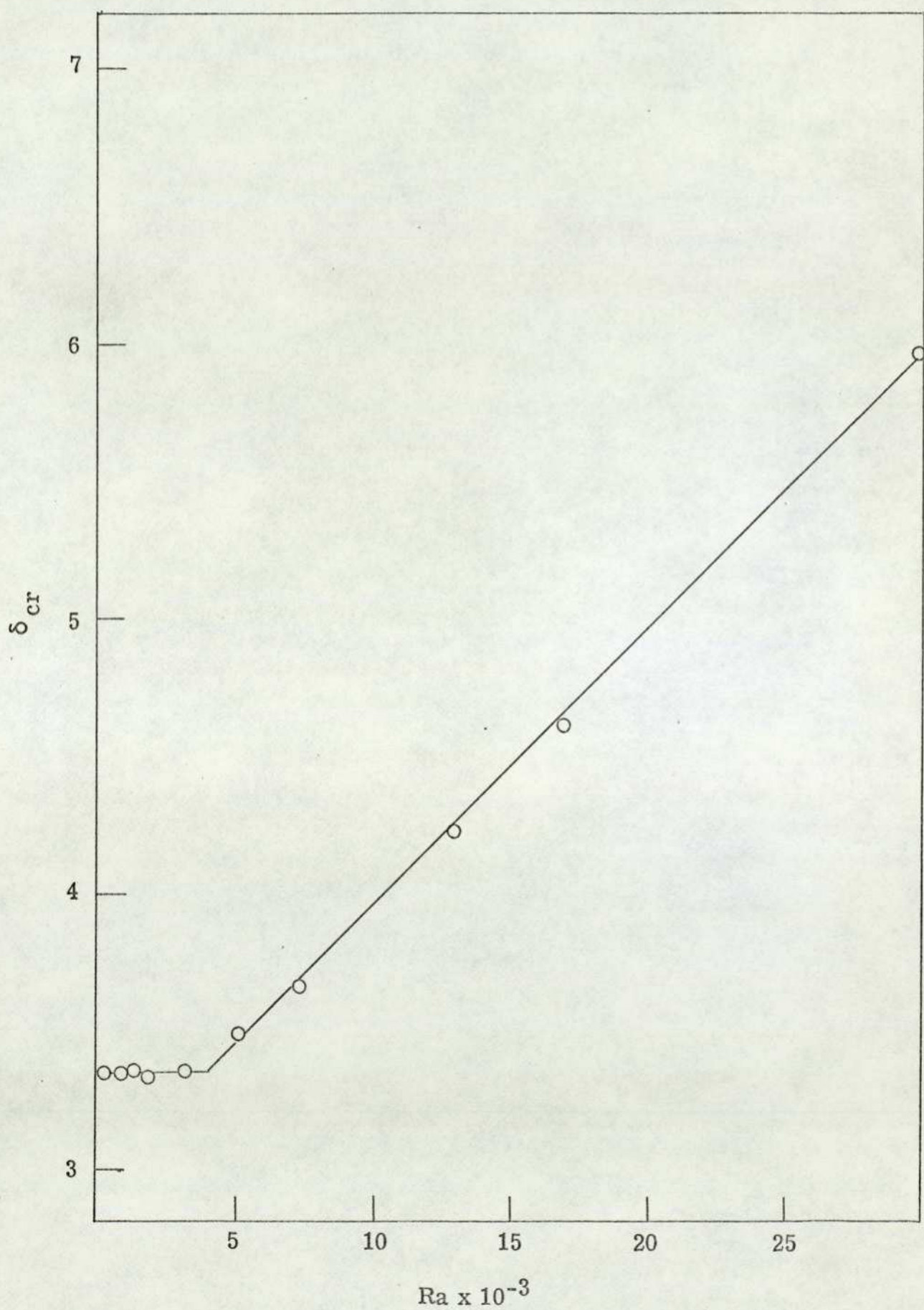
Values of E which satisfy equation 4.8, and
corresponding values of Ra.

n-decane:air = 1:15

P_{cr} (kPa)	T_{cr} (°K)	E (k cal.mole ⁻¹)	δ_{cr}	Ra
5.9	543	44.6	3.35	243
9.1	523	43.9	3.35	626
12.8	513	43.8	3.36	1275
15.0	509	43.8	3.33	1770
20.0	502	43.8	3.36	3211
25.0	498	43.8	3.50	5060
30.0	494	43.8	3.66	7355
40.0	490	43.8	4.22	13235
45.0	488	43.8	4.61	16966
50.0	485	43.8	5.98	30091

Figure 4.10

Variation of δ_{cr} with Ra for a 1:15 n-decane-air mixture



nearly proportional to the square of the density of the gas mixture.

In the case of δ_{cr} , this is brought about because $\delta_{cr} \approx \text{constant} \times [\text{RH}]^a [\text{O}_2]^b$ where the indices a and b are approximately unity.

Slow-combustion/cool-flame boundaries for the other n-decane-air mixtures have been predicted from equation 4.8. A number of values for the initial pressure, P_o , were chosen and corresponding values for the critical initial temperature, T_{cr} , were calculated by trial and error in such a way that the right-hand side of equation 4.8 was equivalent to δ_{cr} . When Ra for the gases was less than 4.0×10^3 , δ_{cr} was taken to be 3.35. However, when Ra was greater than 4.0×10^3 , δ_{cr} was calculated from equation 4.20.

In each evaluation of T_{cr} , the term

$$\left(\frac{Q_w}{\lambda}\right) (P_o = 5.9 \text{ kPa}, T_{cr} = 543^\circ \text{K})$$

in equation 4.8 was corrected using a concentration correction factor (equation 4.21)

$$1.521 \times 10^{12} [\text{RH}]^a [\text{O}_2]^b \quad 4.21,$$

an Arrhenius reaction rate correction factor (equation 4.22)

$$1.594 \times 10^{18} / \exp(E/RT_{cr}) \quad 4.22$$

where $E = 43.8 \text{ k cal.mole}^{-1}$, and a thermal conductivity correction factor (equation 4.23)

$$9.86 \times 10^{-5} / \lambda_{T_{cr}} \quad 4.23$$

The predicted values for T_{cr} for each n-decane-air mixture

are given in Table 4.5 together with the experimentally measured values. Clearly, with the exception of the lowest value for P_0 for each mixture composition, the agreement between the predicted and experimental values is excellent. The discrepancy at low pressures (high temperatures) may probably be accounted for by the small change in the value of E which was shown to take place in the temperature range 523 to 543^oK.

Thus, thermal ignition theory, based on a purely conductive heat transfer in the reacting gases, may be used in conjunction with equation 4.20 to predict accurately the variation with both mixture composition and initial pressure of the minimum temperature for spontaneous ignition in n-decane-air mixtures.

On account of limitations of the apparatus, spontaneous ignition temperatures in n-decane-air mixtures at atmospheric pressure could not be measured. However, spontaneous ignition temperatures for 1:15 n-decane-air mixtures at initial pressures of 70.0kPa, 85.0kPa and 100.0kPa (atmospheric pressure) have been calculated (bottom of Table 4.5) and are clearly quite reasonable.

4.4.4 Application of thermal ignition theory to spontaneous-ignition temperature limits of other alkanes

An attempt has been made to extend the thermal ignition model developed above for n-decane-air mixtures to make possible the prediction of the spontaneous ignition temperature limits for

Table 4.5

Some experimentally observed and predicted values of

T_{cr} for n-decane-air mixtures in the composition

range 1:7.5 to 1:25.0 n-decane : air

Mixture composition n-decane : air	P_o (kPa)	T_{cr} ($^{\circ}K$)	
		observed	predicted
1:7.5	5.7	583	526
	15.3	503	500
	26.0	494	491
	35.0	490	486
	60.0	483	481
1:10.0	7.6	523	520
	15.0	506	503
	26.0	494	492
	39.2	488	486
	60.0	483	482
1:20.0	6.2	543	537
	15.2	513	510
	25.0	501	498
	37.8	493	491
	60.0	488	485
1:25.0	8.0	541	534
	17.0	513	510
	28.0	500	496
	37.0	496	494
	60.0	490	487
1:15.0	70.0	-	482
	85.0	-	481
	100.0	-	480

other alkanes of different molecular weight and molecular structure. The assumption was made that Q , a and b in equations 4.8 and 4.8 (a) do not vary significantly with the molecular weight and structure of the alkane. The overall activation energy, E , for cool-flame combustion has been chosen as the parameter most characteristic of the ignitability of an alkane. (It was shown (Section 4.1.3) that E increases with decreasing ignitability of alkanes.) For the purpose of calculating E , four general classes of alkane structure have been defined, viz:

Class I	$\text{CH}_3 (\text{CH}_2)_n \text{CH}_3$
Class II	$(\text{CH}_3)_2 \text{CH} (\text{CH}_2)_n \text{CH}_3$
Class III	$(\text{CH}_3)_2 \text{CH} (\text{CH}_2)_n \text{CH} (\text{CH}_3)_2$
Class IV	$(\text{CH}_3)_3 \text{C} (\text{CH}_2)_n \text{CH} (\text{CH}_3)_2$

Values of E for alkanes of different molecular weight have been calculated as outlined below for each of the four classes given above.

Slow combustion/cool-flame boundaries for several alkanes of different molecular weight and molecular structure were obtained from the literature or from results reported herein. In each calculation a pair of values of T_{cr} and P_{cr} lying on a slow-combustion/

cool-flame boundary were selected and the concentration correction factor (equation 4.21) was applied. A value for E was then found by trial and error so that, after application of the reaction rate correction factor (equation 4.22), and thermal conductivity correction factor (equation 4.23) equation 4.8 was satisfied. When Ra for the gas mixture was greater than 4.0×10^3 , δ_{cr} in equation 4.8 was calculated from equation 4.20; otherwise it was taken to be 3.35. Thus, the assumption was made that equation 4.20 applies to all the alkane-air or alkane-oxygen mixtures as proposed by Frank-Kamenetskii¹³⁶.

The Rayleigh number of the gas mixture was calculated as described in Section 4.1.5 where Brokaw's rule¹²⁹ was used to estimate C_p and λ and Wilke's estimation method¹³⁰ was used to calculate η . In these calculations, literature values at the appropriate temperature of η ¹³⁸, C_p ¹³⁸ and λ ¹³⁹ were used for the alkane under consideration.

The alkanes considered, together with the corresponding calculated value of E , are given in Table 4.6. It is noteworthy that the values of E calculated for isobutane and n-pentane are in reasonably good agreement with the reported values of $56 \text{ k cal.mole}^{-1}$ ¹²⁴ and $49 \text{ k cal.mole}^{-1}$ ¹¹⁴ respectively, which were calculated from induction period data.

For alkanes having a molecular structure in class I, II, or III, E was found to vary by less than 2% over a considerable portion of the slow-combustion/cool-flame boundary. Thus, equation

Table 4.6

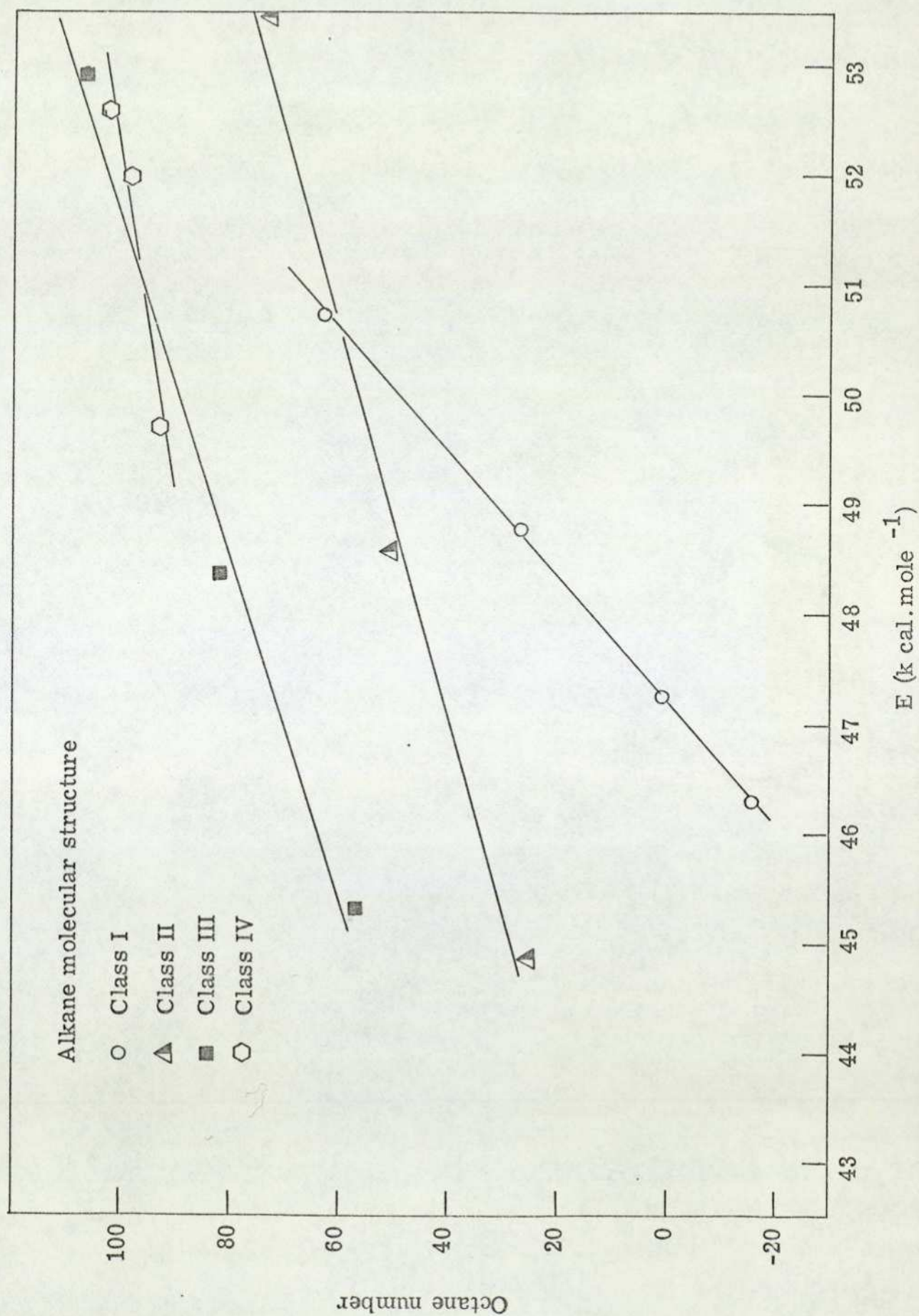
Values of E calculated for alkanes of different
molecular weight and molecular structure

Molecular structure	alkane - oxidant	P _{cr} (kPa)	T _{cr} (°K)	E (k cal.mole ⁻¹)	Reference
Class I	n-butane - O ₂	16.6	558	50.8	123
	n-pentane - O ₂	6.6	558	48.8	114
	n-heptane - air	13.3	538	46.3	64
	n-decane - air	12.8	513	43.8	this work
Class II	isobutane - O ₂	20.0	595	53.5	113
	2-methylpentane - O ₂	13.3	553	48.6	140
	2-methylheptane - air	20.0	521	44.9	this work
Class III	2,3-dimethylbutane - O ₂	30.0	572	52.9	92
	2,4-dimethylpentane - air	41.3	560	48.4	this work
	2,5-dimethylhexane - air	20.0	522	45.1	this work
Class IV	2,2,3-trimethylbutane - O ₂	22.0	578	52.6	this work
	"	60.0	547	51.2	this work
	2,2,4-trimethylpentane-air	76.0	570	51.9	this work
	"	100.0	559	50.3	this work
	2,2,5-trimethylhexane-air	36.0	558	49.2	this work
	"	62.0	528	47.5	this work

4.20 is applicable at least to gas mixtures containing air or pure oxygen and a reasonably volatile alkane having a molecular structure in class I, II or III. For alkanes having a molecular structure in class IV, E has been found to vary slightly with the initial conditions of temperature and pressure. Thus, Table 4.6 shows values for E which were calculated at the low and high pressure extremes of the appropriate slow-combustion/cool-flame boundary.

The variation of octane number, ON, with E for a number of alkanes having a different molecular structure is shown in figure 4.11. It is clear from this figure that different straight-line relationships exist for each class of molecular structure, and that the dependence of ON on E decreases with increasing degree of branching of the carbon chain. For each class of molecular structure, ON increases with increasing E, in agreement with the results of Oberdorfer's studies of the combustion of isomeric hexanes¹²⁶.

Figure 4.11
Variation of E with octane number and
alkane molecular structure



4.4.5 Development of a computer programme for the prediction of the slow-combustion/cool-flame boundaries of low molecular weight alkanes

On the basis of the thermal ignition model developed in Section 4.4.4, a computer programme has been devised which enables the prediction of the spontaneous ignition temperature limits for reasonably volatile alkanes. In principle, an initial pressure, P , is defined and the corresponding limiting temperature, T , for spontaneous ignition is found by an iterative routine. The only input data required to operate the programme is the carbon number and molecular structure class of the alkane, the nature of the oxidant and the composition of the gas mixture, and the size and shape of the reaction vessel.

Physical properties of the gas mixture and appropriate kinetic parameters are calculated in the programme as functions of appropriate input parameters as described below.

Overall activation energy, E

E is calculated as a function of the carbon number, CN , of the alkane for a specified class of molecular structure. The appropriate equations are:

$$\text{Class I} \quad E = 70.17 - 7.81CN + 0.88CN^2 - 0.036CN^3 \text{ kcal.mole}^{-1}$$

$$\text{Class II} \quad E = 72.72 - 7.25CN + 0.74CN^2 - 0.034CN^3 \text{ kcal.mole}^{-1}$$

$$\text{Class III} \quad E = 166.82 - 38.99CN + 4.42CN^2 - 0.181CN^3 \text{ kcal.mole}^{-1}$$

$$\text{Class IV} \quad E = 440.68 - 152.4CN + 19.94CN^2 - 0.873CN^3 \text{ kcal.mole}^{-1}.$$

Thermal conductivity, λ

The thermal conductivities of oxygen and nitrogen vary with temperature in a manner described by equations 4.24 and 4.25 respectively:

$$\lambda_{O_2} = (0.016T + 1.732) \times 10^{-5} \text{ cal. (cm. sec. } ^\circ\text{K)}^{-1} \quad 4.24$$

$$\lambda_{N_2} = (0.013T + 2.696) \times 10^{-5} \text{ cal. (cm. sec. } ^\circ\text{K)}^{-1} \quad 4.25$$

The thermal conductivities of the alkanes were taken from the literature¹³⁹. For alkanes containing an even number of carbon atoms the thermal conductivity is given by equation 4.26:

$$\lambda_{\text{alkane}} = (0.008T + 6.75 - 0.28CN) \times 10^{-5} \text{ cal. (cm. sec. } ^\circ\text{K)}^{-1} \quad 4.26$$

For alkanes containing an odd number of carbon atoms, the thermal conductivity is given by equation 4.27:

$$\lambda_{\text{alkane}} = (0.028T - 2.5 - 0.05CN) \times 10^{-5} \text{ cal. (cm. sec. } ^\circ\text{K)}^{-1} \quad 4.27$$

Heat capacity at constant pressure, C_p

The heat capacities of oxygen and nitrogen vary with temperature according to equations 4.28 and 4.29 respectively:

$$C_{p(O_2)} = (29977.5 + 4.1868T - 1674.7 \times 10^5 / T^2) / 1.34 \times 10^5 \text{ cal. (deg. gm.)}^{-1} \quad 4.28$$

$$C_{p(N_2)} = (27884.1 + 4.2705T) / 1.17 \times 10^5 \text{ cal. (deg. gm.)}^{-1} \quad 4.29$$

Values of C_p for alkanes were obtained from the literature¹³⁸. For alkanes having a molecular structure in classes I to IV, C_p is calcul-

ated from equations 4.30 to 4.33 respectively:

$\left[(0.012CN + 0.009)T + 1.02CN^{1.32} \right] / M$	cal .(deg.gm) ⁻¹	4.30
$0.096CN^{0.96}T^{0.73} / M$	cal .(deg.gm) ⁻¹	4.31
$0.488T^{0.75} / M$	cal .(deg.gm) ⁻¹	4.32
$0.521T^{0.76} / M$	cal .(deg.gm) ⁻¹	4.33.

where M is the molecular weight of the alkane under consideration.

Viscosity, η

In the temperature range 470 to 570°K, the variation with temperature of the viscosity of oxygen and nitrogen is given by equations 4.34 and 4.35 respectively:

$$\eta_{O_2} = 0.414T + 204.7 \quad \mu\text{poise} \quad 4.34$$

$$\eta_{N_2} = 0.355T + 174.3 \quad \mu\text{poise} \quad 4.35$$

where T is measured in °C.

The variation with temperature of the viscosity of alkanes was obtained from the literature¹³⁸, and equation 4.36 was derived to account for the variation of η with both CN and T (°C), viz:

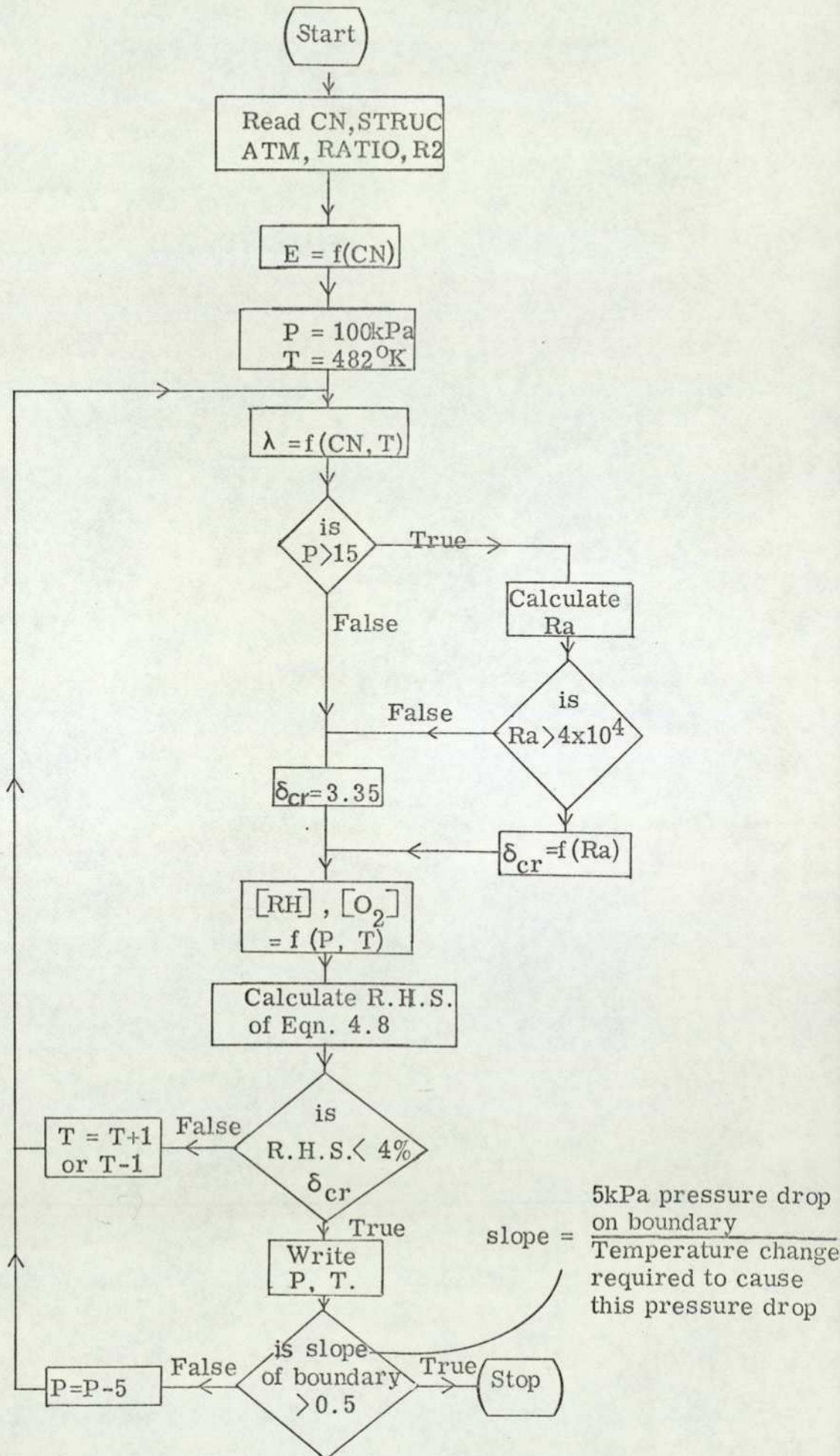
$$\eta_{\text{alkane}} = (0.3 - 0.017CN)T + 116.3 - 17.8CN + 1.67CN^2 - 0.06CN^3$$

μpoise 4.36

The computer programme has been compiled in FORTRAN 4 language and a flowchart describing the operation of the programme is given in figure 4.12. Copies of the programme and a typical output are given in the Appendix. The programme has been used to predict the minimum autoignition temperatures at atmospheric pressure

Figure 4.12

Flowchart of the computer programme



and the low-temperature portion of the slow-combustion/cool-flame boundaries of a number of alkanes. The predicted and observed results are compared in figures 4.13 to 4.16. Clearly, for all the alkanes under consideration, there is satisfactory agreement between predicted and observed results at high pressures. For isobutane and other alkanes having a highly branched carbon chain, there is less satisfactory agreement between the predicted and observed slow-combustion/cool-flame boundaries. It is likely, therefore, that, for these alkanes, E increases significantly with temperature in the low portion of the ignition profile.

Thus, the thermal ignition model developed above explains quite well the variation of the spontaneous-ignition temperature limits of alkanes with both pressure and mixture composition. It is well known that the ignition of an alkane in oxygen occurs as a result of interdependent chain-branching and exothermic processes, and that thermal explosion takes place only when the rate of reaction and, hence, of heat liberation, are high enough for chain-autoacceleration to be replaced by thermal autoacceleration⁷⁴. At low initial pressures, however, reactions leading to cool flames are mainly thermally controlled.

The thermal-ignition model does not, of course, consider in absolute terms degenerate chain-branching as a contributory cause of spontaneous ignition. Because of this, the model cannot explain either the appearance of small pressure lobes on the boundary separating slow-combustion from cool flames, or the existence

Figure 4.13

Observed and predicted spontaneous ignition temperature
limits for alkanes of Class I molecular structure

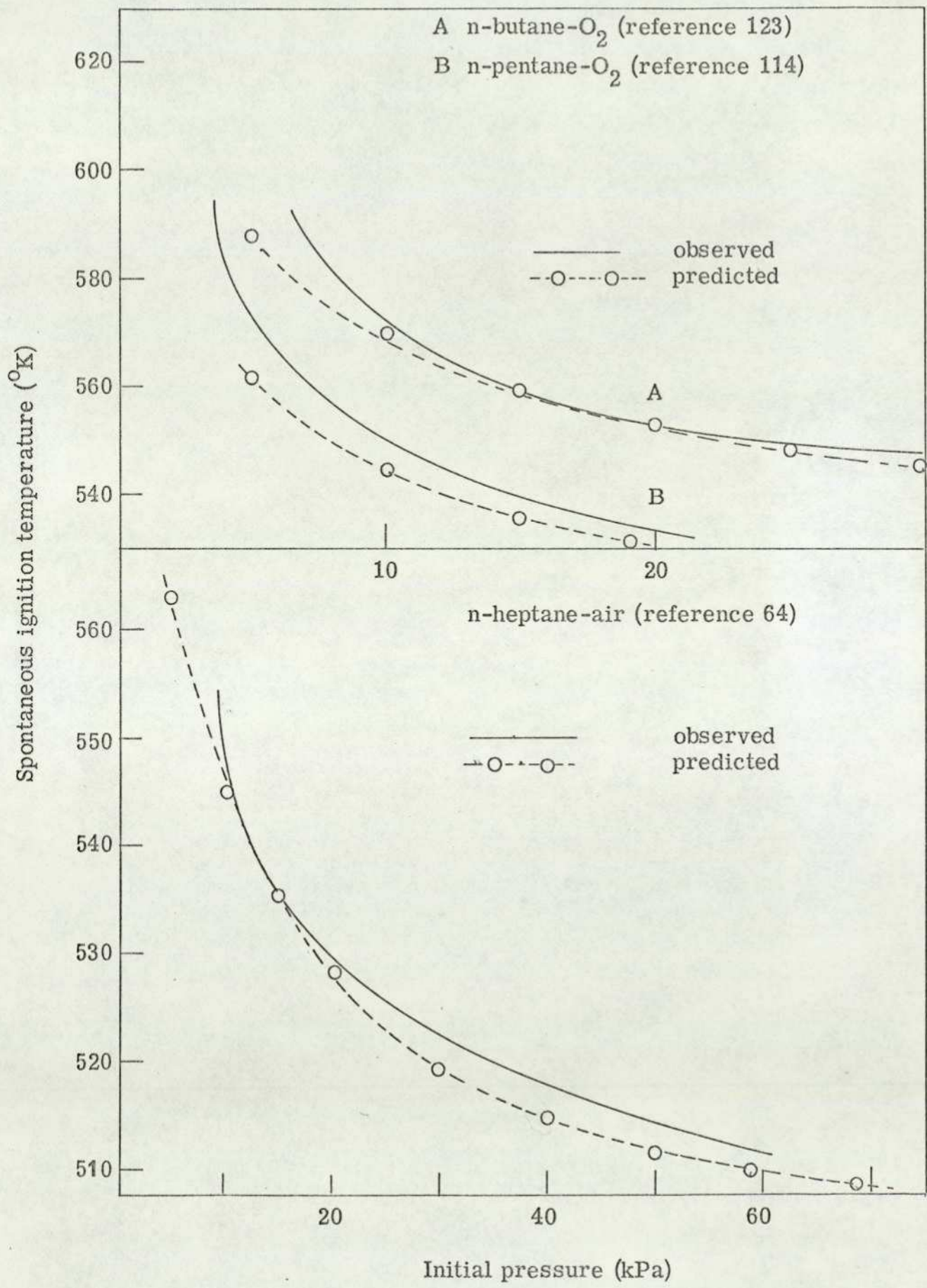
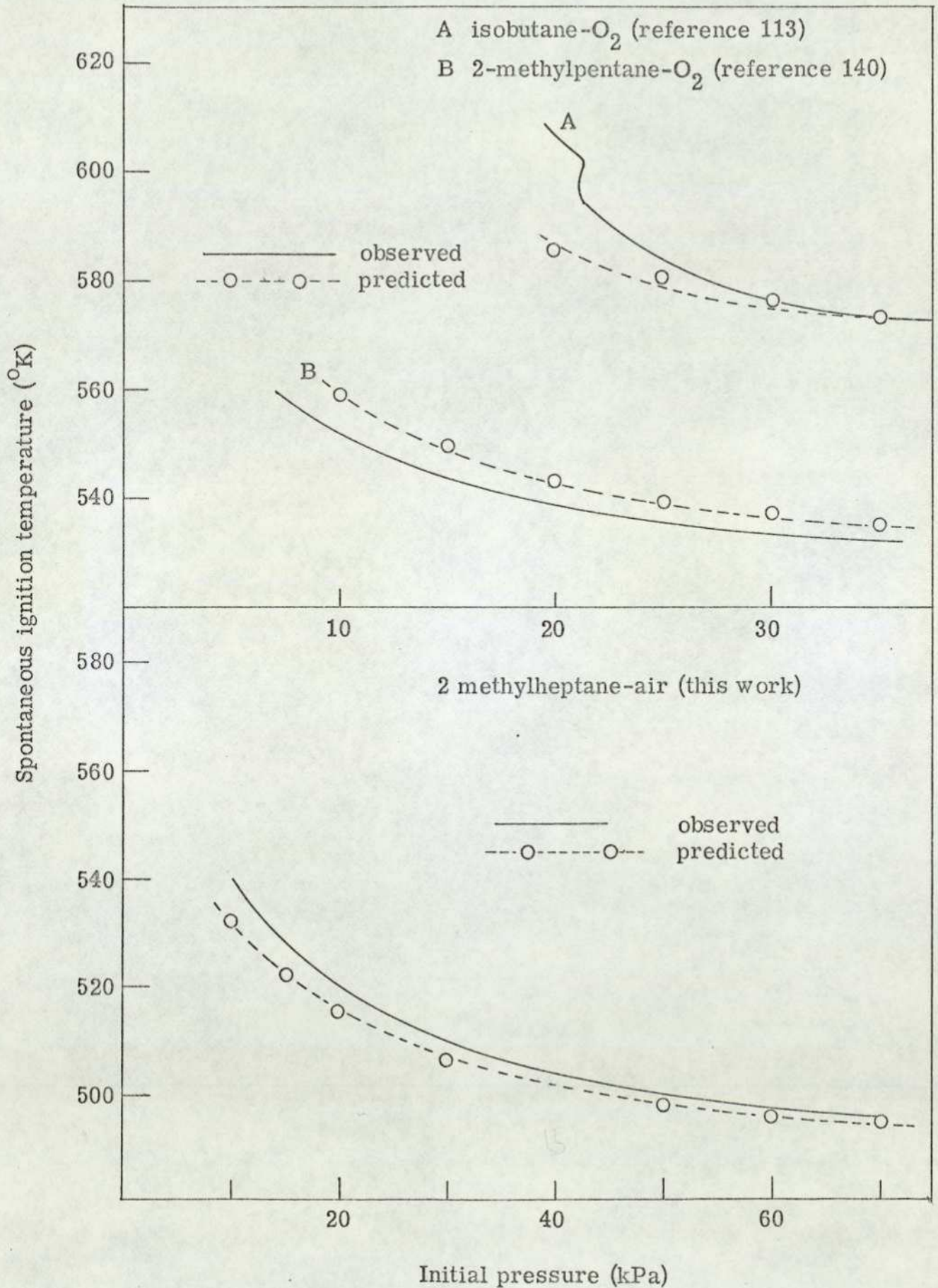


Figure 4.14

Observed and predicted spontaneous ignition temperature
limits for alkanes of Class II molecular structure



Observed and predicted spontaneous ignition temperature
limits for alkanes of Class III molecular structure

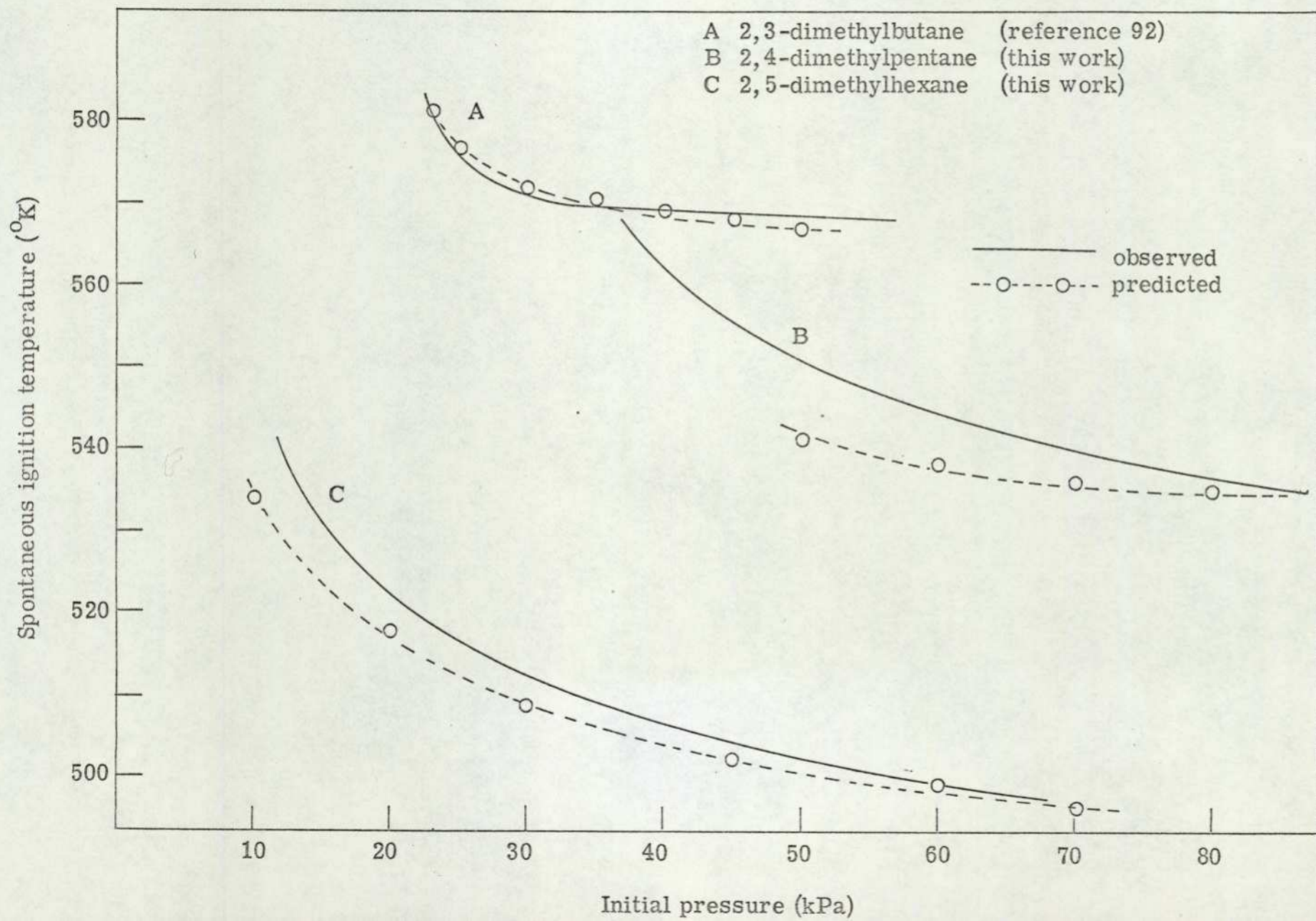
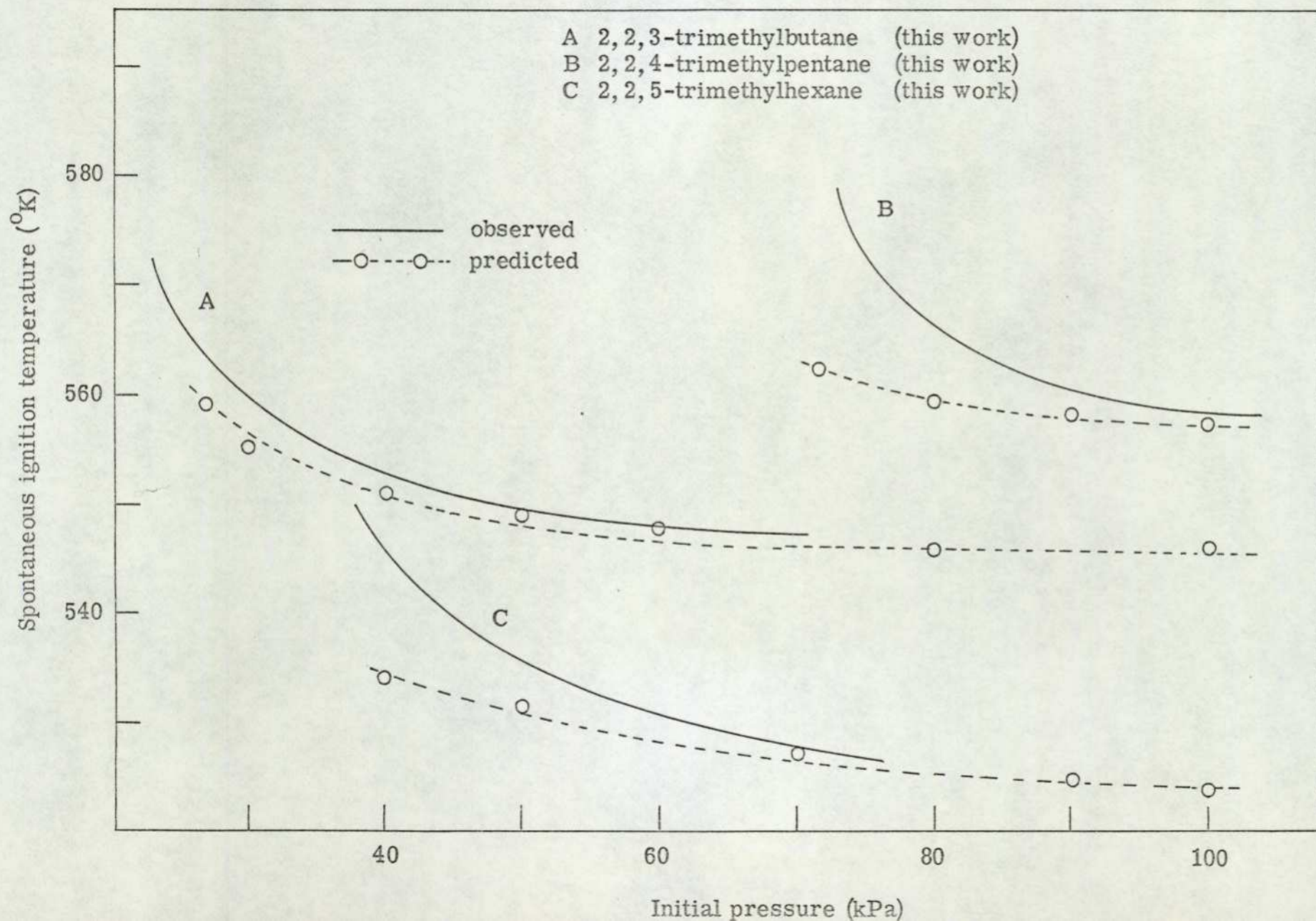


Figure 4.16

Observed and predicted spontaneous ignition temperature
limits for alkanes of Class IV molecular structure



of regions of negative temperature coefficient. The model does, however, distinguish between the ignitability of alkanes by considering the variation of E , which is probably related to the chain-branching process, with molecular structure and molecular weight.

The critical condition for spontaneous ignition in long cylindrical vessels and between long parallel plates (symmetrically heated) has been shown^{97,98} to be attained when δ_{cr} in equation 4.8 is equal to 2.00 and 0.88 respectively. Thus, the spontaneous-ignition limits of alkanes contained in such vessels may be predicted by insertion of the appropriate value for δ_{cr} in equation 4.8. Equation 4.20 relating δ_{cr} to Ra should hold for these vessels, but the value of Ra at which convection becomes significant will probably be correspondingly smaller than the value of 4.0×10^3 for a spherical vessel.

4.4.6 The application of thermal ignition theory to asymmetrically heated n-decane-air mixtures

For n-decane-air mixtures in contact with a hot tube contained in a cooler spherical vessel, spontaneous ignition has been shown to occur (Section 4.3.1) when a more or less constant amount of heat is supplied to the gas mixture. The minimum tube temperature required to cause spontaneous ignition in n-decane-air mixtures at an initial pressure of 55kPa was found to be dependent on the vessel temperature and the tube diameter. The radius of the spherical vessel is also probably a determining parameter.

Clearly, with an initial pressure of 55kPa, even small differences in temperature between the tube and sphere will give rise to significant natural convection. In some cases, this temperature difference was greater than 100°K and under these conditions extensive natural convection currents will exist. In view of this, thermal ignition theory based on a purely conductive heat transfer in the reacting gas cannot be expected to give a satisfactory account of the variation with vessel temperature, T_o , and tube diameter, d_1 , of the minimum tube temperature, T_i , required to cause spontaneous ignition of the gas mixture.

Semenov's equation⁹⁴ based purely on conductive heat transfer

$$r_1 \ln \frac{r_2}{r_1} = \left[\frac{E (T_i - T_o)^2}{2 R T_i^2 Q W} \right]^{\frac{1}{2}} \quad 4.37$$

defines the conditions for spontaneous ignition in a flammable gas mixture contained in a cylindrical annulus, where the inner cylinder is hotter than the outer cylinder. In equation 4.37,

T_i = inner cylinder temperature, $^{\circ}\text{K}$.

T_o = outer cylinder temperature, $^{\circ}\text{K}$.

r_1 = inner cylinder radius, cm.

r_2 = outer cylinder radius, cm.

and other symbols have their usual significance. Semenov demonstrated that equation 4.37 holds provided that r_1 is less than 1 mm. For values of r_1 greater than 1 mm, natural convection was shown to be significant and Semenov proposed⁹⁴ that the inner cylinder is surrounded by a cylindrical laminar gas layer of radius r' within which heat is transferred by conduction. The outer boundary of this layer was assumed to be at a temperature T_o . The left-hand side of equation 4.37 was subsequently modified to

$$r_1 \ln \frac{r'}{r_1} = r_1 \frac{2}{Gr}$$

where Gr is the Grashoff number of the gas. Macdonald¹³⁴ found that the modified form of equation 4.37 did not correlate satisfactorily with the results of his studies of the ignition of aviation kerosene by hot pipes. These studies did, however, reveal that the bulk of the gas mixture surrounding the hot pipe reaches a temperature between

that of the tube and spherical vessel, and that a laminar layer of gas surrounding the pipe was, for practical purposes, non-existent. It is possible that the average bulk temperature of the gas mixture is close to its minimum autoignition temperature corresponding to the experimental conditions (ie. vessel size and initial gas pressure).

Thus, in Macdonald's studies of spontaneous ignition caused by hot pipes¹³⁴, and similar studies reported herein, it is likely that ignition developed within the bulk of the gas rather than at the hot tube or pipe surface. It is possible, therefore, that the critical conditions for spontaneous ignition in the hot-tube-in-a-sphere studies may be predicted from an equation similar to equation 4.8, where δ_{cr} is calculated as a function of the Rayleigh number of the gas as in equation 4.20. Such an approach has been attempted and is described below.

In calculations of the Rayleigh number of the gas, ΔT has been taken to be the temperature difference between the tube and the sphere, and the characteristic dimension of the system, d , has been taken to be the difference between the diameters of the sphere and tube ($d_2 - d_1$). Physical properties of the gas mixture have been estimated at a temperature which is the arithmetic mean of T_i and T_o .

Equation 4.8 has been modified to give equation 4.38:

$$\delta_{cr} = f(Ra)_{(d=d_2-d_1, \Delta T=T_i-T_o)} = \frac{Q w E r_1^2}{\lambda R T_i^2} \quad 4.38$$

in which r_1 is the tube radius and other symbols have their usual significance. The concentrations of n-decane and oxygen in the mixture have been calculated at the arithmetic mean temperature defined above.

For a given vessel temperature and tube radius, T_i was calculated by trial and error until equation 4.38 was satisfied. In these calculations, the concentration correction factor (equation 4.21) and Arrhenius reaction rate correction factor (equation 4.22) were applied as described in Section 4.4.3. In the latter equation, T_i was substituted for T_{cr} .

The predicted values of T_i together with some experimentally observed values are given in Table 4.7 for each of the tubes and for several vessel temperatures. For the 0.64 cm., 0.97 cm. and 1.18 cm. diam. tubes the predicted values are within 2% of the observed values for vessel temperatures less than 453°K. The discrepancy between the predicted and observed values of T_i for the 2.4 cm. diam. tube is on the whole greater than for the other tubes. This may be the result of a significant increase in surface/volume ratio of the system with the latter tube.

Clearly, within the range of experimental conditions used in these studies, equation 4.38 predicts quite well the variation of T_i with T_o and tube diameter. The choice of r_1 as the characteristic dimension in equation 4.38 and of $(d_2 - d_1)$ as the characteristic dimension in calculating Ra was purely empirical. The substitution of T_i for T_{cr} in equation 4.21 was also empirical.

Equation 4.38 has been used in an attempt to predict the results obtained by Macdonald in his studies of the ignition of aviation

Table 4.7

Variation of predicted and observed values
of T_i with vessel temperature and tube diameter.
n-decane : air = 1:15; initial pressure = 55kPa

tube diam. (cm)	vessel temp. (°K)	minimum tube temperature for ignition (°K)	
		Observed	Predicted
0.64	373	6201	617
	393	615	615
	423	607	611
	453	586	607
0.97	423	598	598
	433	593	598
	443	586	591
	453	576	588
1.18	423	592	586
	433	588	584
	443	579	581
	453	566	580
2.40	373	588	562
	443	556	552
	473	520	542

kerosene by hot pipes contained in an 18 in. diam. spherical vessel¹³⁴. The value of E for aviation kerosene was taken to be $43.8 \text{ kcal. mole}^{-1}$, the same as for *n*-decane. The predicted values of T_i are compared with the observed values in Table 4.8. From this table it can be seen that for the 15.2 cm and 7.6 cm diam. pipes, there is a reasonably good agreement between the predicted and observed values of T_i . For the 3.8 cm. diam. and 1.9 cm. diam. pipes there is a large discrepancy between the observed and predicted values of T_i for the lower vessel temperature. This is understandable since the insertion of large values for T_i (viz. 728°K) in the Arrhenius reaction rate correction factor lead to extremely large values for the right-hand side of equation 4.37. These values are several hundred times the value of δ_{cr} calculated from equation 4.20.

Clearly T_i is not an important parameter in determining the rate of heat release preceding spontaneous ignition, and its use as a substitute for T_{cr} in equation 4.21 is limited. This provides further evidence that it is necessary to raise the bulk of the gas mixture to a certain temperature before spontaneous ignition can occur. Nevertheless, as was shown in Section 4.3.2 and 4.3.3, small changes in tube temperature at constant vessel temperature exert a strong influence on kinetic parameters such as the induction period preceding spontaneous ignition and the maximum rate of pressure rise accompanying ignition.

Thus, it may be concluded that, whilst the temperature of the tube probably plays an important role in initiating the reactions

Table 4.8Variations of predicted and observed valuesof T_i with vessel temperature and pipe diameter.kerosene : air = 1:15; initial pressure = 100kPa (1 at m.)

Pipe diam. (cm)	Vessel temp. (°K)	minimum pipe temperature for ignition (°K)	
		Observed	Predicted
1.90	373	923	673
	453	603	612
3.81	373	728	641
	413	623	634
7.62	373	613	607
	423	589	599
15.24	373	580	571
	423	568	568

preceding spontaneous ignition, ignition is unlikely to occur unless the bulk temperature of the gas has attained a certain value. When this temperature has been reached, the rate of heat release from a volume element of the gas mixtures presumably exceeds the rate of heat loss to the surrounding gas and ignition ensues. Similar conclusions were drawn by Macdonald¹³⁴.

Clearly, the method used to predict the conditions for ignition in a hot-tube-in-a-sphere falls short in that it is not on an entirely fundamental basis. However, the complex geometry of such a system does not lend itself to a theoretical treatment, since it lacks an appropriate characteristic dimension and 'end effects' where the tube and sphere are in contact are difficult to take into account.

4.5 Conclusions

n-Decane is a very reactive alkane which undergoes spontaneous ignition in air at temperatures above ca. 480°K and displays cool-flame phenomena at pressures greater than 5kPa. n-Decane-air mixtures exhibit two lobes on the two-stage ignition profile. Kinetic data obtained from pressure-time traces indicate that, in accordance with Lucquin's theory, the lower temperature lobe is associated with an L_1 mechanism and the higher temperature lobe with an L_2 mechanism. The overall activation energy for cool-flame combustion, E , changes at a temperature midway between lobes L_1 and L_2 and is thought to be related to the chain-branching reactions. n-Decane-air mixtures display a two cool-flame region in the temperature range defined by the L_2 lobe.

The ignitability of a number of alkanes decreases in the order n-decane > 2-methylheptane > 2, 5, -dimethylhexane > 2, 2, 5-trimethylhexane > 2, 4-dimethylpentane > 2, 2, 4-trimethylpentane > 2, 2, 3-trimethylbutane. The minimum stability factor calculated for these hydrocarbons increases in the reverse order. It thus appears that the ignitability of an alkane depends on the overall stabilizing effect which the molecule exerts on a hydroperoxide group attached to the carbon atom where the stability factor as a whole is a minimum.

The ignitability in air of fuel mixtures containing n-decane and 2, 2, 5-trimethylhexane is controlled largely by n-decane. In the low temperature region of the ignition profile, the value of E

decreases with increasing 2, 2, 5-trimethylhexane concentration. It is thought that the nonane isomer, which contains a relatively labile hydrogen atom, increases the rate of formation of n-decylhydroperoxides which are probably important chain-branching agents at low temperatures.

Partial replacement of n-decane in the fuel by 2, 2, 5-trimethylhexane has little effect on the position of the 2 cool-flame region in the ignition profile. It is thought likely that similar products of the first cool flame for both these alkanes play an important role in reactions leading to the second cool flame. Consequently, multiple cool-flame phenomena in n-decane and 2, 2, 5-trimethylhexane are probably described by Frank-Kamenetskii's isothermal, two-product theory.

Temperature measurements in reacting n-decane-air mixtures under initial conditions close to the slow-combustion/cool-flame boundary indicate that convective heat transfer becomes significant when the Rayleigh number, Ra , of the gas exceeds a value of ca. 600. At an initial temperature of 543°K , the conductive theory of thermal ignition holds. A maximum stable temperature rise at the centre of the vessel, ΔT_{cr} , can be attained, and a value for E , calculated from the equation $E = 1.6RT_{\text{cr}}^2 / \Delta T_{\text{cr}}$, is in good agreement with the value calculated from induction period data. At an initial temperature of 543°K , reactions leading to cool flame near the boundary with slow combustion are controlled mainly thermally, and the calculated value for Frank-Kamenetskii's δ_{cr} is 3.35, which is

in excellent agreement with the theoretical value of 3.32.

The conductive theory of thermal ignitions predicts the slow-combustion/cool-flame boundary for n-decane-air mixtures for which Ra does not exceed a value of 4.0×10^3 . When Ra is greater than this convective heat transfer is important and δ_{cr} is a function of Ra . This function also applies to other alkane-oxidant mixtures. The overall activation energy has been found to be a parameter characteristic of the ignitability of an alkane. A computer programme, based on thermal ignition theory and the variation of E with alkane molecular weight and molecular structure, predicts the autoignition temperatures and slow-combustion/cool-flame boundaries for alkanes with a carbon number not greater than ten. A minimum of input data is required to operate the programme and predicted results are in good agreement with those observed for alkanes which do not have a highly branched carbon chain. The programme does not take into account the variation of E with temperature and cannot, therefore, explain the appearance of small pressure lobes on the slow-combustion/cool-flame boundaries of some alkanes.

Spontaneous ignition in n-decane-air mixtures surrounding a hot-tube-in-a-sphere appears to depend upon the supply of a critical amount of heat to the gas mixture. Kinetic parameters, such as the induction period preceding spontaneous ignition are very sensitive to small changes in tube temperature. It is likely, therefore, that the chain reactions leading to spontaneous ignition are

initiated at the tube surface. However, the application of thermal ignition theory to the hot-tube-in-a-sphere system indicates that ignition will not occur unless the bulk temperature of the gas has reached a critical value. When this temperature is attained, it is probable that the rate of heat release from a volume element of reacting gas exceeds the rate of heat loss to the bulk of the gas mixture and ignition may then spread throughout the reactant volume.

4.6 Future Work

As a result of predictions derived on the basis of a thermal ignition model of n-decane combustion, it has been concluded that E , the overall activation energy, is a parameter characteristic of the ignitability of an alkane. It would be desirable to be able to calculate E independently for other alkanes from induction period data and pre-ignition temperature rises, and then to compare these calculated values with the predicted ones. Temperature measurements need to be made in convection-free systems and it would therefore be necessary to study alkanes which exhibit cool flames at initial pressures of less than ca. 10 kPa. Any discrepancies between measured and predicted values of E may be due to the unwarranted assumption made in this work that Q for the preflame reactions does not vary significantly with alkane molecular weight or structure. The validity of this assumption could therefore be checked by carrying out analysis of the products. Such measurements would have to be made during the slow combustion reactions preceding cool flames at the boundary with slow combustion for a number of alkanes, including n-decane. From the results of these analyses, Q could be calculated and the degree of variation with alkane molecular weight and structure could be determined. Use of appropriate values for E and Q would enable the validity of the relationship between λ_{cr} and Ra to be checked.

Thermal ignition theory could clearly form a most useful and convenient basis for calculating the conditions required for ignition in asymmetrically heated flammable gas mixtures. Temper-

ature measurements in the reacting gases would help to establish whether or not the criterion for ignition is that the temperature of the bulk of the gas should be raised above a critical value. It would be best to carry out these studies in cylindrical vessels containing heated tubes passing along their axes, as such a system would be simpler to treat from the point of view of thermal ignition theory. A check could also be made on the applicability to asymmetrically heated systems of the relationship between δ_{cr} and Ra .

APPENDIX

The computer programme which was developed to predict spontaneous ignition temperature limits for low molecular weight alkanes (Section 4.4.5) is shown below. Examples of the predicted data for alkanes of each type of molecular structure are also given. The corresponding input data (see beginning of programme for coding) is given on the pages preceding the programme.

INPUT DATA

$$\text{n-Heptane : air} = 1 : 10$$
[illegible]

2-methylheptane : air = 1 : 15

[illegible]


```

MASTER PHD1
DIMENSION TO(100)
C N= THE NUMBER OF ALKANES UNDER CONSIDERATION
C CN= THE CARBON NUMBER OF THE ALKANE
C STRUC=1 TYPE (CH3).(CH2)N.CH3
C STRUC=2 TYPE (CH3).CH.(CH2)N.CH3
C STRUC=3 TYPE (CH3)2.CH.(CH2)N.CH.(CH3)2
C STRUC=4 TYPE (CH3)3.C.(CH2)N.CH.(CH3)2
C ATM=1 IF OXIDANT IS OXYGEN, 2 IF OXIDANT IS AIR.
C RATIO = MOLES OXYGEN/ MOLES ALKANE.
C R2 = THE RADIUS OF THE SPHERICAL REACTION VESSEL (CM.)
C Z=1 IF THERE ARE AN EVEN NUMBER OF CARBON ATOMS IN ALKANE, AND 2
C IF THERE AN ODD NUMBER OF CARBON ATOMS IN ALKANE
READ(1,55)N
55 FORMAT(15)
DO 99 J=1,N
I=1
READ(1,5)CN,STRUC,ATM,RATIO,R2
5 FORMAT(5F10.1)
WRITE(2,201)
201 FORMAT(1H1,10X,58HSPONTANEOUS IGNITION TEMPERATURE LIMITS BY
1C.D.FOSTER///14X,50HA PROGRAMME BASED ON THERMAL IGNITION TH
2EORY///)
R=1.987
WRITE(2,202)R2
202 FORMAT(1H ,31X,16HVESSEL RADIUS = ,F4.1,4H CM.)
KCN=CN
WRITE(2,203)KCN
203 FORMAT(1H0,24X,23HALKANE CARBON NUMBER = ,I3)
IF(STRUC.EQ.1.0)GOTO30
IF(STRUC.EQ.2.0)GOTO31
IF(STRUC.EQ.3.0)GOTO32
IF(STRUC.EQ.4.0)GOTO33
30 E=70.17-7.8133*CN+0.8816*CN*CN-0.03659*CN*CN*CN
MAMS=KCN-2
WRITE(2,204)MAMS
204 FORMAT(1H0,18X,29HALKANE MOLECULAR STRUCTURE = ,
19HCH3.(CH2),11,4H.CH3)
GOTO34
31 E=72.717-7.248*CN+0.7389*CN*CN-0.03367*CN*CN*CN
MAMS=KCN-4
WRITE(2,205)MAMS
205 FORMAT(1H0,18X,29HALKANE MOLECULAR STRUCTURE = ,
115H(CH3)2.CH.(CH2),11,4H.CH3)
GOTO34
32 E=166.819-38.987*CN+4.422*CN*CN-0.1815*CN*CN*CN
MAMS=KCN-6
WRITE(2,206)MAMS
206 FORMAT(1H0,18X,29HALKANE MOLECULAR STRUCTURE = ,
115H(CH3)2.CH.(CH2),11,10H.CH.(CH3)2)
GOTO34
33 E=440.68-152.43*CN+19.939*CN*CN-0.873*CN*CN*CN
MAMS=KCN-7
WRITE(2,207)MAMS
207 FORMAT(1H0,18X,29HALKANE MOLECULAR STRUCTURE = ,
114H(CH3)3.C.(CH2),11,10H.CH.(CH3)2)
34 E=E*(10.0**3)
PEACT=1.521*(10.0**12.0)
C DECIDE WHETHER OR NOT CN IS ODD OR EVEN
CN1=CN/2.0
CN2=CN1-0.5
LCN=CN2
ACN=LCN
BCN=ACN-CN2
IF(BCN.EQ.0.0)GOTO35

```



```

      Z=1.0
      GOTO36
35  Z=2.0
36  IF(ATM.EQ.1.0)GOTO37
      RAT1=RATIO*5.0
      WRITE(2,209)RAT1
209  FORMAT(1H0,32X,19HALKANE : AIR = 1 : ,F4.1///)
      FACT=5.0*RATIO+1.0
      Y1=1.0/FACT
      Y2=RATIO*Y1
      Y3=4.0*Y2
      GOTO38
37  FACT=RATIO+1.0
      WRITE(2,208)RATIO
208  FORMAT(1H0,29X,22HALKANE : OXYGEN = 1 : ,F3.1///)
      Y1=1.0/FACT
      Y2=RATIO*Y1
38  P=100.0
      T=482.0
      WRITE(2,210)
210  FORMAT(1H ,27X,7HINITIAL,9X,7HINITIAL/
127X,8HPRESSURE,6X,11HTEMPERATURE/
228X,5H(KPA),10X,7H(DEG.K)///)
45  IF(ATM.EQ.2.0)GOTO81
      IF(2.EQ.2.0)GOTO8
      TCON1=-0.2805*CN+(0.0086*T+6.756)
      GOTO9
8  TCON1=-0.055444*CN+(0.02825*T-2.499)
9  TCON1=TCON1*10.0**(-5.0)
      TCON2=(0.01627*T+1.732)*10.0**(-5.0)
      RMIX1=1.0/(Y1/TCON1+Y2/TCON2)
      SMIX1=(Y1*TCON1+Y2*TCON2)
      TCOND=0.5*(RMIX1+SMIX1)
      GOTO82
81  IF(2.EQ.2.0)GOTO21
      TCON1=-0.2805*CN+(0.0086*T+6.756)
      GOTO22
21  TCON1=-0.055444*CN+(0.02825*T-2.499)
22  TCON1=TCON1*10.0**(-5.0)
      TCON2=(0.01627*T+1.732)*10.0**(-5.0)
      TCON3=(0.01308*T+2.6961)*10.0**(-5.0)
      RMIX1=1.0/(Y1/TCON1+Y2/TCON2+Y3/TCON3)
      SMIX1=(Y1*TCON1+Y2*TCON2+Y3*TCON3)
      TCOND=0.5*(RMIX1+SMIX1)
82  IF(P.GT.15.0)GOTO39
      DELTA=3.35
      GOTO40
39  W1=14.0*CN+2.0
      W2=32.0
      W3=28.0
      IF(ATM.EQ.2.0)GOTO6
      V12D=2.828*((1.0+(W1/W2))*0.5)
      V21D=2.828*((1.0+(W2/W1))*0.5)
      IF(CN.GT.6.0)GOTO16
      IF(STRUC.EQ.1.0)GOTO16
      IF(STRUC.EQ.2.0)GOTO13
      IF(STRUC.EQ.3.0)GOTO15
      IF(STRUC.EQ.4.0)GOTO17
16  CP1=((0.012*CN+0.0093)*T+1.02*(CN**1.318))/W1
      GOTO18
13  CP1=(0.0958*(CN**0.965)*(T**0.735))/W1
      GOTO18
15  CP1=(0.488*(T**0.748))/W1
      GOTO18
17  CP1=(0.521*(T**0.765))/W1
18  CP2=(29977.5+4.1868*T-(1674.7*10.0**5.0)/(T*T))/133888.0

```



```

RMIX2=1.0/(Y1/CP1+Y2/CP2)
SMIX2=(Y1*CP1+Y2*CP2)
CP=0.5*(RMIX2+SMIX2)
DENS=(P*0.0001203*(W1+RATIO*W2))/(T*FACT)
T=T-273.0
V1=(0.304-0.0167*CN)*T+116.3-17.8*CN+
11.668*(CN**2.0)-0.0588*(CN**3.0)
V2=0.414*T+204.7
V12=((1.0+((V1/V2)**0.5)*((W2/W1)**0.25))**2.0)/V12D
V21=((1.0+((V2/V1)**0.5)*((W1/W2)**0.25))**2.0)/V21D
V=V1/(1.0+Y2*V12/V1)+V2/(1.0+Y1*V21/Y2)
V=V*10.0**(-6.0)
T=T+273.0
RA=(3.6*(DENS**2.0)*CP*(R2**3.0)*1.6*R*(T**2.0))/(TCOND*V*E)
IF(RA.GT.4000.0)GOTO50
DELTA=3.35
GOTO40
6  V12D=2.828*((1.0+(W1/W2))**0.5)
   V13D=2.828*((1.0+(W1/W3))**0.5)
   V21D=2.828*((1.0+(W2/W1))**0.5)
   V31D=2.828*((1.0+(W3/W1))**0.5)
   V23D=2.828*((1.0+(W2/W3))**0.5)
   V32D=2.828*((1.0+(W3/W2))**0.5)
   IF(CN.GT.6.0)GOTO24
   IF(STRUC.EQ.1.0)GOTO24
   IF(STRUC.EQ.2.0)GOTO26
   IF(STRUC.EQ.3.0)GOTO27
   IF(STRUC.EQ.4.0)GOTO28
24  CP1=((0.012*CN+0.0093)*T+1.02*(CN**1.318))/W1
    GOTO29
26  CP1=(0.0958*(CN**0.965)*(T**0.735))/W1
    GOTO29
27  CP1=(0.488*(T**0.748))/W1
    GOTO29
28  CP1=(0.521*(T**0.765))/W1
29  CP2=(29977.5+4.1868*T-(1674.7*10.0**5.0)/(T*T))/133888.0
    CP3=(27884.1+4.2705*T)/117152.0
    RMIX2=1.0/(Y1/CP1+Y2/CP2+Y3/CP3)
    SMIX2=(Y1*CP1+Y2*CP2+Y3*CP3)
    CP=0.5*(RMIX2+SMIX2)
    DENS=(P*0.0001203*(W1+(W2+W3*4.0)*RATIO))/(T*FACT)
    T=T-273.0
    V1=(0.304-0.0167*CN)*T+116.3-17.8*CN+
11.668*(CN**2.0)-0.0588*(CN**3.0)
    V2=0.414*T+204.7
    V3=0.355*T+174.3
    V12=((1.0+((V1/V2)**0.5)*((W2/W1)**0.25))**2.0)/V12D
    V13=((1.0+((V1/V3)**0.5)*((W3/W1)**0.25))**2.0)/V13D
    V21=((1.0+((V2/V1)**0.5)*((W1/W2)**0.25))**2.0)/V21D
    V23=((1.0+((V2/V3)**0.5)*((W3/W2)**0.25))**2.0)/V23D
    V31=((1.0+((V3/V1)**0.5)*((W1/W3)**0.25))**2.0)/V31D
    V32=((1.0+((V3/V2)**0.5)*((W2/W3)**0.25))**2.0)/V32D
    V=V1/(1.0+Y2*V12/V1+Y3*V13/V1)
1+V2/(1.0+Y1*V21/Y2+Y3*V23/Y2)
2+V3/(1.0+Y1*V31/Y3+Y2*V32/Y3)
    V=V*10.0**(-6.0)
    T=T+273.0
    RA=(3.6*(DENS**2.0)*CP*(R2**3.0)*1.6*R*(T**2.0))/(TCOND*V*E)
    IF(RA.GT.4000.0)GOTO50
    DELTA=3.35
    GOTO40
50  DELTA=0.0001*RA+2.96
40  RH=P*0.0001203/(FACT*T)
    OX=RATIO*RH
    TFACT=1.594*(10.0**18.0)/(EXP(E/(R*T)))
    CONC=(RH**0.87)*(OX**0.91)*PFACT*TFACT*0.00009859/TCOND

```



```

RHS=(CONC*E*(R2**2.0))/(R*(T**2.0))
DIFF1=RHS-DELTA
DIFF2=DELTA-RHS
IF(DIFF1)41,42,43
41  FRAC2=DIFF2/DELTA
    IF(FRAC2.LT.0.05)GOTO42
    T=T+1.0
    GOTO45
43  FRAC1=DIFF1/DELTA
    IF(FRAC1.LT.0.05)GOTO42
    T=T-1.0
    GOTO45
42  WRITE(2,211)P,T
211  FORMAT(1H ,F33.1,F16.1)
    I=I+1
    TO(I)=T
    IF(I.EQ.2)GOTO46
    DTO=TO(I)-TO(I-1)
    IF(DTO.GT.10.0)GOTO99
46  P=P-5.0
    T=TO(I)
    GOTO45
99  CONTINUE
999  STOP
    END

```

T, LENGTH 1623, NAME PHD1

A PROGRAMME BASED ON THERMAL IGNITION THEORY

VESSEL RADIUS = 5.0 CM.

ALKANE CARBON NUMBER = 7

ALKANE MOLECULAR STRUCTURE = $\text{CH}_3.(\text{CH}_2)_5.\text{CH}_3$

ALKANE : AIR = 1 : 10.0

INITIAL
PRESSURE
(KPA)INITIAL
TEMPERATURE
(DEG.K)

100.0	506.0
95.0	506.0
90.0	506.0
85.0	506.0
80.0	507.0
75.0	507.0
70.0	508.0
65.0	509.0
60.0	509.0
55.0	510.0
50.0	511.0
45.0	513.0
40.0	515.0
35.0	517.0
30.0	519.0
25.0	523.0
20.0	528.0
15.0	535.0
10.0	545.0
5.0	563.0

A PROGRAMME BASED ON THERMAL IGNITION THEORY

VESSEL RADIUS = 5.0 CM.

ALKANE CARBON NUMBER = 8

ALKANE MOLECULAR STRUCTURE = (CH₃)₂.CH.(CH₂)₄.CH₃

ALKANE : AIR = 1 : 15.0

INITIAL PRESSURE (KPA)	INITIAL TEMPERATURE (DEG.K)
100.0	493.0
95.0	493.0
90.0	493.0
85.0	494.0
80.0	494.0
75.0	494.0
70.0	495.0
65.0	496.0
60.0	496.0
55.0	497.0
50.0	498.0
45.0	500.0
40.0	502.0
35.0	504.0
30.0	506.0
25.0	510.0
20.0	515.0
15.0	522.0
10.0	532.0
5.0	549.0

A PROGRAMME BASED ON THERMAL IGNITION THEORY

VESSEL RADIUS = 5.0 CM.

ALKANE CARBON NUMBER = 8

ALKANE MOLECULAR STRUCTURE = (CH₃)₂.CH.(CH₂)₂.CH.(CH₃)₂

ALKANE : AIR = 1 : 15.0

INITIAL PRESSURE (KPA)	INITIAL TEMPERATURE (DEG.K)
100.0	495.0
95.0	495.0
90.0	496.0
85.0	496.0
80.0	496.0
75.0	497.0
70.0	497.0
65.0	498.0
60.0	499.0
55.0	500.0
50.0	501.0
45.0	502.0
40.0	504.0
35.0	506.0
30.0	509.0
25.0	513.0
20.0	518.0
15.0	524.0
10.0	534.0
5.0	552.0

A PROGRAMME BASED ON THERMAL IGNITION THEORY

VESSEL RADIUS = 5.0 CM,

ALKANE CARBON NUMBER = 9

ALKANE MOLECULAR STRUCTURE = (CH₃)₃C.(CH₂)₂CH.(CH₃)₂

ALKANE : AIR = 1 : 15.0

INITIAL PRESSURE (KPA)	INITIAL TEMPERATURE (DEG.K)
------------------------------	-----------------------------------

100.0	524.0
95.0	524.0
90.0	525.0
85.0	525.0
80.0	525.0
75.0	526.0
70.0	527.0
65.0	527.0
60.0	528.0
55.0	529.0
50.0	531.0
45.0	532.0
40.0	534.0
35.0	536.0
30.0	539.0
25.0	543.0
20.0	549.0
15.0	556.0
10.0	567.0

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