SPREAD OF FLAME ON A LIQUID SURFACE

A Thesis submitted for
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by

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ABSTRACT

Published values of open and closed flash points have been reviewed in the light of a theory developed. Differences are explained in terms of the rate at which vapour diffuses from a liquid surface under different conditions. It is concluded that only the closed flash point has any basic significance.

Experimental measurements of the rate of spread of flame across a liquid surface were made for a flame confined to a long parallel sided channel. The effects of initial temperature, liquid depth and channel width were determined. Liquids used were propanol, butanol, amyl alcohol and hexanol. It was found that the effects of liquid depth and channel width were only important when the initial temperature was less than the closed flash point.

Attention was concentrated on this region, in which preheating of the liquid by the spreading flame is the mechanism which controls the rate of spread. The temperature variations in a liquid while a flame spreads across its surface were therefore measured. Qualitative explanations of observed effects are given and a quantitative theory is developed which expresses convective heat transfer effects in the liquid in terms of an effective thermal conductivity. The mechanism of heat transfer from the flame to the liquid is discussed.

For initial temperatures greater than the closed flash point the rate of spread of flame is not affected by heat transfer processes in the liquid. Increasing the initial temperature, by increasing the concentration of vapour, increases the rate of spread. When the vapour/air mixture at the surface becomes stoichiometric no further increase occurs. Maximum rates of spread measured were 3-5 times the laminar burning velocity of the stoichiometric mixture.

Factors affecting the period between the ignition of a liquid at a wick and the first spread of flame from the wick were also studied experimentally.

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NOMENCLATURE

a	a limit of an integral
b	2b = width of strip heat source
$\bar{b}$	dimensionless form of b; $\bar{b} = b/2 \sqrt{\frac{pc}{Kt}}$
B	dimensionless form of b; $B = C_{2x}.vb$
c	calorific value of mixture or specific heat
C_1	a constant introduced in Chapter 5; $C_1 = \frac{\pi pc}{2Q}$
C_{2x}	a constant introduced in Chapter 5; $C_{2x} = \frac{pc}{2K_1}$
C_{2z}	a constant introduced in Chapter 5; $C_{2z} = \frac{pc}{2(K_3K_1)^{\frac{1}{2}}}$
C_A	a concentration of vapour which is a function of time and position.
C_e	a concentration of vapour immediately above a liquid surface
D	diffusion coefficient
E,F	constants in the expression $C_e = \exp \lceil E + F.t \rceil$
f(x)	a function of x
F	the ratio of an effective thermal conductivity to a measured thermal conductivity
F_x	F, based on the effective thermal conductivity in the x direction
F_z	F, based on the effective thermal conductivity in the z direction
$\lceil I \rceil$	stands in place of an integral
k	literature value of thermal conductivity
K	(Chapter 2) $\frac{P\theta_c}{P\theta_o}$
K	an effective thermal conductivity
K_1,K_2,K_3	values of K in the x,y,z directions respectively.
$K_o(u)$	the modified Bessel function of the second kind of order zero.
l	the distance between the liquid surface and a plane at which a boundary condition is defined (Chapter 2)

$l/2$	the distance between a surface and a plane at which a boundary condition is defined (Chapter 5), hence liquid depth.
L_o	the distance between a flame front and the point on a liquid surface where the first temperature rise occurs.
L	the distance between the points on a liquid surface at which the first temperature rise occurs and at which the temperature = T
Lo.2	the value of L for which $\frac{T-T_L}{T_c-T_L} = 0.2$
Lo.5	the value of L for which $\frac{T-T_L}{T_c-T_L} = 0.5$
L	(in Chapter 2) temperature of liquid at t = o
M	rate of heating of liquid in flash point determination
n	an integer, used to describe the general term of an infinite series
N,O	constants in the expression $\ln p_e = N.T + O$
p (or p_e)	vapour pressure of liquid at temperature T
p_s	the partial pressure of a vapour in its stoichiometric mixture with air.
P	atmospheric pressure
q,Q	the heat flux from a heat source
t	(Chapter 2) time for which diffusion has been taking place
t	(Chapter 3) measured time for flame to spread 26 cm.
t	(Chapter 5) time for which heating has been taking place
$t_{induction}$	the time between the ignition of a liquid at a wick and the first spread of flame from the wick.
T	(Chapter 2) temperature of liquid at time t; T = L + M.t.
T	a variable temperature
T_b	boiling point range quoted by manufacturers for their products
T_c	measured temperature of liquid surface immediately below flame front
$\overline{T_c}$	mean value of T_c

T_F closed flash point

T_L initial temperature of liquid

T_s liquid temperature at which $p = p_s$

T' a critical temperature for flame propagation.

v (or v flame) rate of spread of flame, or velocity of moving heat source.

v' a value of v corrected to a reference temperature.

V_{Air} the velocity of a superimposed air current

V_{liquid} the velocity of an artificially created liquid current.

x a variable distance

$\bar{x}$ dimensionless form of x; $\bar{x} = \frac{x}{2}\sqrt{\frac{pc}{Kt}}$

X dimensionless form of x; $X = C_{2x}.vx$

y a variable distance; in Chapter 2, y denotes a height above a liquid surface with the surface as the plane of origin.

y % of a liquid boiling in the range T_b

z a variable distance; in Chapter 2, z denotes a distance from the plane of origin when this is not the surface

Z dimensionless form of z; $Z = C_{2z}.vz$

Z_n^+ $C_{2z}.\, v\left[(z - 1/2)^2 + (2nl + 1/2 - z)^2\right]^{\frac{1}{2}}$

Z_n^- $C_{2z}.\, v\left[(z - 1/2)^2 + (2nl - 1/2 - z)^2\right]^{\frac{1}{2}}$

θ a variable temperature which is zero at $t = o$ (i.e. $\theta = T - T_L$ and is a temperature rise)

θ_F $T' - T_L$

θ_i (Chapter 2) temperature at $t = o$ }

θ_c (Chapter 2) closed flash point } also used as subscripts

θ_o (Chapter 2) open flash point }

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CHAPTER FOUR — THE SPREAD OF FLAME ACROSS A LIQUID SURFACE

Experimental Work, Part II

CHAPTER ONE

INTRODUCTION

1.1. General Introduction

The factors controlling the burning of liquids received little systematic investigation until comparatively recently. Up to 1939 the majority of the information available on the subject was in the form of flash point data and, with a few isolated exceptions, no attempts were made to arrive at an understanding of the mechanisms involved in the burning of a liquid. By 1939 however, interest in fire research was growing and the outbreak of the second world war with the resultant enormous increase in fire damage gave added importance and a new sense of urgency to this work. During this period the emphasis was on investigating methods of controlling fires but, as with any ad hoc research programme, it was evident that these investigations would be more effective if combined with an increasing knowledge of the mechanism of burning at the free surface of a liquid. At the end of the war research on these lines continued for it was clear that with the vastly increased demand for petroleum products the problem of liquid fires should not be underestimated.

A different interest in the burning of liquids, which was stimulated from comparative quiescence during the war and which has developed considerably since then, arises from the use of liquid fuels as a source of energy. The invention of the jet engine and the ramjet engine together with the increasing use of oil fired furnaces demanded an improved knowledge of the factors affecting the rate of burning of a liquid.

While the problems of extinguishing a fire associated with a stored liquid and of maintaining a fire in association with

a liquid fuel are diametrically opposed they both benefit from contributions to our understanding of the transfer processes involved, i.e. the transfer of matter from the liquid surface to the reaction zone, and the transfer of heat from the reaction zone to the liquid. Thus the work of Burgoyne, Cohen and Taylor (1,2) on the propagation of flame through a suspension of oil droplets in air, which was carried out to determine the causes of crank case explosions in marine engines, is also of interest in relation to the burning of the spray of fuel from a nozzle in a combustion chamber. It is of interest to note that much of the information obtained so far on the burning of liquids depended neither on advanced practical techniques nor on complicated theoretical reasoning. A considerable amount of the valuable work which laid the foundations of our present knowledge of the subject could equally well have been carried out thirty years earlier. The comparatively undeveloped state of the subject in 1939 say was due therefore not to technical difficulties but to a lack of interest.

1.2. The burning of liquids in bulk

One of the first accounts of experimental work on the burning of petroleum products was given by Hall (3) in 1925 and although the problem was kept under review by the fire protection officers of refineries not a great deal was published on this subject until twenty years later. Hall's work was directly concerned with the causes of boilover in tank fires, boilover being a description of the situation which sometimes occurs with fires of petroleum products when the product starts to foam with sufficient violence to carry liquid over the rim of the storage tank. This work showed that the primary cause of boilover was the formation of steam from water which was present in a layer at the bottom of the tank but that this formation of steam could only take place if the phenomenon described as 'heat wave' formation

occurred. The existence of this 'heat wave' (now known as hot zone) was deduced from thermocouple records. These showed that at a point in the oil the temperature remained constant for some time after ignition, then rose rapidly, then became constant again. The time at which the rapid rise occurred was a linear function of depth. Thus when oils of a certain type are burning two zones are formed - a hot zone and a cold zone - between which a well defined boundary exists, and in each zone the temperature varies little with depth. The boundary between these zones moves downwards at an approximately constant rate which is several times greater than the rate at which the surface moves. If the hot zone reaches a water layer at the bottom of the tank steam is produced which may produce foaming in the oil and boilover may occur.

Further evidence showed that the formation of a hot zone only occurs in products having a wide range of boiling points; it does not occur with a pure substance for instance. Hot zone formation is caused by the large differences in volatility and latent heat between the various components of a product with a wide boiling range. When ignition of such an oil occurs the lighter more volatile components are distilled off at the surface and burned leaving behind a layer of hot heavy ends. Because of its high temperature this layer continues to float on the cold oil; heat transfer from the hot zone to the cold oil has the effect of distilling off more light ends from the cold oil and in their passage to the surface these vapours stir the hot zone thus maintaining it at a uniform high temperature. Thus as the boundary of the hot zone passes down through the oil, the oil is progressively stripped of its most volatile components. When this stripping is complete i.e. when the hot zone has spread through all the oil, a second hot zone may be formed in a similar way.

These findings of Hall's were confirmed by Burgoyne and Katan (4) who were concerned with evolving the most effective ways of fighting fires in petroleum storage tanks. By experiments on

both hot zone forming and non hot zone forming oils they showed that the injection of air at the base of the storage tank aids fire fighting by agitating the liquid and reducing the temperature of the surface. This effect is more important with hot zone forming oils because it reduces the risk of boilover when fire fighting foams are applied to the surface.

Similar findings were reported by Pavlov and Khovanova (5) in 1953 but this paper seems merely to confirm Hall's findings and not to present anything new.

Many other measurements of burning rate and temperature distributions have been reported, mainly for non hot zone forming substances, and theoretical treatments for these quantities have been suggested. One such theoretical temperature distribution has been given by Khudyakov (6) who by considering only heat transfer by conduction in the liquid and taking a steady state temperature distribution relative to the moving surface obtained the expression $\frac{t - t_o}{t_s - t_o} = e^{-Kx}$ where t is the temperature at a point x on a stationary system of axes, t_s is the surface temperature, t_o is the initial temperature and K is a constant. The manner in which the equation was derived shows that $K = (\frac{vpc}{k})$ where v is the rate of burning of the liquid surface and $\frac{k}{pc}$ is the thermal diffusity. The experimental section of this paper shows that the temperature gradients can be expressed in the form given but that there are considerable differences between experimental and calculated values for k. These differences are attributed to the effects of radiation from the flame and to the hot zone phenomenon referred to above.

A similar approach was used by Reid (7) to the problem of the steady temperature distribution in a semi-infinite liquid. He again assumes that there is no convective heat transfer in the liquid but he includes a term of the form $Aa \exp \left[- a (x-1) \right]$ in his differential equation to include the effects of heat transfer by radiation into the liquid. This form for the temperature

distribution was checked by Hildenbrand and Whitaker (8) who carried out measurements on burning liquid nitrate esters. They found that Reid's suggested distribution gave fair agreement with their experimental results.

A comprehensive study of fires in liquids was made by Rasbash and Rogowski (9) who studied alcohol, petrol, benzole and kerosine fires in a vessel 30 cm. in diameter. As well as studying the changes occurring in the liquid, i.e. temperature distributions, rates of burning, and changes in composition, they studied the temperature, dimensions, upward velocity and emissivity of the flames. They describe different appearances of the flame and its relation to the liquid surface. From the experimental results it was deduced that with alcohol fires heat transfer to the liquid was mainly by conduction whereas for the others it was mainly by radiation. This difference was thought to be a cause of the different appearances of the flames. A further point of interest in this paper is in the use of a result of Spaldings (10) (see 1.3) to obtain a semi-theoretical value for the burning rate in an alcohol fire. Alcohol was chosen as being more appropriate because of the small contribution of radiation to the total heat transfer. The authors showed that there was a good measure of agreement between the theoretical and calculated values.

Similar measurements, although not on such a comprehensive scale, were made by Krueger and Radusch (11) on ethanol and gasoline fires. They found that the liquid burning rate was markedly increased by air movements but that the temperature distribution was not affected to the same extent. With gasoline the burning rate decreased with time; the maximum burning rate increased with tank diameter (in the range 12-30 cm.) Temperature measurements showed that the temperature falls off rapidly below the surface of the liquid even after long burning times. This is in contrast to the behaviour of hot zone forming substances.

A different approach to the problem of burning liquids is

described by Faure and Pugnet (12) who wished to determine the distribution of pressure, temperature and velocity resulting from the convection currents associated with large surface fires. Experimental results were obtained for the distributions of these quantities above heated flat plates and above liquid fires. In each case the heat source was 50 cm. in diameter. The paper includes a theoretical consideration of natural convection, based on the work of Chia-Shun-Yih (13), which gives the distribution of velocity and temperature in a semi-infinite medium above a point source of heat. Although no agreement between the experimental results and the theoretical predictions was reported it is of interest to note the use of this somewhat unusual approach to the problem of liquid fires. A considerable body of data on the burning of liquids at a free surface now exists; it seems likely that a greater understanding of the problem now depends as much on the use of new approaches to explain existing data as on the compilation of fresh data.

A remarkably wide range of sizes of vessel was used in experiments described by Blinov and Khudyakov (14). These experiments, on burning rates and flame heights, were carried out in vessels ranging in size from 0.37 cm. diameter to 22.9 meters diameter. This work demonstrates the danger of basing conclusions on results obtained over a small range of vessel diameters because three regimes of behaviour are clearly established viz. laminar, transition, and turbulent. For example, the work of Krueger and Radusch referred to above was all conducted in the transition region. For all the oils tested by Blinov and Khudyakov the relationship between rate of burning and pan diameter was substantially the same. At first the rate of burning decreases with increasing vessel diameter, the product of the two remaining approximately constant. This is described as the laminar flow regime and corresponds to a Reynolds number of less than 20 (based on the

properties of the cold vapour). For vessel diameters between 6 cm. and 40 cm. the rate of burning passes through a minimum, increases, and then levels off to a constant value with increasing vessel diameter. This is described as a transition region; it corresponds to Reynolds numbers of 20 to 500. For greater vessel diameters the burning rate is independent of vessel diameter and burning is described as turbulent. In a review of this article (15) Hottel suggests a simplified semiquantitative analysis of the heat transfer from the flame to the liquid; he shows that if heat transfer from the vessel rim, from the flame by convection, and from the flame by radiation are considered then an expression can be obtained with the same relationship between burning rate and vessel diameter as is observed experimentally.

This article is therefore of considerable value in differentiating between the various types of behaviour which may be encountered with liquid fires and contains useful information on burning rates and flame lengths.

Further work on the burning of liquids has been concerned more directly with the extinction of fires above liquids. Thus work has been done on the effect of water sprays on liquid fires and the effect of inert substances on such fires. This work while of undoubted value in its relation to fire fighting techniques is not of such direct interest to a study of the factors controlling the burning of liquids.

1.3 The burning of liquids as fuels

When considering the design of a combustion chamber the behaviour of liquid fuels when burning as droplets is often of great importance. Many fundamental studies have been carried out of both freely moving and suspended droplets either alone or in the presence of other droplets. One such study, by Godsave(16), gave

experimental results for the rate of burning and drop life of single droplets suspended on a fine silica filament together with a theoretical expression for the mass burning rate of a droplet in terms of the geometry and physical properties of the system. In common with several other studies however this treatment is specific to the burning of droplets and no attempt is made to render the theory general.

A general theory of liquid fuel burning has been developed by Spalding (10) (17); because of its general nature and the fact that it can be used in the analysis of liquid fires in bulk, this theory will be considered here in some detail. The theory is developed by writing down the material balance equations for each component together with a heat balance equation and applying boundary conditions appropriate to heterogenous combustion. By assuming equality between the thermal and molecular diffusivities the equations can be written in a common form involving a dimensionless variable as also can the boundary conditions. This dimensionless variable (b) then represents either temperature or concentration. In general, when considering the combustion of a liquid fuel, it is required to know the mass transfer rate of fuel at the surface of the fuel. Since the equation to be solved is a second order one two boundary conditions are needed and the most convenient ones will usually be the values of b at the surface of the fuel and at infinity in the gas stream, i.e. b_s and b_g. With this information, no attempt is made to solve the differential equation it is simply stated that the mass transfer rate at the surface is controlled by the difference $(b_g - b_s)$ since this difference determines the gradient at the surface. This difference is then described as the transfer number, $B = b_g - b_s$, which may be considered as a non-dimensional driving force for mass transfer.

There is a different form of this transfer number for each chemical element involved and one for the heat balance.

All of these forms however must give the same value for B and the choice of a form to use is therefore dictated by the information available.

In addition to the transfer number the mass transfer rate is affected by the geometry of the system and by the gas flow conditions. Expressions for this rate are given by Spalding for a number of special cases and a general method for predicting mass transfer rates is given based on analogy with heat transfer. By use of the 'stagnant film' theory it can be shown that $\frac{m'' \times c}{k \ln(1+B)} = Nu$ where m'' = mass transfer rate/unit area; x = a typical dimension c and k are properties of the gas; B is the transfer number and Nu is the Nusselt number calculated from heat transfer data for a corresponding system using values of the Reynolds number or Grashof number based on the data of the problem.

The results of a considerable amount of experimental work were considered in the light of this theory by Spalding who found that good agreement existed between predicted burning rates and experimental rates. However the value of the theory lies as much in the light which it sheds on the possible effects of changing the conditions under which combustion is taking place as in the accurate prediction of burning rates.

1.4. The spread of flame across a liquid surface

The interest in this topic lies not in the possibility of directly applying any information gained as a result of a study of it to a particular problem but rather in the light which such information sheds upon the interaction between a flame and a liquid surface in general. The only previous investigation of this topic of which any report was found in the literature was conducted by T.Kinbara; details of this work were published in a series of eight papers between 1930 and 1942. Of these papers seven were

published in Japanese together with abstracts in English (18-24) while the eighth (25) was published in English.

Kinbaras work consisted mainly of determining the rate of spread/temperature curves for eight organic liquids and for various mixtures of two inflammable liquids and of one inflammable liquid with water. The liquids were burned in a brass vessel and the flames progress was observed photographically.

The rate of spread/temperature curves are considered in three parts corresponding to three different states of the liquid. In the first part the velocity increases very slowly with temperature corresponding to the state where the vapour pressure of the liquid is insufficient to provide a combustible mixture and the liquid must be preheated by the flame before propagation can occur. In the second part the velocity increases rapidly with temperature to a maximum value and in the third part after attaining its maximum velocity, a gradual decrease in the velocity takes place. These latter parts correspond to the combustion of the air and the vapour of the liquid without preheating but in the third part an insufficiency of oxygen exists.

Kinbara's interest was centred on the two higher temperature regions and very few of his measurements were made in the lower temperature region. As a result of this he came to the conclusion that the rate of spread was independent of the width of the channel along which this flame was propagating provided that this width exceeded 1.5 cm. and also that the rate of spread was independent of the depth of the liquid for depths greater than 0.05 cm.

The temperature corresponding to the maximum velocity was found by Kinbara to be a temperature of the liquid having a vapour pressure close to that of the stoichiometric mixture with air. This also held for the mixtures of inflammable liquids with water. For increasing concentrations of water, the temperature of

maximum rate of spread increased in such a way that the partial pressure of the inflammable component remained constant. The maximum rate of spread however decreased with increasing concentration of water.

In addition to these measurements Kinbara also studied the effect of covering the combustion vessel and of inducing air currents across the surface of the liquid. His papers contain mainly quantitative descriptions of this work and do not contain any definite conclusions. Two of the papers deal with the combustion of benzene; they contain photographs of the various types of flame structure observed and descriptions of the photographs. One of the structures observed is compared with that obtained with gaseous mixtures of benzene and air in a tube.

In reference (24) a method is described for determining the variation in composition in the vapour above a liquid surface by determining the changes in refractive index. Kinbara carried out several sets of measurements using this method and found that in his circumstances the partial pressure of vapour in the air fell off linearly from its equilibrium vapour pressure at the surface to approximately 10% of this value 3 cm. from the surface and then to zero 5 cm. from the surface. This type of variation was found in each case. It is not possible to say quite what his experimental circumstances were as this paper is in Japanese and no English abstract is available.

In the light of this past work by T. Kinbara it was decided that the emphasis in the present investigation should be on the low temperature region, with a view to elucidating the mechanisms which control the rate of spread of flame when preheating must occur, but that sufficient experimental work should be conducted with higher liquid temperatures to check the main conclusions of Kinbara.

CHAPTER TWO

SOME PROPERTIES OF INFLAMMABLE LIQUIDS

2.1. Introduction

During the investigation into the factors affecting the rate of spread of flame across a liquid surface, it was considered desirable to review critically the information available on those properties of inflammable liquids which might be relevant to the investigation. Factors considered for each property were the method of its determination, the underlying physical significance of the property, and the way in which variations in the property might affect the spread of flame across a liquid surface. The properties which were studied were the closed flash point, the open flash point and the fire point and each of these will be discussed in turn.

2.2. The Closed Flash Point

Methods of determining the closed flash point differ little in principle. In each method a quantity of liquid is heated in a standard closed cup at such a rate that its temperature changes in a standard manner, and a source of ignition is applied at standard intervals. The closed flash point is considered to be that temperature at which a flash is first observed to spread through the vapour above the liquid.

The physical significance of this type of measurement is clear. The temperature recorded is that temperature of the liquid surface, which coincides in time with the vapour above the liquid surface becoming inflammable at the height of the igniting source. Thus there will always be a delay between the vapour becoming inflammable at the liquid surface and the observation of the flash point due to the separation of the igniting source from the surface.

Although stirring of the vapour phase will reduce this delay it will not eliminate it. The magnitude of this delay is discussed in more detail below (2.4.2).

The significance of the closed flash has been discussed by Burgoyne and Williams-Leir (26) who mentioned the existence of an error due to the finite rate at which diffusion occurs and therefore considered an ideal closed flash point. They concluded that at an ideal closed flash point θ_c the equilibrium vapour pressure of the liquid $P\theta_c$ is equal to the lower limit of inflammability of the vapour in air (y%) multiplied by the atmospheric pressure (P) i.e. $P\theta_c = \frac{y}{100} \cdot P$.

In this paper values of the closed flash point for different liquids calculated from their vapour pressure/temperature curves and lower limit of inflammability data were compared with experimentally determined values. It was observed that the calculated and experimental values were usually of the same order and in general the calculated values were lower. This difference can be accounted for by considering the effect of diffusion from the surface to the igniting source (see 2.4.2.)

2.3. The Open Flash Point

In the previous section criticisms were advanced against existing methods of making closed flash point determinations and reasons were given for these criticisms. In the present section it is hoped to demonstrate the validity of such criticisms by applying similar reasoning to open flash point determinations, translating this reasoning into mathematical form and using the resulting equation to analyse published experimental values for open flash points.

2.3.1. Methods of Determination

In the handbook on standard testing methods published by the Institute of Petroleum (27) two methods are given for determining the open flash point of a liquid. These methods are known as the Cleveland Open Cup method and the Pensky-Martens Open Flash Point method; in most respects they are alike and they will be described only in broad outline. In each case dimensions are given for the liquid container, which is to have vertical sides and is to be open to the atmosphere, and it is specified that the liquid shall be heated at the rate of 9-11°F/min. Mention is made of the need for adequate screening round the vessel for stray draughts would render the results unreliable. In the Cleveland method a pilot flame is swept across the mouth of the cup at prescribed intervals whereas in the Pensky-Martens method a pilot flame is fixed above the liquid surface. The temperature of the liquid is recorded when a flash travels through the vapour from the pilot flame and this temperature is called the open flash point. From the point of view of the results obtained the most important difference between the two methods is the distance between the pilot flame and the liquid surface. In the Cleveland method the flame is swept in a plane $\frac{3}{8}$" above the liquid surface whereas in the Pensky Martens method the flame is fixed $\frac{7}{8}$" above the liquid surface. In each case the flame is approximately on a level with the rim of the cup.

2.3.2. Theoretical considerations

For the purposes of this analysis the open flash point will be defined as "the temperature of a liquid surface when the vapour at a prescribed height above the surface becomes inflammable, the liquid having been heated in a prescribed way". In other words the open flash point occurs when the concentration of vapour at the

appropriate height is equal to the lower inflammability limit. It is this approach which will now be put to the test.

In Case I of the Appendix an expression is derived whereby the concentration of inflammable component in the vapour phase can be calculated at any height and at any time during an open flash point determination. An important assumption in the derivation is that the vapour is diffusing to infinity in an undisturbed manner i.e. that the vessel is perfectly shielded from draughts. This expression is:-

$$\frac{C_A}{C_e} = \frac{1}{2}\left[e^{-\sqrt{F/D}y} \operatorname{erfc}\left(\frac{y}{2\sqrt{Dt}} - \sqrt{Ft}\right) + e^{\sqrt{F/D}y} \operatorname{erfc}\left(\frac{y}{2\sqrt{Dt}} + \sqrt{Ft}\right)\right] \quad - (2.7)$$

The value of the ratio $\frac{C_A}{C_e}$ is plotted as a function of the two dimensionless groups $\left(\frac{y}{2\sqrt{Dt}}\right)$ and $(\sqrt{Ft})$ in Fig 2.1.

The significance of the symbols in equation (2.7) is as follows:-

C_A = concentration of diffusing vapour at a height y after t seconds.

C_e = concentration of diffusing vapour at the liquid surface after t seconds.

D = diffusion coefficient of vapour in air.

y = height above the liquid surface.

t = time for which diffusion has been taking place.

F = a measure of the way in which C_e varies with time thus $C_e = \exp(E + Ft)$.

By means of equation (2.7) it is possible to calculate the theoretical concentration of vapour at the height of the igniting source at the open flash point of any liquid for which the vapour pressure/temperature relationship and the diffusion coefficient of the vapour in air are known. If the assumptions concerning the significance of the open flash point which were made above are valid then this concentration should be equal to that

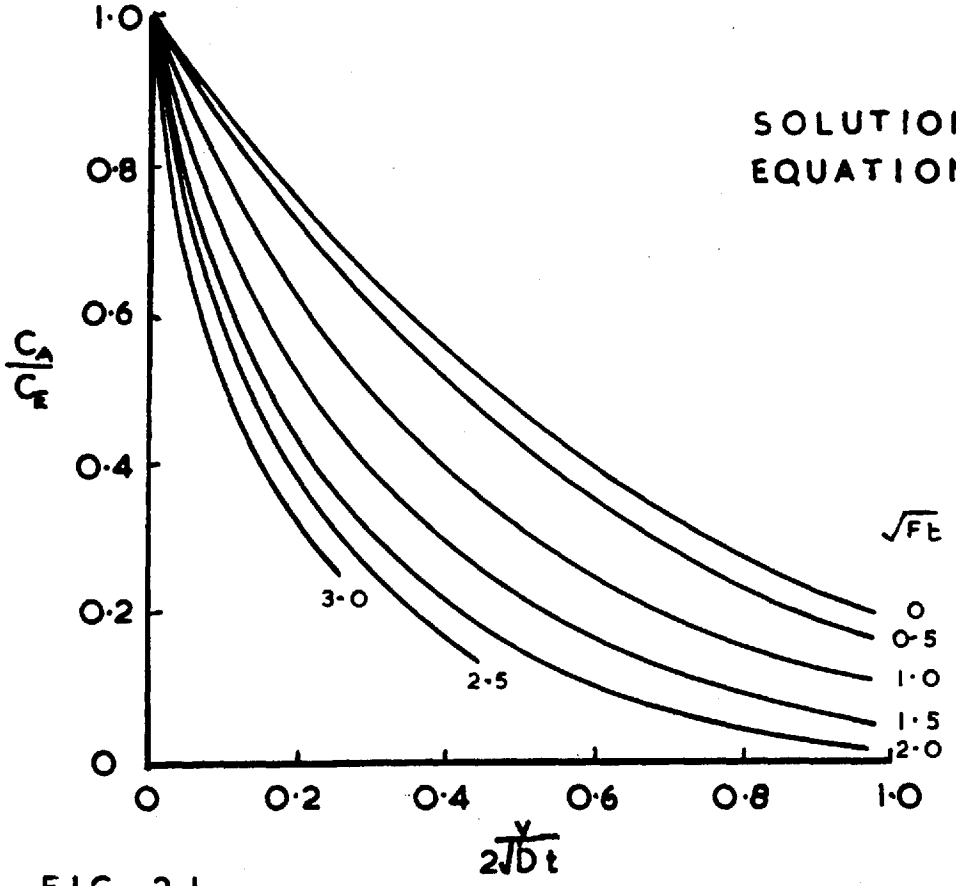

SOLUTIONS OF
EQUATION 2.7
1·0
0·8
0·6
0·4
0·2
0
$\frac{C_A}{C_E}$
$\sqrt{Ft}$
0
0·5
1·0
1·5
2·0
3·0
2·5
0
0·2
0·4
0·6
0·8
1·0
$\frac{y}{2\sqrt{Dt}}$

FIG. 2.1

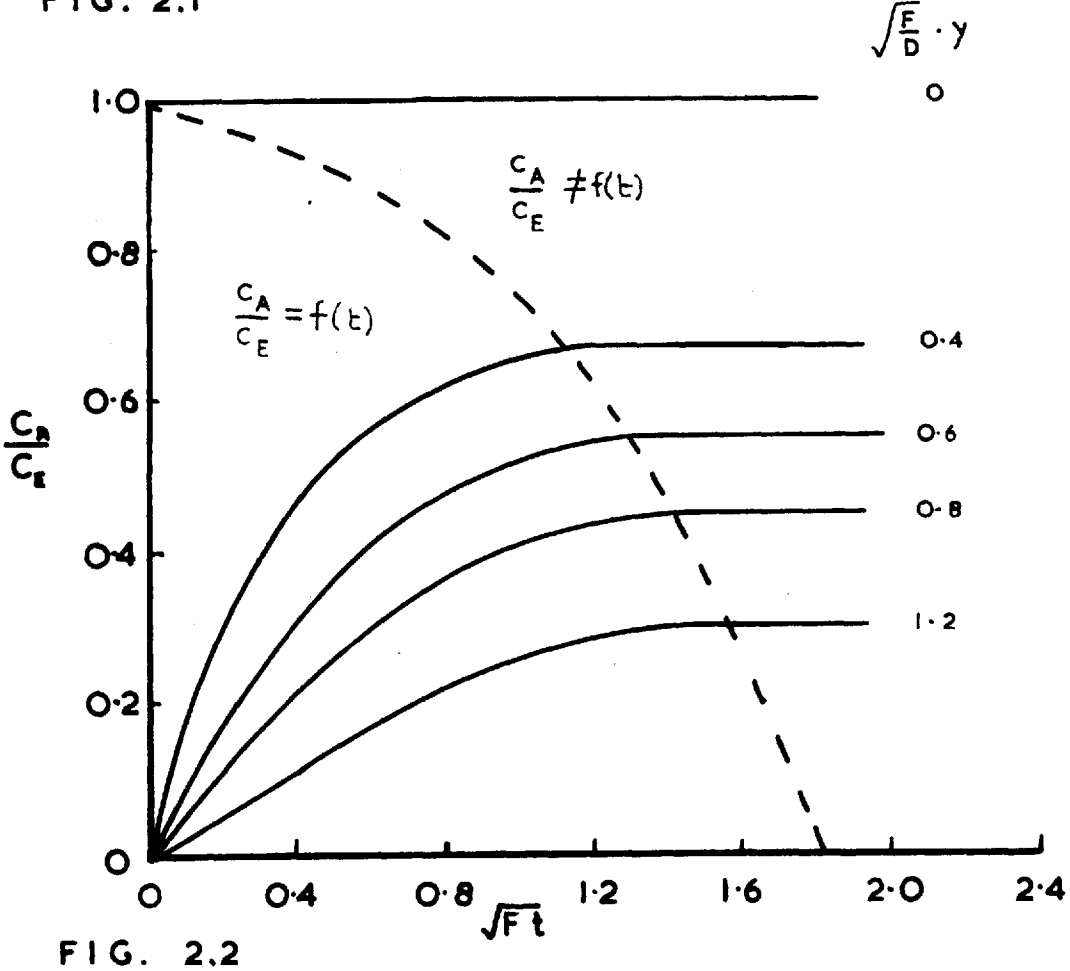

$\sqrt{\frac{F}{D}} \cdot y$
0
1·0
$\frac{C_A}{C_E} \neq f(t)$
0·8
$\frac{C_A}{C_E} = f(t)$
0·4
0·6
0·8
1·2
0·6
0·4
0·2
0
$\frac{C_B}{C_E}$
0
0·4
0·8
1·2
1·6
2·0
2·4
$\sqrt{Ft}$

FIG. 2.2

of the lowest limit mixture. As discussed above this latter concentration may be calculated from the closed flash point, to a good approximation.

In order that the validity of equation (2.7) might be checked a literature survey was made. This survey revealed thirteen substances (Table 2.1) for which the following information was available:- vapour pressure/temperature data (28), diffusion coefficient (29), open and closed flash points(30)(31); and a further twenty four substances (Table 2.2) for which only the flash point data and vapour pressure/temperature data were available.

It is important to note that in no case was it stated which method was used for determining the open flash point.

For each of the thirteen substances in Table 2.1 the following series of operations was carried out:-

(i) it was assumed that the determination of the open flash point was made by the Cleveland method, i.e. with the igniting source $\frac{3}{8}$" above the liquid surface.

(ii) it was assumed that heating was started at 20°C and the time required to raise the liquid to its open flash point at a heating rate of 9°F/min. was calculated.

(iii) A value for F was calculated using the vapour pressure/temperature data for the liquid.

(iv) The vapour pressure of the liquid at its open flash point was recorded.

(v) Values of y = $\frac{3}{8}$", t from (ii), F from (iii), C_e from (iv) and D were substituted into equation (2.7) to give C_A the concentration of vapour at the height of the igniting source.

These calculated values of C_A are given in column four of Table 2.1. It will be noted that for the first seven substances listed in Table 2.1 the values of C_A calculated with y = $\frac{3}{8}$" agree closely with the values given in column two for the concentration of vapour at the closed flash point. For the remaining six substances however the calculated value is consistently too high.

The calculations were repeated for these six substances with $y = \frac{7}{8}$", i.e. assuming that the determinations had been made by the Pensky-Martens method, and these values are given in column five of Table 2.1. It can be seen that these values are very much closer to the experimental values given in column two.

These calculations may therefore be taken to indicate that equation (2.7) gives a good indication of the changing conditions during an open flash point determination and that the concentration of vapour at the height of the igniting source when the flash is observed is equal to the concentration of vapour at the closed flash point.

TABLE 2.1

(the units of columns 2-5 are mm.Hg.)

Substance	$P_{\theta c}$	P1.1.	$(C_A)_{y=\frac{3}{8}"}$	$(C_A)_{y=\frac{7}{8}"}$	$\left(\frac{C_A}{C_e}\right)_{y=\frac{3}{8}"}$	$\left(\frac{C_A}{C_e}\right)_{y=\frac{7}{8}"}$
p-iso-pentanol	10.6	9.1	10.3		0.75	
ter-pentanol	11.5	9.1	9.7		0.65	
acetic acid	31.8	30.4	32.0		0.83	
xylene	4.2		4.1		0.70	
ethyl benzene	5.5		6.0		0.67	
n-amyl acetate	3.7		3.1		0.70	
ethyl butyrate	16.0		15.8		0.78	
n-propanol	10.6	16.3	20.2	14.3	0.79	0.55
iso butanol	14.5	12.9	25.4	18.2	0.78	0.57
n-pentanol	6.2	9.1	12.9	9.1	0.71	0.54
n-butanol	8.2	12.9	18.9	12.6	0.80	0.54
iso-amyl acetate	5.4		10.1	5.6	0.78	0.52
butyl acetate	6.9		10.1	6.7	0.74	0.49

Further information of considerable value may be obtained from Table 2.1. A study of columns six and seven reveals that the value of the ratio $\frac{C_A}{C_e}$ at a particular height is approximately the same for each liquid. If these concentrations are expressed in terms of partial pressures this may be written $\frac{P\theta_c}{P\theta_o} = K$ where $P\theta_c$ = vapour pressure at the closed flash point, $P\theta_o$ = vapour pressure at the open flash point and K is a constant the magnitude of which depends on the apparatus used for the determination. In order to investigate the applicability of this simplification the value of the ratio $\frac{C_A}{C_e}$ was calculated for the twenty four liquids mentioned above. These results are given in Table 2.2.

TABLE 2.2.

GROUP I	K > 0.62			GROUP II	K < 0.62		
Substance	$P\Theta_c$	$P\Theta_o$	$K=\frac{P\Theta_c}{P\Theta_o}$	Substance	$P\Theta_c$	$P\Theta_o$	$K=\frac{P\Theta_c}{P\Theta_o}$
Octyl acetate	20	25	0.80	Methyl aniline	12	20	0.60
Methyl cello-solve acetate	25	31	0.80	Maleic anhydride	27	45	0.60
Phenol	14	18	0.78	Cellosolve	13.8	22.7	0.60
Glycol	2.6	3.4	0.76	Nitro-methane	54	91	0.59
Methyl Salicylate	13	17	0.76	Dibutyl phthalate	2.1	3.6	0.58
Tetralin	9	12	0.75	Benzalde-hyde	11	19	0.58
Benzyl Alcohol	14	19	0.74	Nitro-ethane	25	45	0.56
Acetic Anhydride	19.9	27.4	0.73	Dimethyl aniline	7.3	14	0.52
Carbitol	15	21	0.72	Dimethyl phthalate	9	18	0.50
Dichloro-benzene	19	28	0.68	Glycerol	7	14	0.50
Naphthalene	7.4	11	0.68	Cymene	46	10.5	0.44
				Stearic acid	2.8	7	0.40
				diethylene glycol monobutyl ether	1.7	4.7	0.37

As can be seen from Table 2.2. these additional experimental values of the ratio $K = \frac{P\Theta_c}{P\Theta_o}$ lie in two groups with ranges 0.37 - 0.60 and 0.68 - 0.80. At first sight it would appear that the difference between these two groups corresponds to the difference in value of the theoretical ratio for the two different methods of determination.

In order to gain further information on this point a simple statistical test was applied to the data. Four sets of values of K exist viz. (i) experimental, $K > 0.62$ (18 substances); (ii) experimental, $K < 0.62$ (19); (iii) theoretical $y = \frac{3}{8}$" (13); (iv) theoretical, $y = \frac{7}{8}$" (6). "Students" t test (32) was used to test the null hypothesis that each of these four groups were samples drawn at random from the same universe. This test showed that the differences between groups (i) and (ii) and between (i) and (iv) are highly significant. It showed also that the differences between groups (i) and (iii) and between groups (ii) and (iv) are not significant.

These results were taken as further evidence in favour of the proposition that experimental results for open flash points fall into one of two groups depending on the method used and that these experimental results can be predicted by means of the expression $\frac{P\Theta_c}{P\Theta_o} = K$, with a reasonable degree of accuracy. For a Cleveland determination the mean value of K found was 0.75, and for a Pensky-Martens determination the mean value was K = 0.53. Moreover these two groups of experimental results correspond closely with the different values of the theoretical ratio $\frac{C_A}{C_e}$ calculated for $y = \frac{3}{8}$" and $y = \frac{7}{8}$", namely 0.74 and 0.53 respectively.

2.3.3. The variation of open flash point with the height of the igniting source

In the previous section it was demonstrated that theoretically the value obtained for an open flash point will depend on the height of the igniting source, and certain conclusions were reached as a result of this. In order that this might be confirmed experimentally, an investigation was carried out in the Chemical Engineering Department of Imperial College by Mr. J.L.A. Alexander. This work has been reported fully elsewhere (33).

The experimental work which concerns the present discussion was carried out in a Pensky Martens Open Flash Point Apparatus with the following three major modifications:-

(i) the source of ignition was changed from a pilot flame to a spark discharge.

(ii) the height of the electrodes from the surface was made adjustable over the range 0-1.5 inches.

(iii) the cup was further protected from draughts by the addition of a sleeve, the upper rim of which was 2" above the surface of the liquid.

The two most important sets of results obtained with this apparatus by Alexander are shown in Fig 2.3 and 2.4. They show the variation in Open Flash Point with the height of the igniting source for n-hexanol and carbitol respectively.

Theoretical predictions of Open Flash Point

By means of equation (2.7) it is possible to find the concentration of vapour at a given height after a given time of heating. It is more difficult to reverse the process and calculate the time of heating necessary to give a particular concentration at that height, that is to say to carry out the calculation necessary for the prodiction of the Open Flash Point.

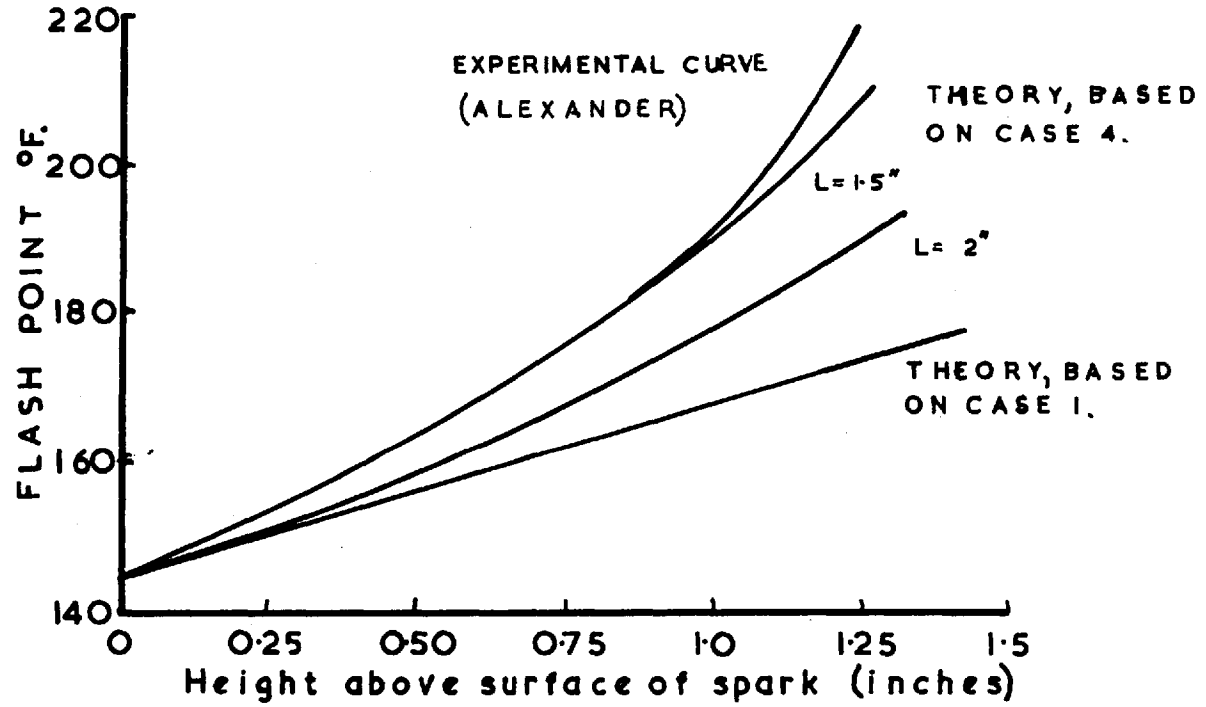


FIG. 2.3 DATA FOR HEXANOL

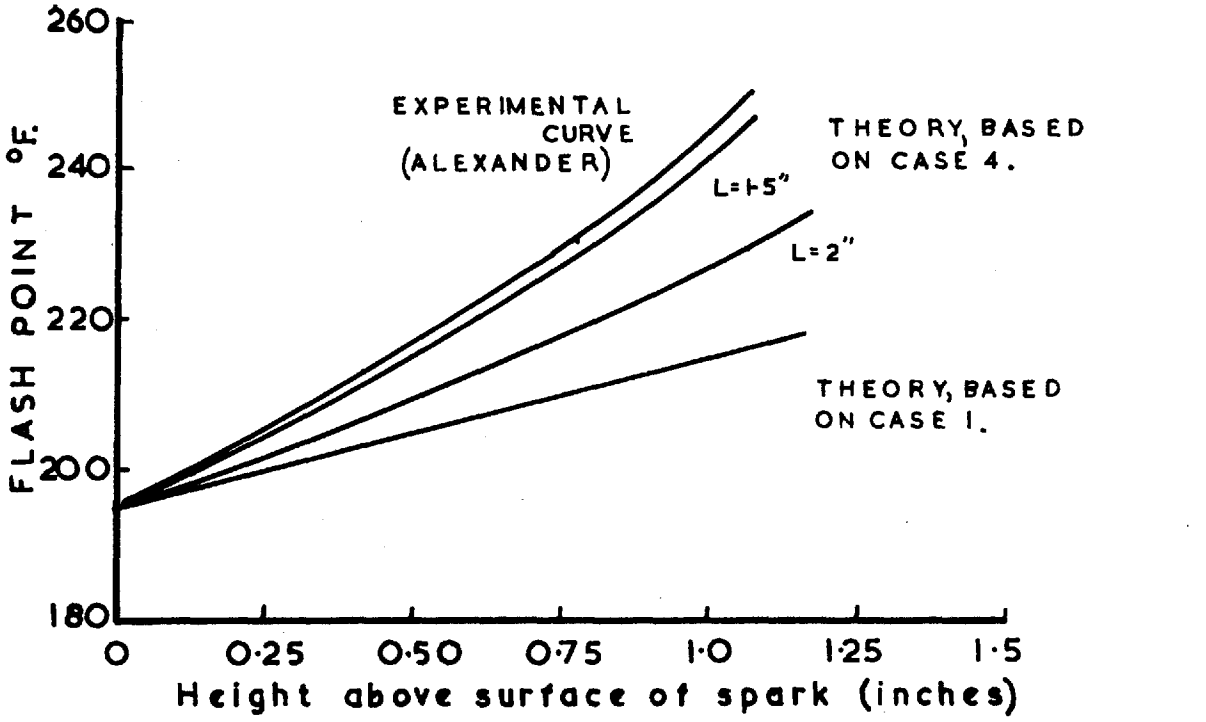


FIG. 2.4 DATA FOR CARBITOL

THE VARIATION IN OPEN FLASH POINT WITH HEIGHT OF IGNITING SOURCE

Either a graphical or an approximate numerical method must be used. The first few values obtained by graphical means showed that in the regions of interest the ratio $\frac{C_A}{C_e}$ was independent of temperature. The reason for this became apparent when equation (2.7) was replotted as $\frac{C_A}{C_e} = f\left[(\sqrt{Ft}), (\sqrt{\frac{F}{D}}.y)\right]$ - Fig. 2.2. This graph shows that as $\sqrt{Ft}$ increases $\frac{C_A}{C_e}$ tends to a value of $e^{-\sqrt{\frac{F}{D}}.y}$ and having confirmed that this region was the appropriate one to use it was assumed that $\frac{C_A}{C_e} = e^{-\sqrt{\frac{F}{D}}.y}$ - (2.7B)

At the open flash point then $\frac{P\Theta_c}{P\Theta_o} = e^{-\sqrt{\frac{F}{D}}.y}$ or $\ln P\Theta_c + \sqrt{\frac{F}{D}}.y = \ln P\Theta_o$

Now the time of heating $t = \frac{\ln P\Theta_o - \ln P\Theta_1}{F} = \frac{\ln P\Theta_c - \ln P\Theta_1 + \sqrt{\frac{F}{D}}.y}{F}$

$$= t' + \sqrt{\frac{t'}{\ln (P\Theta_c/P\Theta_1) D}} \cdot y$$

where t' = time to heat to Θ_c the closed flash point

$$\Theta_o = \Theta_1 + Mt \; ; \quad \Theta_c = \Theta_1 + Mt'$$

$$\therefore \Theta_o = \Theta_c + M\sqrt{\frac{\Theta_c - \Theta_1}{M \ln(P\Theta_c/P\Theta_1) D}} \cdot y$$

$$= \Theta_c + y\sqrt{\frac{M(\Theta_c - \Theta_1)}{(\ln P\Theta_c - \ln P\Theta_1) D}} \qquad - (2.7c)$$

Thus from (2.7c) the open flash point should be a linear function of the height of the igniting source.

For n-hexanol :- $\Theta_c = 145^\circ F$; $M = 10^\circ F/min.$; $D = 0.059^2 cm/sec.$

$\Theta_1 = 70^\circ F$ (say); $P\Theta_c = 13.5mm$ Hg.; $P\Theta_1 = 1$ mm Hg.

$$\therefore \Theta_o = 145 + y\sqrt{\frac{0.17(75)}{0.059 \ln 13.5}}$$

$$= 145 + 9.1\, y \text{ where } y \text{ is in cm.}$$

This line, and a similar line for carbitol, were drawn on Fig. 2.3 and 2.4.

A comparison between these lines and the experimental lines shows two things clearly:

i) values of the open flash point predicted by theory are consistently too low.

ii) they do not increase at an increasing rate as do the practical values.

It was therefore concluded that the boundary conditions used in solving Case I in the Appendix were too simple. In spite of the additional shielding of the cup from draughts and the fact that the determinations were made in a closed fume cupboard it was made unmistakably clear that the assumption that diffusion took place in an undisturbed manner from the liquid surface to infinity was not justified. A fresh solution of the differential equation was therefore obtained by assuming that disturbing effects reduced the concentration of vapour to zero at a distance l from the liquid surface. This solution is given as Case 4 in the Appendix.

This modified solution was used to predict values for the open flash point firstly with l = 2" i.e. assuming that the vapour concentration was reduced to zero at the rim of the cup, and secondly with l = 1½". These fresh predictions are again plotted on Figs 2.3 and 2.4. It can be seen that the theoretical curves are now of the same form as the experimental curves and that in each case the curve with l = 1½" corresponds almost exactly with the experimental curve. This demonstrates how vulnerable an open flash point determination is to disturbing effects even under the most carefully controlled experimental conditions.

2.4. Discussion

2.4.1. The fire point

This property has not been discussed previously for two reasons. Firstly, there is an almost complete lack of experi-

mental data concerning it and it is not therefore possible to test the validity of any theories concerning it; secondly, because it is a different type of property from a flash point. In principle the fire point is the minimum temperature of a liquid at which the rate of evaporation is sufficient to maintain a flame above the liquid. Present methods of determining the fire point probably give too low a value for this quantity because their criterion for determining the fire point is that the liquid shall have been heated to its fire point before the flame is extinguished rather than that the liquid shall be at its fire point when the vapour is ignited.

A method based on igniting the liquid and then cooling it until the flame is extinguished and recording the temperature at which extinction occurs would seem to offer more scope for a systematic analysis.

2.4.2. The closed flash point

In case III of the Appendix to this chapter an expression is derived, (equation 2.14) whereby the difference between the closed flash point as measured and the true closed flash point can be calculated for the case where there is no disturbance of the vapour phase. Substituting the data for hexanol into this expression gives a value of $\frac{C_A}{C_e} = 0.82$ for an experimental closed flash point of 145°F. If it is assumed that C_A is the equilibrium concentration at the true closed flash point (as defined by Burgoyne and Williams-Leir) and C_e is the equilibrium concentration at the experimental closed flash point then, for $\frac{C_A}{C_e} = 0.82$, the value of the true closed flash point would be 140°F. An expression for the case where the vapour is stirred has been derived (34) by assuming that stirring is perfect in the vapour phase except for a surface film in which the resistance to mass transfer is concentrated. Any numerical values used for the thickness of this film would be arbitrary however and no numerical solution will be given.

When any physical property of a substance is measured it is important that the nature of the property be understood for such an understanding will enable a closer approach to the true value of the property to be made. It would seem that when present methods for determining flash points were developed the physical significance of the flash point was but imperfectly understood because these methods give results which are controlled by two factors viz:- the true closed flash point of the substance under test and the rate of diffusion of vapour from the liquid surface to the igniting source.

The true closed flash point as defined by Burgoyne and Williams-Leir (loc.cit) is a fundamental physical property of an inflammable substance (insofar as the lower limit of inflammability may be regarded as fundamental). Values of the flash point determined by existing I.P. methods give a value higher than the true closed flash point because the concentration of vapour at the surface is changing continuously and there is a finite delay before the effect of any change can be observed at the height of the igniting source. The magnitude of the delay between the vapour at the surface becoming inflammable and the vapour at the igniting source becoming inflammable will be governed by the diffusivity of the vapour in air, the separation of the igniting source from the surface and by whether or not the vessel is closed.

The differences between the true and the experimental values of closed flash point are in general less than 5°C (26) (35) and a possible explanation of these differences has been advanced above by reference to theoretical diffusion rates. The I.P. methods therefore give a value for the closed flash point which is fairly close to the true value and they are reasonably convenient to use for liquids with flash points greater than room temperature. An account of the difficulties which arise when adapting this method for use with liquids whose flash points are below room temperature (e.g. petrol, acetone, ether) has been given by Dawson (35).

A continuous flow method for determining flash points has been described in a United States Bureau of Mines report (36). In this method air is bubbled through a liquid contained in a glass vessel and a spark is passed through the air as a source of ignition. The glass vessel is contained in a thermostat bath the temperature of which is increased until the spark ignites the air/vapour mixture. By suitable design conditions can be achieved whereby the air bubbles leaving the liquid are very nearly saturated with vapour at the temperature of the liquid. This flow method enables the true flash point to be approached more closely in practice than the unsteady state methods at present in use. Moreover it can be used very conveniently at low temperature if a suitable freezing mixture is available.

2.4.3. Open Flash Points

A review of published data shows that the difference between open and closed flash points may be anything up to 20°C and it has been shown that the magnitude of observed differences is consistent with the view that the differences were caused by diffusion effects. These differences would not be important if it could be established that an open flash point determination measured a physical property which differed in some fundamental or practical way from the closed flash point. In fact the evidence points the other way to the conclusion that an open flash point determination measures nothing new - rather it measures a temperature which is arbitrarily related to the closed flash point. The amount by which the open flash point of a liquid exceeds the closed flash point can be varied at will by changing the distance between the igniting source and the liquid surface. It would be possible to construct an open flash point apparatus in which no flash would be observed until the liquid has reached its boiling point.

Attempts have been made to justify the use of the open flash point by claiming that it gives a better indication of the hazards involved in storing liquids in open vessels. It is not difficult to see that such an attitude can be dangerously misleading. If the temperature of a liquid exceeds its true closed flash point then the concentration of vapour near the surface exceeds the lower limit of inflammability. Therefore, regardless of the fact that the concentration of vapour six inches above the surface may not lie within the inflammable range, the vapour may still be ignited near the surface. The assumption that when a liquid is stored in the open the critical temperature, with respect to ignitibility of its vapour, is the open flash point is not therefore valid and a belief in it may lull one into a false sense of security.

In conclusion then, let it be said that both open and closed flash point determinations are revealed as attempts to measure the true closed flash point on to which are superimposed intrinsic errors due to the finite rate at which diffusion occurs and the lack of equilibrium in the system. However, while the closed flash point method gives an approximation to the true closed flash point which is sufficiently good for all save the most exacting circumstances, the open flash point method gives a result so much in excess of the required value that it can be dangerously misleading. In these circumstances there seems little point in continuing to make determination by the latter method.

Appendix to Chapter Two

The variation in concentration of vapour above a liquid surface with height and time

A list of the symbols used in the Appendix

t = time for which diffusion has been taking place.

y = height above the surface, surface as plane of origin.

z = distance from plane of origin when this is not the surface.

l = distance between plane of origin and surface in the latter case.

C_A = concentration of diffusing vapour at a height y after time t

C_e = concentration of diffusing vapour at liquid surface.

L = temperature of liquid at $t = o$.

M = rate of heating of liquid

T = temperature of liquid at time $t = L + Mt$

N, O = constants in the expression $\ln p_e = N.T + O$

p_e = vapour pressure of liquid at temperature T

E, F = constants in the expression $C_e = \exp [E + F.t]$

$E = N.L + O$ (dimensionless); $F = N.M$ (dimensions, time $^{-1}$) when p_e and C_e are in the same units.

$$F = \frac{\ln (Pe_2/Pe_1)}{(T_2-T_1)/M.}$$

D = diffusion coefficient.

It is possible, by reference to mass transfer theory, to set up differential equations describing the variations in concentration of a substance A in a vapour phase when it is evaporating from a liquid surface and diffusing through that vapour phase. These equations are solved below for four special cases after certain limiting assumptions have been made. The main limiting assumptions are:-

i) that the solutions deal only with the one-dimensional flow of mass from an infinite liquid surface.

ii) that mass transfer is by diffusion only, disturbing effects being ignored.

iii) that Stephan flow is not considered, i.e. it is assumed that the concentration of the substance diffusing is small.

CASE I - Open Flash Point Determination

Initial Conditions

i) that at t = o the concentration of A is zero throughout the vapour phase. In the absence of any information to the contrary this assumption must be made. $(C_A)_{t = o} = o$

ii) that at infinite distance from the liquid surface the concentration gradient is zero. $y = \infty \quad \frac{\partial C_A}{\partial y} = o$

iii) that the variation in concentration of A at the liquid surface is given by $(C_A)_{y=o} = C_e = e^{E + Ft}$ where C_e is the concentration corresponding to the equilibrium vapour pressure of the liquid at the temperature attained after time t, and E and F are constants.

That this is so can be shown as follows:-

The temperature of the liquid surface varies as $T = L + Mt$ where L = initial temperature of the liquid (say 20°C) and M is the rate of heating (10°F/min as specified).

Over a small range of temperature the variation in equilibrium vapour pressure of a liquid may be written

$\ln p_e = N.T + O$ without great error where N and O are constants. In the case of n-propanol (see Table 2.3) the straight line through the points at 20°C and 40°C on a graph of $\ln p_e$ v T would go through the point (30°C, 27.0 mm.), that is to say over this small range the maximum error involved is approximately 2%.

Table 2.3

Vapour Pressure Data For n-propanol

T°C	20	30	40
mm.Hg	14.5	27.6	50.2

On combining these two expressions it can be seen that $\ln p_e = (N.M)t + (N.L + O)$ or $p_e = \exp[(N.M)t + (N.L + O)]$
Therefore it is justifiable to write $C_e = e^{E + Ft}$ at $y = o$.

Differential Equations:-

The basic equation for unsteady state mass transfer is

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial y^2} \qquad - (2.1)$$

taking the Laplace transform of this equation

$$\overline{\frac{\partial C_A}{\partial t}} = D \frac{\partial^2 \overline{C_A}}{\partial y^2} \qquad - (2.2)$$ - indicates the Laplace Transform

The Laplace transform of F(t) is defined as $\overline{F(t)} = \int_o^\infty e^{-pt} F(t)dt$

whence $\overline{\frac{\partial C_A}{\partial t}} = \int_o^\infty e^{-pt} \frac{\partial C_A}{\partial t} . dt = [\overline{C_A}\, e^{-pt}]_o^\infty + p \int_o^\infty e^{-pt} C_A . dt$

$$= o \; C_{A_{t=\infty}} - 1. \; C_{A_{t=o}} + p\overline{C_A}$$

but $C_{A_{t=o}} = o$ from the initial conditions $\therefore \quad \overline{\frac{\partial C_A}{\partial t}} = p\,\overline{C_A} \qquad - (2.3)$

substituting (2.3) in (2.2) $\quad \frac{\partial^2 \overline{C_A}}{\partial y^2} - P/D \; \overline{C_A} = o$

the solution of this differential equation is

$$\overline{C_A} = Ae^{\sqrt{P/D}.y} + Be^{-\sqrt{P/D}.y} \qquad - (2.4)$$

differentiating w.r.t.y $\frac{\partial \overline{C_A}}{\partial y} = A\sqrt{P/D}\, e^{\sqrt{P/D}Dy} - B\sqrt{P/D}\, e^{-\sqrt{P/D}Dy}$

$$- (2.5)$$

substituting the boundary conditions y = o, $C_A = C_e$ in (2.4)

$$\overline{C_e} = A + B$$

$y = \infty \quad \frac{\partial C_A}{\partial y} = o$ in (5) $\qquad o = A.\infty - B.o \quad \therefore \quad A = o$

$$\therefore \quad B = \overline{C_e} = \int_o^\infty e^{E + Ft}.e^{-pt}.dt = \frac{e^E}{F-P}\left[e^{(F-P)t}\right]_o^\infty \text{ for } p>F$$

$$= \frac{e^E}{P-F}$$

substituting for A and B in (2.4) $\overline{C_A} = \frac{e^E}{P-F}.\, e^{-\sqrt{P/D}.y} \qquad - (2.6)$

this is in the form $\overline{C_A} = \frac{e^{-qy}}{p-\alpha}$ where $q = \sqrt{P/K}$, q and k being real and positive, and α unrestricted. From tables of inverse transforms (37)

$$C_A = e^E.\tfrac{1}{2}\, e^{Ft}\left[e^{-\sqrt{F/D}.y}\operatorname{erfc}\left(\frac{y}{2\sqrt{Dt}} - \sqrt{Ft}\right) + e^{+\sqrt{F/D}y}\operatorname{erfc}\left(\frac{y}{2\sqrt{Dt}} + \sqrt{Ft}\right)\right]$$

$$- (2.7)$$

Of the dimensionless groups $(\sqrt{F/D}.y)$ $(\sqrt{Ft})$ and $\left(\frac{y}{2\sqrt{Dt}}\right)$ only two are independent. Equation (27) may therefore be written

$$\frac{C_A}{C_e} = F\left[\left(\frac{y}{2\sqrt{Dt}}\right)\left(\sqrt{Ft}\right)\right] \qquad - (2.8)$$

since $e^{E+Ft} = C_e$.

CASE II Storage Tanks:-

Here the problem is concerned with a volume of vapour occupying the space above a liquid stored in a closed tank and the circumstances under which a potentially inflammable concentration of vapour will spread through this volume.

Initital conditions

i) At $t = o$ $C_A = o$ throughout the vapour

ii) that the liquid surface is at a constant temperature $C_A = C_e \neq F(t)$

iii) that no mass transfer takes place across the plane corresponding to the roof of the tank. In this case it is more convenient to consider this limiting plane to be at zero height and the liquid surface at height l. To avoid confusion, systems of this type will be described using a variable height z. Therefore the intial conditions become

$$(C_A)_{t=o} = o; \quad z = o \quad \frac{\partial C_A}{\partial z} = o ; \quad z = l \quad C_A = C_e \neq F(t)$$

Solution of the equations

Equations (4) and (5) of Case I apply in this case also.

Thus $$\overline{C_A} = Ae^{\sqrt{P/D}\, z} + Be^{-\sqrt{P/D}z} \qquad - (2.4)$$

$$\frac{\partial \overline{C_A}}{\partial z} = A\sqrt{P/D}\, e^{\sqrt{P/D}z} - B\sqrt{P/D}\, e^{-\sqrt{P/D}\,z} \qquad - (2.5)$$

substituting $z = o$ $\frac{\partial C_A}{\partial z} = o$ in (2.5) $o = A - B$ i.e. $A = B$

$z = l$ $C_A = C_e$ in (2.4) $$\frac{C_e}{P} = A\left[e^{\sqrt{P/D}\, l} + e^{-\sqrt{P/D}\, l}\right]$$

substituting for A and B in (2.4)

$$\overline{C_A} = \frac{C_e}{P} \frac{e^{\sqrt{P/D}z} + e^{-\sqrt{P/D}z}}{e^{\sqrt{P/D}l} + e^{-\sqrt{P/D}l}}$$

$$= \frac{C_e}{P}\left[e^{-\sqrt{P/D}(l-z)} + e^{-\sqrt{P/D}(l+z)}\right]\left[1+e^{-2\sqrt{P/D}l}\right]^{-1}$$

Expanding the second bracket

$$\overline{C_A} = \frac{C_e}{P}\left\{\sum_{n=o}^{\infty} (-1)^n e^{-\sqrt{P/D}\left[(2n+1)l-z\right]} + \sum_{n=o}^{\infty} (-1)^n e^{-P/D\left[(2n+1)l+z\right]}\right\}$$

Inverting

$$\frac{C_A}{C_e} = \sum_{n=o}^{\infty}(-1)^n \operatorname{erfc}\left[\frac{(2n+1)l-z}{2\sqrt{Dt}}\right] + \sum_{n=o}^{\infty}(-1)^n \operatorname{erfc}\left[\frac{(2n+1)l+z}{2\sqrt{Dt}}\right]$$

- (2.9)

or in terms of dimensionless groups $\frac{C_A}{C_e} = F\left[\left(\frac{l}{2\sqrt{Dt}}\right)\left(\frac{z}{2\sqrt{Dt}}\right)\right]$ - (2.10)

CASE III Closed Flash Point Determinations

In this case it is assumed that vapour is diffusing in an undisturbed manner from the liquid surface to the vessel roof and that there is no stirring of the vapour phase.

Initial Conditions

i) At $t = o$ $C_A = o$ throughout the vapour.

ii) At $z = l$ $C_A = e^{Et+Ft}$ as discussed in Case I.

iii) At $z = o$ $\frac{\partial C_A}{\partial z} = o$ as discussed in Case II.

Solution of the Equations:-

Equations (2.4) and (2.5) of Case I are again used and the above initial conditions are substituted into them.

substituting at $z = o$ $\frac{\partial C_A}{\partial z} = o$ into (2.5) $o = A - B$ i.e. $A=B$

$C_A = e^{Et+Ft}$ at $z = l$ into (2.4) $\frac{e^E}{P-F} = A\left[e^{\sqrt{P/D}l} + e^{-\sqrt{P/D}l}\right]$

substituting for A and B in (2.4)

$$\overline{C_A} = \frac{e^E}{P-F}\left[\frac{e^{\sqrt{P/D}z} + e^{-\sqrt{P/D}z}}{e^{\sqrt{P/D}l} + e^{-\sqrt{P/D}l}}\right]$$

Dividing through by $e^{\sqrt{P/D}l}$ and expanding the denominator as before

$$\overline{C_A} = \frac{e^E}{P-F}\left\{\sum_{n=o}^{\infty}(-1)^n e^{-\sqrt{P/D}\left[(2n+1)l-z\right]} + \sum_{n=o}^{\infty}(-1)^n e^{-\sqrt{P/D}\left[(2n+1)l+z\right]}\right\}$$

Inverting:-

$$\frac{C_A}{C_e} = \sum_{n=o}^{\infty}\tfrac{1}{2}\left\{e^{-\sqrt{F/D}\left[(2n+1)l-z\right]}\operatorname{erfc}\left[\frac{(2n+1)l-z}{2\sqrt{Dt}} - \sqrt{Ft}\right]\right.$$
$$\left. + e^{\sqrt{F/D}\left[(2n+1)l-z\right]}\operatorname{erfc}\left[\frac{(2n+1)l-z}{2\sqrt{Dt}} + \sqrt{Ft}\right]\right\}$$
$$+ \sum_{n=o}^{\infty}\tfrac{1}{2}\left\{e^{-\sqrt{F/D}\left[(2n+1)l+z\right]}\operatorname{erfc}\left[\frac{(2n+1)l+z}{2\sqrt{Dt}} - \sqrt{Ft}\right]\right.$$
$$\left. + e^{+\sqrt{F/D}\left[(2n+1)l+z\right]}\operatorname{erfc}\left[\frac{(2n+1)l+z}{2\sqrt{Dt}} + \sqrt{Ft}\right]\right\} \quad - (2.11)$$

Expressing this in dimensionless groups

$$\frac{C_A}{C_e} = F\left[\left(\frac{1}{2\sqrt{Dt}}\right)\left(\frac{z}{2\sqrt{Dt}}\right)(\sqrt{Ft})\right] \qquad - (2.12)$$

Case IV Open Flash Point Determinations - Revised

In the light of further investigations it became apparent that the treatment outlined for open flash point determinations in Case I was inadequate. The reason for this was that the physical model on which the treatment was based was oversimplified. In Case I it was assumed that the vapour diffused in an undisturbed manner from the liquid surface to infinity. Later work suggested however that shielding, far from being perfect, was largely ineffective. It was therefore decided to solve the differential equations assuming that the concentration of diffusing vapour A was reduced to zero, at a distance l from the liquid surface, by the effect of draughts or other disturbing factors.

Initial Conditions

i) At $t = o$ $C_A = o$ throughout the vapour

ii) At $z = l$ (i.e. at the liquid surface) $C_A = e^{E+Ft}$ as before

iii) At $z = o$ $C_A = o$

Solution of the equations

Solving for the constants in equation (2.4) using the above conditions gives $A = -B$

and $$A = \frac{e^{E}}{P - F}\left[e^{\sqrt{P/D}l} - e^{-\sqrt{P/D}l}\right] - 1$$

substituting for A and B in equation (4)

$$\overline{C_A} = \frac{e^{E}}{P-F}\left[\frac{e^{\sqrt{P/D}z} - e^{-\sqrt{P/D}z}}{e^{\sqrt{P/D}l} - e^{-\sqrt{P/D}l}}\right]$$

solving as before

$$\frac{C_A}{C_e} = \frac{1}{2}\sum_{n=o}^{\infty} e^{-\sqrt{F/D}\left[(2n+1)l-z\right]}\operatorname{erfc}\left[\frac{(2n+1)l-z}{2\sqrt{Dt}} - \sqrt{Ft}\right] + e^{\sqrt{F/D}\left[(2n+1)l-z\right]}\operatorname{erfc}\left[\frac{(2n+1)l-z}{2\sqrt{Dt}} + \sqrt{Ft}\right]$$

(continued overleaf)

$$- \tfrac{1}{2} \sum_{n=0}^{\infty} e^{-\sqrt{F/D}\left[2n+1\ 1+z\right]} \operatorname{erfc}\left[\frac{2n+1\ 1+z}{2\sqrt{Dt}} - \sqrt{Ft}\right]$$

$$+ e^{\sqrt{F/D}\left[2n+1\ 1+z\right]} \operatorname{erfc}\left[\frac{2n+1\ 1+z}{2\sqrt{Dt}} + \sqrt{Ft}\right] \qquad - (2.13)$$

Expressing this in terms of dimensionless groups

$$\frac{C_A}{C_e} = F\left[\left(\frac{1}{2\sqrt{Dt}}\right)\left(\frac{z}{2\sqrt{Dt}}\right)\ (\sqrt{Ft})\right] \qquad - (2.14)$$

CHAPTER 3

THE SPREAD OF FLAME ACROSS A LIQUID SURFACE
EXPERIMENTAL WORK - PART I

3.1. Preliminary work

At the start of the experimental investigation into spread of flame across a liquid surface preliminary work was carried out to gain information on the following points prior to the design of a larger scale apparatus.

i) The suitability of different inflammable liquids for use in larger scale experimental work.

ii) The maximum size of apparatus which it would be convenient to use.

iii) The relative merits of various methods of ignition of inflammable liquids.

iv) The precautions which would be necessary to minimize the effect of outside disturbances such as draughts.

This preliminary work was carried out in metal vessels which were already available. Two such vessels were used one being 9" x 7" x 1" and the other being 7" x $1\frac{1}{2}$" x $\frac{1}{2}$".

i) When making a choice of inflammable liquid it had to be borne in mind that the terms of reference of the research programme specified the use of a liquid of low volatility. Other controls on the choice were imposed by the cost and availability of the different suitable liquids. Small scale experimental work was conducted with the following liquids at room temperature:- Tetralin, butanol, propylene glycol, ethyl phthalate, ethylene glycol, cyclohexanone, amyl alcohol, cyclohexanol and hexanol.

Tetralin, which was used extensively in the other preliminary work because it was available in large quantities, showed itself to be inconvenient for larger scale work. When burning, tetralin releases large quantities of soot, in common

with other aromatic hydrocarbons. This soot is released in the vapour phase from where it is deposited freely on any adjacent solid surfaces thus rendering the vessel in which the tetralin is burning extremely dirty. Furthermore the liquid becomes contaminated as burning continues and after a short while becomes heavily discoloured. In view of the above factors which would render experimental work with tetralin exceedingly unpleasant it was decided not to consider further at this stage tetralin or any other aromatic liquid.

Of the remaining liquids the alcohols emerged as the most suitable. The rate of spread of flame across an amyl alcohol surface (measured as 0.3"/sec. at room temperature and 2"/sec. at 45°C) lay in the range in which it was planned to take measurements and the liquid was clean to handle and clean while burning. Moreover the adjacent members of the homologous series, butanol and hexanol, would serve as useful comparisons when the effects of liquid volatility and other physical properties were studied. It was therefore decided to start experimental work using amyl alcohol.

ii) It was considered desirable to carry out experimental work in a fume cupboard. This fact placed the limitations on the size of the large scale apparatus. It was found experimentally that the fume cupboard available was quite capable of handling the products of combustion from a 63 sq.in. surface of burning tetralin. The physical size of the fume cupboard rather than its handling capacity was therefore controlling. This was:- width of door 41.5"; inside width 44"; depth beyond door 15".

iii) A method of igniting a liquid of low volatility (i.e one which could not be ignited directly) was required which would give reproducible behaviour and which, when used in conjunction with a parallel sided channel, would give rise to a flame spreading with a substantially straight flame front. Various methods of ignition were tried which involved segregating part of the involatile liquid behind a barrier and then applying heat either

from a coal gas/air flame or by adding a small quantity of more volatile liquid and igniting that. The barrier would be removed when a flame was established and this flame would then be able to spread. All such methods proved unsatisfactory in some respect. The simplest method tried, that of igniting the liquid at a wick running the width of the channel, proved to be the best. The flame readily established itself on the wick and, after a warming up period, it would spread with a straight flame front. Reproducible behaviour was obtained by this means.

iv) The preliminary experimental work showed that some form of control against the effects of draughts was necessary. In the absence of screens such factors as the amount by which the flame cupboard door was open had a noticeable effect on the spreading flame. With side screens 5" high however no such effects were observed.

3.2. Apparatus

3.2.1. The experimental vessel

When considering the programme of work for which an experimental vessel would be needed, prior to the design of such a vessel, it was concluded that provision should be made for the investigation of the effect of the following factors on the rate of spread of flame across a liquid surface:-

the initial temperature of the liquid, the physical properties of the liquid, the depth of the liquid, the width of the flame front. In order to reduce the complexity of the problem it was decided to confine the flame to spreading along a channel which was long in comparison with its width. This condition meant that the practical situation could be represented by a two dimensional model with a resultant simplification of any theoretical analysis. In terms of the experimental work involved, this simplification necessitated the study mentioned above of the effect of the flame (i.e. the channel) width.

With the experience and information gained in the preliminary work a larger scale apparatus was designed in which operating conditions, as discussed above, could be closely controlled and accurate measurements taken. This apparatus will now be described in detail under three headings viz:- the temperature regulating system, the combustion trough, and the screens.

The temperature regulating system:- Of the methods available for controlling the temperature of the inflammable liquid in the combustion vessel it was thought that partial immersion of the combustion vessel in a constant temperature water bath would give a satisfactory control. Desirable qualities for such a system are that it should give as uniform a temperature to the liquid in the combustion vessel as possible, that it should be easy to adjust, and that any temperature setting could be reproduced. It was considered likely that a water bath would prove satisfactory on each of these points and this method was therefore adopted.

It was decided to make the water bath as large as possible, bearing in mind that it had to be fitted into a fume cupboard. This resulted in the dimensions of the water bath (A) being fixed at 40" x 9" x 3". With a vessel of this shape it would have been difficult to incorporate a heater, thermostat, and stirrer. A separate constant temperature water bath (B) 18" x 10" x 10", from which water could be circulated to bath A was therefore provided in which a Techne 'Tempunit' was installed.

This 'Tempunit'comprised an electric heater, a thermostat giving a temperature control of 0.1°C over the range 15 - 80°C, and a means of circulating water between the tank and an outside system.

The water bath (A) was therefore provided with inlet and outlet pipes, 1" x ¼" i.d., which were mounted one above the other at the same end of the bath. Circulation of the water was achieved by admitting the water through the upper pipe and by inserting a baffle which was mounted on six feet so as to be 1" above the

base of the water bath. This baffle covered the complete area of the water bath except for a 1" gap at the end distant from the inlet pipe. The water was therefore constrained to flow along the top of this baffle and to return underneath it.

Since the water level in tank (B) was greater than in the water bath (A) water flowed from B into A under the influence of gravity, the flow in the reverse direction being controlled by the circulating attachment on the 'tempunit'. It was not possible to balance these flows exactly and they were therefore adjusted so that the water bath (A) was tending to fill. A float operated micro-switch brought a pump into action when the water level in A reached a certain height thus increasing the flow into B, and cut the pump out when the level had dropped sufficiently. By this means the water level in A was controlled within limits $\frac{1}{4}$" apart.

In order to reduce heat losses both vessels A and B were lagged where possible with asbestos cloth and asbestos board. When the system had reached equilibrium the temperature in A would vary by less than 1°C from end to end at a temperature of 50°C and this equilibrium temperature in A would be 1 - 2°C lower than the control temperature in B.

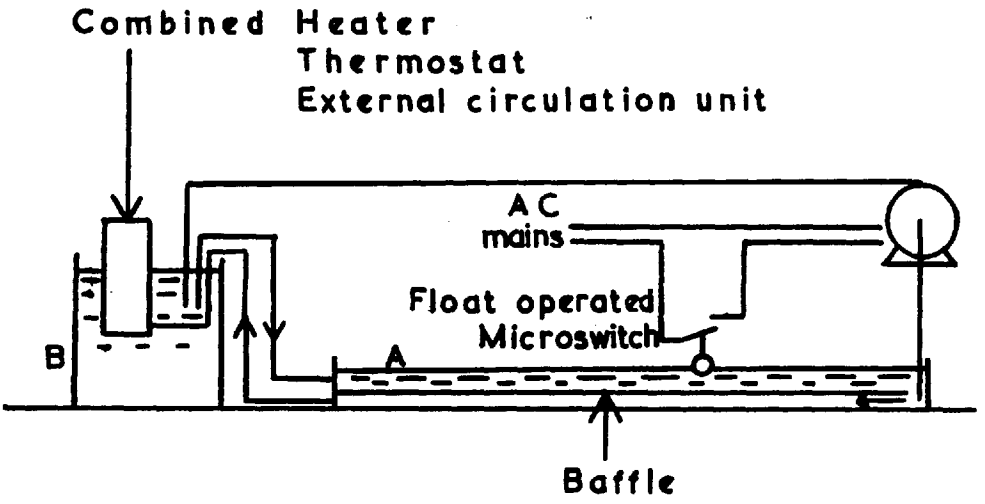
The temperature regulating system is shown in diagrammatic form in Fig. 3.1. while detailed dimensions of the water bath (A) together with details of the supports for the combustion vessel are given in Fig. 3.2.

The combustion vessel

The combustion vessel consisted of a brass trough 38" x 4.5" x 1". Two fixed marks were inscribed on the base of this vessel $10\frac{1}{4}$" apart, one being 13" from the nearest end.

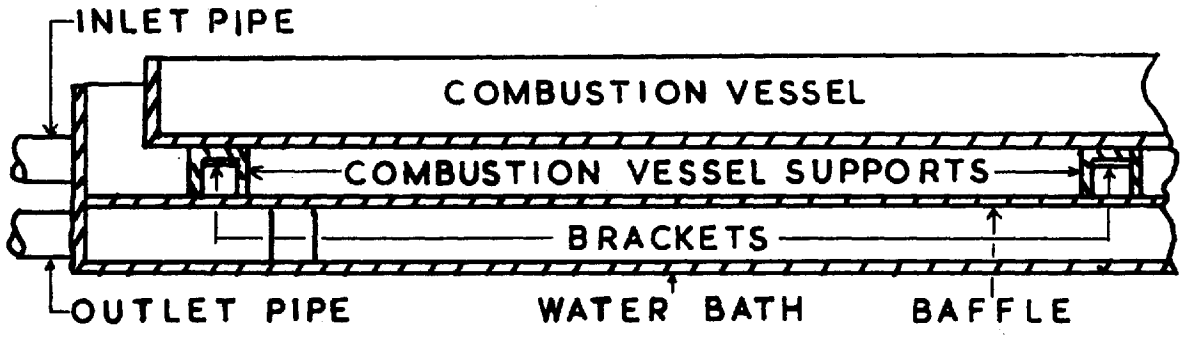
The screens

Initially it was intended to use asbestos sheets bolted to brass angle as screens. In use however the brass angle became distorted by the heat rendering this method valueless. These



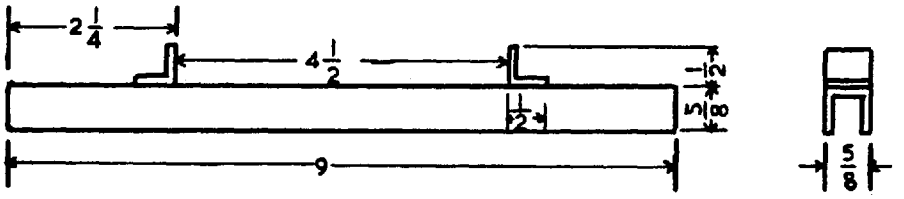
A The experimental vessel
B Constant temperature water bath

FIG 3.1 THE TEMPERATURE CONTROL SYSTEM

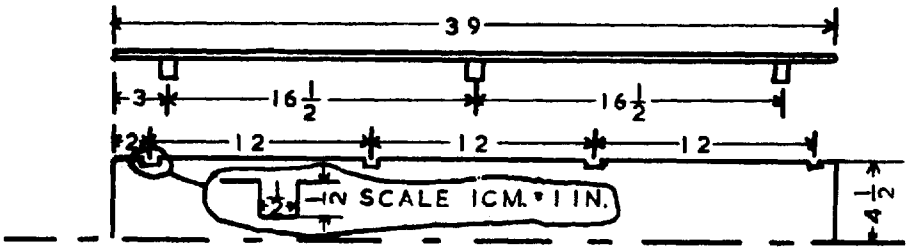


3.2A ASSEMBLY DRAWING (SECTIONAL ELEVATION)

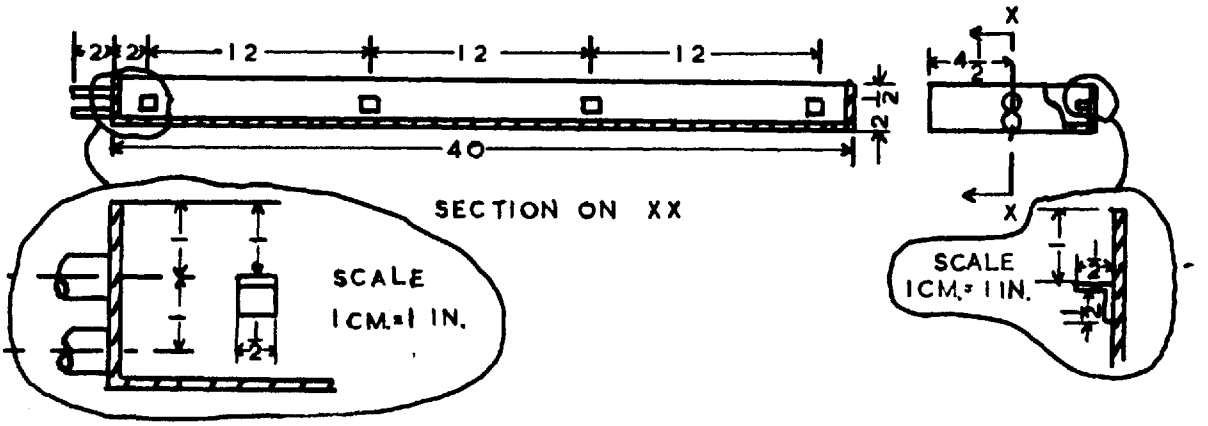
FIG.3.2 THE EXPERIMENTAL VESSEL



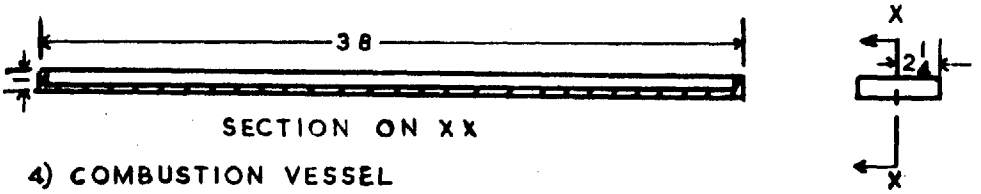
1) COMBUSTION VESSEL SUPPORT



2) BAFFLE



3) WATER BATH



4) COMBUSTION VESSEL

NO.	COMPONENT	SCALE	NO. OFF	MATERIAL	THICKNESS
1	COMBUSTION VESSEL SUPPORT	1 CM.= 1 IN.	4	BRASS	1/8 IN
2	BAFFLE	1 CM.= 4 IN.	1	BRASS	16 GAUGE
3	WATER BATH	1 CM.= 4 IN.	1	BRASS	16 GAUGE
4	COMBUSTION VESSEL	1 CM.= 4 IN.	1	BRASS	16 GAUGE

ALL DIMENSIONS IN INCHES

3.2B DETAILS OF COMPONENTS

screens were therefore replaced by Sindanu, $\frac{3}{8}$" thick and 8" high which was both heat resistant and self supporting.

Since on occasions flames spread around the ends of the Sindanu screens, the original asbestos screens were modified and laid on the combustion vessel outside the main screens so as to prevent the access of air to those portions of the liquid surface which it was not intended to ignite.

The main screens were held in position by clamps.

3.2.2. The method used for timing high rates of spread

The average rate of spread of flame was measured by timing its progress between two fixed marks 26 cm. apart. For intervals greater than three seconds visual observation and timing with a stop watch was considered sufficiently accurate but for shorter intervals it was felt that a different means of timing would be necessary. Of the methods available for timing the flames rate of spread it was considered that methods which gave a direct indication of a time interval would be more useful than photographic methods which would involve further measurements. The possibility of initiating a counter by means of a signal from a photo electric cell was investigated experimentally but the method was found to be unsatisfactory due to the low light emission from the flame front and the distance which it was necessary to allow between the liquid surface and the photo electric cell. The second method of initiation to be investigated was the operation of micro switches by the fusion of nylon threads. Apart from the minor practical difficulty of handling the very fine nylon thread used (0.08 mm. diameter) this method proved both reliable and convenient.

The circuit used was as follows:- the output from a 1000 c/s signal generator was fed to a decatron counter via two micro switches. These switches, which were operated through brass levers, were connected so that in their normal operating positions one completed the circuit while the other one broke it.

To prepare the timing apparatus for a run the micro switches were clamped above the combustion vessel some 3" above the level of the screens with one switch above each of the fixed marks on the base of the combustion vessel. To the lever on each switch a length of nylon thread was attached, the other end of which was tied to a short length of thin metal which rested on the base of the combustion vessel. This piece of metal was held in position by placing each end of it underneath one of the sindanu screens. Having attached the nylon thread to the switch, the height of each switch was adjusted so that the tension in the nylon thread held the operating lever of the switch down against the compression of a spring in the switch. In this position the circuit through the switch nearer to the wick was open whereas that through the farther switch was closed.

At the start of a run the decatron counter was reset to zero and the liquid was ignited. As the flame spread to the far end of the trough each nylon thread was fused in turn. When the first thread was fused the circuit was completed through the first micro switch as the operating lever was released. This enabled the signal from the signal generator to be counted by the decatron counter. When the second thread was fused the circuit was broken again and no further signal reached the counter. The reading on the counter then gave the time interval between the operation of the two switches to 0.001 seconds.

Errors in the use of this method could arise from variations in the time between the arrival of the flame at the nylon thread and the operation of the switch. However this delay is likely to be similar for the operation of each switch and these errors will tend to cancel each other. Moreover the nature of the experimental work was such that an answer to 0.001 seconds was not required; 0.05 seconds being sufficiently accurate.

3.2.3. The method used for studying temperature variations in the liquid

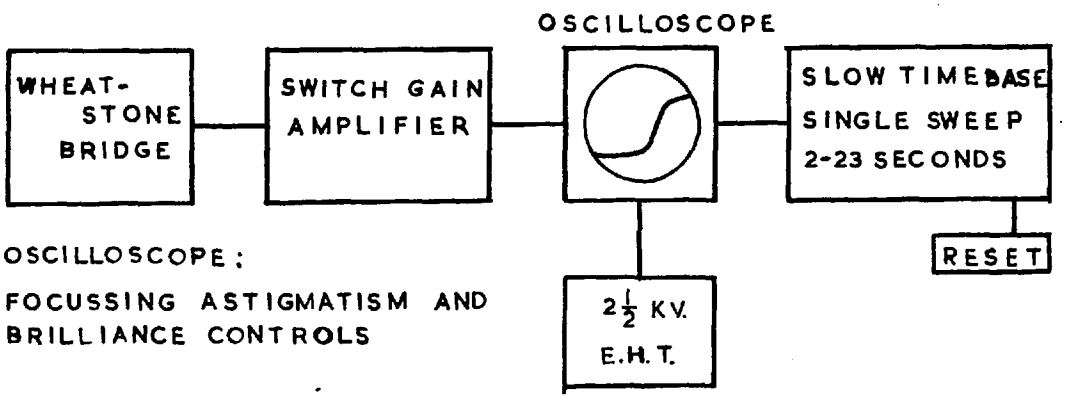
Because it was concluded at an early stage of the work that heat transfer processes in the liquid played an important part in controlling the rate of spread of flame across a liquid surface an apparatus was designed and constructed to measure temperature variations in a liquid as a flame spread across its surface.

In this apparatus a thermistor was included as one arm of a Wheatstone Bridge and the out-of-balance voltage from this bridge was amplified and fed on to the Y plates of an oscilloscope. The X plates of the oscilloscope were linked to a single sweep time base. A diagram of this apparatus is given as Fig. 3.3

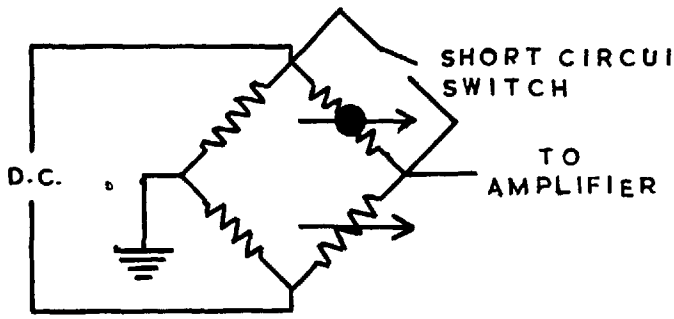
The range of this instrument was such that in the vertical direction temperatures from 20°C to 90°C could be measured while the time base could be varied from two to twenty three seconds. The calibration of the temperature axis is given in Fig. 3.4. This calibration was checked periodically but was not found to vary appreciably. The time base when checked was found to be linear, within the limits needed.

To complete the instrument a camera was constructed on the front of the oscilloscope to give a focussed image of the screen on a photographic plate, and a push button switch was provided with one of its leads connected to each lead of the thermistor. By this means the thermistor could be short circuited, giving a distinctive deflection on the oscilloscope screen. This enabled the trace on the screen to be related to the position of the flame relative to the thermistor by pressing the switch at predetermined positions of the flame front.

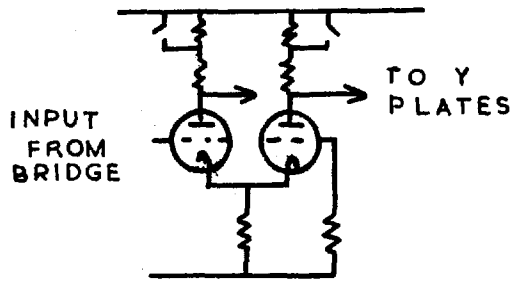
The temperature sensitive element of the thermistor was approximately 1 mm. across and it was sealed in a thin glass tube. Having a low heat capacity it responded rapidly to changes in temperature, the maximum temperature gradient which it could



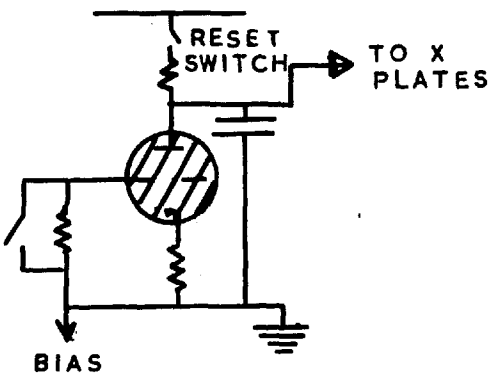
SCHEMATIC DIAGRAM



WHEATSTONE BRIDGE



"LONG TAILED PAIR" DEFLECTION AMPLIFIER



TIME BASE

FIG. 3.3 THE APPARATUS FOR MEASURING TEMPERATURE VARIATIONS.

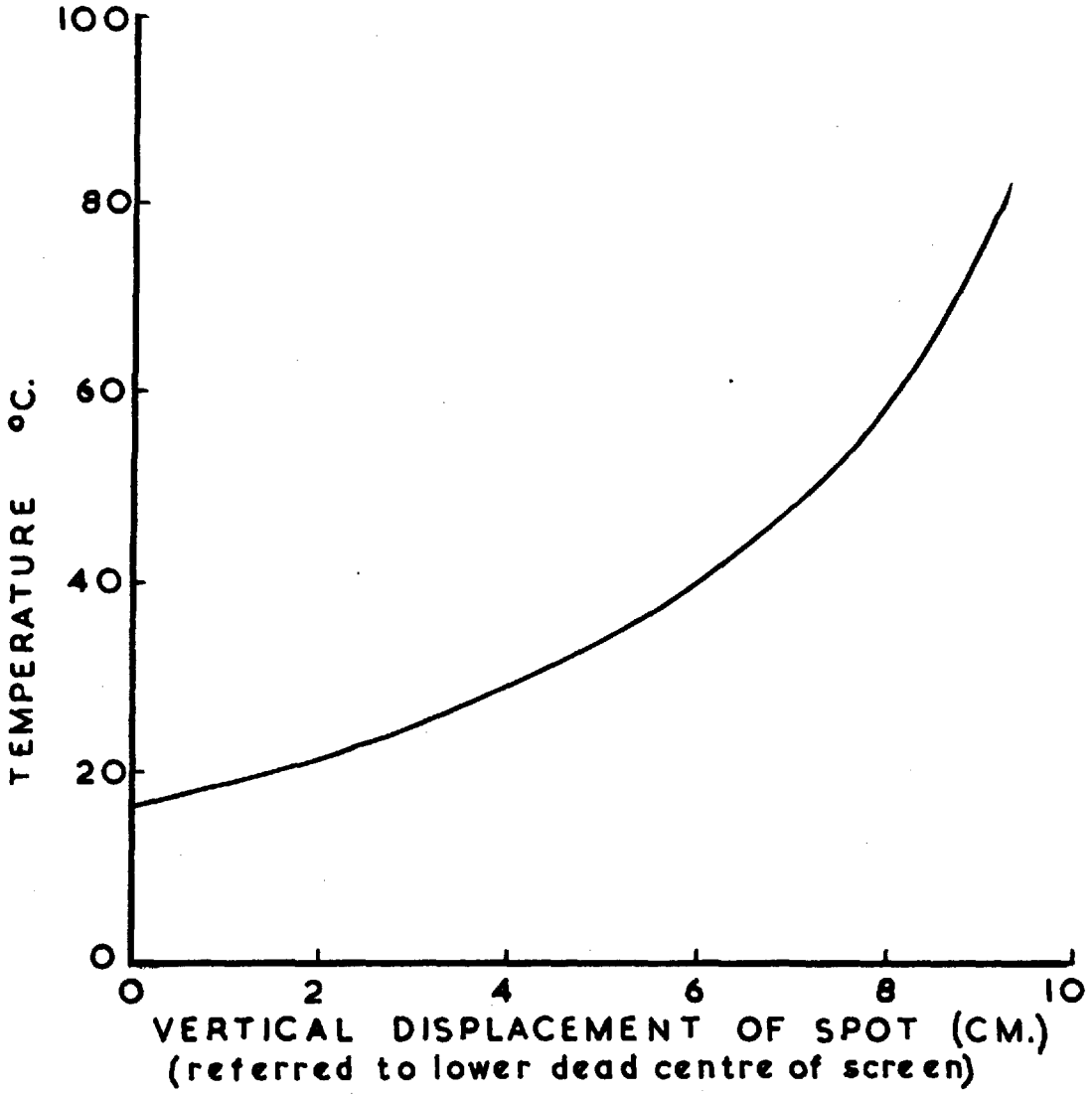


FIG. 3.4 OSCILLOSCOPE CALIBRATION

cope with being of the order of 200°C/second. During experimental work no temperature gradients of anything approaching that order were encountered. The thermistor inevitably gave a value for the temperature which was integrated over a range of depths but owing to the small size of the temperature sensitive element this effect was not important.

3.3. Experimental Procedure

When the first set of runs were carried out in the apparatus described in 3.2.1. it soon became apparent that careful controls were necessary if reproducible results were to be obtained. Fifty three preliminary runs were made as a result of which it was concluded that the inflammable liquid must be changed and the Sindanu screens cooled to room temperature between runs.

The effect of using the same batch of liquid for more than one run was to decrease the rate of spread of the flame although this effect only became marked after three or four runs. A possible explanation of this change lies in the effect of small percentages of water as a diluent on the rate of spread (see 3.4.1.3) and the fact that the liquid in the trough could become contaminated with water. The changing composition of amyl alcohol when exposed to the air due to the absorption of water would be reflected in the increasing specific gravity with time of a sample which was exposed to the air. The results of measurements on such a sample are given in Table 3.1.

TABLE 3.1.

Time of Exposure (min.)	Specific Gravity
0	0.8082
15	0.8096
30	0.8101
45	0.8109
60	0.8115
150	0.8118

Accordingly it was decided to carry out each run with a fresh batch of liquid, either as supplied by the manufacturers or re-distilled to the manufacturers specifications (quoted as a minimum percentage boiling in a given temperature range).

The necessity for cooling the screens is more obvious since the rate of spread is sensitive to changes in temperature. The screens were either allowed to cool naturally between runs or they were sprayed with water and then dried.

The following experimental procedure was therefore adopted. Before a run it was decided what initial temperature, channel width, volume of liquid and liquid to use. (the normal practice for a set of runs was to use the same liquid, the same volume of liquid and the same channel width and to vary the initial temperature).

For each run an estimate of the flame's rate of spread, based on previous experience, was made in order to decide which method to adopt for timing the flame's progress. If the flame was expected to spread at less than 8 cm./sec. (i.e. an interval greater than 3 sec. between passing the different fixed marks) then measurements were made using a stop watch and observing the flame's progress visually. If a rate of spread greater than 8 cm./sec. was expected then arrangements were made for using the method described in 3.2.2.

The thermostat was set to an appropriate value and the temperature regulating system was brought into operation and allowed to come to equilibrium. The specified volume of liquid was then added and, when it had reached a steady temperature, its temperature was measured and recorded. The screens were put into position and adjusted to their appropriate separation, and the wick was placed across the channel so formed, 2" from one end and 11" from the first fixed mark. If appropriate, the nylon threads for the electronic timer were fixed in position at this stage. The liquid was then ignited at the wick and the time taken for the flame to spread between the two fixed marks was measured as discussed above, and recorded. After the flame had passed the

second fixed mark the free end of the channel was covered with a piece of asbestos board and an asbestos cloth was placed over the top of the Sindanu screens. By thus cutting off the air supply the flame was extinguished. This method of extinction proved completely satisfactory.

At the conclusion of the run the liquid was transferred to a residues bottle to await redistillation and the screens were cooled.

By adopting such a standard experimental procedure a fair degree of reproducibility was obtained between runs carried out under identical conditions. The reproducibility of the results is discussed in quantitative terms in 3.4.2.

3.4. Results

3.4.1. The variation of rate of spread with initial temperature

It was stated above (3.2.2.) that in order to determine the rate of spread of flame across a liquid surface two fixed marks were inscribed on the base of the combustion vessel and the interval between the flames arrival at the first mark and its arrival at the second mark was measured and recorded. In order to justify the use of such a measurement, which can only give the average rate of spread over the distance between the fixed marks, a preliminary experiment was carried out. A series of marks was made on the base of the combustion vessel at 1" intervals and the normal experimental procedure was adopted up to the moment of ignition. After ignition however the time was recorded when the flame reached each mark for a distance of 25" from the wick. The time-distance relationship of the flame is shown in Fig. 3.5. This run was carried out using amyl alcohol 250 ml. at 22.5°C with a channel width of 1.3 inches (cf. Table 3.4).

From Fig 3.5 it can be seen that after an initial induction period of 30 seconds the flame spreads at a rate greater than its equilibrium rate up to 7" from the wick. Between 7" and 9" there is a transition stage before the flame adopts its

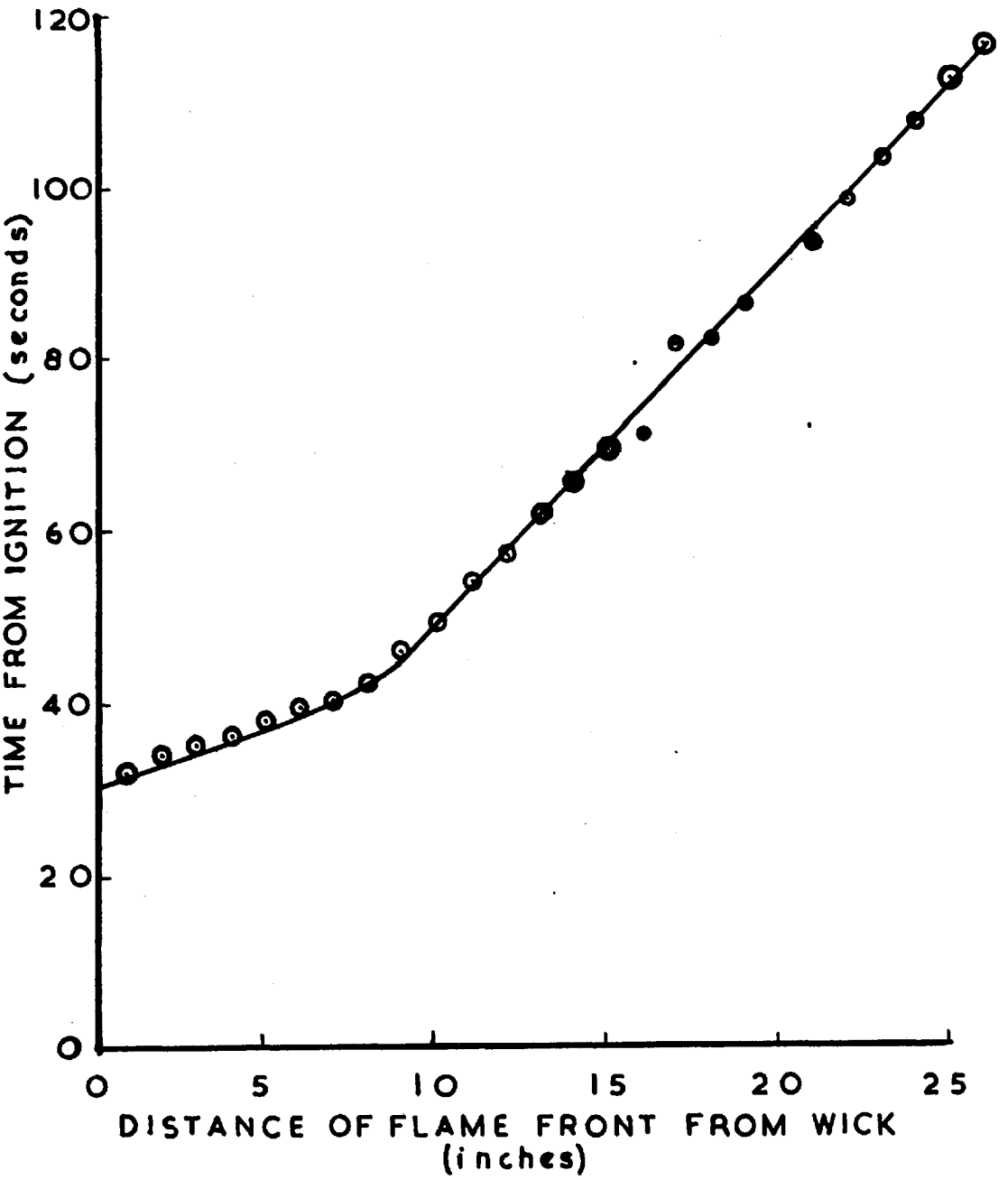


FIG. 3.5 THE PROGRESS OF A TYPICAL FLAME ALONG THE COMBUSTION VESSEL.

equilibrium rate of spread. It then continues at that rate over a considerable distance. The slope of the straight line through the points corresponds to an average rate of spread of 0.62 cm/sec.

The closeness of the points in Fig. 3.5 to a straight line shows that the use of an average rate of spread is justified because the value obtained will be independent of the position or the separation of the fixed marks, provided that a sufficient distance is allowed between the wick and the fixed marks. Since the distance allowed in the combustion vessel for this purpose was 11" it is to be expected, in the light of the above experiment, that the steady state rate of spread will have been attained before the first fixed ~~rate~~ mark is reached.

Having established that the average rate of spread as measured did not depend on the position of the fixed marks relative to the wick, the effects of various parameters on the rate of spread were determined experimentally. These parameters were liquid depth, channel width, the percentage of water as a diluent in the inflammable liquid, and the nature of the inflammable liquid.

The experimental results obtained are tabulated in the Appendix to this chapter as Tables 3.2 - 3.15 and 3.17 - 3.18. For each Table, representing one set of results, the values of the above parameters were kept constant and runs were carried out at a series of initial temperatures. For each run the initial temperature and the time taken to travel 26 cm. are recorded together with the average rate of spread. Where times are quoted to the nearest second or 0.1 second they were measured with a stopwatch. Where three decimal places are quoted the measurement was made using the electronic timer described in 3.2.2.

The values of the parameters appropriate to each set of results are summarised on the first page of the Appendix.

A critical discussion of these results together with a consideration of their reproducibility and a description of the modes of propagation observed is given in 3.4.2.

3.4.1. The effect of liquid depth

The effects of varying the liquid depth were investigated using amyl alcohol and hexanol at a channel width of 1.3 inches and the results obtained are given in Tables 3.2 - 3.9.

On Fig. 3.6 all the experimental points of Table 3.4 are plotted in the form log v against T_L, together with an estimate of the best line through these points. It is apparent that to plot all the 148 points given by Tables 3.2 - 3.9 on the same graph would be to obscure any trends which might be present. Estimates of the best line through each set of points were therefore made, as for the set in Table 3.4, and these are shown on Fig 3.7, which is again in the form log v against T_L. Fig 3.8 shows the best line of Table 3.4 plotted as v , on a linear scale, against T_L. This graph helps to emphasise the very large changes which occur in the rate of spread of flame as the temperature of the liquid increases, and to demonstrate the need for a log v against T_L plot, with equal weighting given to percentage changes, to illustrate the effect of changing the liquid depth.

3.4.1.2. The effect of channel width

The effect of varying the channel width was studied using amyl alcohol and hexanol, 250 ml. per run, and channel widths of 0.9", 1.3" and 2.5". The results obtained are given in Tables 3.4 and 3.9 - 3.12. Estimates of the best line through each set of points are plotted in Fig. 3.9 as log v against T_L.

3.4.1.3. The effect of small percentages of water as a diluent

In the section on experimental procedure (3.3) it was stated that irreproducible results were obtained if the inflammable liquid became contaminated with water. The effect of small percentages of water as a diluent was therefore studied under controlled conditions using solutions of 1, 2 and 4% by volume of water in amyl alcohol. (Water and amyl alcohol are not completely

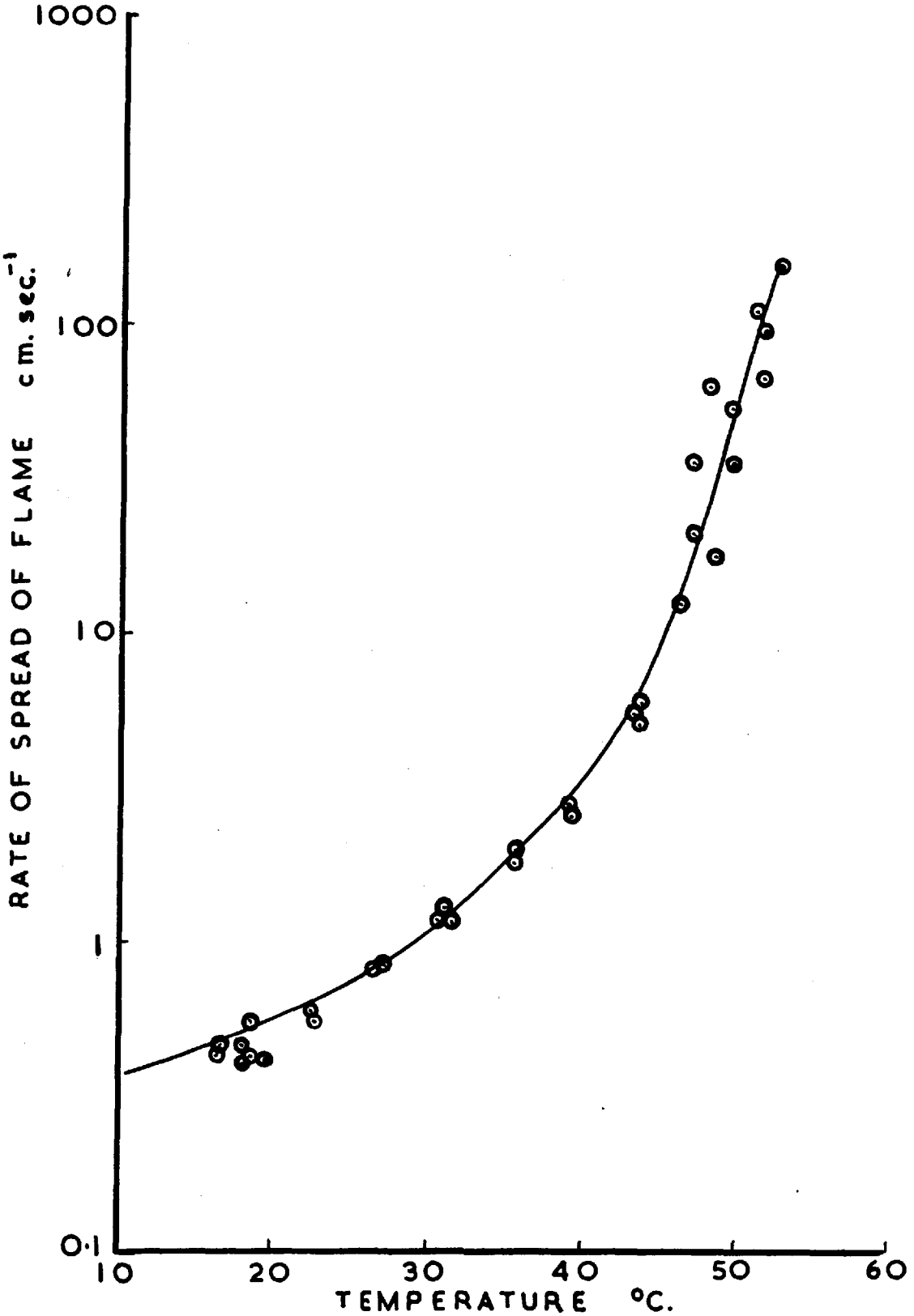


FIG. 3.6 THE RESULTS OF A COMPLETE SET OF RUNS (TABLE 3.4)

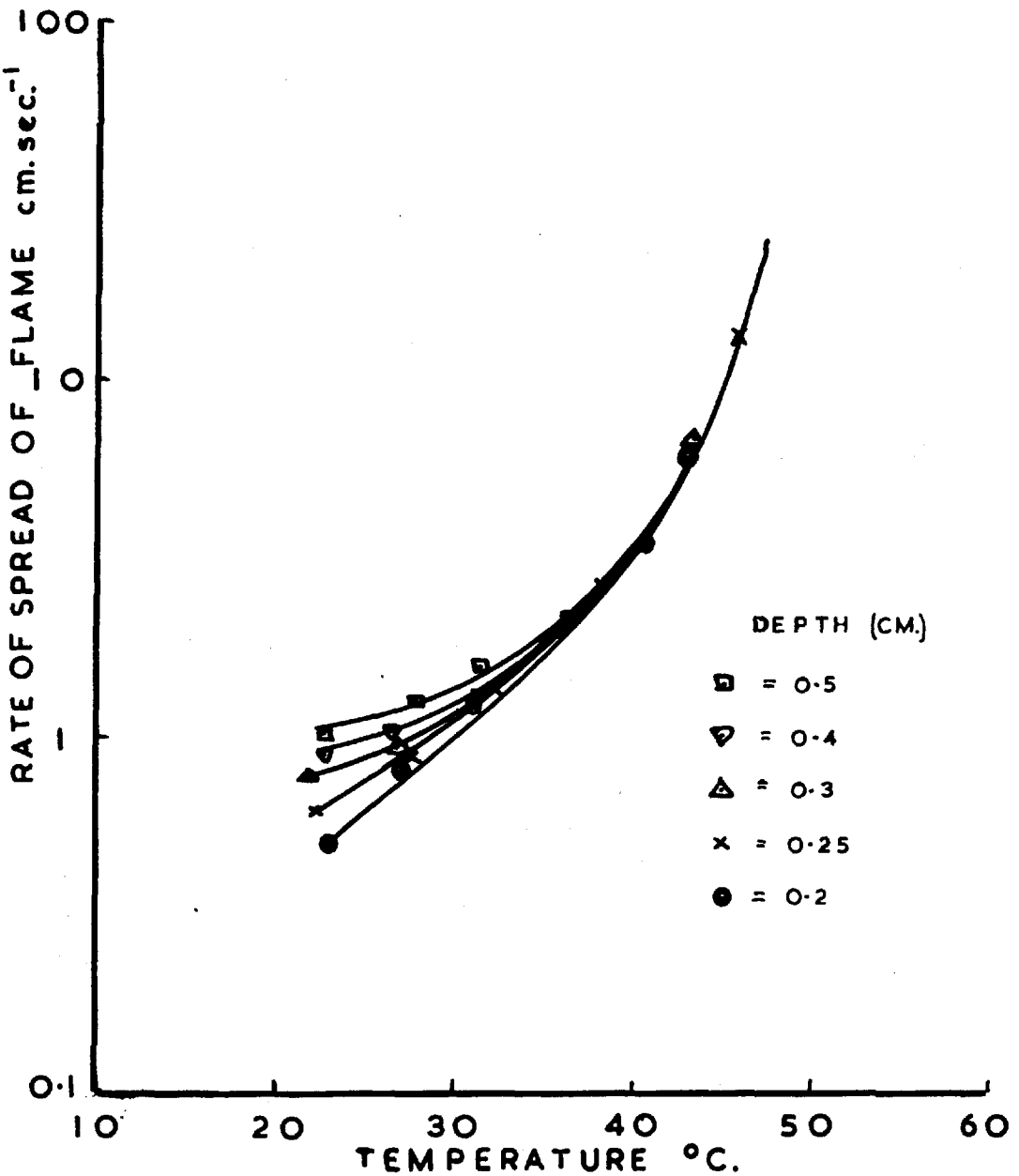


FIG. 3.7 RESULTS FOR AMYL ALCOHOL
The effect of liquid depth

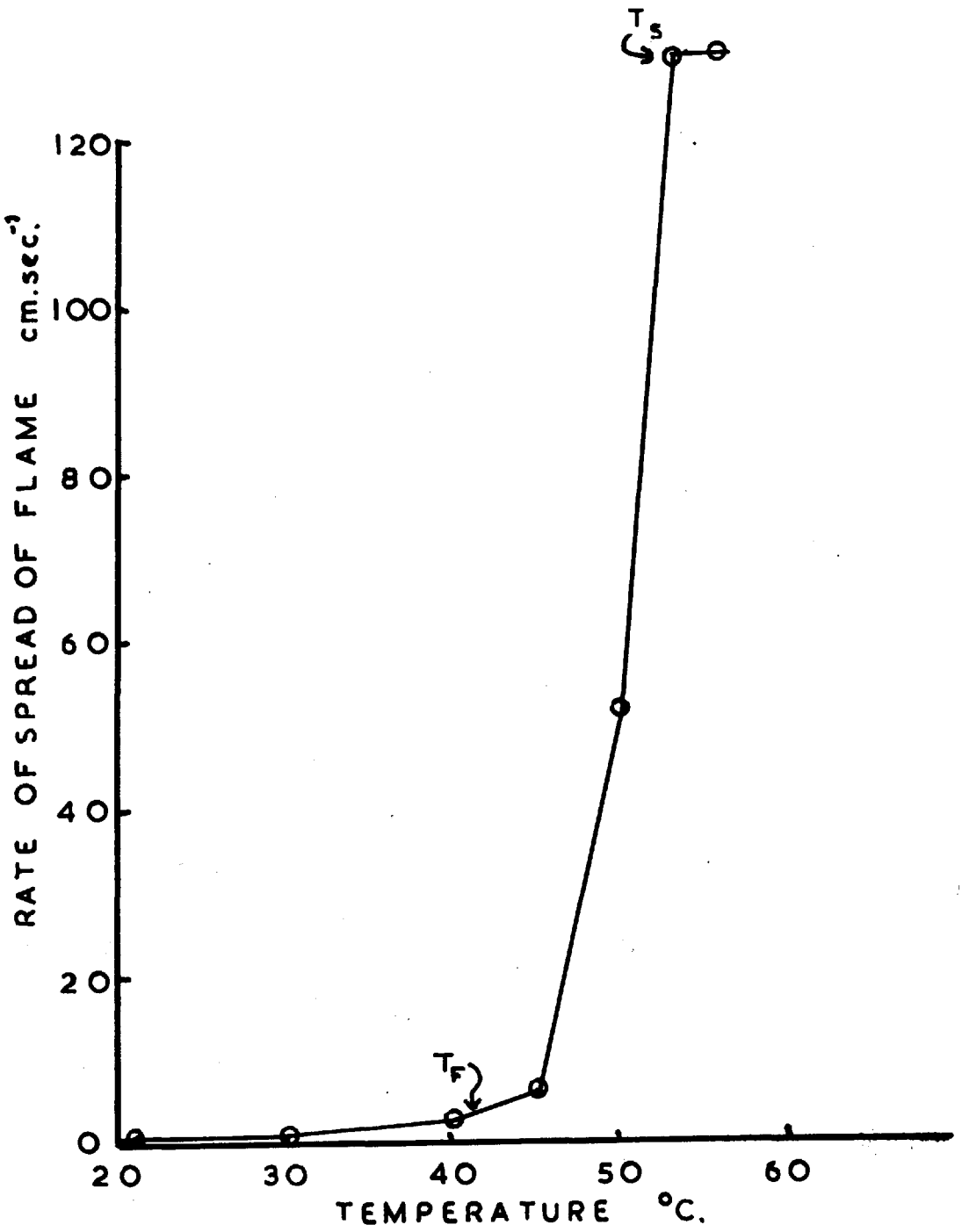


FIG. 3.8 RESULTS FOR AMYL ALCOHOL

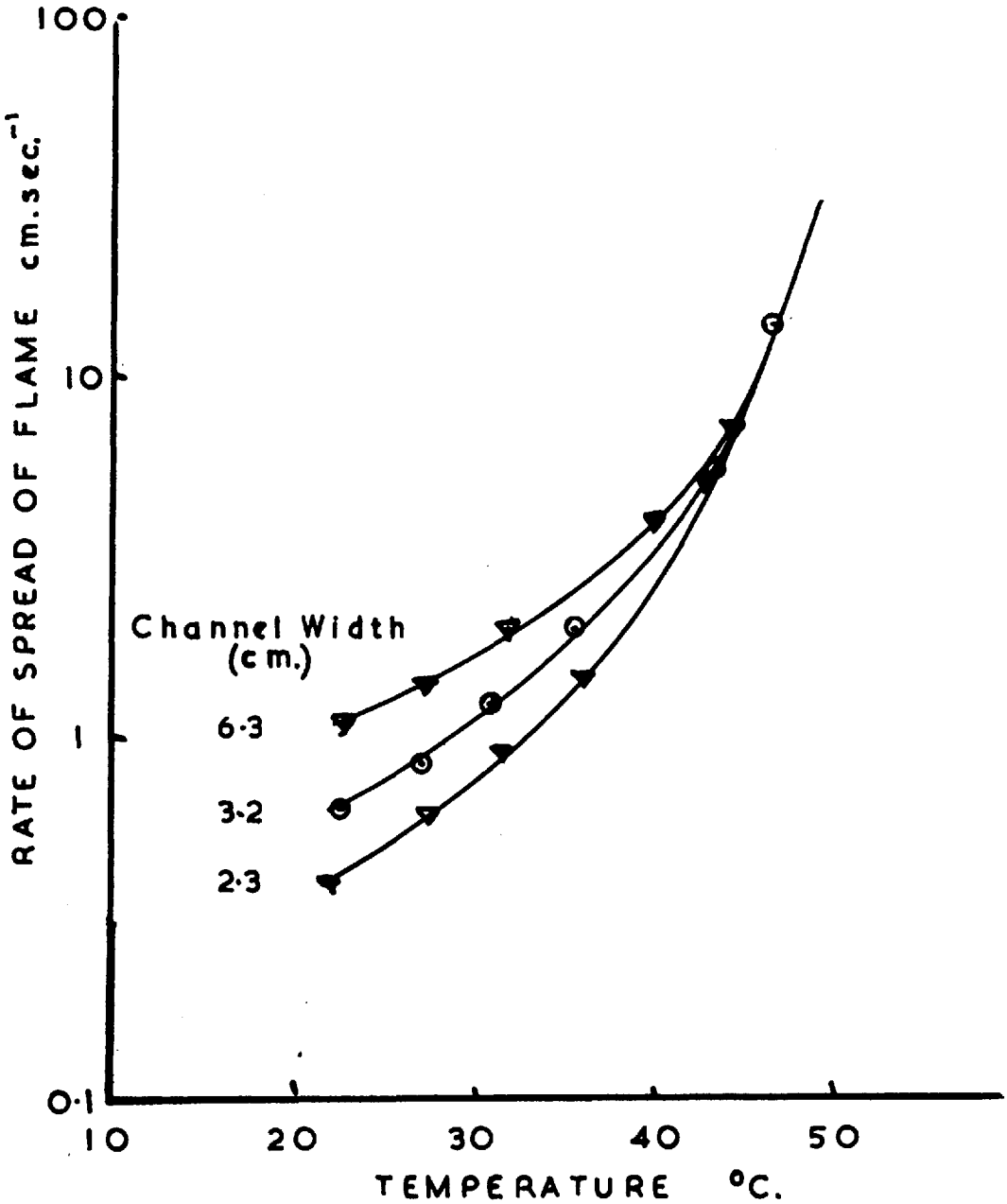


FIG. 3.9 RESULTS FOR AMYL ALCOHOL
THE EFFECT OF CHANNEL WIDTH

miscible, a saturated solution of water in amyl alcohol being approximately 5% by volume of water). The runs were carried out using 250 ml. of solution per run and channel width of 1.3 inches. The results are given in Tables 3.13 - 3.15 and the estimates of the best lines through these points are plotted in Fig. 3.10 as log v against T_L. The results of Table 3.4, for amyl alcohol under the same conditions with no water in solution, are also shown in Fig. 3.10.

3.4.1.4. The results for different inflammable liquids

In addition to amyl alcohol and hexanol, experiments were carried out using propanol and butanol. A summary of some properties of these liquids is given in Table 3.16 while their vapour pressure/temperature curves are plotted in Fig. 3.11. The following abbreviations will be used in this section:-

T_F, the closed flash point of the liquid (Ref.31) °C

T_S, the temperature at which the vapour pressure of the liquid = P_S °C

P_S, the partial pressure of vapour in the stoichiometric mixture with air mm.Hg

P, the partial pressure of vapour at a temperature T mm. Hg.

T_b, the boiling point range quoted by the manufacturers (B.D.H) °C

y, the minimum percentage of liquid boiling in the range T_b %

TABLE 3.16

Substance	T_b	y	P_S	T_F	T_S	$\frac{P}{P_S}$ at T_F
n-propanol	96-99	95	32.3	23	32.5	0.54
n-butanol	116-118	95	24.5	35	44.7	0.54
iso amyl alcohol (3-methyl butanol)	128-132	95	19.7	41	50.7	0.52
n-hexanol	157	-	16.5	62	65.2	0.80*

* Because of thehigh values of this ratio, the flash point of hexanol was measured by the method described in reference (36).

The value obtained was $T_F = 58^oC$ $(\frac{P}{P_S} = 0.60)$

The results for propanol and butanol, obtained using 250 ml. per run and a channel width of 1.3 inches, are given in Tables 3.17 and 3.18. Averaged results are plotted in Fig 3.12. together with those for amyl alcohol and hexanol under the same conditions (Tables 3.4 and 3.9) in the form log v against T_L. For each liquid the temperatures T_F and T_S are indicated on Fig 3.12.

3.4.2. Discussion on the results of 3.4.1.

Before embarking on a discussion of the information which may be obtained from the results of 3.4.1, as plotted in Figs.3.6 - 3.12, the validity of basing conclusions on measurements of the average rate of spread of flame across a liquid surface will be considered. The significance of the results could be questioned if evidence showed that measurements made with a particular set of conditions were not reproducible or if physical conditions over which there was no control, e.g. barometric pressure, laboratory temperature and humidity, exerted a greater influence on the results than did those factors which were controlled experimentally, or if the rate of spread of flame was changing from end to end of the trough.

An indication of the reproducibility of the results can be obtained from Fig. 3.6 on which the thirty two results quoted in Table 3.4 are plotted. In the temperature range 16 - 20°C some scatter is apparent but as the temperature increases this scatter decreases. Up to 45°C the points lie closely grouped but above this temperature the points become more scattered so that the drawing of a best line through them becomes more difficult. In the temperature range 45 - 50°C the rate of spread is changing very rapidly with temperature and these increased discrepancies may result from small errors in temperature

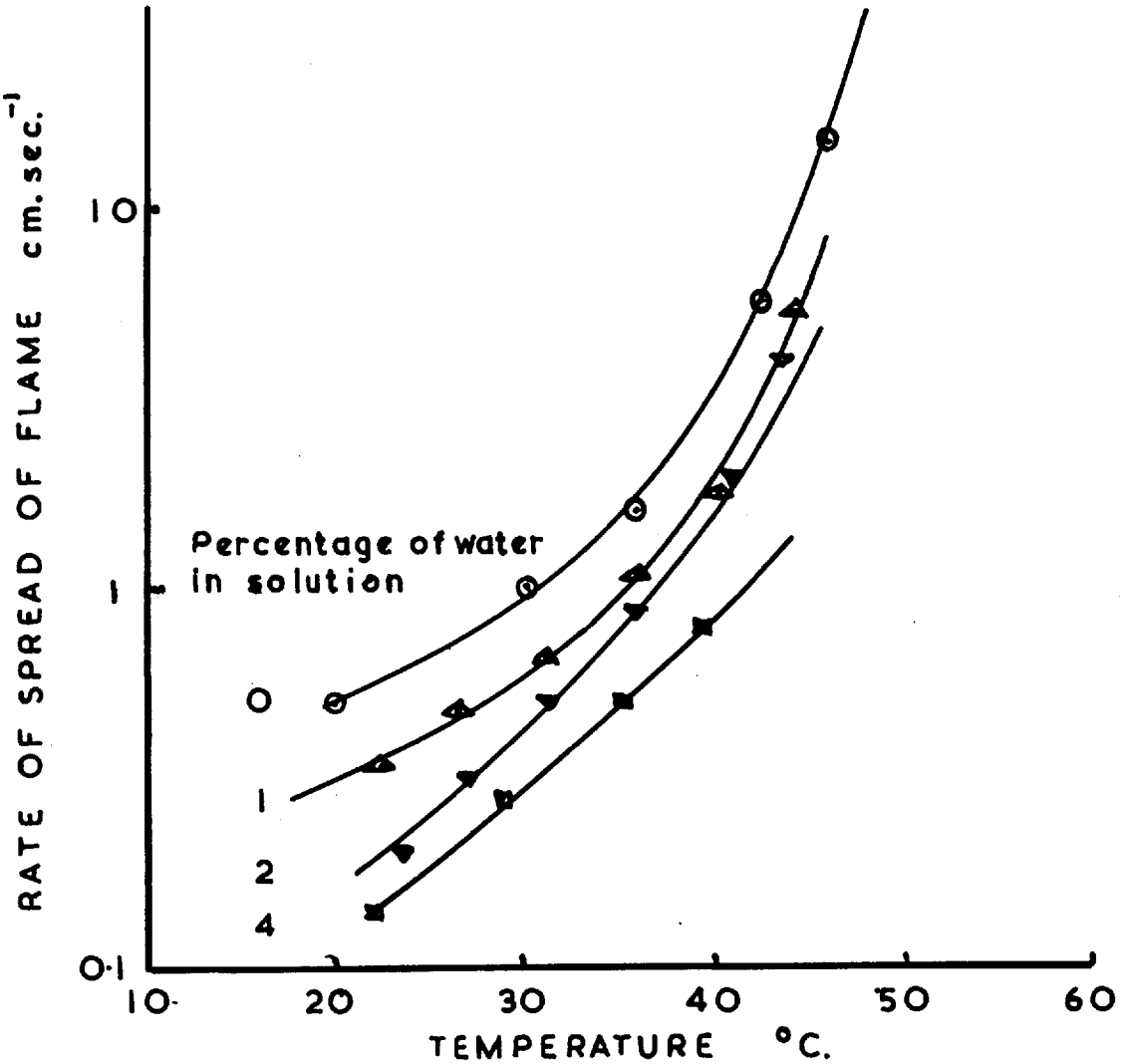


FIG. 3.10 THE RESULTS FOR SOLUTIONS OF WATER IN AMYL ALCOHOL

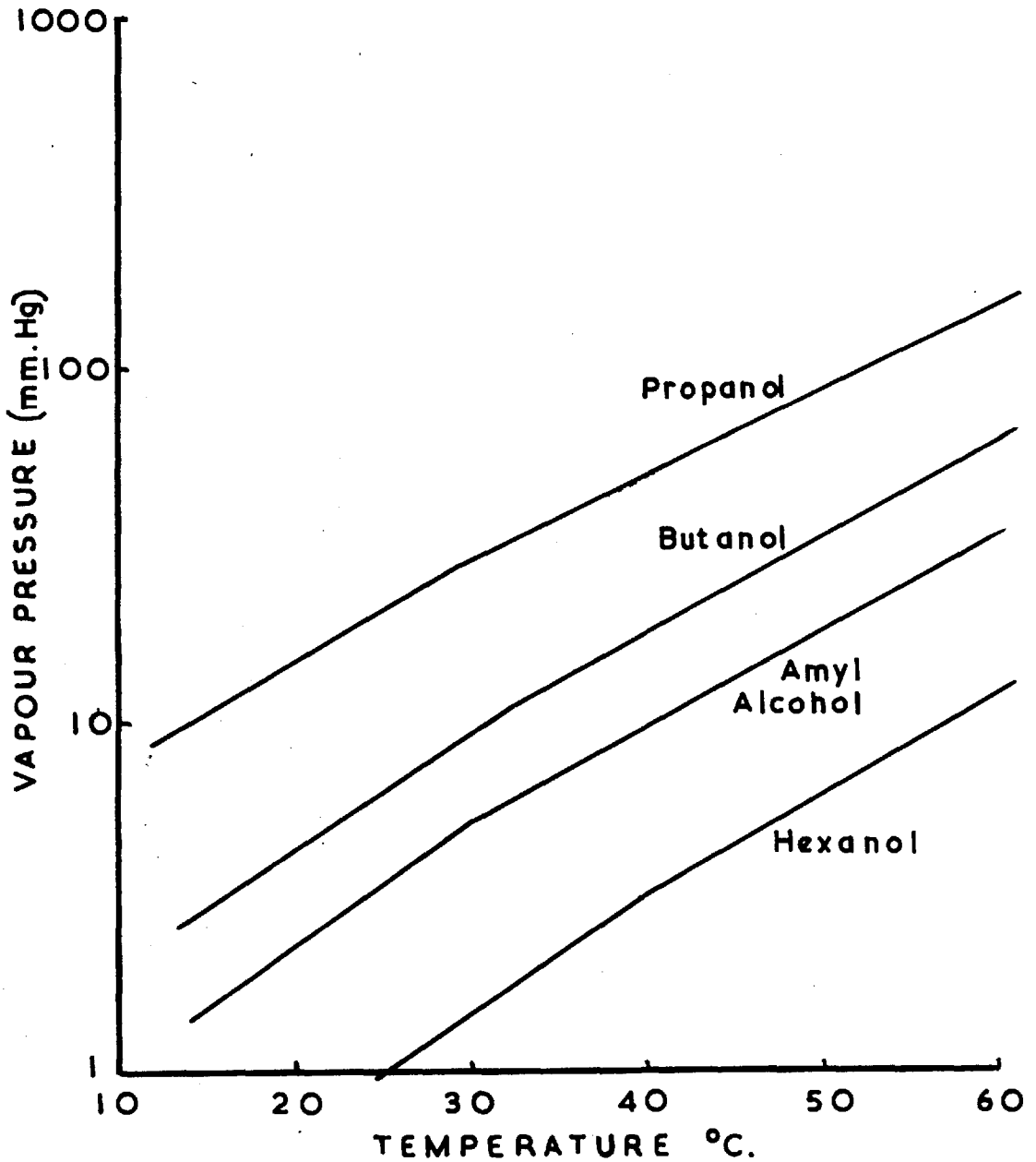
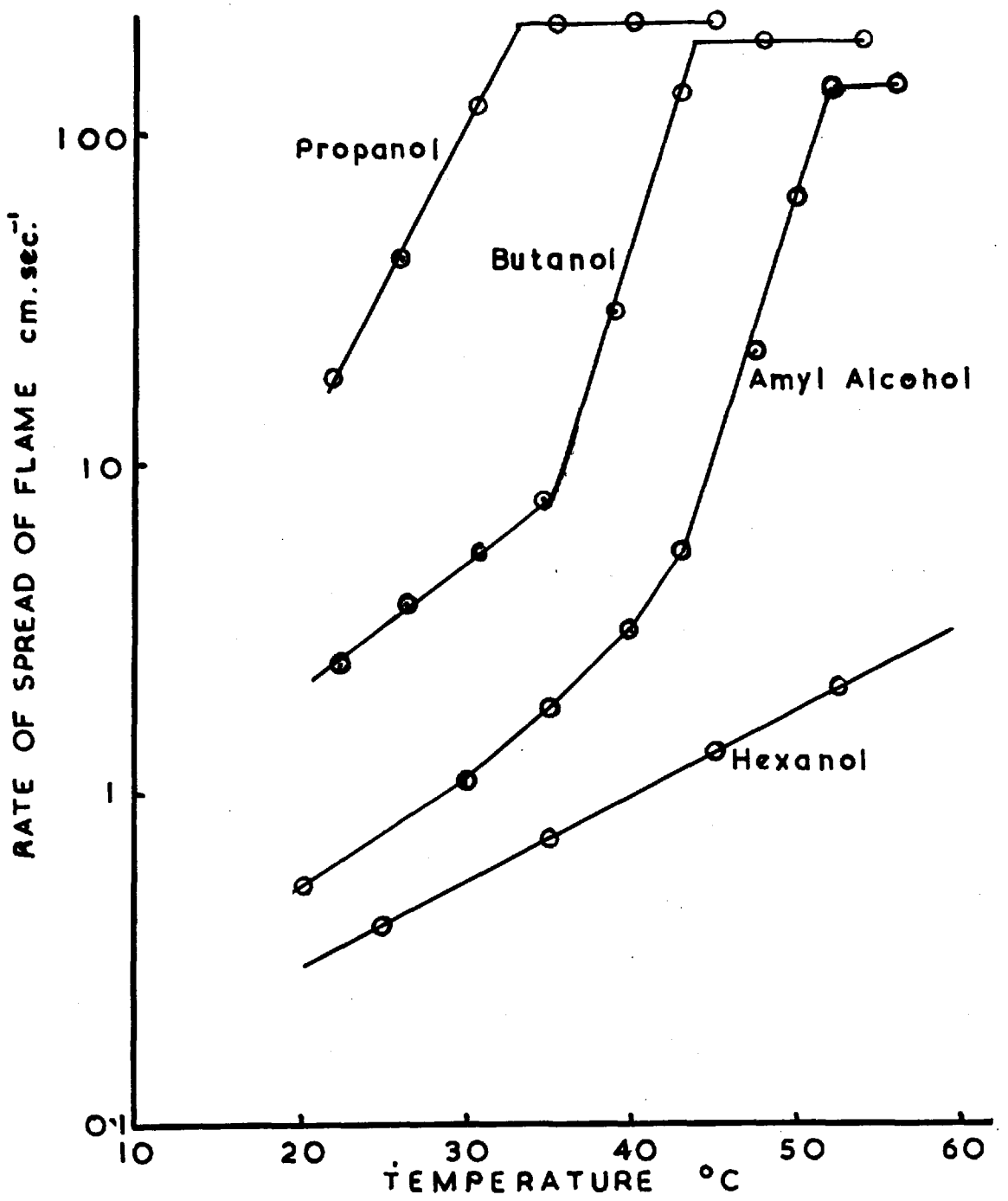


FIG. 3.11 VAPOUR PRESSURE DATA

FIG. 3.12 EXPERIMENTAL RESULTS FOR DIFFERENT LIQUIDS

	T_F	T_S
PROPANOL	23	32·5
BUTANOL	35	44·7
AMYL ALCOHOL	41	50·7
HEXANOL	58	65·2



measurement as well as random variations in the rate of spread. This scatter is not so pronounced in the higher temperature runs with propanol and butanol (Table 3.17, 3.18).

If the results for hexanol from Table 3.8 are considered (selected because of the large variation in t from 12 - 200 seconds) then all the points lie within 10% of the best line and fifteen out of seventeen lie within 5%. This degree of reproducibility (90% of points within 5% of the best line) is exceeded by many of the sets of runs.

As the runs in a particular set were made over a period of several days and in some cases additional runs were made months later this degree of reproducibility may be taken as an indication that the effect of random changes in uncontrolled conditions is small in comparison with the effect of controlled changes.

It has already been shown (Fig.3.5) that the rate of spread of flame does not vary with distance from the wick when that distance is greater than 6 - 7". This is confirmed in part by results in Table 3.3 which show that moving the wick over a distance of 5" relative to the fixed marks does not affect the measured rate of spread between the fixed marks.

With this background information, the average rate of spread of a flame as measured was accepted as a meaningful quantity and one whose variations could profitably be subjected to an intensive investigation.

Modes of flame propagation

When the mechanisms controlling the rate of spread of flame across a liquid surface are considered it becomes apparent that two distinct types of behaviour must exist. The distinguishing feature between these two types will be the relation of the initial concentration of vapour above the liquid surface to the lower limit of inflammability of the vapour.

When the initial concentration is less than the lower limit of inflammability sufficient preheating of the liquid by the spreading flame must occur to give a concentration of vapour within the inflammability range. In such circumstances the rate of spread of the flame will be governed both by the amount of preheating necessary and the rate at which this preheating will take place.

When the initial concentration of vapour exceeds the lower limit of inflammability no preheating of the liquid is necessary although it may still occur. Control over the rate of spread of flame is then exercised directly only by occurrences in the vapour phase (although they in turn are related to the state of the liquid phase).

If, in the above discussion, the concentration of vapour at a particular liquid temperature can be considered in terms of the vapour pressure exerted by the liquid at that temperature, then the boundary between the two types of behaviour will be the true closed flash point of the liquid, as discussed in Chapter 2.

Evidence for the existence of these two regions may be found in the experimental results given in 3.4.1. Fig 3.8 shows the marked increase in the gradient of the curve through the experimental points in the region of initial temperature 40 -45°C. In the ten degrees from 30°C to 40°C the rate of spread increases by a factor of three. In the ten degrees from 40°C to 50°C however the rate of spread increases by a factor of twenty. The closed flash point of amyl alcohol is approximately 41°C. Although this increase in gradient is most marked on a graph of v , on a linear scale, against T_L it is also apparent on a graph of v , on a logarithmic scale, against T_L.Fig. 3.12 shows the experimental results for all four liquids used plotted on such a basis. For propanol, flash point 23°C, all experimental points lie in the region where the vapour phase is controlling and no marked discontinuity in gradient is apparent. For butanol, flash point 35°C,

there is a very marked change in gradient at T_L = 35°C and such a change is apparent, to a lesser degree, for amyl alcohol at T_L = 41°C. All the results for hexanol were obtained with liquid temperatures less than the closed flash point. These results suggest that two different types of behaviour may be distinguishable in practice and these types of behaviour will now be considered in the light of the earlier remarks about modes of propagation.

Liquid phase controlling

It was suggested above that when the initial temperature of the liquid is less than the closed flash point of the liquid the rate of spread of flame will be controlled by the amount of preheating of the liquid necessary and by the rate at which preheating occurs. These points are considered in detail in 3.4.3. and in Chapter 5. In this section however the only aspect of this suggestion which will be considered is the broad one that when T_L T_F, heat transfer processes in the liquid phase will be controlling. From this it follows that when $T_L < T_F$, environmental factors affecting heat transfer processes in the liquid such as the depth of liquid, or the width of liquid surface burning will have an effect on the flame's rate of spread and that this effect will diminish as T_L approaches T_F.

Experimental evidence in favour of this view is shown on Figs. 3.7 and 3.9. The results plotted on Fig. 3.7 show the effect of liquid depth on the flames rate of spread. For amyl alcohol, flash point 41°C, at an initial temperature of 23°C the rate of spread is halved by decreasing the liquid depth from 0.5 cm to 0.2 cm. whereas at 38°C the curves for the five different liquid depths used have merged together and no measurable differences exist between the rates for different depths. At 23°C, increasing the depth by 25% from 0.2 cm to 0.25 cm. increases the flames rate of spread by 33%. The same percentage increase from 0.4 cm to 0.5 cm however increases the rate of spread by only 10%, suggesting that a state is being approached in which further increases in depth would not affect the rate of spread.

This indication that the rate of spread of flame will become independent of depth for depths greater than some critical value, together with the fact that increases in rate of spread result from increases in depth when the depth is less than that critical value, leads to further conclusions as to the temperature distribution in the burning liquid. If, in the vertical plane passing through the flame front, the temperature distribution in the liquid were substantially uniform then increases in depth, at a particular initial temperature, would mean that a greater amount of heat would have to be supplied to achieve a particular surface temperature. Such an increase in heat requirement would result in a reduction of the flames rate of spread. If however the bulk of the temperature rise occurred near the surface with steep temperature gradients resulting in a vertical direction then the net amount of heat necessary to achieve a particular surface temperature would be largely independent of liquid depth. The controlling factor in such a case would be the rate at which heat was lost from this hot surface film. It follows that the nearer this hot film is to a heat sink maintained at the initial temperature (e.g. the bottom of the combustion vessel) the greater will be the losses from it. Therefore as the depth of liquid is increased the gross heat requirement is decreased because the net requirement remains constant and the heat losses from the surface film are reduced. Such a reduction in heat requirement would lead to increased rates of spread.

Since the experimental evidence shows that an increase in depth increases the rate of spread it is probable that steep temperature gradients are produced in a vertical direction in a liquid as a flame passes across its surface.

The results plotted on Fig. 3.9 show the effect of channel width on the flames rate of spread. Here again the effect is most noticeable at low temperatures, an increase in

width from 0.9" to 2.5" increasing the rate of spread by a factor of three at 23°C. The effect of changing the channel width persists until an initial temperature of approximately 43°C. This feature suggests that the rate of heat transfer to the liquid per unit width of flame front increases as the scale of operations increases. An increase in rate of this kind has previously been reported in connection with liquid fires (4) (9) and in the present circumstances an additional factor in favour of such an increase may result from the heat transferred to the sindanu screens becoming a decreasing percentage of the total heat released as their separation is increased.

Visual observation of the spreading flame yielded information on the shape of the flame front and the manner in which the flame progressed. In all save a very small number of the runs carried out the flame spread with a straight flame front which was perpendicular to its direction of propagation. Slight deviations from straightness occurred near the screens where the flame was slightly retarded but this curvature did not extend across very much of the channel width.

At initial temperatures approaching the flash point flames were observed to spread steadily and without fluctuation, their instantaneous rate of spread corresponding to their average rate of spread. At lower initial temperatures however a different mode of propagation was apparent for often the flame would advance into a region but would not become established there. Having advanced, it would then retreat a little only to advance again a short time later. This type of flickering advance would be superimposed on to a steady progress of the mean position about which the flame was fluctuating. These fluctuations occurred on quite a small scale being of the order of one second in duration and one centimetre in amplitude. Their frequency varied considerably and as the initial temperature was increased so this mode of propagation changed into the more stable one described above.

The strictly local character of these fluctuations is confirmed by the results shown in Fig.3.5 since only in one case (after seventeen seconds) is there a noticeable deviation from the straight line corresponding to the average rate of propagation in spite of the fact that during this run, carried out with amyl alcohol at 23°C, visible fluctuations occurred.

This type of behaviour may result from a difference between the flash point and the fire point of the liquid concerned. (These properties have been discussed in Chapter 2). When the flame advances in the fluctuating manner described above it seems probable that its advance into a region coincides with the attainment of its flash point by the liquid in that region but the rate of increase of temperature is not sufficient to raise the liquid to its fire point before the flames goes out. The flame front then returns to a region where combustion is already self supporting and, after a delay sufficient for the evaporation of an inflammable concentration of vapour, it advances again. This successive advancing and retreating supplies sufficient heat to stabilise the flame in a new position ahead of the old one. In terms of temperatures this explanation suggests that relative to a temperature profile moving at the average rate of spread of the flame, the flame is fluctuating between the positions corresponding to the flash point and the fire point. While the rate at which the temperature profile moves will be controlled by heat transfer considerations the superimposed local variations in rate will be controlled by mass transfer considerations.

It seems probable therefore that the flame first reaches a point on a liquid surface when the temperature at that point is equal to the flash point of the liquid. The propagation of the flame is however stabilised about the point slightly behind the flame front where the liquid has been heated to its fire point.

Vapour phase controlling

The evidence of the previous section tends to confirm the view that when the initial temperature of a liquid is below its flash point the rate of spread of flame across its surface is controlled by heat transfer processes in the liquid phase. There is no sharp transition to a state in which the composition of the vapour phase becomes controlling but as the initial temperature of the liquid approaches the flash point so the effect of environmental factors decreases. With amyl alcohol, flash point 41°C, the effect ofchannel width disappears at 43°C. It seems likely that for an amyl alcohol surface at a temperature greater than 43°C the rate of spread of flame will be controlled by the initial composition of the vapour phase.

At the flash point of a liquid the vapour composition at its surface is that of the lower limit mixture and the concentration of vapour decreases rapidly with distance from the surface. As the temperature of the surface is increased so the vapour concentration at the surface increases until at a temperature T_S the composition of the vapour is that of the stoichiometric mixture with air.

Fig. 3.12 shows that a pronounced discontinuity in the gradient of the rate/temperature curves occurs for propanol, butanol, and amyl alcohol at temperatures close to T_S. Contrary to the findings of T. Kinbara (25) no evidence was found to suggest that the rate passed through a maximum at this temperature although for propanol T_S was exceeded by 10°C giving a vapour pressure of 96 mm.Hg. as opposed to 32.3 mm. Hg at T_S.

The rapid increases in rate observed for each liquid between T_F and T_S must result from the enrichment of the vapour present before ignition occurs. Such an increase in rate is known to occur in the fundamental burning velocity of an inflammable mixture as its concentration is raised from that of the lower limit mixture towards the stoichiometric.

The evidence suggests therefore that for $T_L > T_F$ the rate of spread is independent of the condition of the bulk of the liquid but is dependent on the initial concentration of vapour above the surface. This dependence results from the increase in reaction rate with final flame temperature as manifested by the increase in burning velocity with mixture strength. It is probable that other factors will come into play apart from this but their control must be exercised in the vapour phase.

3.4.3. Temperature profile measurements

In section 3.2.3 the desirability of measuring the variations of temperature in an inflammable liquid as a flame passed across its surface was discussed and an apparatus for carrying out such measurements was described. The calibration and operating characteristics of this apparatus are also described in 3.2.3.

For a run in which temperature variations were to be measured the experimental procedure was similar to that outlined in 3.3. In addition to this procedure the thermistor was placed in the combustion vessel with its temperature sensitive element vertically above the fixed mark distant from the wick and just below the surface of the inflammable liquid. The connections to the thermistor were led in from the end distant from the point of ignition. A further mark was inscribed on the combustion vessel 3" from the position of the tip of the thermistor.

Before a run was started the time base of the oscilloscope was set to a value conveniently greater than the time which, it was anticipated, the flame would take to spread 3". A photographic plate (Ilford, HP3) was then exposed to the image of the oscilloscope screen and, by re-setting the oscilloscope with the thermistor in its operating position, a trace was obtained on the plate corresponding to the initial temperature of the liquid. By thus calibrating each plate against an independently

determined reference temperature, a constant check was maintained on the temperature calibration of the apparatus.

During a run the normal measurement, of the time taken for the flame to spread 26 cm. was made and in addition the oscilloscope was reset when the flame was slightly more than 3" from the tip of the thermistor. By momentarily short circuiting the thermistor (see 3.2.3) as the flame passed the 3" mark and again as the flame reached the temperature sensitive element of the thermistor, marks were obtained on the photographic plate which enabled the trace of the changing temperature in the liquid to be related to the position of the flame relative to the thermistor.

The plate was then processed and, to be interpreted, was placed in the half plate adaptor from a full plate dark slide. To this half plate adaptor was attached a piece of millimetre ruled tracing paper which was calibrated in terms of time and temperature for the image of the oscilloscope screen. By illuminating the plate from underneath when in this frame the trace of the temperature variation could be re-drawn on the calibrated paper whence it could be described in terms of temperature and time co-ordinates, referred to the time of the flame passing the 3" mark. By knowing the average rate of spread of the flame the trace could then be expressed in terms of a curve showing how the temperature at a point varies with the distance of an approaching flame from that point. By postulating a steady state propagation of the flame this curve may in turn be regarded as showing the steady state variation in temperature with distance ahead of the flame front on a system of axes whose moving origin is the flame front.

In Tables 3.19 - 3.21 the results obtained for the measurement of temperature variations are summarized. For each run T_L and v , the initial temperature of the liquid and the average rate of spread of the flame, are given. In the third

column, T_c is the temperature recorded at the instant of the flame reaching the tip of the thermistor, as indicated by short circuiting the thermistor. For each of the liquids used the mean value of T_c was calculated and all the temperature-distance curves were adjusted so that at zero distance from the flame front they all passed through the same temperature, i.e. $\bar{T}_c$. This minor adjustment brought the results into line with the suggestions as to the mode of propagation which were made in 3.4.2. The mean value of T_c is given at the top of each table and in column four the value of the adjustment necessary for each run is given.

In no case does this adjustment exceed 0.5 seconds with a standard deviation from zero adjustment of 0.15 seconds, based on all the runs, demonstrating that there is considerable justification for such an adjustment. From the temperature-distance curves, adjusted in this way, three values of distance were noted. The first one, L_o, is the distance between the flame front and the position of the first measurable temperature rise. The second, $L_{o.2}$, is the distance between the position of the first temperature rise and the point where 20% of the temperature rise has occurred, i.e. where $\frac{T - T_L}{T_c - T_L} = 0.2$. The third, $L_{o.5}$, is the corresponding distance for $\frac{T - T_L}{T_c - T_L} = 0.5$. The final two columns give the values of the ratio $\frac{L_{o.2}}{L_o}$ and $\frac{L_{o.5}}{L_o}$ for each run.

TABLE 3.19 Results for butanol $\bar{T}_c = 37^\circ C$

$T_L{}^\circ C$	v cm/sec.	$T_c{}^\circ C$	correction (sec)	L_o cm.	$L_{o.2}$cm.	$L_{o.5}$cm	$\frac{L_{o.2}}{L_o}$	$\frac{L_{o.5}}{L_o}$
22.0	2.4	35	+ 0.1	4.4	2.8	3.5	0.63	0.79
21.9	2.3	36	+ 0.1	3.7	2.5	3.0	0.66	0.82
27.0	2.6	37	0	2.3	1.3	1.6	0.55	0.72
26.5	2.6	35	+ 0.1	2.9	1.6	2.1	0.55	0.73
31.0	4.0	39	- 0.1	2.0	1.0	1.4	0.50	0.70
31.1	3.8	39	- 0.1	2.1	1.3	1.6	0.61	0.76
35.0	6.2	37	0	1.3	0.7	1.0	0.54	0.76
						Mean value	0.58	0.75
						Standard Deviation	0.05	0.04

TABLE 3.20 Results for amyl alcohol $\bar{T}_c = 41^\circ C$

$T_L{}^\circ C$	v cm/sec.	$T_c{}^\circ C$	correction (sec)	$L_o$cm.	$L_{o.2}$cm.	$L_{o.5}$cm	$\frac{L_{o.2}}{L_o}$	$\frac{L_{o.5}}{L_o}$
22.0	0.6	39	+0.1	2.8	1.7	2.2	0.60	0.77
22.0	0.7	41	0	3.4	1.3	2.4	0.39	0.72
27.5	0.9	42	-0.1	3.0	1.2	2.2	0.39	0.74
27.0	1.0	43	-0.2	2.7	1.4	2.1	0.55	0.76
31.3	1.3	38	+0.2	2.7	1.5	2.2	0.57	0.81
31.4	1.4	41	0	3.2	1.9	2.6	0.61	0.82
35.3	2.0	39	+0.1	2.1	1.2	1.6	0.56	0.76
35.5	2.0	41	0	1.7	0.9	1.3	0.51	0.74
39.5	3.2	44	-0.3	0.7	0.4	0.5	0.54	0.76
						Mean value	0.52	0.76
						Standard Deviation	0.08	0.03

TABLE 3.21 Results for hexanol $\bar{T}_c$ = 57°C

T_L°C	v cm/sec.	T_c°C	correction (sec)	$L_o$cm.	$L_{o.2}$cm.	$L_{o.5}$cm.	$\frac{L_{o.2}}{L_o}$	$\frac{L_{o.5}}{L_o}$
22.2	0.4	56	+0.3	5.8	1.8	4.6	0.33	0.80
21.2	0.3	59	-0.5	6.7	3.6	5.0	0.53	0.75
27.5	0.5	55	+0.1	7.8	5.1	6.9	0.65	0.89
27.1	0.4	57	0	7.6	4.9	6.5	0.65	0.86
31.5	0.6	57	0	4.6	2.4	3.6	0.53	0.78
31.2	0.6	59	-0.2	3.6	1.9	2.8	0.53	0.77
39.5	1.2	56	+0.2	2.2	1.1	1.4	0.51	0.62
40.5	1.2	61	-0.1	2.9	1.2	1.9	0.42	0.67
44.5	1.7	55	+0.2	4.1	2.2	3.2	0.46	0.64
48.0	1.8	57	0	2.0	0.9	1.3	0.54	0.79
52.0	2.5	56	+0.1	3.1	2.4	2.7	0.80	0.90
					Mean value		0.54	0.78
					Standard Deviation		0.10	0.09

The results are presented in this way because all the temperature profiles measured were of the same general shape and each one could, within limits, be represented by the same general curve, $\left(\frac{T - T_L}{T_c - T_L}\right)^{0.4} = \left(\frac{L}{L_o}\right)$ where T_c and L_o have already been defined and T is the temperature at a distance L from the position of the first temperature rise, i.e. $L_o - L$ from the flame front. The power 0.4 was calculated using the mean values of $\frac{L_{o.2}}{L_o}$ and $\frac{L_{o.5}}{L_o}$ for all the above runs namely $\frac{L_{o.2}}{L_o} = 0.54$ and $\frac{L_{o.5}}{L_o} = 0.77$.

In order to examine whether or not the same curve could be used to express the results for the three different liquids, "Students" t test was applied to the data to test the null hypothesis that each of the three sets of results was a sample drawn at random from the same universe. This test showed that the differences between the three sets are not significant and they

may therefore be treated in terms of a single correlation. In addition variations in the values of these ratios for a particular liquid appeared to be due to random causes since no correlation could be found with any other variable. It was considered that these factors justified the use of a single curve to represent the results for all twenty seven runs, since any result could be adequately specified by substituting T_c and L_o in the expression $(\frac{T - T_L}{T_c - T_L})^{0.4} = (\frac{L}{L_o})$. This expression is plotted in Fig. 3.13 on which are also shown the mean experimental values of $\frac{L_{0.2}}{L_o}$ and $\frac{L_{0.5}}{L_o}$.

To examine the way in which L_o varies with changing experimental conditions, Fig. 3.14 shows L_o plotted against $T_c - T_L$ for each liquid. There is a statistically significant linear correlation between L_o and T_L for each liquid, the following straight line relationships being obtained:-

For butanol:- $L_o = -0.21\ (T_L - 40.7)$

correlation coefficient =-0.95, degrees of freedom = 5

correlation is highly significant

For amyl alcohol:- $L_o = -0.11\ (T_L - 52.6)$

correlation coefficient = -0.74, degrees of freedom = 7

correlation is significant

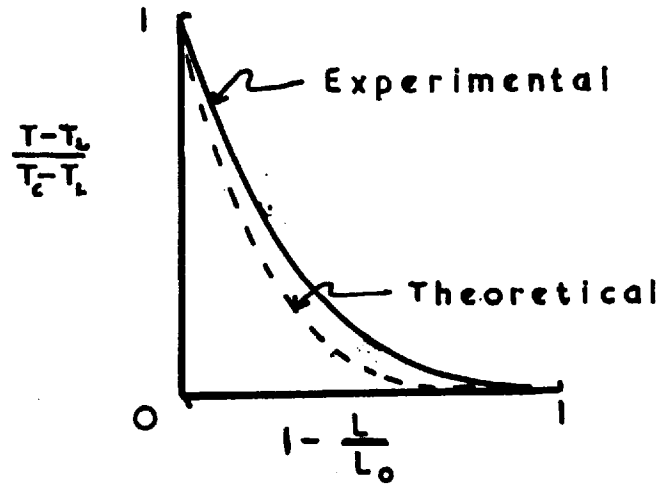
For hexanol:- $L_o = -0.16\ (T_L - 63.6)$

correlation coefficient = -0.79, degrees offreedom = 9

correlation is highly significant

Although these temperature profiles are discussed in detail in Chapter 5 some of the more important results will be considered here. Firstly, in 3.4.2 it was suggested that before a flame can enter a particular region the liquid must first have been preheated to its flash point if its initial temperature were lower than its flash point. The values of T_c listed in Tables 3.19 - 3.21 tend to confirm this, T_c being the measured temperature to which the liquid was preheated at the moment of the flames arrival. For a particular liquid these values of T_c lie close together; differences may be due either to a genuine variation in T_c or to

FIG. 3.13 THE TEMPERATURE PROFILE AHEAD OF THE FLAME



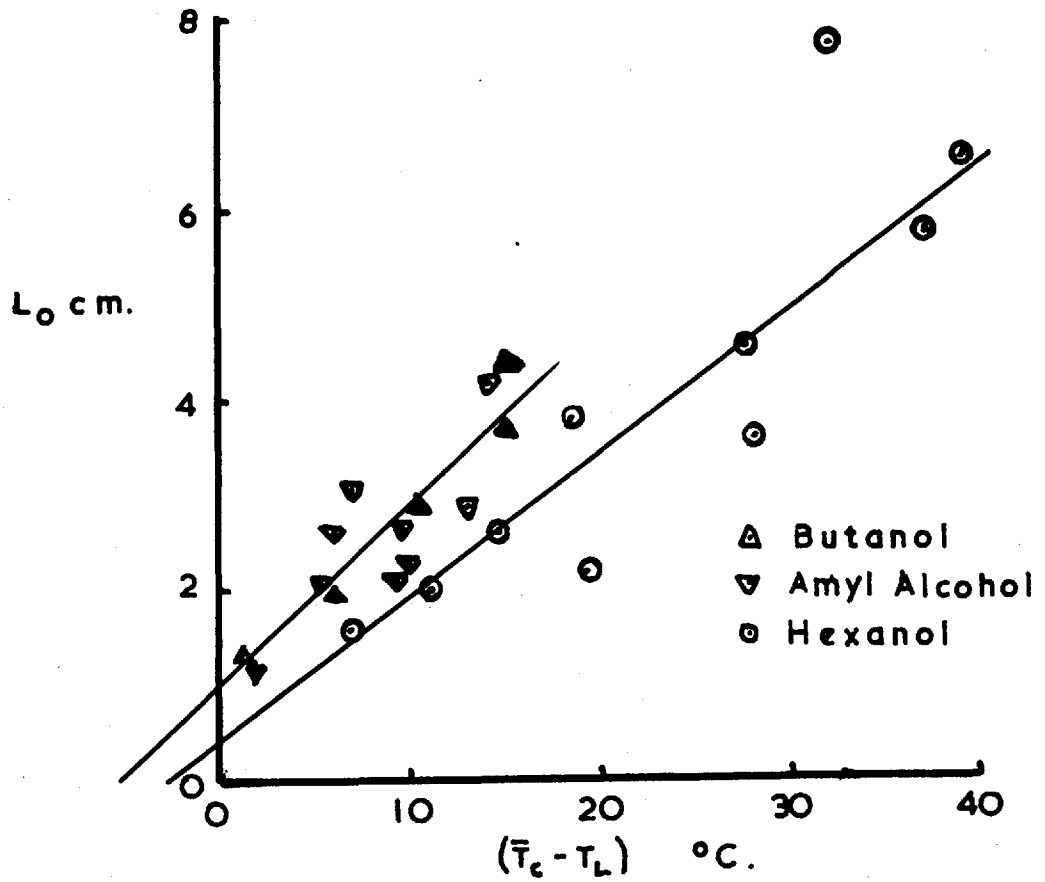


FIG. 3.14 THE VARIATION IN L_0 WITH T_L

a minor error in the synchronisation of the flames position with the temperature profile. The latter explanation seems more likely since most deviations could have been produced by an error of less than 0.2 seconds in the synchronisation.

A comparison of $\bar{T}_c$ with the value of the flash point for each liquid (Table 3.15) shows a close agreement:-

Butanol:- Flash point = 35°C; $\bar{T}_c$ = 37°C

Amyl Alcohol:- Flash point = 41°C; $\bar{T}_c$ = 41°C

Hexanol:- Flash point = 58°C; $\bar{T}_c$ = 57°C

This close agreement is further evidence in favour of the suggestion made concerning the flame's mode of propagation when $T_L < T_F$.

In the correlations between L_o and T_L for each liquid a further temperature appears. This temperature is an extrapoloted value of T_L for $L_o = 0$. In 3.4.2 the possiblity of the flash point being the significant temperature in connection with the flames first arrival at a point and the fire point being the significant temperature in connection with the stabilisation of the flame at a point was mentioned. This suggests a possible significance for the temperatures appearing in the correlation between L_o and T_c. The difficulties involved in the measurement of the fire point were discussed in Chapter 2 and it is not possible to make a direct comparison between these temperatures and the fire points of the liquids concerned. For butanol and hexanol these temperatures are 4°C and 6°C higher than the values determined for $\bar{T}_c$, but for amyl alcohol the difference is 12°C. Since it is for amyl alcohol that the scatter of the experimental points is greatest this value is the least reliable of the three. This comparison between the extrapolated values of T_L for L_o=0 and $\bar{T}_c$ tend to support the view that flame propagation is stabilised at a point where the temperature is a few degrees higher than the flash point and this temperature may be the fire point. Further evidence is necessary before the case for this viewpoint can be stated more strongly however. These matters are discussed further in Chapter 5.

APPENDIX TO CHAPTER THREE

Experimentally determined values of the rate of spread of flame across a liquid surface

List of symbols used

T_T = temperature setting of thermostat ^{o}C

T_L = temperature assumed by inflammable liquid ^{o}C

t = time measured for flame to spread 26cm. seconds

v = average rate of spread of flame = $\frac{26}{t}$ cm/sec.

CONTENTS

TABLE 3.2

T_T	T_L	t	v
25	22.4	Flame did not spread	
25	23.1	"	
30	27.0	"	
35	31.5	"	

TABLE 3.3

25	22.3	60.5	0.43
25	22.5	52.5	0.50
25	22.9	55.5	0.47
25	23.0	58.5	0.44
25	23.1	56.0	0.46
25	23.3	53.3	0.48
30	27.4	26.5	0.98
30	27.5	25.5	1.02
30	27.5	31.5(1)	0.83
30	27.4	30.0(2)	0.87
30	27.5	31.2(3)	0.83
30	27.6	30.0(4)	0.87
35	31.7	19.5	1.33
35	31.7	19.4	1.34
40	35.5	13.0	2.00
40	36.1	13.3	1.95
45	39.0	8.7	2.98
45	40.5	7.4	3.51
45	40.8	7.6	3.42

(1) wick 2" from end
(2) " 3" " "
(3) " 5" " "
(4) " 7" " "

TABLE 3.4

TT	T_L	t	v
19	16.4	59	0.44
19	16.4	58	0.45
20	18.4	48.2	0.54
20	19.5	63.0	0.41
20	18.0	56.0	0.46
20	18.9	61.5	0.42
20	18.0	60.0	0.43
25	22.5	44.2	0.59
25	22.8	44.8	0.58
30	26.5	31.4	0.83
30	27.0	31.0	0.84
35	31.0	19.6	1.33
35	31.0	22.0	1.18
35	30.5	22.0	1.18
40	35.5	13.2	1.97
40	35.0	13.5	1.93
45	39.0	8.8	2.95
45	39.0	9.0	2.89
50	43.5	4.4	5.90
50	43.5	4.8	5.42
50	43.1	4.465	5.82
53	46.1	2.0	13.00
55	47.0	0.685	37.96
55	47.0	1.194	21.78
55	47.5	0.408	63.72
56	48.7	1.418	18.33
57	49.4	0.700	37.14
58	49.5	0.430	60.46
60	52.7	0.197	132.0
60	51.0	0.226	115.0
60	51.5	0.265	98.1
60	51.7	0.313	83.1

TABLE 3.5

T_T	T_L	t	v
20	17.4	39.0	0.67
20	17.8	45.5	0.57
25	22.0	39.0	0.67
25	22.0	35.0	0.74
25	22.0	32.2	0.81
25	23.2	32.5	0.80
25	22.3	35.0	0.74
30	26.7	24.5	1.06
30	27.8	18.5	1.41
30	27.0	32.0	0.81
30	27.0	29.7	0.88
30	27.0	27.5	0.95
30	27.0	27.3	0.95
35	31.7	19.4	1.34
35	31.7	19.9	1.31
35	31.2	20.0	1.30
45	39.2	10.3	2.52
45	40.2	7.8	3.33
45	40.5	9.8	2.65
45	40.5	9.1	2.86
45	39.2	8.4	3.10

TABLE 3.7

25	23.0	26.0	1.00
25	23.0	22.4	1.16
30	27.7	16.6	1.57
30	27.4	19.7	1.32
30	31.4	15.7	1.66
35	31.4	16.0	1.63
40	36.1	14.7	1.76
40	36.3	12.5	2.08
50	43.0	4.3	6.05

TABLE 3.6

T_T	T_L	t	v
20	19.0	30.6	0.85
20	19.0	27.0	0.96
25	23.2	30.6	0.85
25	23.2	31.4	0.83
25	22.5	23.2	1.12
25	23.0	26.0	1.00
25	23.2	25.8	1.01
25	23.2	23.0	1.09
25	23.0	28.4	0.92
30	26.3	21.0	1.24
30	26.5	24.1	1.08
30	26.9	25.5	1.02
30	27.0	17.0	1.53
30	27.	23.0	1.13
30	27.0	22.2	1.17
35	31.0	15.0	1.73
35	31.0	14.9	1.74
35	31.1	14.0	1.86
35	31.0	19.5	1.33
35	31.0	19.2	1.35
40	35.5	10.8	2.41
40	35.6	10.6	2.45
40	35.6	10.0	2.60
40	36.1	12.5	2.08
45	40.1	6.4	4.06
45	40.0	6.4	4.06
50	43.0	4.0	6.50
50	43.0	4.2	6.19

TABLE 3.8

T_T	T_L	t	v
25	23.2	194	0.13
25	23.6	200	0.13
30	27.5	68	0.38
30	27.8	72	0.36
35	31.7	49.4	0.53
35	31.6	43.8	0.59
40	35.7	35.7	0.73
40	35.7	36.3	0.72
45	40.0	28.5	0.91
45	41.0	31.0	0.84
45	41.0	26.2	0.99
50	44.9	22.9	1.14
50	45.0	22.1	1.18
55	47.5	16.3	1.59
55	47.0	18.3	1.42
60	51.4	13.3	1.95
60	50.8	12.7	2.05

TABLE 3.9

T_T	T_L	t	v
25	23.1	80	0.33
25	23.2	64	0.41
25	23.8	64	0.41
30	27.2	42	0.62
30	28.3	50	0.52
35	31.6	36.7	0.71
35	31.6	36.7	0.71
40	36.3	34.1	0.76
40	36.4	31.1	0.84
40	36.2	32.4	0.80
45	41.0	26.1	1.00
45	41.0	28.4	0.92
50	45.0	27.7	1.15
50	44.7	21.1	1.23
55	48.9	14.3	1.82
55	48.4	16.4	1.59
60	51.9	12.5	2.08
60	51.5	13.6	1.91

TABLE 3.10

T_T	T_L	t	v
25	23.3	65.0	0.40
25	23.3	86.3	0.30
25	23.2	77.8	0.33
30	27.5	32.4	0.80
30	27.6	48.4	0.54
30	27.5	31.5	0.66
35	31.7	24.5	1.06
35	31.6	26.3	0.99
40	35.5	19.0	1.37
40	35.3	25.3	1.03
40	36.0	19.2	1.35
45	39.4	14.0	1.86
45	39.6	10.4	2.50
45	39.4	10.4	2.50
50	44.3	3.5	7.43
50	44.2	5.4	4.81

TABLE 3.11

T_T	T_L	t	v
25	23.0	21.7	1.20
25	23.1	23.6	1.10
25	23.4	23.0	1.13
30	27.0	17.3	1.50
30	27.3	19.1	1.36
30	27.7	18.0	1.44
35	31.9	13.1	1.98
35	31.9	13.6	1.91
40	36.4	10.5	2.48
40	36.4	10.4	2.50
45	40.4	6.3	4.13
45	40.0	6.4	4.06
50	42.7	4.9	5.31
50	42.5	4.0	6.50

TABLE 3.12

T_T	T_L	t	v
25	23.9	47.0	0.55
25	23.9	48.5	0.54
30	28.0	36.0	0.72
30	27.8	35.0	0.74
35	33.0	27.8	0.94
35	32.8	28.5	0.91

TABLE 3.13				TABLE 3.14			
T_T	T_L	t	v	T_T	T_L	t	v
25	22.6	78	0.33	25	23.5	122	0.21
25	22.7	78	0.33	25	23.5	128	0.20
30	26.7	58	0.45	30	26.8	91	0.29
30	26.8	57	0.46	30	27.0	87	0.30
30	26.3	41	0.63	30	27.0	68	0.38
30	26.3	57	0.46	30	27.0	87	0.30
30	27.0	57	0.46	30	27.0	86	0.30
35	31.2	30	0.87	35	30.5	49	0.53
35	31.1	35	0.74	35	31.1	45	0.58
35	31.2	39	0.67	35	31.1	49	0.53
35	31.6	40	0.65	35	31.0	50	0.52
35	31.2	40	0.65	40	35.5	30	0.87
40	35.8	14.7	1.77	40	35.5	27	0.96
40	35.7	16.3	1.60	40	35.5	32	0.81
40	36.0	23.2	1.13	40	36.4	24	1.08
40	35.9	24.0	1.08	45	39.3	14.0	1.86
40	35.5	25.0	1.04	45	39.7	13.3	1.95
45	40.0	18.0	1.44	45	39.7	13.0	2.00
45	40.5	13.0	2.00	50	43.5	5.3	4.90
45	40.0	13.0	2.00	50	43.0	6.0	4.33
45	40.0	13.6	1.91				
45	39.5	11.0	2.36				
50	43.7	4.6	5.65				
50	44.1	5.0	5.20				

TABLE 3.15

T_T	T_L	t	v
25	22.3	174	0.15
27	24.1	200	0.13
27	24.2	160	0.16
30	26.7	133	0.20
35	30.5	91	0.29
35	30.5	94	0.27

TABLE 3.15 (cont'd)

T_T	T_L	t	v
40	35.2	42	0.62
40	35.2	62	0.42
40	35.0	54	0.48
40	35.2	66	0.39
40	35.2	65	0.40
45	39.2	34	0.76

TABLE 3.17

25	21.7	1.383	18.80
25	22.2	1.493	17.4
25	22.1	1.527	17.0
30	26.0	0.574	45.3
30	26.0	0.669	38.9
30	26.0	0.816	31.9
35	31.0	0.218	119.3
35	30.5	0.212	122.6
35	30.5	0.205	126.8
40	35.3	0.124	209.7
40	35.5	0.117	222.2
45	39.2	0.136	191.2
45	38.5	0.116	224.1
50	43.0	0.113	230.1
50	43.0	0.386	67.4
50	42.5	0.128	203.1
50	52.0	0.131	198.5

TABLE 3.18

25	22.2	9.7	2.68
25	22.2	9.9	2.63
30	26.6	7.0	3.71
30	26.5	7.0	3.71
35	30.9	5.1	5.10
35	30.6	5.0	5.20
40	34.9	2.7	9.63
40	35.3	2.3	11.30
45	39.2	0.751	34.6
45	39.0	0.957	27.2
50	43.0	0.201	129.4
50	42.7	0.202	128.7
55	46.2	0.138	188.4
55	46.3	0.137	189.8
60	52.7	0.136	191.2
60	52.5	0.128	203.1

CHAPTER FOUR

THE SPREAD OF FLAME ACROSS A LIQUID SURFACE -

EXPERIMENTAL WORK PART II

4.1. The experimental vessel

In Chapter 3 experimental work carried out using a combustion trough 40" long and 5" wide was described. As a result of the experience gained in this section of the experimental work it was concluded that there were matters of interest which could be studied more conveniently in a smaller experimental vessel. These matters were the effect of liquid flow on the flame's rate of spread, the effect of superimposed air currents on the flame's rate of spread, and the factors affecting the induction period i.e. the period between the ignition of the liquid at a wick and the flame spreading from the wick. Furthermore it was decided to study the shape of the flame front in the plane perpendicular to its width and any visible manifestations of the interaction between the spreading flame and the liquid surface. This necessitated the construction of an experimental vessel in which both the walls containing the liquid and the screens protecting the spreading flame from draughts were transparent.

Two experimental vessels of this type were constructed. In each case the base and ends of the vessel were made from aluminium channel $1\frac{1}{4}$" x $\frac{3}{4}$". In order that the results obtained might be directly comparable with those obtained in the larger apparatus it was decided to use a wall separation of 1.3". Since the use of metal channel offered the easiest means of construction $1\frac{1}{4}$" outside width channel was purchased, this size being available only in aluminium. The piece of channel for the base, 12" long in one case and 10" in the other, was used with its open side downwards. At each end a piece of channel 1" long was stuck vertically with its open side facing inwards.

For the vessel 12" long, sheets of 'Armourplate' glass, 3/16" thick, were used for the walls. 'Armourplate' is a registered trade name of Pilkington Bros Ltd., for a surface toughened glass prepared by rapidly cooling the surfaces of the hot glass. It is claimed for this glass that it will resist the stresses resulting from a local temperature difference of 250°C. In practice it was found that this glass resisted all the thermal stresses to which it was subjected in the course of the experimental work. For the vessel 10" long sheets of ruby mica 0.005" thick were used for the walls. This vessel was constructed because of the superior optical qualities of mica. Owing to the susceptibility of the mica sheets to damage and the difficulty in obtaining replacement sheets of that size (10" x 4") this vessel was only rarely used.

The walls were stuck to the base with a ½" overlap and to complete the trough, were stuck to the ends as well. The adhesive used throughout was 'Araldite' epoxy resin of the type distributed in two tubes, one of resin and one of hardener. This adhesive was the only one of several tried which had sufficient heat resistant and solvent resistant properties for the satisfactory construction of a combustion vessel of the type required.

In order that measurements of rates of spread might be made, two lines 3" apart were inscribed on the base of each vessel, the first one being 2" from the end.

The dimensions of the glass sided vessel were such that the addition of 50 ml. of liquid gave a liquid depth of 0.5 cm. This compares with a volume of 500 ml. of liquid required to give such a depth in the larger vessel.

When it was required to take measurements at a temperature greater than r oom temperature the small combustion vessels were heated by an electric fire element which was placed underneath the channel forming the base of the combustion vessel. The rate of heating was controlled by supplying the element from a Variac auto-transformer. This system was not very satisfactory however and the majority of

measurements were taken at room temperature.

4.2. Steady state propagation

All the measurements made under this heading were made by the methods described in Chapter 3, sometimes with minor modifications. To measure high rates of spread for example the nylon threads were tied to a strip of metal which was laid in the combustion vessel. Two right angle bends in this strip of metal took it clear of the end of the trough and it was clamped to a block outside the trough to hold it in position.

4.2.1. Measurements of rates of spread

A series of runs was carried out using n-butanol to determine whether the duration of the induction period affected the steady state propagation of the flame or if these two phenomena could be treated independently. It was suggested in Chapter 3 that the flames behaviour could be considered in terms of an induction period, a transition period and a steady state period and it would be desirable in any analysis of the steady state period to regard events in that region as being independent of events in the induction period. In Table 4.1 the measured times for n-butanol to spread 3" under different conditions are recorded. Three different wicks were used and in 4.5 results are given to show that changing the size of the wick alters the length of the induction period. The first column in Table 4.1 gives the temperature at which the run was carried out, the second column gives the time measured and the third column gives the average velocity corrected to a temperature of 22°C by means of the formula $v' = v - (T - 22)\ 0.2$ where v' is the velocity corrected to 22°C and v is the velocity measured at an initial temperature of T°C. This formula is based on the results for butanol in Table 3.17.

TABLE 4.1		25ml.n-butanol; depth=0.25cm.	
	$T^{o}C$	t sec	v' cm/sec.
Wick I	23.0	34	2.0
Height 0.6cm.	23.5	3.7	1.8
$\bar{v}'$= 1.94 cm/sec	24.0	3.8	1.6
σ = 0.22	24.0	3.0	2.1
	25.0	2.7	2.2
Wick II	24.5	3.2	1.9
Height 0.9 cm.	24.0	3.8	1.6
$\bar{v}'$= 1.80 cm/sec	24.5	3.6	1.6
σ = 0.17	23.5	3.4	1.9
	23.0	3.4	2.0
Wick III	21.5	3.0	2.6
Height 1.2cm.	22.0	3.0	2.5
$\bar{v}'$= 2.06 cm/sec	25.0	3.0	2.0
σ = 0.43	25.0	3.7	1.5
	24.5	3.4	1.7

"Students" t test shows that the differences between these three sets of results are not significant. It is probable therefore that the equilibrium rate of spread of a flame is independent of the duration of the induction period.

In Table 4.2 are given the results of flame spread measurements made in the small vessel using butanol and amyl alcohol.

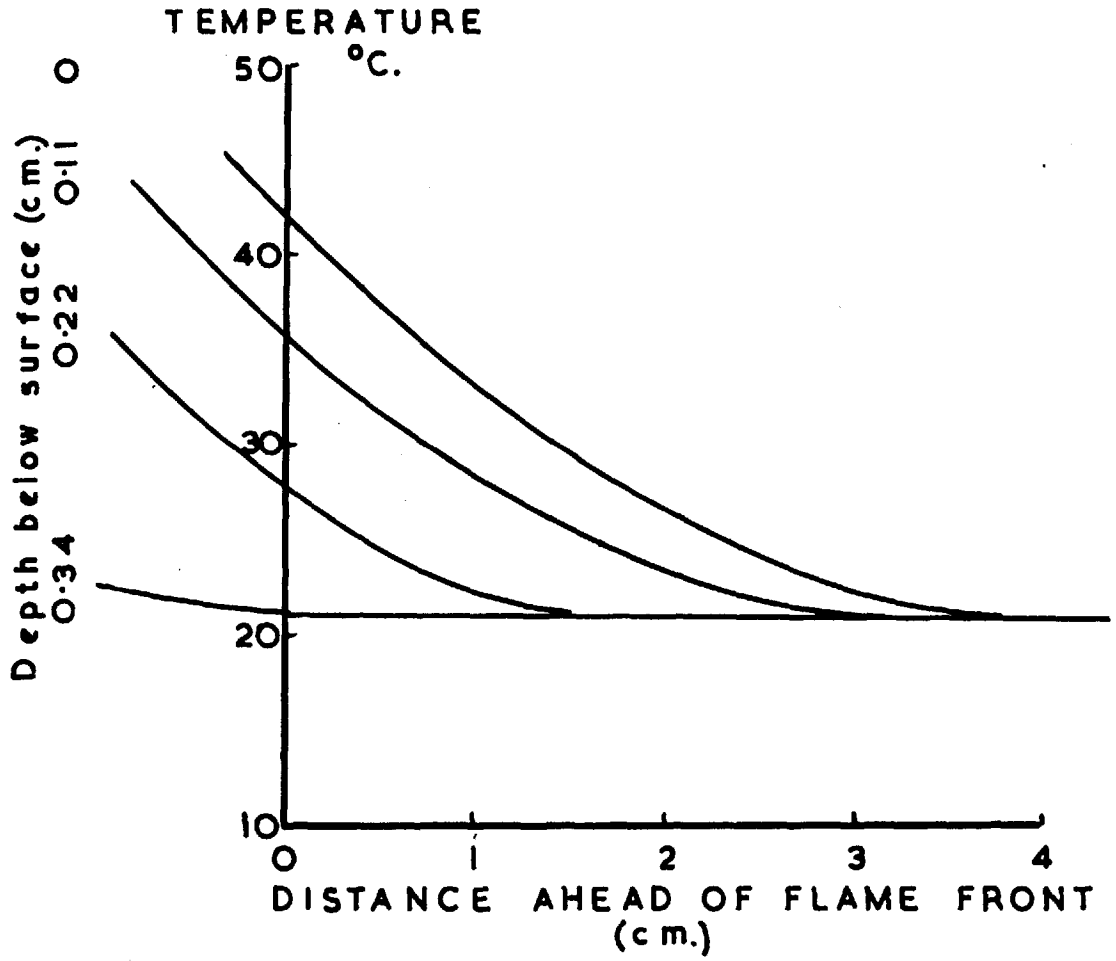
TABLE 4.2

Liquid	Depth (cm)	T°C	t sec	v cm/sec.
Butanol	0.05	22	did not	propagate
"	0.10	24.5	5.4	1.41
"	0.10	24.5	6.6	1.15
"	0.10	27	3.2	2.38
"	0.15	22.5	4.2	1.81
"	0.15	25	3.9	1.95
"	0.15	25	4.6	1.65
"	0.20	24.5	4.4	1.73
"	0.20	25	3.0	2.54
Amyl alcohol	0.25	21	9.3	0.82
"	0.25	22	10.0	0.76
"	0.25	23	8.7	0.87
"	0.25	26	7.0	1.09
"	0.25	28	7.4	1.03

4.2.2 Measurements of temperature profiles

When measuring temperature profiles in the small combustion vessels the same experimental procedure was adopted as for measurements in the large vessel. In addition to measurements made with the tip of the thermistor at the surface of the liquid three runs were carried out with the tip submerged to different depths. For these runs the submergence of the thermistor tip was measured using a travelling telescope. The results obtained from measurements in the glass sided trough are given in Table 4.3; they are presented in a way similar to that adopted in Tables 3.18 - 3.21.

All the profiles measured were of the same form as those measured in the larger vessel with the exception of those made with the thermistor tip submerged. These results are plotted in Fig. 4.1 to show the variation of temperature with depth in different positions relative to the flame.



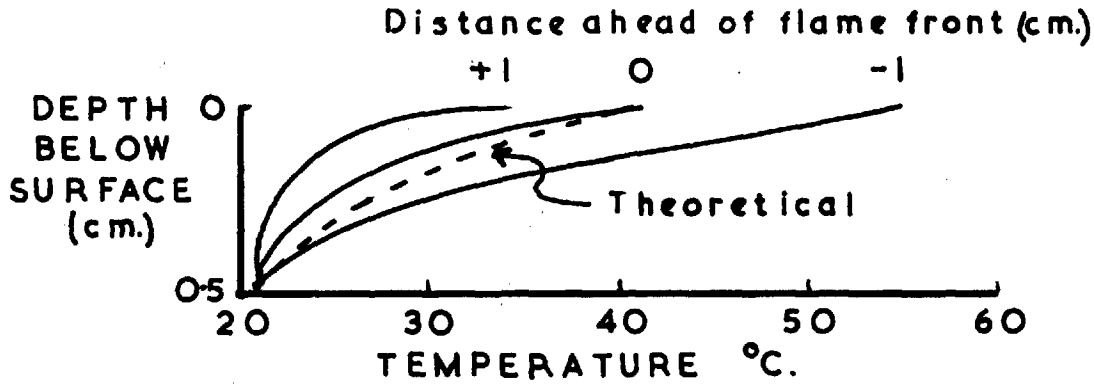


FIG. 4.1 THE VARIATION IN TEMPERATURE BELOW THE LIQUID SURFACE

LIQUID AMYL ALCOHOL
DEPTH 0·5 cm.

TABLE 4.3

Liquid	Depth of Liquid	Submergence of Thermistor	T_L	v	T_F	L_o
	cm.	cm.	°C	cm/sec.	°C	cm.
Amyl alcohol	0.2	0	18	0.66	38	3.7
Amyl alcohol	0.3	0	20	0.91	40	3.4
Amyl alcohol	0.4	0	21	1.00	41	3.3
Amyl alcohol	0.5	0	21	1.52	38	3.2
Amyl alcohol	0.5	0.114	22	1.43	36	3.2
Amyl alcohol	0.5	0.215	23	1.27	29	1.5
Amyl alcohol	0.5	0.336	23	1.52	23	0
Hexanol	0.25	0	20	0.40	56	5.6

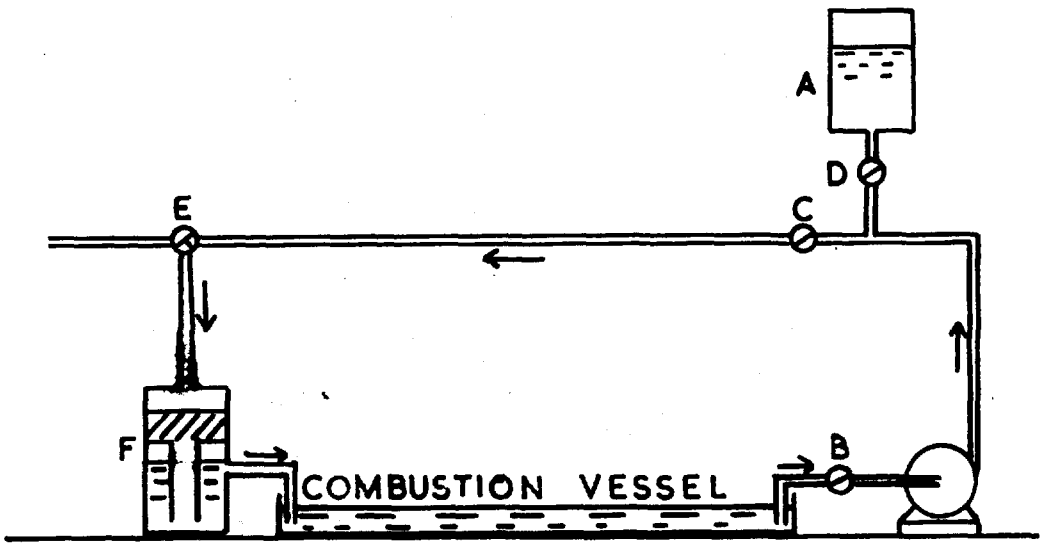
4.2.3. A comparison between the results of 3.4 and 4.2

A comparison between the results obtained in the large combustion vessel and those obtained in the small one shows that they are very similar although not exactly the same. For example the mean rate of spread of flame across butanol at 22°C as measured is slightly lower in the small vessel than in the large. Whether there exists a genuine difference between the two rates or whether the observed difference is a chance one arising from the inherent small degree of irreproducibility in the measurements can not definitely be established. Factors which might alter the flame's rate of spread are the difference in the nature of the walls of the channel (sindanu or glass) or in the different conditions at the base of the vessel. In the larger vessel the base is of brass in contact with a large heat sink whereas in the smaller vessel the base is of aluminium in contact only with air on its lower face. In contrast, the measurements of rate of spread of flame across an amyl alcohol surface show an increase from the larger vessel to the smaller vessel. A possible explanation of this change is contained in Fig. 3.5. This shows that in the steady state the time

for the flame to travel 3" is approximately 12 seconds at 22.5°C. However the time taken for the flame to travel from a point 7" from the wick to one 10" from the wick is only 9-10 seconds as this region is part of the transition stage of the flames spread. Since the measurements in Table 4.2 were made over this range it is probable that for amyl alcohol the steady state rate was not measured. The actual values obtained were much closer to the 9-10 second range than to 12 seconds. The values of the velocities in Table 4.3 are also somewhat higher than the comparable ones obtained in the large vessel. These discrepancies are not sufficient to remove the usefulness of the smaller vessel but they do serve to indicate some of its limitations. The temperature profile measurements show no important difference between the results for the different vessels. The values of L_o for amyl alcohol or hexanol at 20°C are approximately the same whether measured in the large or in the small vessel. The fact that L_o remained approximately the same for five different depths of amyl alcohol at the same initial temperature while v increased from 0.66 cm/sec. to 1.52 cm/sec. is of interest. It demonstrates that the correlations between L_o and T_L given in 3.4.3 (e.g. $L_o = 0.11\ (52.6-T)$) have a wider range of applicability than is at first apparent since L_o does not appear to be a function of liquid depth. This feature together with the variations of temperature with depth below the surface in the liquid as the flame approaches (Fig. 4.1) are further discussed in Chapter 5. It should be noted here however that the results shown on Fig. 4.1 are evidence in favour of the suggestions made in 3.4.2 concerning the temperature distribution in the burning liquid since they confirm that the bulk of the temperature rise occurs near the surface.

4.3. The effect of liquid flow on the flame's rate of spread

The effect on the flames rate of spread of flowing the inflammable liquid past the wick was investigated using the experimental arrangement shown in Fig. 4.2. The inlet and outlet tubes were of copper turned over and rendered oval. The system was primed from the



A LIQUID RESERVOIR
B,C,D TWO WAY TAPS
E THREE WAY TAP
F FILTER & CAPACITY

FIG 4.2 APPARATUS FOR STUDYING THE EFFECTS OF LIQUID MOVEMENT

reservoir A by judicious adjustments of taps B, C, D and E, the three way tap E being used to remove air locks and any surplus liquid from the system. The vessel F acted both as a filter to remove balsa wood particles, which were added to visualise the flow, and as a capacitance to render the system more stable. The centrifugal pump was supplied from a Variac by which means the rate of circulation of liquid was controlled. In order that the wick should not act as a weir it was raised on to supports at each end and the liquid was allowed to flow underneath it.

To carry out a run the system was primed with the liquid to be burned and the pump was brought into operation on a suitable voltage. Immediately before the liquid was ignited a series of small balsa wood particles was dropped into the flowing liquid and the time taken for each one to travel 3" was measured and recorded. When satisfactory agreement as to the mean rate of flow of the liquid had been obtained the liquid was ignited and the induction time and the time taken for the flame to travel 3" were measured. The flame was then extinguished.

Runs were carried out using butanol with the wick at either the inlet or the outlet end i.e. with the flow supporting and opposing the flames progress in turn. The initial temperature was measured for each run and all lay in the range 20-23°C. The results obtained are plotted on Fig. 4.3 as v_{flame} against v_{liquid} and as $t_{induction}$ against v_{liquid}. This shows that when the flame is travelling in the same direction as the liquid its velocity relative to the liquid is nearly constant over the range measured, from 0-6 cm/sec. When spreading against the liquid flow its relative velocity decreases at first and then increases again until it exceeds the velocity measured with the liquid stationary. Under these conditions the flame was never observed to be swept back by the vigour of the flow. The induction time is observed to increase with liquid flow rate for both conditions suggesting that the induction period is one in which hot liquid accumulates near the wick and that any tendency to disperse this accumulation inhibits the spread of the flame. For a liquid of high flash point

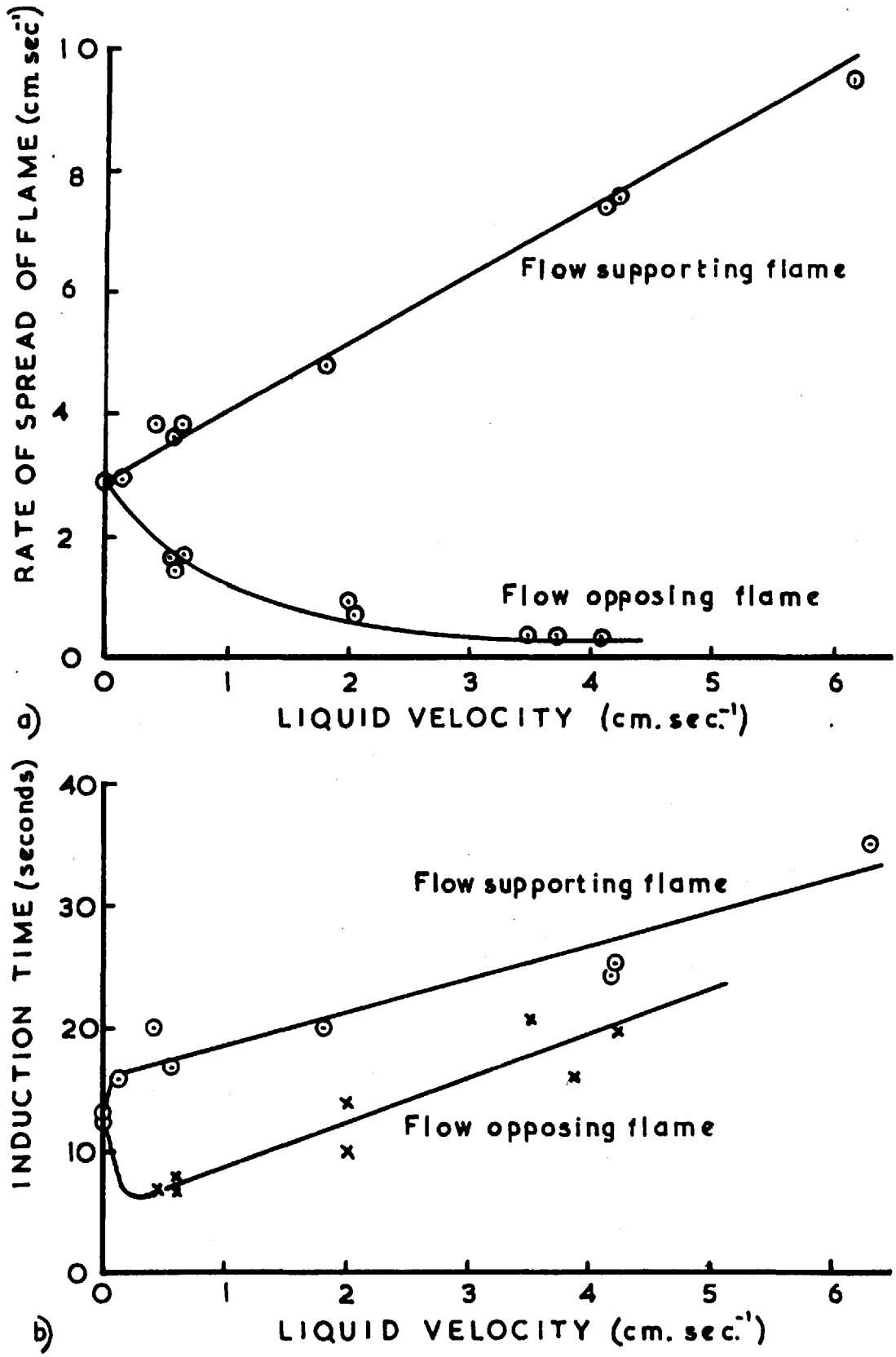


FIG 4.3 THE EFFECT OF LIQUID MOVEMENT ON

a) The rate of spread of flame
b) The induction time

it would appear to be easier to prevent the spread of flame during the induction period than during the steady state period.

4.4. The effect of superimposed air currents on the flame's rate of spread

In order that the effect of superimposed air currents on the flame's rate of spread might be studied a centrifugal blower was clamped to a bench and the combustion vessel was placed 3" from its outlet. The centrifugal blower was supplied from a Variac and for different supply voltages the pitot pressures in different parts of the combustion vessel were measured. As would be expected the linear velocity of the air current decreased as the distance from the blower increased. The maximum decrease measured was of 30% from the value 3" from the blower to the value 12" from the blower. In view of the fact that the current of air was confined only by the vertical walls and not at the top of the vessel such a decrease is not particularly large. The values recorded and plotted for the air velocity were those measured 9" along the trough i.e. 12" from the blower.

Runs were carried out using propanol and amyl alcohol with the air current supporting or opposing the flames progress. For the runs with amyl alcohol induction times and the times to travel 3" were measured and these are plotted as $t_{induction}$ and v_{flame} against v_{air} in Fig. 4.4. For the runs with propanol the times to spread 3" only were measured using the electronic timer described in 3.2.2. These results are also plotted on Fig. 4.4.

Propanol and amyl alcohol were used for this work because the disturbances to the system were applied in the vapour phase and, according to the analysis in 3.4.2, vapour phase processes are controlling for propanol at room temperature whereas liquid phase processes are controlling for amyl alcohol. Fig 4.4 shows that for air currents up to 100 cm/sec. the flames rate of spread across an amyl alcohol surface changes by only 20% depending on whether the flow is supporting or opposing the flames progress. Above this value a supporting current had a more

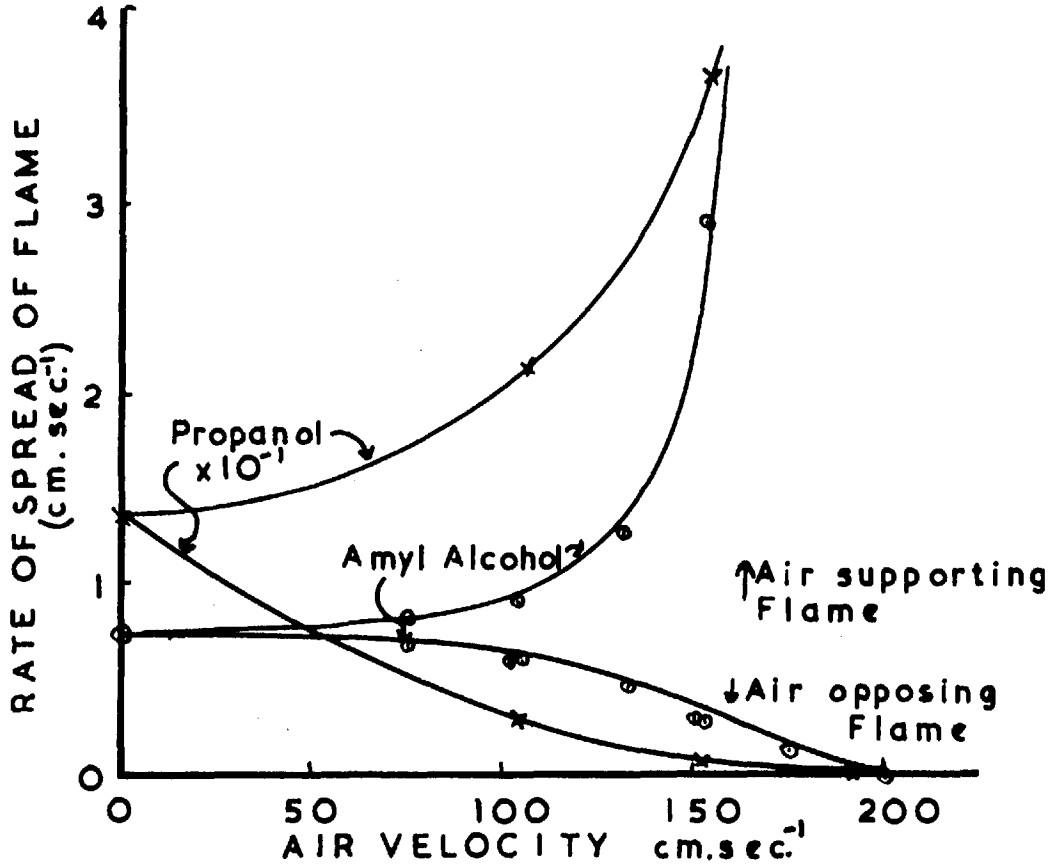
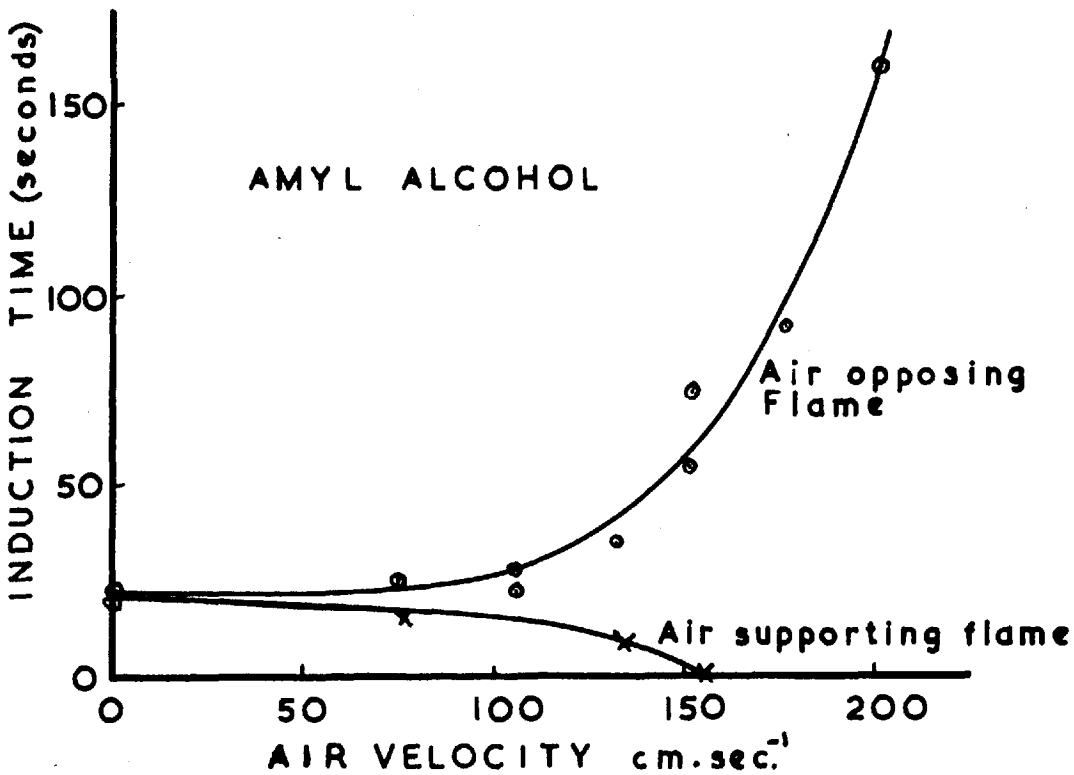


FIG. 4.4 THE EFFECTS OF SUPERIMPOSED AIR CURRENTS



profound effect, for example increasing the air velocity from 120 cm/sec. to 150 cm/sec increased the rate of spread by 150%. The flame was not observed to spread completely across amyl alcohol against an air current in excess of 190 cm/sec. The induction time increased steadily as the velocity of the air current increased when the flame was trying to spread against the flow. With the air flow supporting it however the induction time was progressively reduced until with wind velocities greater than 150 cm/sec. it became too small to measure. This effect resulted from the flame at the wick being blown forward on to the liquid surface with a resultant increase in the heat transfer to the liquid.

The results for propanol show similar trends to those for amyl alcohol and again an opposing wind of velocity 200 cm/sec. is sufficient to stop the flames progress. Results obtained with the air current supporting are liable to error because the nylon threads were fused by the top of the flame which was being blown along ahead of the position where the flame front met the liquid surface. The trends revealed are probably correct though since these errors tend to affect both nylon threads by a similar amount.

4.5. The induction period

Although the major interest in the study of the spread of flame across a liquid surface was focussed on the factors affecting the steady state rate of spread of flame it was felt that an investigation of the events leading up to the attainment of this steady state condition would be of value.

Accordingly a series of experiments was carried out in the small combustion vessel to determine whether or not the delay between the ignition of the liquid at the wick and the observation of the first spread of flame from the wick (hereinafter referred to as the induction period) was a reproducible property of the system and if so what factors affected the duration of this period. Furthermore measurements of temperatures were made near the wick to determine the way in which heat spread through the liquid during the induction period in an attempt to determine the critical conditions for the spread of flame from the wick.

4.5.1. The effect of wick size on induction time

Thirty runs were carried out using butanol at room temperature to determine whether or not induction times were reproducible under controlled conditions and to what extent they were affected by the size of the wick used. The set of runs was carried out using three different wicks (as described in Table 4.1) and two different depths of liquid, five runs being carried out at each of the six different combinations resulting. The order in which these runs were performed was randomised to minimise any possible long term effects. The results obtained are given in Table 4.4

TABLE 4.4

Volume,ml	Wick	Measured induction time	Mean times(sec)
25	I(0.6cm)	8.0,9.0,8.8,7.6,8.2	8.3
25	II(0.9cm)	9.8,9.0,9.1,9.6,9.2	9.6
25	III(1.2cm)	11.5,11.0,11.2,9.5,10.4	10.7
40	I	15.5,16.8,17.0,17.5,14.0	16.2
40	II	21.8,18.9,17.8,18.2,17.8	18.9
40	III	19.5,18.6,19.2,21.2,17.5	19.2

These results show that under controlled conditions the induction time as a measure of the behaviour of an inflammable liquid is reproducible. It may therefore be regarded as having some direct physical significance rather than as a phenomenon controlled by apparently random causes.

For each of the two volumes of liquid used, there is a small but clear cut difference between the induction times measured for the three different wicks. The reason for making this investigation was to see if increasing the size of the wick increased the rate of burning and in turn the rate of heat transfer to the liquid. Such a change would however have been reflected in a decrease in induction time with

increasing wick size. Visual observation suggested that the reason for the increase in induction time with increasing wick size was caused by the extra time which the flame took to spread down the wick from the top, where it was ignited, to the surface of the liquid. Since these times were of the same order as the differences between the results for different wicks, i.e. about one second, it is probable that the bulk of the heat transferred to the liquid was released in the area close to the liquid surface and the effect of altering the wick size is simply to alter the time which occurs between ignition at the top of the wick and a flame becoming established on the wick adjacent to the liquid surface. As the results of Table 4.4 show, the effect of altering the liquid depth is very much greater than the effect of changing the wick size. This feature of the work was further investigated; the results are given in 4.5.2.

4.5.2. The effect of liquid depth on induction time.

TABLE 4.5

Liquid	Volume used, ml.	Measured induction time, sec.	Mean time
Butanol	20	9.2, 10.4, 10.1	9.9
"	30	14.8, 15.8, 13.8	14.8
"	40	18.8, 18.0, 18.0	18.3
"	50	22.0, 21.8, 24.8	22.8
Amyl alcohol	20	18.4, 18.0, 17.5	18.0
"	30	26.8, 26.8, 28.0	27.2
"	40	34.5, 33.8, 36.4	34.9
"	50	43.2, 43.8, 46.2	44.3
Hexanol	20	78.5, 79.4, 83.0, 77.5	79.6
"	30	116, 127, 120	121
"	40	163, 180, 205	183

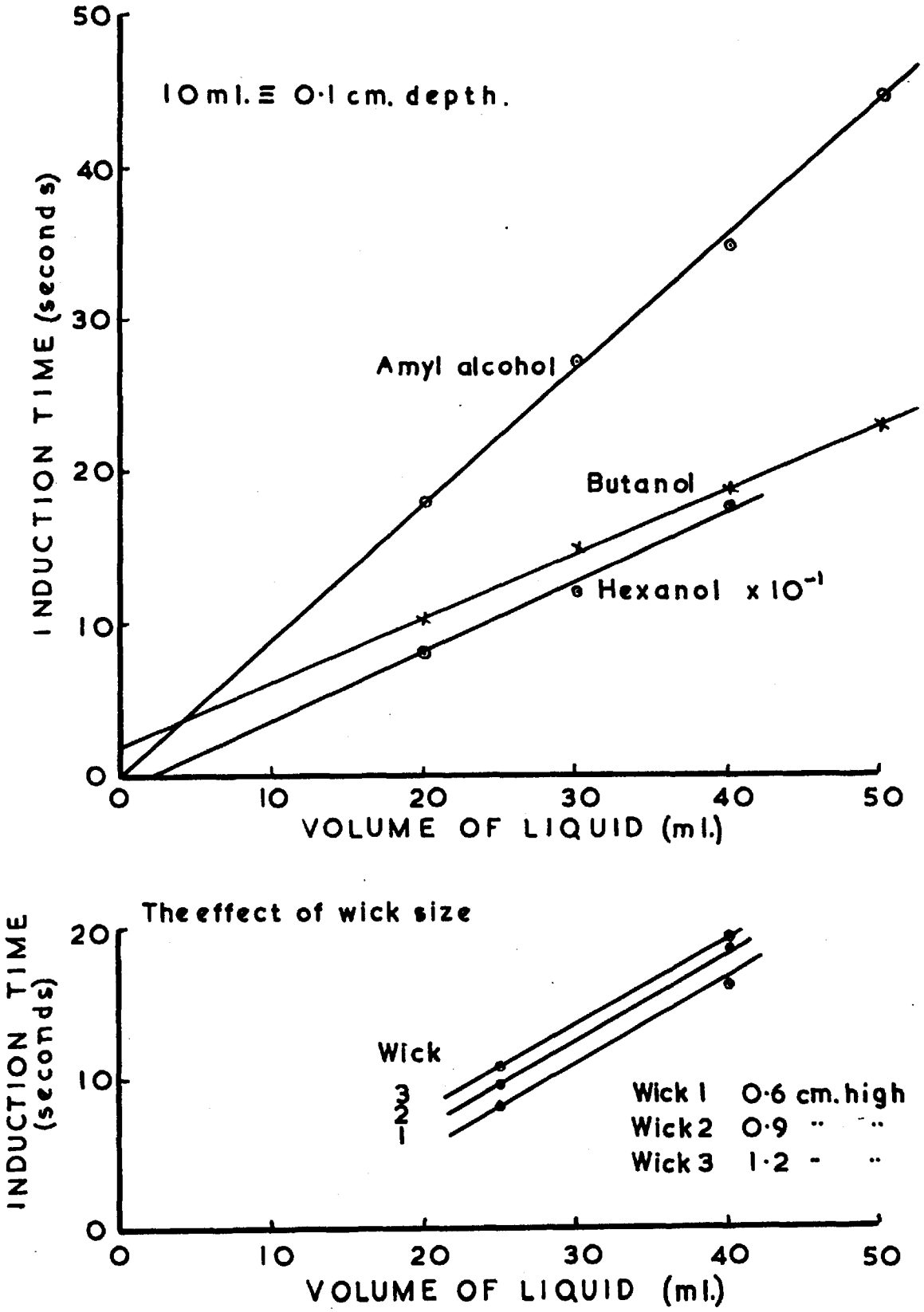


FIG. 4.5 FACTORS AFFECTING INDUCTION TIMES

The values of mean induction time given in Table 4.4 are plotted, against the volume of liquid used, in Fig 4.5. It can be seen that for each liquid it is approximately true to say that the ratio of the induction times for two different depths of liquid is the same as the ratio of the depths. An implication of this result is that during the induction period there is very little variation of temperature with depth in the liquid since doubling the liquid depth requires a doubling of the heating time. Visual observation shows that during the induction period an eddy becomes established in the liquid near the wick. Thus hot liquid from the surface is continuously circulated through the depth of the liquid. This would give rise to a more even temperature distribution than would otherwise result which in turn would account for the variation in induction time with liquid depth.

The differences between the induction times for different liquids are considered in 4.5.3.

4.5.3. The spread of hot liquid from the wick

In order to obtain further information on the factors controlling the induction period temperature profiles near the wick were measured. A further study of the manner in which heat spread through the liquid was made by photographing the position of the boundary between hot liquid and cold liquid. Owing to the difference in refractive index this boundary could be observed and the variations in its position were related to the temperature of the liquid as measured directly.

4.5.3.1. Temperature measurements

Runs were carried out with butanol, amyl alcohol, and hexanol using the apparatus described in 3.2.3 to measure the way in which the liquid temperature near the wick varied during the induction period. The procedure adopted was to clamp the thermistor with its temperature sensitive element at the surface of the liquid a known distance from the wick. For a run the oscilloscope was reset and the liquid ignited at the wick. Marks were made on the photograph of the trace by short

circuiting the thermistor at a known time after ignition, at the time of the flame spreading from the wick, and at the time of the flame reaching the thermistor (when the distinction could be made between the latter pair of times). When runs were repeated under the same conditions very similar results were obtained.

Fig. 4.6 shows the results obtained using 25ml. of butanol per run with the thermistor at distances of 1.2 cm., 4 cm., and 6 cm. from the wick. In the upper graph the temperature variations at each of these distances are plotted. It is evident that 1.2 cm. from the wick the liquid is preheated to the temperature close to the closed flash point of n-butanol, i.e. 36°C, at the moment of the flame spreading from the wick. However at 4 cm. and 6 cm. from the wick the liquid is preheated only to 27°C and 24°C respectively at the moment of the flame passing those points. In the lower graph of Fig. 4.6 the results are re-plotted in a different form to show the variation of temperature with distance from the wick at different times from ignition.

The corresponding graphs for results obtained using 50 ml. of n-butanol and 25 ml. of amyl alcohol are given as Figs. 4.7 and 4.8 respectively. In the latter case the temperatures when the flame passed the 4 cm., 8 cm., and 12 cm. marks were 30°C, 29°C, and 36°C respectively. For purposes of comparison the results for butanol and amyl alcohol are re-plotted on the same graph (Fig. 4.9) together with additional results for n-hexanol.

4.5.3.2. The optical effects of the temperature variations in the liquid

The refractive index of a liquid varies considerably with temperature. If there are temperature gradients in a liquid then rays of light passing through the liquid will be deflected as a consequence of the refractive index gradients. The effects of such non-uniformities of refractive index in an optical path have been described as schlieren. In recent years, with the development of techniques based on the interpretation of schlieren images, this word has takeon on a specialised meaning and it is now most commonly used in connection with certain

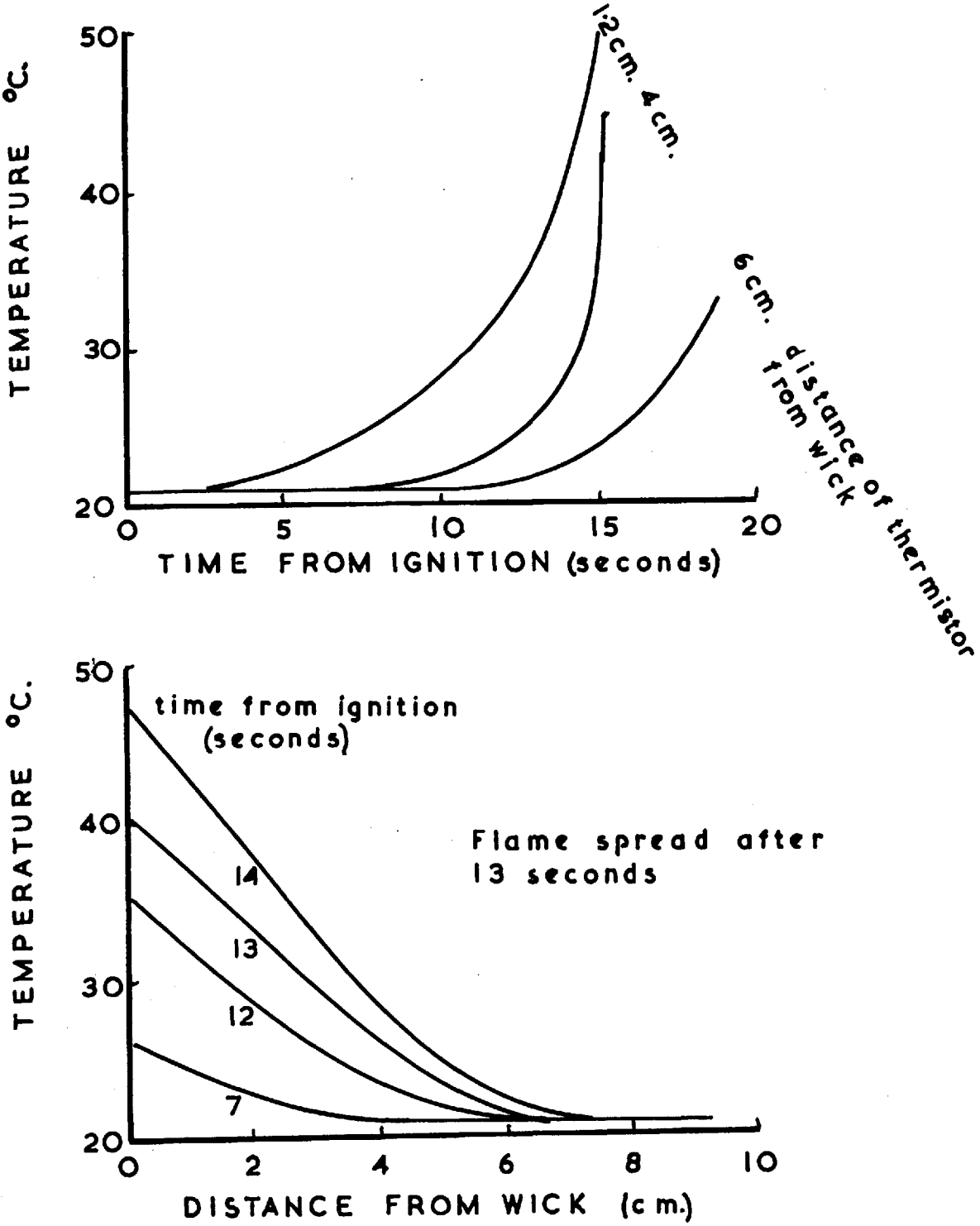


FIG. 4.6 INDUCTION PERIOD TEMPERATURE PROFILES 25ml BUTANOL.

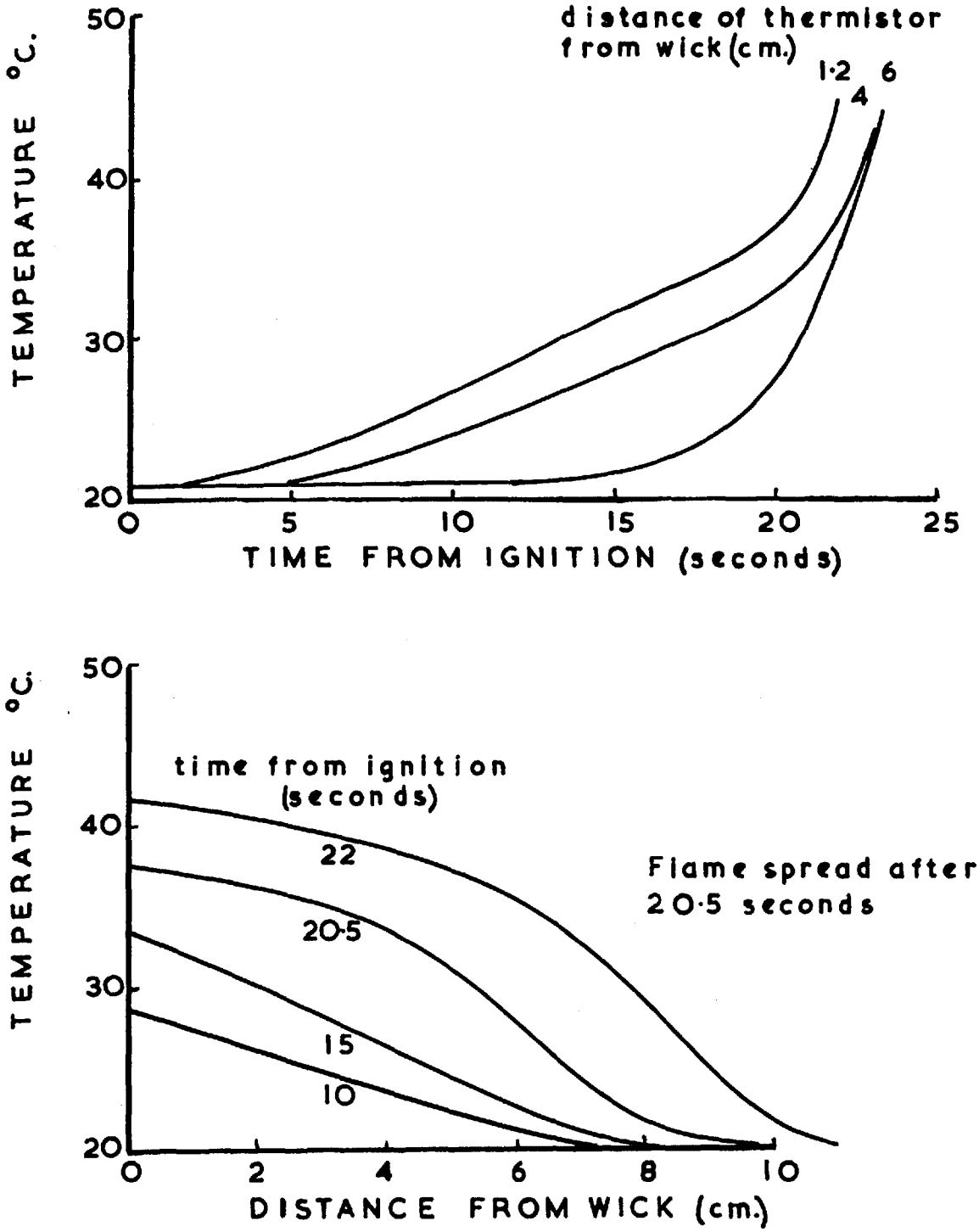
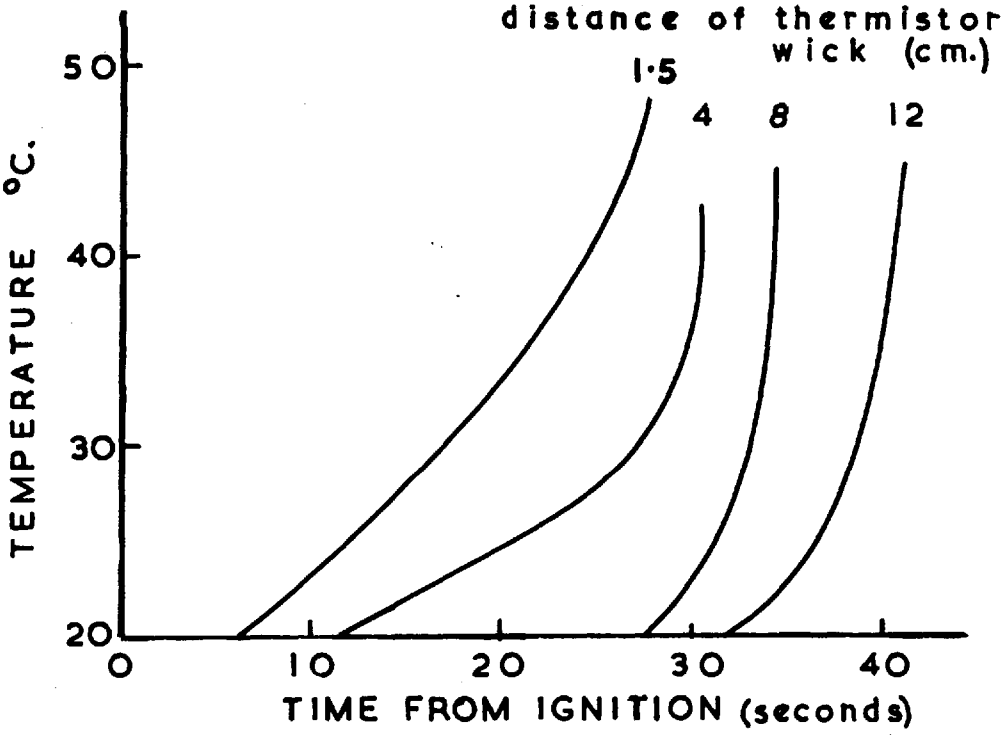


FIG. 4.7 INDUCTION PERIOD TEMPERATURE PROFILES 50ml. BUTANOL.



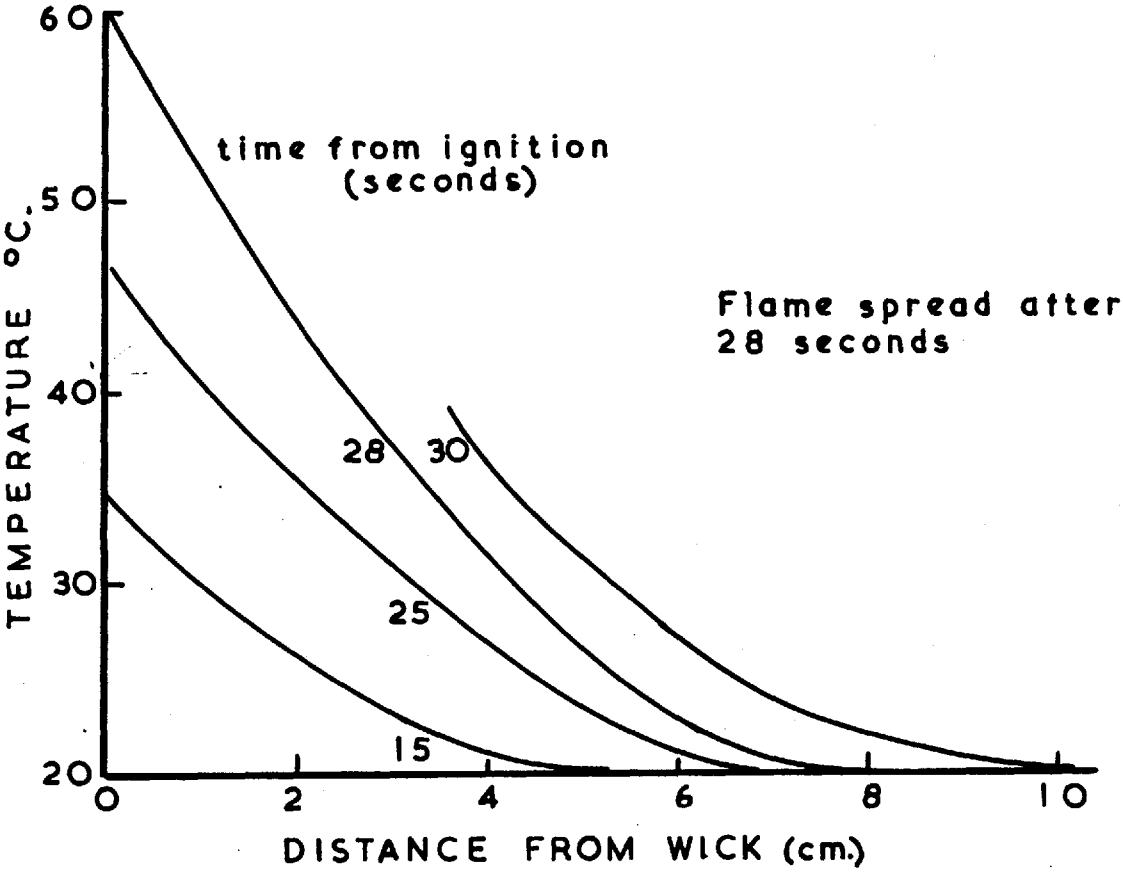
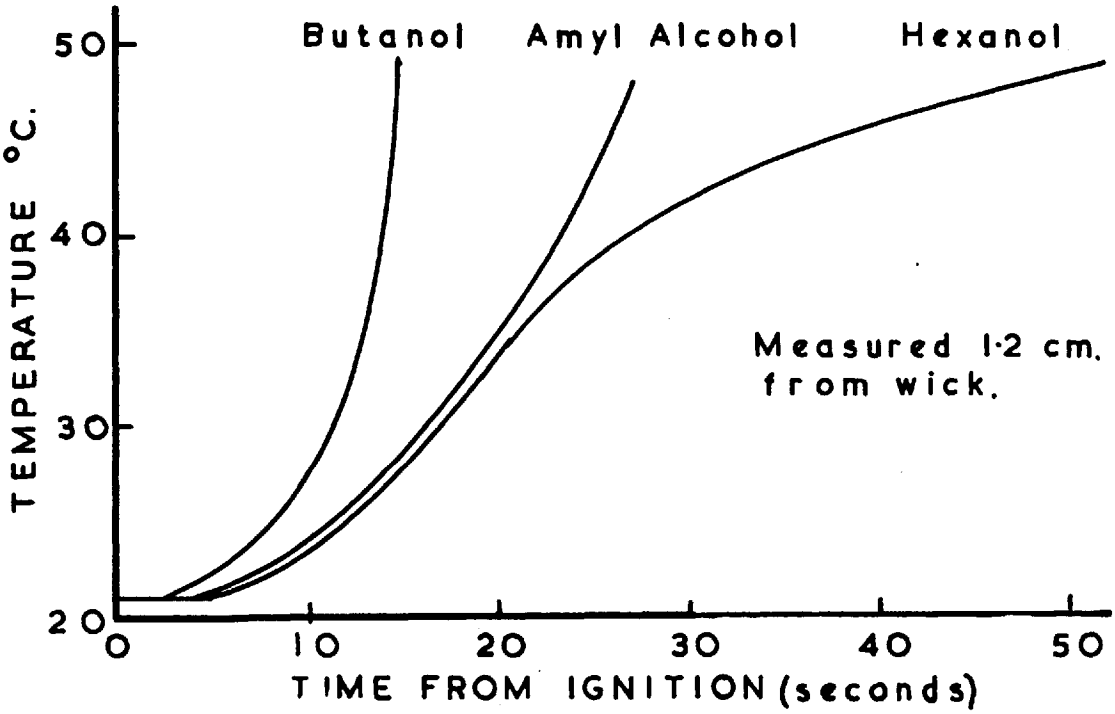


FIG. 4.8 INDUCTION PERIOD TEMPERATURE PROFILES 25 ml. AMYL ALCOHOL



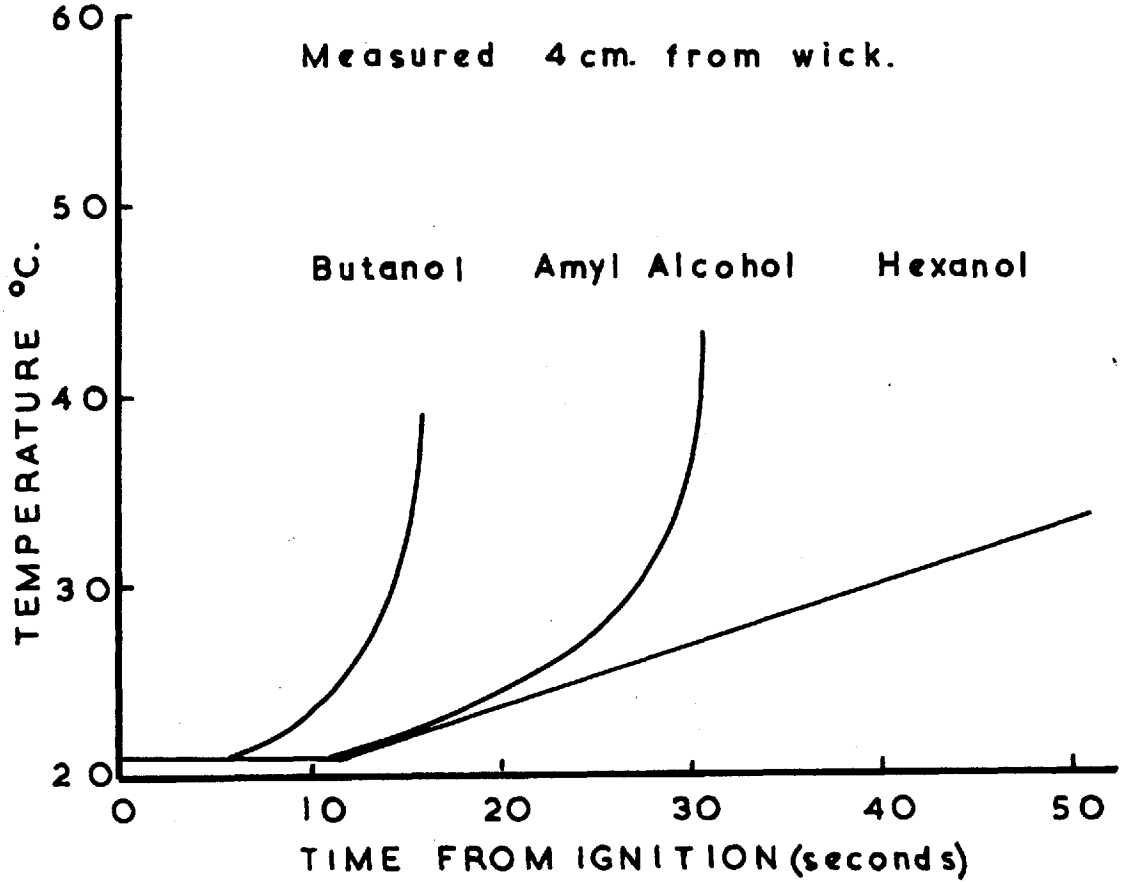


FIG.4.9 A COMPARISON OF INDUCTION PERIOD TEMPERATURE PROFILES

optical systems (38). However in this thesis the word 'schlieren' will be used in its more general sense. The expression 'schlieren boundary' is used to describe the boundary between a region in which no optical disturbances are observed and a region in which temperature gradients give rise to a distorted image of the liquid. This boundary can be observed with the naked eye and photographed by casting a shadow of the liquid on to a photographic plate.

During the induction period increases in temperature of the liquid near the wick gave rise to a schlieren boundary which moved away from the wick as the induction period proceeded. In order to determine to which temperature of the liquid this boundary corresponded and to trace its progress during the induction period arrangements were made to photograph the position of this boundary at frequent intervals.

A thin sheet of paper was attached to the outer face of one of the glass walls of the combustion vessel. The vessel was illuminated from the other side from a pinhole source of light, formed by focussing the light from a high pressure mercury vapour lamp on to a pinhole in a screen. This illumination caused a shadow of the liquid in the combustion vessel to be thrown on to the paper screen; when the liquid was burning at the wick the schlieren boundary could be observed on this screen.

A U.S. Army aerial camera, with a focal plane shutter and film winding gear operated by a 24 volt D.C. electric motor, was modified by removing its original lens and fitting an extending front with a 13.5cm. focal length camera lens. With this arrangement a 90% life size image was produced on the film; each frame was $5\frac{1}{2}$" square and a standard film contained fifty frames. During a run this camera was focussed on to the screen attached to the combustion vessel and photographs were taken at one second intervals during the induction period. Results obtained using 25ml. and 50 ml. of butanol are shown in Fig. 4.10 where the position of the schlieren boundary in relation to the wick is plotted as a function of time for each run. It is of interest to note that the position of this boundary a certain time after ignition is approximately the same for both runs until the end of the induction period for the 25 ml. run is approached.

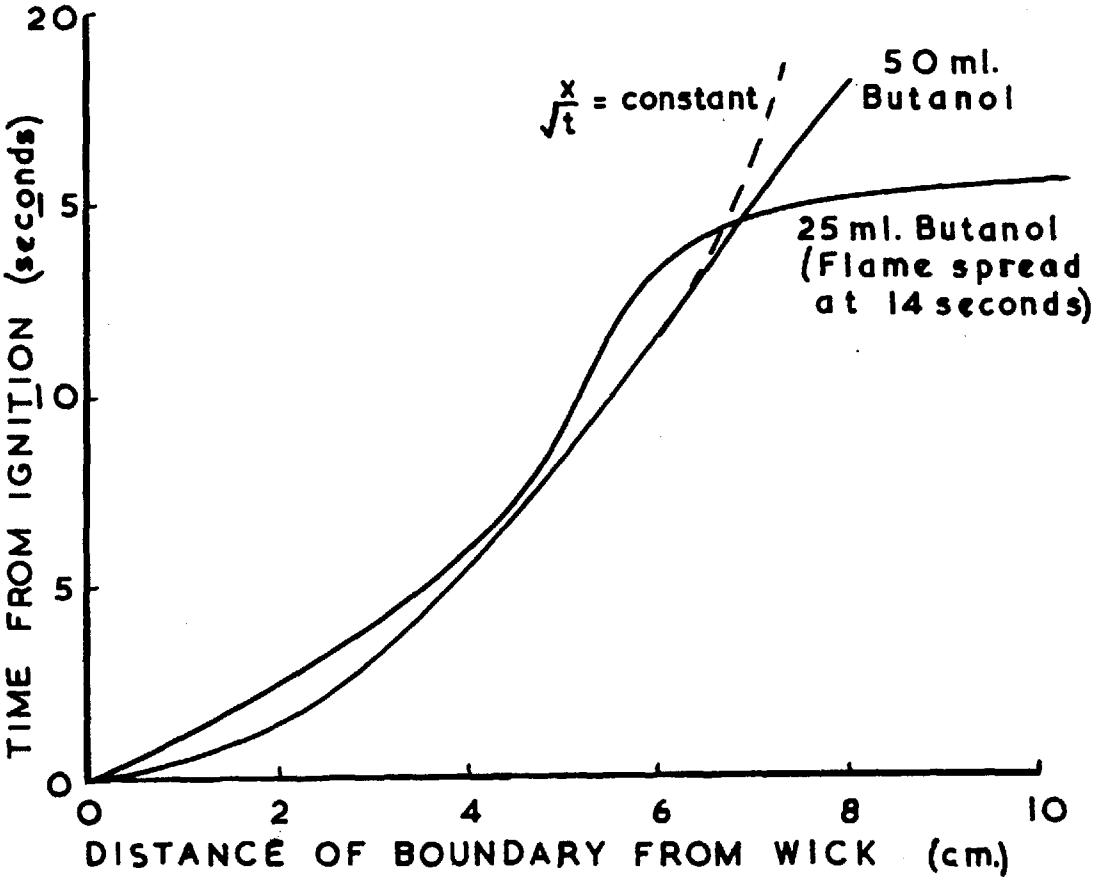


FIG. 4.10 THE MOVEMENT OF THE SCHLIEREN BOUNDARY DURING THE INDUCTION PERIOD.

A comparison between the position of the schlieren boundary and the shape of the temperature profiles is instructive. For 25 ml. of butanol Fig. 4.10 shows that seven seconds from ignition the schlieren boundary is 4.4 cm. from the wick while at twelve and thirteen seconds from ignition it is 5.6 cm. and 5.8 cm. from the wick respectively. Fig. 4.6 shows that when the temperatures were measured directly the first observed temperature rise 4.4 cm. from the wick occurred after 7 seconds while at 5.6 cm. after 12 seconds a temperature rise of 0.3°C had occurred and at 5.8 cm. after 13 seconds the rise was 0.9°C. For 50 ml. of butanol the schlieren boundary had reached 4 cm. and 6 cm. from the wick after 5.5 seconds and 11.7 seconds respectively. When measured directly (Fig. 4.7) the temperature rise at (4 cm. 5.5 seconds) was 0.3°C and at (6 cm. 11.7 seconds) it was 0.6°C.

4.5.4. Discussion

The above measurements of the phenomena occurring during the induction period together with visual observation of convection currents in the liquid suggest that the following sequence of events occurs when a liquid is ignited at a wick. Heat transfer from the flame to the liquid gives rise to a region near the wick where considerable recirculation of liquid occurs. Beyond this region a further convection current becomes established which produces a net flow of liquid away from the wick at the surface. When some critical condition is achieved, the flame spreads from the wick and overtakes this convection current but during this period the flame is still stabilised at the wick because the liquid has not been sufficiently preheated to maintain combustion above it. As the flame reaches the extent of this convection current the transition to the stabilisation of the flame at a moving point on the surface occurs and the steady state rate of spread and temperature profiles become established.

From the available evidence it would seem that the duration of the induction period is controlled mainly in the zone of recirculation next to the wick. Temperature measurements 1-2 cm. from the wick

(which is about the limit of the zone of recirculation) show that when the flame first spreads from the wick the temperature at this point has risen to or beyond the closed flash point of the liquid. The circumstances where the liquid is heated above its closed flash point without the vapour above it becoming ignited (which is a strictly local condition confined to the vicinity of the wick) may arise because the chimney effect of the flame burning on the wick draws the surrounding air and vapour to it. Therefore until the rate of evolution of vapour increases the inflammable vapour may be drawn into the flame instead of the flame spreading into the inflammable vapour. In these circumstances it is difficult to deduce a critical condition for the spread of flame from a wick and this matter is obviously one which would benefit from further experimental investigation.

It is evident however that whatever the nature of this critical condition it must be directly related to the temperature of the zone of recirculation; because of the way in which the induction time varies with liquid depth it has been suggested that the temperature of this zone is substantially uniform throughout. Reference to Fig. 4.9 shows that it is far more difficult to heat this zone by 10°C from 50°C to 60°C than it is from 20°C to 30°C. The temperature/time curve for hexanol at 1.2 cm. from 25 seconds onwards is characteristic of a region which is being supplied with heat at a constant rate and which is losing heat at a rate proportional to its temperature. Induction times for hexanol (Table 4.5) are disproportionately large for this reason.

The transition period, which occurs after the flame has started to spread from the wick and before the steady state conditions of propagation have been achieved, is the least important of the three types of behaviour which may be distinguished, viz;- induction, transition, steady state propagation.

The transition period did not seem to control the flames behaviour in any way. In the vast majority of investigations made the flame spread from the wick and the transition to steady state propagation occurred. In the only circumstances where the flame failed to

propagate (amyl alcohol, 0.15 cm. depth), the flame showed no tendency to spread from the wick. This failure is therefore a further matter relating to the induction period which requires examination.

A situtation was never encountered in which the flame spread from the wick and then failed to propagate completely. Thus, once the induction period had been successfully completed, the transition to steady state propagation always occurred.

The state of information on the induction period may be summarised as follows. Preliminary measurements on matters affecting the duration of the induction period have been made. Qualitative explanations of some of these results have been given and other matters which require investigation have been discussed. At this stage it is not possible to arrive at any definite quantitative explanation of the controlling phenomena nor is it possible to state the critical condition which characterises the ending of the induction period. Further experimental work would make such information more accessible.

CHAPTER 5

THE FLAME AS A HEAT SOURCE

5.1. Introduction

In earlier chapters it was suggested that when the initial temperature of a liquid is less than the closed flash point of that liquid the rate of spread of flame across its surface is controlled by heat transfer processes. Any detailed analysis of the experimental results should therefore be based on a consideration of the effects of heat transfer from the flame to the liquid surface and from the liquid surface to the bulk of the liquid. In the present state of knowledge of heat transfer processes it is impossible to determine these effects exactly; any estimate of the rate of convective heat transfer from the flame to the liquid, for example, must be based on empirical formulae derived for different circumstances.

Even if a reliable estimate of the rate of heat transfer to the liquid could be made it would still be necessary to consider how this heat would spread through the liquid. It is quite possible to set up the differential equations for combined conduction and convection in a gas or liquid, based on Fourier's equation for heat conduction (37), and the hydrodynamic equations for motion in a fluid under the influence of external forces such as the buoyancy forces which give rise to convective heat transfer (39)(40). These equations can not however be solved as they stand. Solutions for them have been obtained by making limiting assumptions and applying them to the most simple circumstances (41) but the applications of these methods in their present state appear to be few. An alternative approach is to apply the similitude theory of Frank-Kamenetskii (42) for which the equations are re-written in terms of dimensionless co-ordinates. Any critical conditions relevant to the equations may then be regarded as functions only of the

dimensionless parameters which result. Only a small amount of information can be conveyed by this means however and it was felt that a more complete means of interpreting the results would be desirable. In the following pages such a method is outlined; it consists of solving the heat transfer equations for conduction only and applying the solutions to the experimental results. It was found that by adopting this procedure a qualitatively consistent picture of the observed experimental trends was obtained. Moreover for many of the experimental results a quantitatively consistent picture was obtained by substituting a value for the liquid thermal conductivity many times greater than the experimentally determined one. Thus apparently many aspects of the flames behaviour may be described by treating the effects of convective heat transfer in terms of an 'effective thermal conductivity' and the equations for heat conduction.

In the following pages a detailed description of this approach is given together with its applications to the experimental results. The necessary solutions to the equations are given in an appendix.

5.2. Steady state propagation

Before proceeding to a detailed discussion of the experimental results in terms of the 'effective thermal conductivity' approach the physical model for which the differential equations are solved will be considered. First of all the model is a two dimensional one. Variations along the flame front are not considered and it may therefore be regarded as an infinite flame front spreading across an infinite liquid surface. Secondly the flame is considered as a strip source of heat (width 2b, heat flux Q) moving at a constant velocity (v) across the surface of the liquid in a direction normal to itself. Since a steady state has been achieved conditions relative to the flame are constant with time. The system is therefore considered in terms of moving rectangular axes (velocity v) on which the liquid surface is in the plane $z = \frac{1}{2}$ and the strip source of heat is in the plane $z = \frac{1}{2}$ and extends from $x = -b$ to $x = b$. The direction of motion of the strip source is taken as the x negative direction. Thirdly the inflammable liquid is considered

in terms of an isotropic solid bounded by two infinite parallel planes. Across one of these planes (the liquid surface at $z = \frac{1}{2}$) a strip source of heat is moving as described above. At the other plane (the bottom of the liquid at z = o) no temperature rise occurs. Since the liquid is in contact, through the metal base of the combustion vessel, with a heat sink maintained at the initial temperature of the liquid this is a realistic condition to adopt. The temperature rise at a point (x,z) is given by equation (5.4) of the Appendix to this chapter. This equation is in a dimensionless form.

$$C_1 V\theta = \int_{X-B}^{X+B} \sum_{n=-\infty}^{\infty} e^{u} Ko\left[(u^2+(Zn^{+})^2)^{\frac{1}{2}}\right] - \sum_{n=-\infty}^{\infty} e^{u}\, Ko\left[(u^2+(Zn^{-})^2)^{\frac{1}{2}}\right] . du \qquad - (5.4)$$

Ko(u) is the modified Bessel function of the second kind of order zero

$X = \frac{pcvx}{2K} = C_2 vx$

$B = \frac{pcvb}{2K} = C_2 vb$

θ = temperature rise

$Zn^{+} = \frac{pcv}{2K}\left[(z-1/2)^2 + (2nl+1/2 -z)^2\right]^{\frac{1}{2}}$

$Zn^{-} = \frac{pcv}{2K}\left[(z-1/2)^2 + (2nl - 1/2 - z)^2\right]^{\frac{1}{2}}$

$C_1 = \frac{\pi pc}{2Q}$

k, p, c = thermal conductivity, density and specific heat respectively.

The numerical solution of equation (5.4) is discussed in detail in the Appendix to this chapter. At this stage the solution for the surface temperature only will be considered (z=1/2).

If equation (5.4) is written as

$$C_1 V\theta = \left[I\right]_{X-B}^{X+B}$$

then the values of $\left[I\right]_0^a$ are plotted in Fig. 5.1 against (a), with

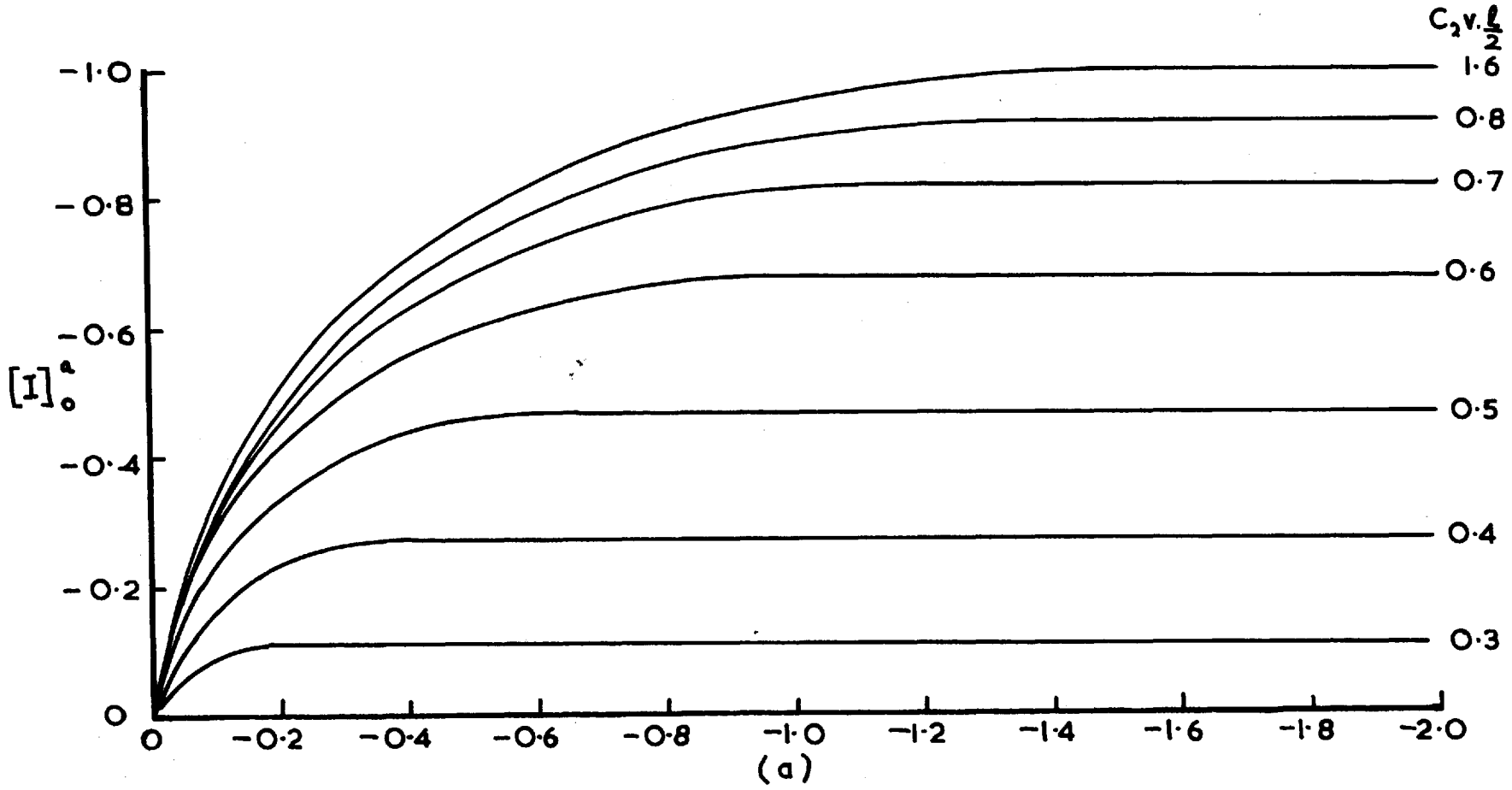


FIG. 5.1 THE SOLUTION OF EQUATION 5.4 FOR THE SURFACE TEMPERATURE CASE.

$C_2.1/2.v$ as a parameter, for the surface temperature case, $z = 1/2$. Only values for $a < o$ are given because the progress of the flame is controlled by changes occurring in the liquid ahead of it and this direction has been taken as negative. Thus, from Fig. 5.1, if $X+B = -1$, $X-B = -2$, and $C_2.1/2.v = 0.8$ then $C_1V\theta = (-0.88) - (-0.92) = 0.04$.

(since $\int_{a_1}^{a_2} f(x)dx = \int_{0}^{a_2} f(x)dx - \int_{0}^{a_1} f(x)\,dx$)

5.2.1. Factors affecting the steady state rate of spread of flame

It has been shown experimentally that the rate of spread of flame across a liquid surface is affected by the nature of the liquid, the temperature of the liquid, the depth of the liquid, and the width of the channel to which the flame is confined. In this section the observed experimental effects of changes in these parameters will be compared with the effects predicted by Equation (5.4)

In Chapter 3 it was suggested that propagation of a flame is stabilised at the point on a liquid surface where the temperature has reached a critical value (T' say). This point has the same velocity as the flame front (v). T' is a constant for a particular liquid. From Equation (5.4) a relationship between v and θ_F, the temperature rise at the flame front, can be deduced. At the flame front $x = -b$

$$\therefore \quad C_1V\theta_F = \left[I\right]_{-2B}^{o} = -\left[I\right]_{o}^{-2B}$$

This corresponds to the form in which Fig. 5.1 is plotted. Fig 5.1 may therefore be regarded as a graph of $C_1V\theta_F$ against $v.\frac{b}{K}$ with $v.1/2.\frac{1}{2k}$ as a parameter. Of these quantities only θ_F ($\theta_F = T'-T_L$ where T_L is the initial temperature of the liquid) and $1/2$ are varied independently; v is a dependent variable and the other quantities are properties of the system. From Fig. 5.1 it can be seen that if the experimental data were to be plotted in the form $v\,(T'-T_L)$ against v they should tend to a constant value of $v(T' - T_L)$. Moreover, if the results lie in

the region where $2B > 1.3$ there should be a single curve for the experimental data when plotted in the form $v\,(T' - T_L)$ against $v.l/2$.

In order to obtain information on this latter point the first prediction must first be verified and a value of T' determined. If $v\,(T'-T_L)$ tends to a constant value (A say) as v increases, when

$$v\,(T'- T_L) = A \text{ then } \quad \frac{A}{v} = T' - T_L.$$

If $\frac{1}{v}$ is plotted against T_L therefore the data should tend to a straight line of negative slope and intercept T' on the temperature axis. Figs 5.2, 5.3, and 5.4 show typical results for butanol, amyl alcohol, and hexanol plotted in this way. (Tables 3.4, 3.9, 3.18). For each liquid the data tend to a straight line of negative slope as predicted. Values of T', found by extrapolation, are

Butanol $T' = 42^{\circ}C$

Amyl alcohol $T' = 48^{\circ}C$

Hexanol $T' = 62^{\circ}C$

Using these values for T' the results for butanol (four liquid depths), amyl alcohol (five liquid depths), and hexanol (two liquid depths) were plotted in the form $v\,(T' - T_L)$ against $v.l/2$. (Figs. 5.6, 5.7, and 5.8). For purposes of comparison the form of such a curve predicted by Equation 5.4 is also shown (Fig. 5.5). Points of similarity between the predicted and experimental curves are that in each case $v\,(T' - T_L)$ increases to a constant value and also that the experimental results for different liquid depths all lie near the same curve for a particular liquid. The co-ordinates of the point at which $v\,(T' - T_L)$ becomes constant can be estimated from each graph. These are

Fig. 5.5 Predicted $C_1V\theta = 1.0$ $C_2.v.l/2 = 1.3$

Fig. 5.6 Butanol $V\theta = 50$ $v.l/2 = 0.6$ $\therefore$ $C_1=0.020$, $C_2= 2.2$

Fig. 5.7 Amyl alcohol $V\theta = 25$ $v.l/2 = 0.5$ $\therefore$ $C_1=0.040$, $C_2 =2.6$

Fig. 5.8 Hexanol $V\theta = 22$ $v.l/2 = 0.3$ $\therefore$ $C_1=0.045$, $C_2 =4.3$

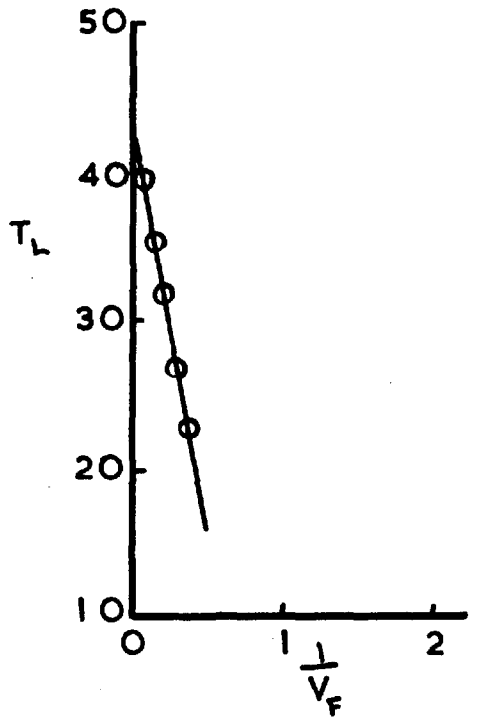


FIG. 5.2 BUTANOL

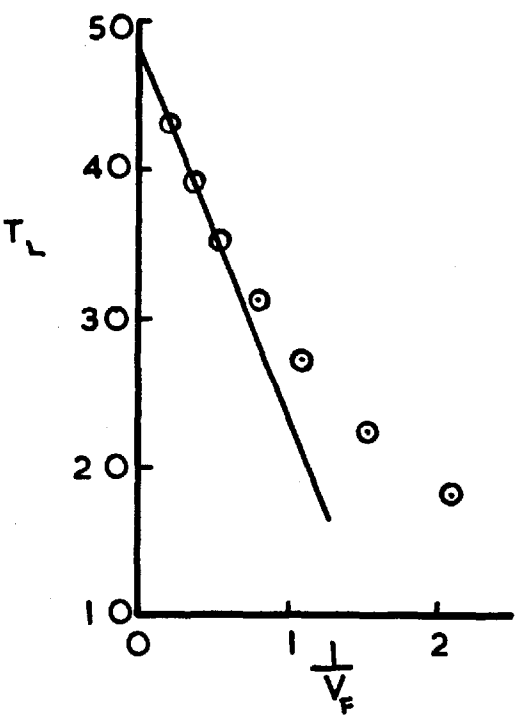


FIG. 5.3 AMYL ALCOHOL

FIG. 5.2 - 5.4 EXPERIMENTAL DATA
THE VARIATION OF $\frac{1}{V_F}$ WITH T_L

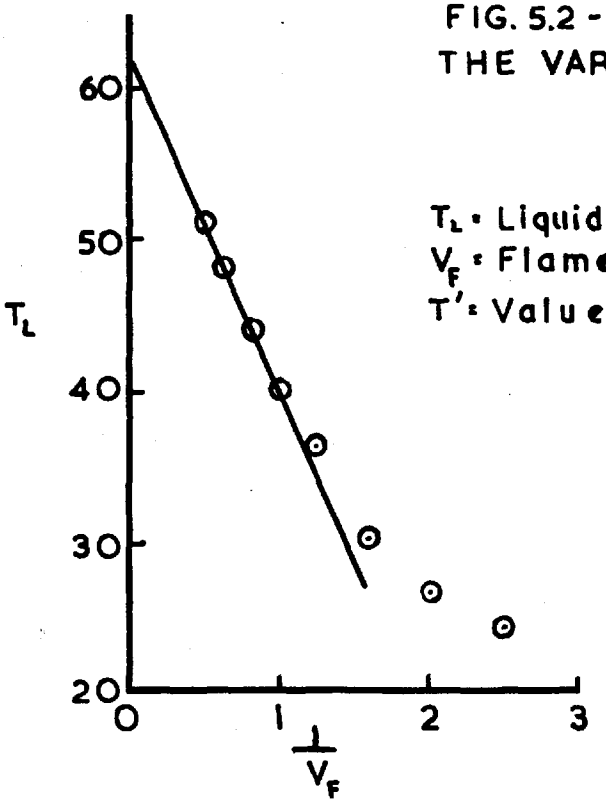


FIG. 5.4 HEXANOL

T_L = Liquid initial temperature (°C)
V_F = Flame's rate of spread (cm.sec.$^{-1}$)
T' = Value of T_L at $\frac{1}{V_F} = 0$

Butanol	$T' = 42$ °C.
Amyl Alcohol	$T' = 48$ °C.
Hexanol	$T' = 62$ °C.

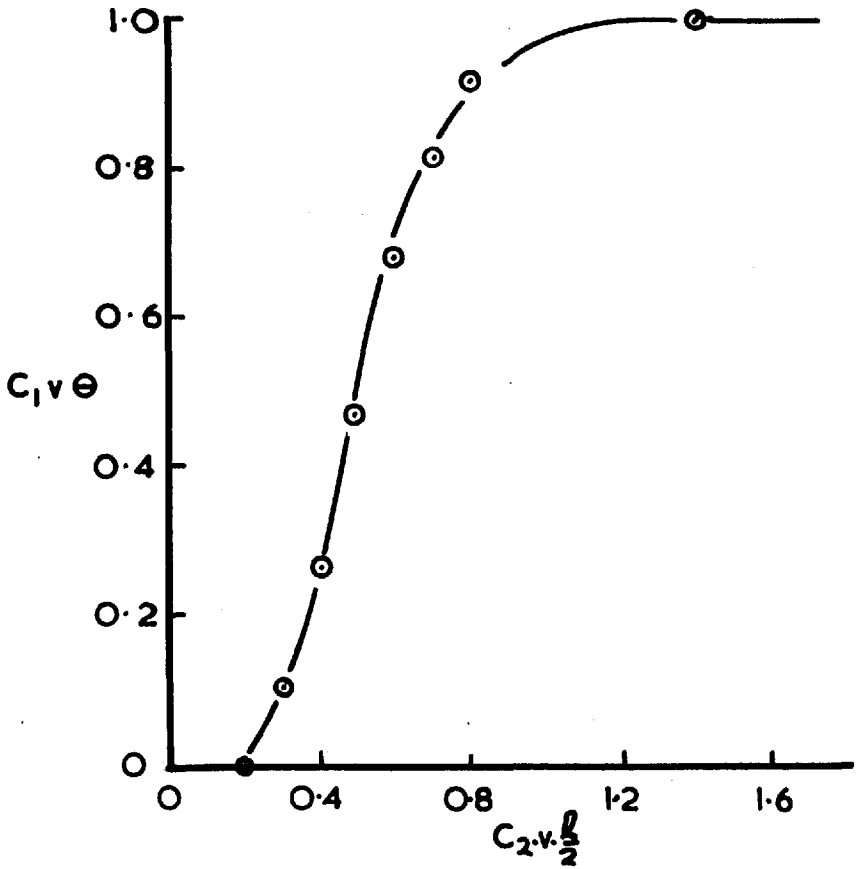


FIG. 5.5 THEORETICAL FORM OF RELATIONSHIP (FROM FIG. 5.1)

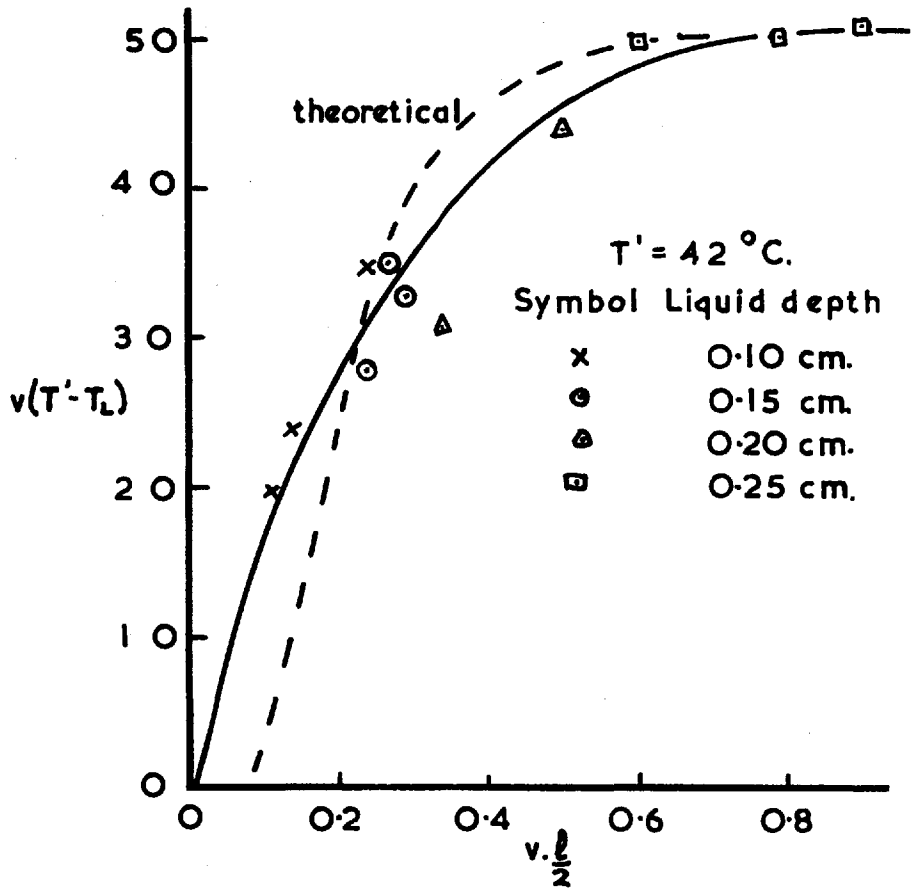


FIG. 5.6 EXPERIMENTAL RESULTS FOR BUTANOL.

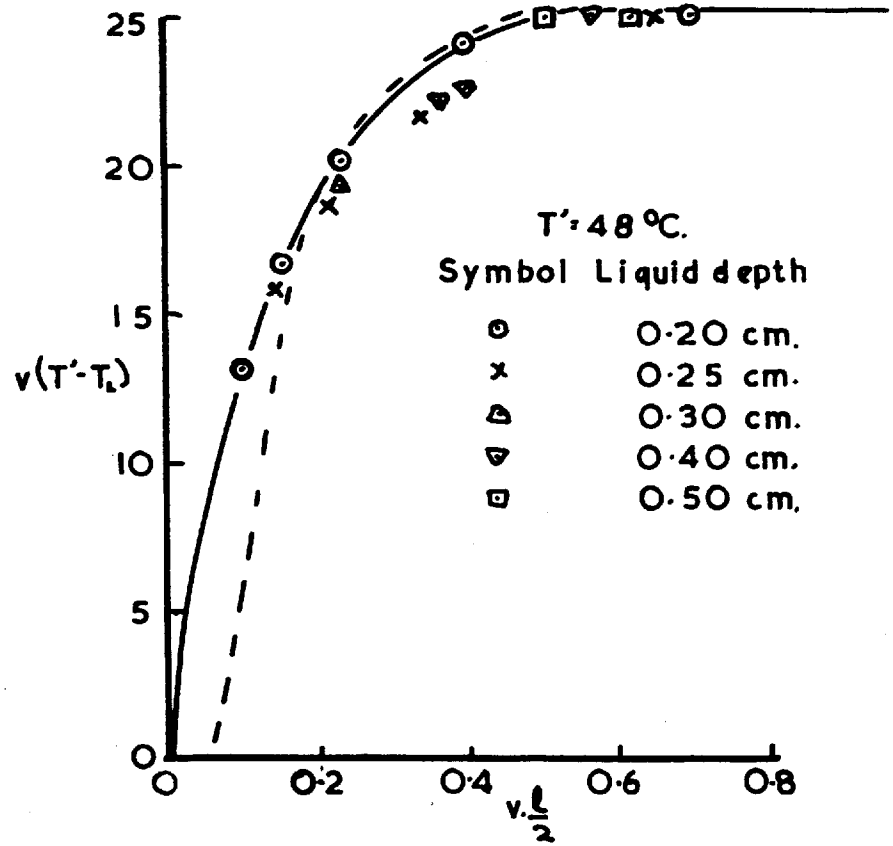


FIG. 5.7 EXPERIMENTAL RESULTS FOR AMYL ALCOHOL.

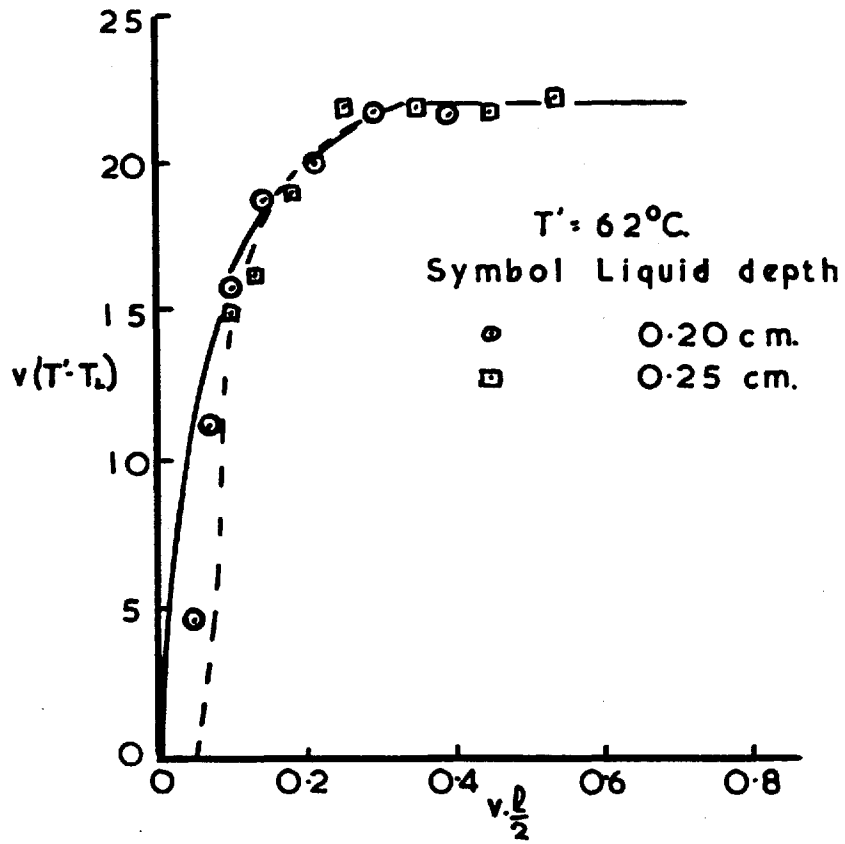


FIG. 5.8 EXPERIMENTAL RESULTS FOR HEXANOL.

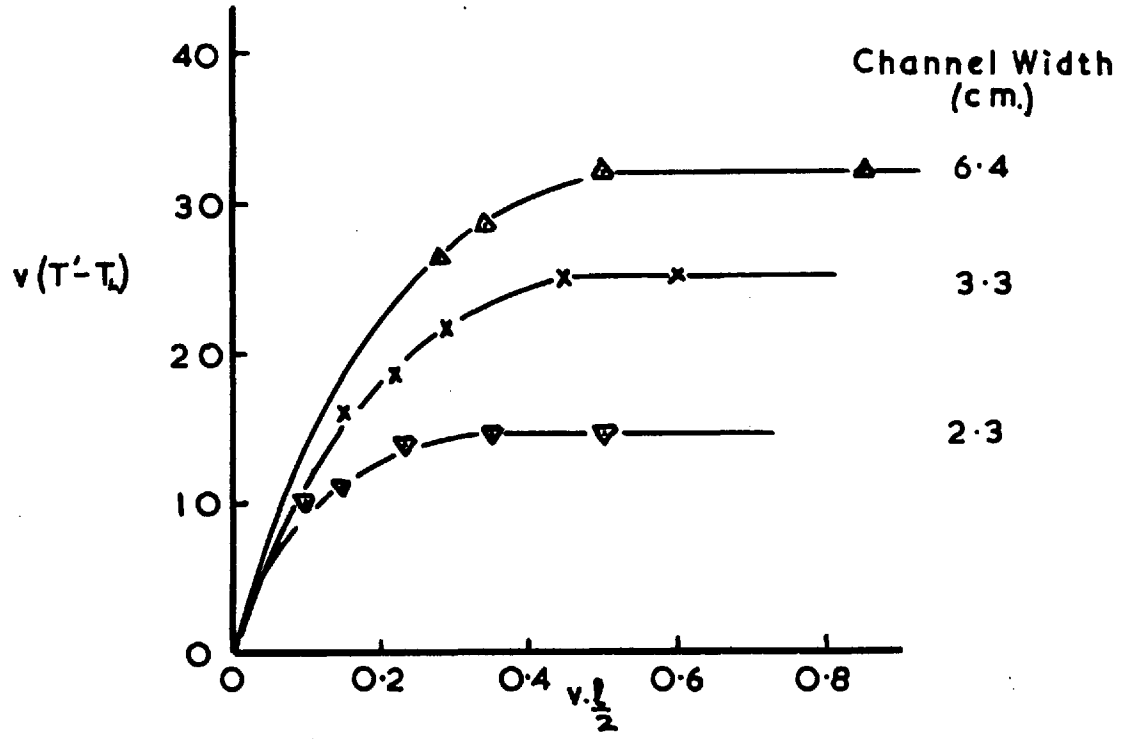


FIG. 5.9 EXPERIMENTAL RESULTS FOR AMYL ALCOHOL
The effects of Channel Width.

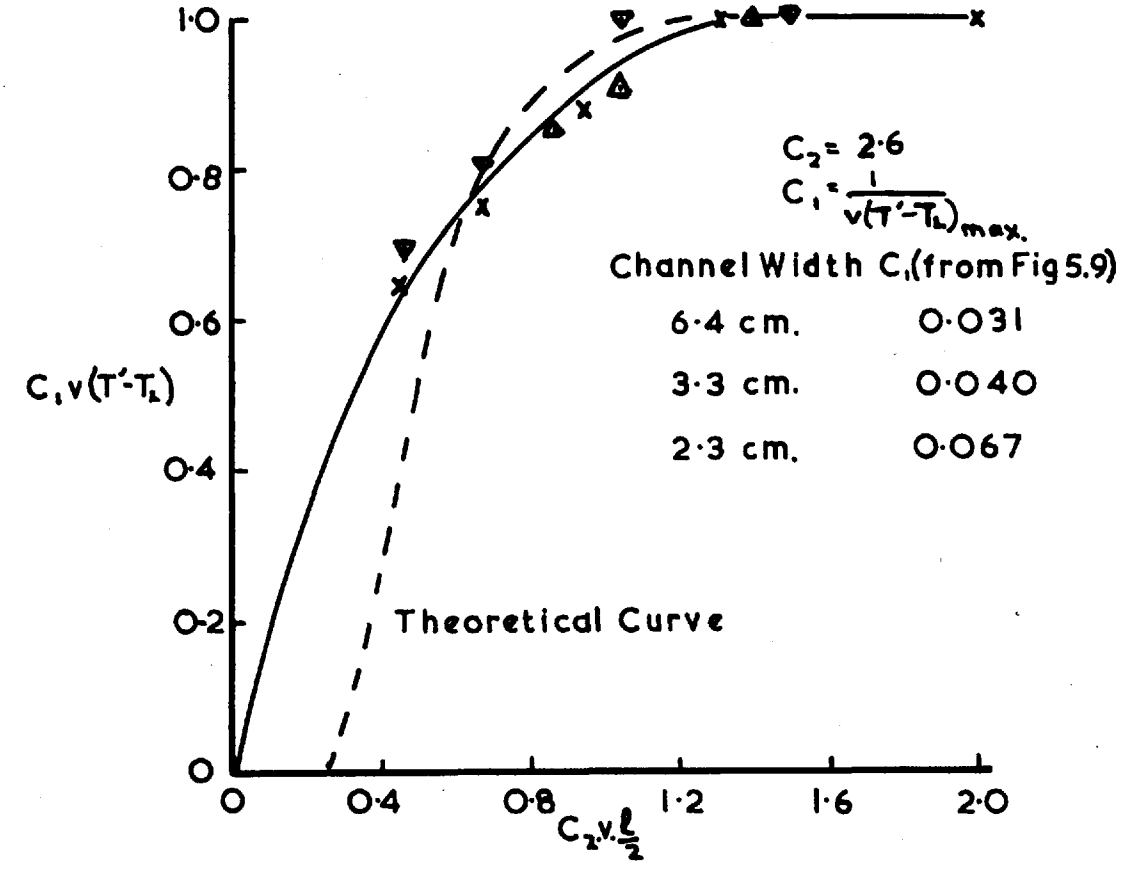


FIG. 5.10 AN ALTERNATIVE FORM OF FIG. 5.9

Using appropriate values for C_1 and C_2 the predicted curve was then re-plotted on Figs. 5.6 - 5.8 (the dotted line). This enables a more direct comparison to be made in each case.

The effect of channel width

In the above discussion all the results considered were obtained using a channel width of 1.3 inches. For amyl alcohol results were also obtained using channel widths of 0.9 and 2.5 inches (Tables 3.10 and 3.11) at a liquid depth of 0.25 cm. It will be assumed that the effect of altering the channel width is to alter Q, the value of the heat flux from the flame to the liquid. Although the amount of heat liberated by the flame in passing over a given area of liquid surface is not affected by the channel width, it was suggested in Chapter 3 that at small channel widths a greater proportion of this heat is absorbed by the screens thereby reducing the net heat flux to the surface. In Fig. 5.9 the results for the three different channel widths are plotted in the form $v\,(T' - T_L)$ against $v.l/_2$. The same trends are revealed for each curve while the constant value of $v\,(T' - T_L)$ is different in each case. These values are

Channel width 0.9 inches $(V\theta)_{max} = 15$ $C_1 = 0.067$

Channel width 1.3 inches $(V\theta)_{max} = 25$ $C_1 = 0.040$

Channel width 2.5 inches $(V\theta)_{max} = 32$ $C_1 = 0.031$

Since C_1 is proportional to $1/Q$ this variation is as expected. Using a value of $C_2 = 2.6$ and appropriate values of C_1 the results of Fig. 5.9 are re-plotted in Fig. 5.10 in the form $C_1V\,(T'-T_L)$ against $C_2.v.l/_2$, together with the predicted curve. The three sets of experimental results now lie on a single curve of the same general form as the predicted curve.

5.2.2. Temperature variations in the liquid

The way in which the temperature of the liquid ahead of the flame varies can be predicted from Equation (5.4). Two matters of interest here, for the purposes of comparison with the experimental

results, are the distance ahead of the flame of the point at which the first temperature rise occurs and the shape of the temperature profile between the flame and this point. Equation (5.4) has been written

$$C_1V\theta = \left[I\right]_{X-B}^{X+B}$$

At the position of the first temperature rise $C_1V\theta = 0$

$$\therefore \quad \left[I\right]_0^{X+B} = \left[I\right]_0^{X-B}$$

From Fig. 5.1 for $C_1V\theta_F = 0.92$ for example, this first occurs when $X + B = 1.1$. This value of X+B therefore corresponds to the position of the first temperature rise. A corresponding value of $(X+B) - (X+B)'$ say - can be measured for several values of $C_1V\theta_F$. These values are plotted in Fig. 5.11 in the form $C_2V.L_o$ against $C_1V\theta_F$. Since at the flame front $x = - b$, distances ahead of the flame front may be written in terms of $L = x + b$. Therefore $(X + B)' = C_2V\ (x + b) = C_2V.L_o$.

Fig. 5.11 shows that there is a straight line relationship between $C_1V\theta_F$ and C_2VL_o. There is therefore an exactly similar relationship between $C_1\theta_F$ and C_2L_o. Equation (5.4) therefore predicts the following relationship between L_o the distance between the flame and the point at which the first temperature rise occurs, and θ_F $(= T' - T_L)$.

$$L_o = 1.3.\ \frac{C_1}{C_2}.\ \theta_F$$

In Chapter 3 the following correlations between experimentally determined values of L_o and T_L were derived.

Butanol	$L_o = 0.21\ (40.7-T_L)$	$\frac{C_1}{C_2} = 0.161$
Amyl alcohol	$L_o = 0.11\ (52.6-T_L)$	$\frac{C_1}{C_2} = 0.085$
Hexanol	$L_o = 0.16\ (63.6-T_L)$	$\frac{C_1}{C_2} = 0.123$

Thus, equation 5.4 correctly predicts a linear relationship between L_o and T_L. The values for T' in the above correlations may be

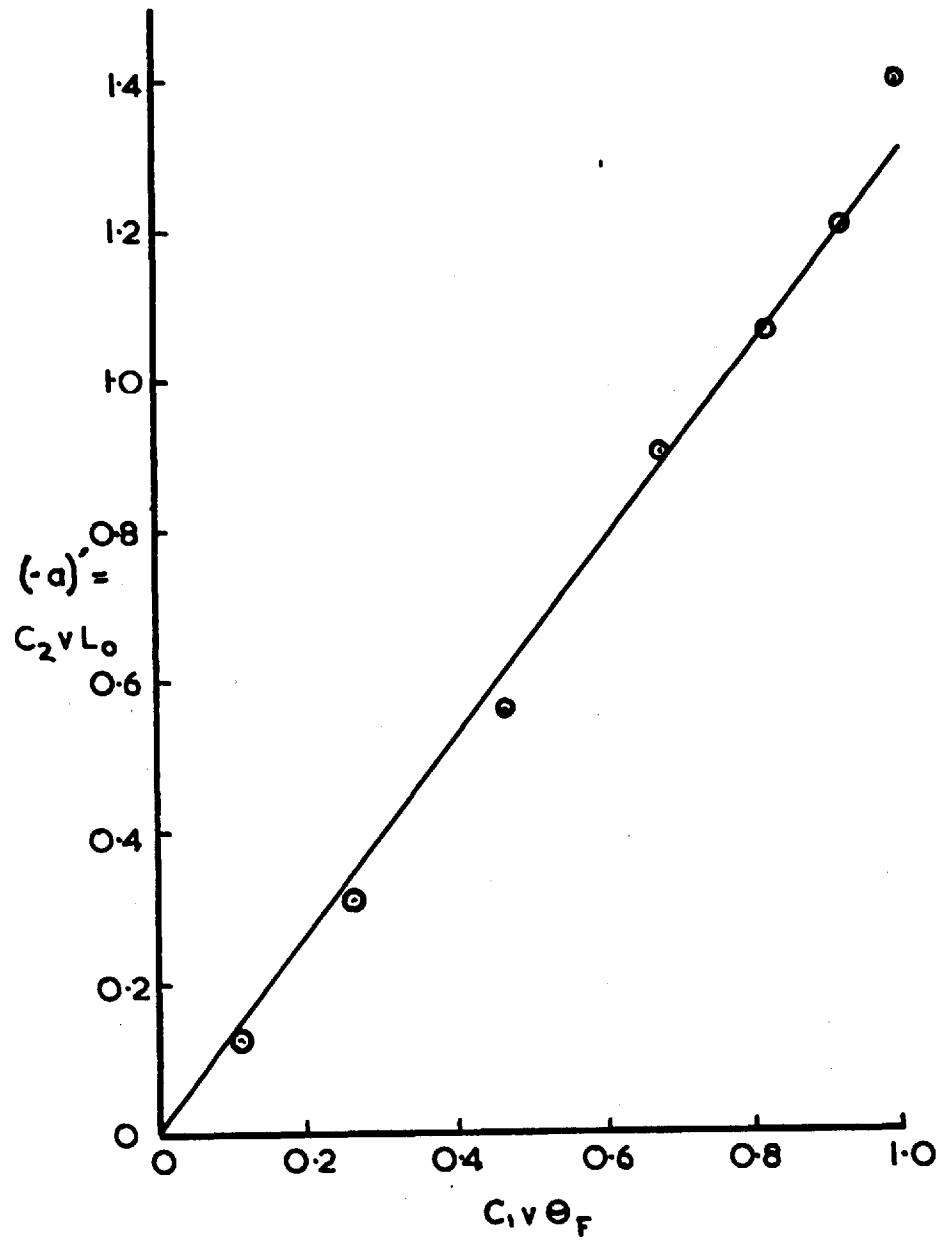


FIG. 5.11 THE VALUES OF (-a) AT WHICH $[I]_o^a$ BECOMES CONSTANT (FROM FIG. 5.1)

compared with those obtained in the previous section. Butanol (42°C) and hexanol (62°C) compare closely. Amyl alcohol (48°C) does not compare so closely but statistically, the above value of 52.6°C for T' is the least significant of the three.

A further point of agreement between predicted and experimental values for L_o exists. Theory predicts that at a particular value of T_L there is a single value of L_o for all liquid depths. This was confirmed experimentally (Table 4.3).

The shape of the temperature profile ahead of the flame may be predicted as follows. For $C_2.v.1/2 = 1$, for example (assuming $2B > 1.3$, so that $\lceil I \rfloor_o^{X-B} = -1$)

when $\frac{\theta}{\theta_F} = 0 \quad \lceil I \rfloor_o^{X+B} = -1 \quad X + B = -1.3$

$$\frac{\theta}{\theta_F} = 0.2 \quad \lceil I \rfloor_o^{X+B} = -0.8 \quad X + B = -0.55$$

$$\frac{\theta}{\theta_F} = 0.5 \quad \lceil I \rfloor_o^{X+B} = -0.5 \quad X + B = -0.20$$

Adopting the notation of Chapter 3 (Tables 3.19 -21)

$$\frac{L_o.2}{L_o} = 1 - \frac{0.55}{1.3} = 0.58 \; ; \quad \frac{L_o.5}{L_o} = 1 - \frac{0.20}{1.30} = 0.84.$$

Further investigation shows that the predicted values of these ratios are independent of the values of $C_2.v.1/2$ or 2B. The predicted temperature profile is plotted on the same graph as the experimental one (Fig. 3.13). It is of the same general form as the experimental one but somewhat displaced from it. Theory predicts that a single curve should represent temperature profiles for all circumstances and this was confirmed experimentally.

Temperature variations in the bulk of the liquid can be predicted from Equation 5.4 (but not from Fig. 5.1 which applies only to surface temperatures). The result of an experimental determination of the variation of temperature with depth is shown in Fig. 4.1. A theoretical

profile, which was calculated for the circumstances of the determination, is also shown.

These profiles are of similar shape but the agreement between them is not particularly good. They both confirm that the bulk of the heat transferred into the liquid is concentrated near the surface as was suggested in Chapter 3.

5.2.3. The significance of the constants C_1 and C_2

In 5.2.1 values of C_1 and C_2 were obtained from rate of spread/initial temperature curves, while in 5.2.2 values of $\frac{C_1}{C_2}$ were obtained from temperature measurements. These two sets of values do not agree. For instance, from 5.2.1. values of C_1 and C_2 for butanol are $C_1 = 0.020$ and $C_2 = 2.2$, giving a value of $\frac{C_1}{C_2} = 0.009$, whereas from 5.2.2, $\frac{C_1}{C_2} = 0.161$. A possible explanation of this difference lies in the fact that in 5.2.1 values of C_1 and C_2 were derived from measurements on quantities which were controlled by the flow of heat downwards through the liquid, while in 5.2.2, $\frac{C_1}{C_2}$ was derived from measurements based on the flow of heat parallel to the surface. It would therefore appear that the liquid is behaving not as an isotropic solid as assumed but as an anisotropic solid with an 'effective thermal conductivity' which is greater in the horizontal direction than in the vertical direction. This is reasonable since the bulk of the heat transferred to the liquid is concentrated near the surface and the convection currents will therefore be concentrated there as well. The convection currents along the surface will be far more effective in transferring heat than eddies in the bulk of the liquid.

The derivation of Equation 5.4 was therefore repeated for an anisotropic solid with conductivities K_1, K_2, K_3 in the x, y and z directions respectively and its principal axes of conductivity parallel to the geometric axes. This change does not alter the form of the equation at all, it merely alters the significance of the constants which become:-

$$C_1 = \frac{\pi\rho c}{2Q}\left(\frac{K_3}{K_1}\right)^{\frac{1}{2}}; \qquad C_2 = \frac{\rho c}{2K_1} \quad \text{when multiplied by}$$

quantities measured in the x direction = C_{2x}; $C_2 = \frac{\rho c}{2(K_1 K_3)^{\frac{1}{2}}}$ when multiplied by quantities measured in the z direction = C_{2z}.

In 5.2.1, $C_2 = C_{2z}$; In 5.2.2, $C_2 = C_{2x}$.

In Table 5.1 all the values of C_1 and C_2 are summarized together with the values of Q, K_1, K_3, calculated from them. For each liquid pc = 0.5 c.g.s. units.

TABLE 5.1

Quantity	Channel width (inches)	Butanol	Amyl alcohol	Hexanol	Amyl alcohol (revised)
C_1	1.3	0.020	0.040	0.045	0.040
$\frac{C_1}{C_{2x}}$	1.3	0.161	0.085	0.123	0.108
C_{2z}	1.3	2.2	2.6	4.3	2.6
K_1	1.3	2.0	0.53	0.68	0.68
K_3	1.3	0.0064	0.020	0.0048	0.013
Q	1.3	2.2	3.7	1.4	2.7
C_1	0.9		0.067		0.067
Q	0.9		2.2		1.6
C_1	2.5		0.031		0.031
Q	2.5		4.8		3.5
Fx		5000	1300	1700	1700
Fz		16	50	12	34
T'		42	53	62	48

In this table all quantities are expressed in c.g.s. units. Published values for the thermal conductivity of butanol, amyl alcohol, and hexanol show a variation of only 1% for the different liquids. The average thermal conductivity of these three liquids is

$$k = 0.00039 \text{ cal./cm}^2\text{.sec. } (^\circ\text{C/cm.})$$

In Table 5.1 the factor $Fx = \frac{K_1}{k}$ and $Fz = \frac{K_3}{k}$.

The first set of values given for amyl alcohol in Table 5.1 is based on the correlation $L_o = 0.11\ (52.6 - T_L)$. Statistically, this is the most significant correlation between the experimentally determined values of L_o and T_L. However it has been shown above that the temperature, 52.6°C, should correspond with the value of T' determined from the rate of spread/initial temperature data. For amyl alcohol T' = 48°C. An agreement between these two temperatures exists in the data for butanol and hexanol. To be consistent therefore the correlation between L_o and T_L should, for amyl alcohol, be of the form $L_o = m\ (48 - T_L)$. Determining m from the data of Table 3.20 by the method of least squares gives

$$L_o = 0.14\ (48 - T_L)$$

The set of results in Table 5.1 headed - amyl alcohol (revised) - is therefore based on the value m = 0.14 instead of m = 0.11. While this is not the most significant value, it is the one based on the most consistent argument.

The significance of the numerical values of K_1, K_3 and Q will be considered in section 5.4.

5.2.4 A single curve for all rate of spread measurements

An examination of Figs. 5.6, 5.7, 5.8 and 5.10 suggests that all rate of spread measurements can be expressed in terms of a single curve. Accordingly the best smooth curve through each set of data was replotted on a single graph; the four curves lay close together and an average curve was estimated from them. This curve is plotted as Fig.5.12 in the form $\frac{C_1}{C_{2z}} \cdot \frac{(T' - T_L)}{(1/2)}$ against $C_1 V\ (T' - T_L)$. With the aid of this curve the rate of spread of flame across a liquid surface at a particular temperature and liquid depth can be estimated for circumstances for which T', C_1, C_{2z} are known. C_{2z} and T' are properties of the liquid which so far are known only for butanol, amyl alcohol, and hexanol. C_1 depends on properties of the liquid and on the heat flux, which is affected by the width of the channel.

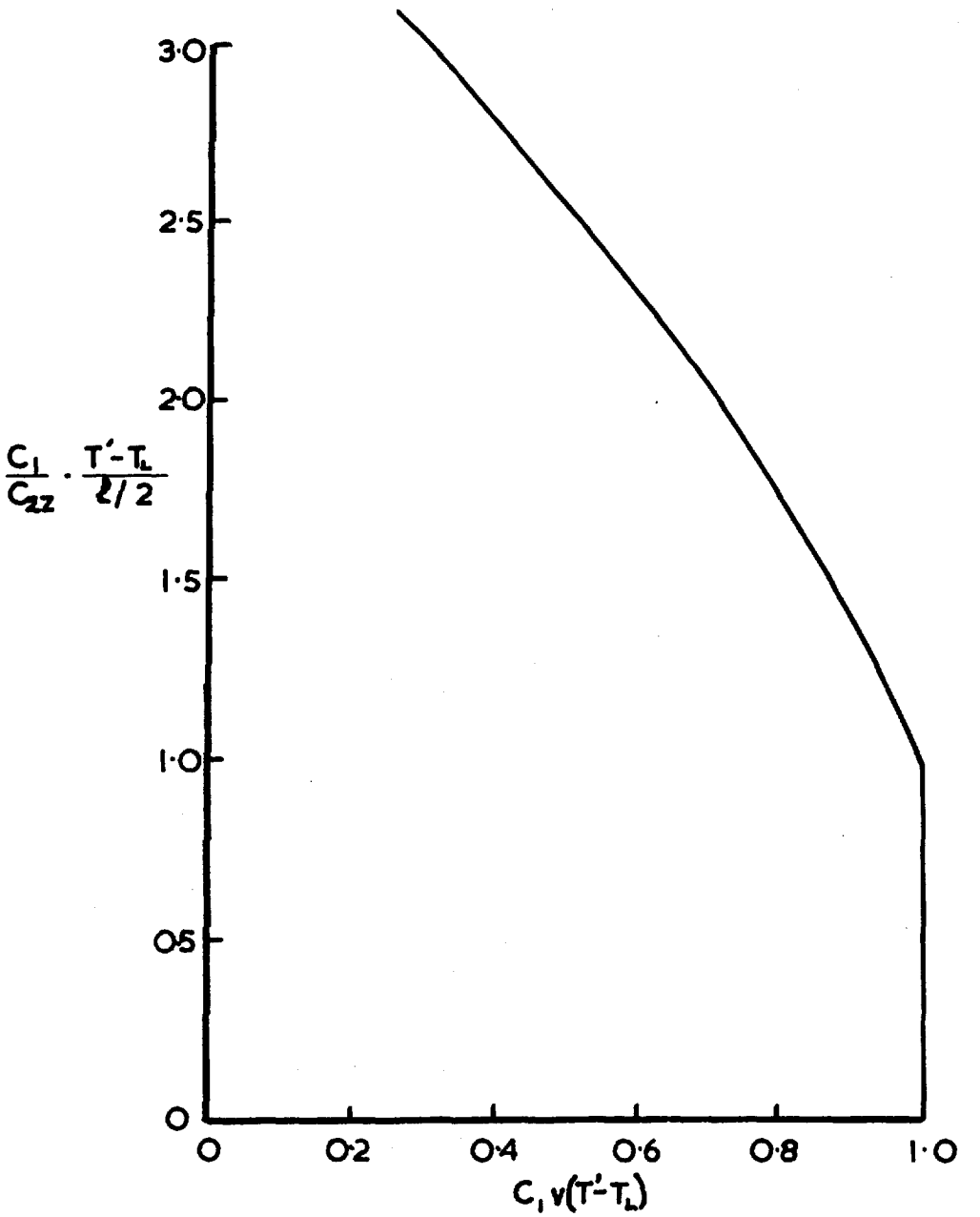


FIG. 5.12 THE CURVE GIVING THE BEST REPRESENTATION OF THE DATA ON THE RATE OF SPREAD OF FLAME

C_1, C_{22}, T' = Properties of the liquid and the experimental conditions.

$\ell/2$ = Liquid depth (ALL IN C.G.S. UNITS)

T_L = Liquid initial temperature

v = Flame's rate of spread

In order to estimate a rate of spread in a particular set of conditions the following procedure is adopted T', C_1 and C_{2z} are found by reference to Table 5.1. For a particular value of T_L, the liquid initial temperature, and 1/2, the liquid depth, the value of $\frac{C_1}{C_{2z}} \frac{(T' - T_L)}{(1/2)}$ is found and, by reference to Fig. 5.12, the corresponding value of $C_1 V (T' - T_L)$. From this value, v is easily calculated.

This procedure was adopted for the conditions of a 1 in 4 sample of all the experimental rate of spread measurements of Chapters 3 and 4 (neglecting those which were vapour phase controlled) and the values predicted by Fig. 5.12 were compared with the experimental ones. Expressing them in terms of the ratio $\frac{V \text{ (predicted)}}{V \text{ (experimental)}}$ gave the following distribution of values.

$\frac{V \text{ (predicted)}}{V \text{ (experimental)}}$	0.5 - 0.7 1.5 - 1.7	0.7 - 0.9	0.9 - 1.1	1.1 - 1.3	1.3 - 1.5
Percentage in range	2 2	7	63	24	2

Fig. 5.12 therefore gives a reasonably good idea of the value of v under certain circumstances, without being highly accurate. The variation between predicted and experimental values is roughly comparable with the variation in the measurement repeated under the same conditions. Since the experimental results were determined for thirteen different combinations of liquid, liquid depth, and channel width and over a temperature range of 40°C this agreement is promising.

5.3 The induction period

The 'effective thermal conductivity' approach can be applied to the induction period but the result is not so satisfactory as in the case of steady state propagation, partly because of the shortage of experimental data and partly because the situation is more complicated. A description has already been given of how, during the induction period, a region of intense recirculation becomes established in the liquid next to the wick. This would have the effect of obliterating any temperature gradients in the vertical direction in that region. It was found experi-

mentally that doubling the liquid depth doubled the induction time, which is consistent with this view.

Induction times therefore are controlled by a mechanism which it is not possible to analyse by the 'effective thermal conductivity' approach. The variations in temperature outside this zone of recirculation can however be analysed in this way. The temperature rise at the surface of a semi-infinite solid which is heated by a stationary strip source of heat is given by Equation 5.6 of the Appendix.

$$\theta = \frac{q}{\pi}\sqrt{\frac{t}{K}}\int_{\bar{x}-\bar{b}}^{\bar{x}+\bar{b}}\left[\int_{z^2}^{\infty} e^{-u}\,\frac{du}{u}\right].dz \qquad - \quad (5.6)$$

where $\bar{x} = \frac{x\sqrt{pc}}{2\sqrt{Kt}}$ $\qquad \bar{b} = \frac{b}{2}\sqrt{\frac{pc}{Kt}}$

If this equation is written

$$\frac{\theta}{q}\pi\sqrt{\frac{K}{t}} = [I]_{\bar{x}-\bar{b}}^{\bar{x}+\bar{b}}$$

then Fig. 5.13 represents $[I]_{a}^{\infty}$

From equation (5.6) it is apparent that the position of the first temperature rise corresponds to some critical value of $(\bar{x} - \bar{b})$, while from Fig. 5.13 it can be seen that this critical value is $(\bar{x} - \bar{b}) = 1.6$. Since $(x - b)$ represents the distance between the heat source and the position of the first temperature rise (= a say) it follows that the movement of this position should be given by the expression $\frac{a}{\sqrt{t}}.\sqrt{\frac{pc}{4K}} = 1.6$.

Fig. 4.10 shows an experimentally determined relationship between (a) and (t). In order to provide a comparison with the above form a curve of the form $\frac{a}{\sqrt{t}}$ = constant is plotted to give the best approximation to the experimental curve for 50 ml. butanol. From t = o to t = 15 seconds there is no noticeable difference between the predicted and experimental forms of this curve. From the experimental curve $\frac{a}{\sqrt{t}} = 1.75$ giving a value of $\sqrt{\frac{pc}{4K}} = \frac{1.6}{1.75}$. This corresponds to a value of K = 0.45 cal./cm^2. sec. (°C/cm) (F = 370).

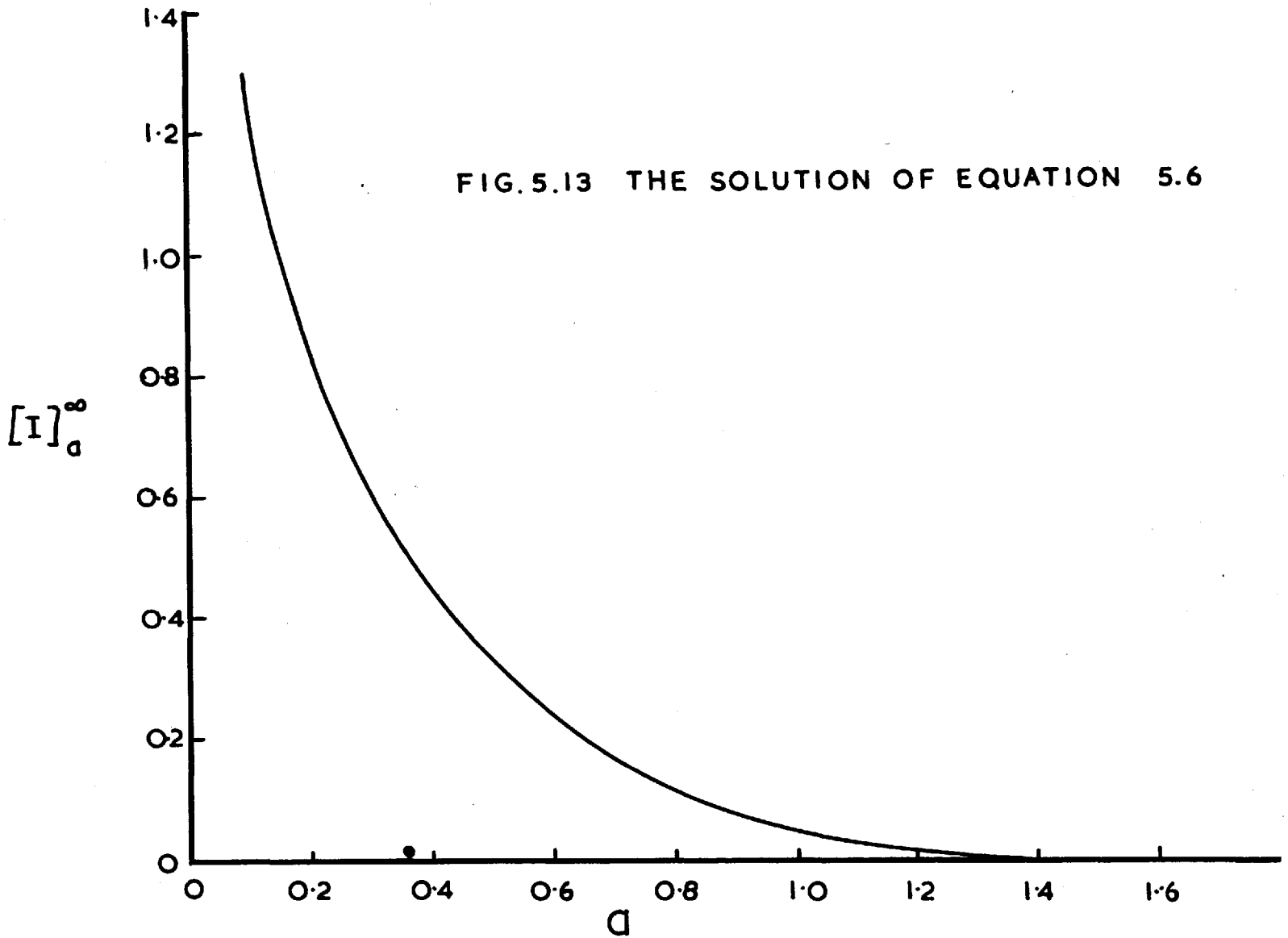


FIG. 5.13 THE SOLUTION OF EQUATION 5.6

Equation (5.6) can also be used to predict the variation with time of the temperature rise at a point. This variation when plotted in the form $\frac{\theta}{\sqrt{t}}$ against $\frac{x}{\sqrt{t}}$ should give a curve of the same form as Fig. 5.13. If the temperature variations of Figs. 4.6 - 4.9 are plotted in this way then points of similarity and dissimilarity emerge. The results for butanol, amyl alcohol, and hexanol (for the first 25 seconds) are similar in form to the curve of Fig. 5.12 but no exact comparison can be made. They have in common the general description that the temperature increases at an increasing rate. However even this point of similarity is lost for hexanol after 25 seconds, when the temperature starts to increase at a decreasing rate (i.e. there is a point of inflexion in the temperature/time curve). Points of dissimilarity between the predicted and experimental forms lie in the fact that results for different values of x do not lie on a single curve when plotted in this way, and in the detailed shape of the curves.

It was therefore concluded that while Equation 5.6 correctly predicted the relationship $\frac{a}{\sqrt{t}}$ = constant for the position of the first temperature rise it stood in need of modification for predicting other aspects of the changes occurring during the induction period. It was decided that such modifications could more usefully be made when further experimental investigation of the induction period had led to a clearer understanding of the controlling mechanism.

5.4 Discussion

The 'effective thermal conductivity' approach correctly predicts several qualitative relationships between experimentally determined quantities relevant to the rate of spread of flame across a liquid surface. Extensions of this approach to the induction period have been made but with less satisfactory results.

The following relationships have been predicted by the 'effective thermal conductivity' approach and verified by experiment for steady state propagation:-

i) When the rate of propagation, v, and the liquid initial temperature, T_L, are plotted together in the form $v\ (T' - T_L)$ against v the value

of $v\ (T'-T_L)$ increases as v increases until it attains a constant value.

ii) When the results for different liquid depths ($l/2$) are plotted in the form $v\ (T' - T_L)$ against $v.l/2$ they lie on a single curve.

iii) When allowance is made for the different net heat flux to the surface at different channel widths, the results for different channel widths lie on a single curve.

iv) A linear relationship exists between the distance ahead of the flame at which the first temperature rise occurs (L_o) and the liquid initial temperature, of the form

$$L_o = m\ (T' - T_L)$$

v) The value of L_o is independent of the liquid depth at a particular initial temperature.

vi) The values of T' obtained by extrapolating the rate of spread/initial temperature data when plotted in the form $1/v$ against T_L, and the value of T' obtained by extrapolating the position of first temperature rise/initial temperature data are the same for a particular liquid. (This did not apply to the data for amyl alcohol).

vii) The temperature profile ahead of the flame when plotted in the form $\frac{T - T_L}{T' - T_L}$ against $\frac{L}{L_o}$ is the same for each liquid and for each liquid depth.

The actual shapes of the predicted and experimental curves for (i) and (vii) differed to some extent, but, as stated, the overall trends were identical.

In addition to this qualitative agreement quantitatively consistent solutions were obtained for all the above seven relationships if it was assumed that the liquid was behaving as an anisotropic solid with a thermal conductivity K_1 in the horizontal direction and K_3 in the vertical direction. Since the rate of spread of flame is controlled by the flow of heat downwards through the liquid, as is shown by the effect of liquid depth, the constants relevant to K_3 are found from the effect of liquid depth on the rate of spread. On the other hand, the position of the first temperature rise is controlled by the flow of heat parallel to the surface and information is thereby obtained on K_1.

Values of K_1 and K_3 are given in Table 5.1 for each liquid, together with F_x and F_z, the factors by which k, the experimental thermal conductivity, must be multiplied to give K_1 and K_3. (This discussion will be confined to the revised results for amyl alcohol as these are based on a more consistent argument and are numerically more consistent than the original results).

The values of F_x and F_z may be regarded as a measure of the relative importance of convection and conduction as heat transfer mechanisms in the circumstances of the experiments. The pattern of heat transfer in a liquid across the surface of which a flame is spreading is one of high temperature rises near the surface and slow convection currents along the surface away from the flame. This is consistent with the high values obtained for F_x, which show that from 2000-5000 times more heat is being transferred ahead of the flame by these surface currents than would be transferred by conduction alone.

A factor of some thousands is not surprising when rates of heat transfer by conduction and convection are compared directly. The rate of heat transfer per unit area due to conduction is equal to k x (temperature gradient) while the rate due to convection is equal to vpc.T, where v is the velocity of the convection current. The ratio of heat transfer by convection to heat transfer by conduction is therefore $F = \frac{vpcT}{k\frac{dT}{dx}}$

Typical values (from the literature or as measured) for the quantities in this expression could be T = 20°C; $\frac{dT}{dx}$ = 10°C/cm.; pc = 0.5 c.g.s. units; k = 0.0004 c.g.s. units. These give $F = \frac{V.0.5.20}{0.004}$ = 2500 v. Thus a convection current of only 0.8 cm/sec. is required to give a value of F = 2000 in these circumstances.

The heat transfer into the bulk of the liquid is only 16-34 times greater than that which would result from conduction alone. This suggests that the bulk of the liquid is disturbed by the effects of convection, giving rise to some heat transfer by the movement of hot liquid, but that this disturbance is gentle compared with that which takes place at the surface.

The highly directional effect of convective heat transfer in the liquid which is suggested by the large differences between K_1 and K_3 is therefore consistent with the observed effects of the flame on the liquid and with a priori reasoning.

In Table 5.1 values are given for Q, the heat flux from the flame to the liquid, expressed in cal./sq. cm. sec. Since no values for 2b, the width of the strip heat source, have been specified during the analysis of the experimental data there is no means of cross checking to find whether these values are reasonable in terms of the total heat release per unit width of flame front.

If it is assumed that the flame is 1 cm. high and is spreading through a weak limit mixture of alcohol vapour with air (which is an approximate representation of the actual situation) then the rate of heat release per unit width of flame front = c.v.1 cal/cm.sec. where c = calorific value per unit volume of mixture, cal./c.c. For a 1.5% mixture of amyl alcohol (calorific value 790 kg./mole) with air, $c = \frac{1.5}{100}\cdot\frac{790000}{22400}$ = 0.52 cal/c.c. $\therefore$ rate of heat release from flame front = 0.5 v. cal./cm. sec.

This rate of heat release compared with the values of Q in Table 5.1 suggests that either the heat transfer to the liquid which controls the rate of spread is concentrated near the flame front, or the heat released in the flame front only represents a fraction of the heat transferred from the flame to the liquid in the controlling region, or the values of Q in Table 5.1 are too high.

A consideration of the way in which a flame spreads across a liquid surface shows that all the hot products of combustion formed in the flame front are retained, at any rate temporarily, between the flame front and the liquid surface. It is therefore likely that the chief mechanism by which heat is transferred to the liquid surface is through the proximity of products of combustion at 1200°C to the liquid surface. This is consistent with the view expressed above that at the effective edge of the heat source the liquid temperature is slightly above the

liquid closed flash point, i.e. that this edge is behind the flame front. With alcohol flames, where radiation from the flame is not important, all the evidence is consistent with the view that the heat from the flame enters the liquid at or behind the flame front and any preheating of the liquid is caused by the transmission of heat through the liquid. With highly luminous flames it is possible that heat from the flame will be transferred to the liquid surface ahead of the flame as well. This might give rise to the position where T' was less than the closed flash point because the leading edge of the heat source was ahead of the flame. Since however the flame front is not very high (about 1 cm.) the geometric factor for radiation between the flame and the liquid surface will be low. The behaviour of liquids giving non luminous flames may differ in points of detail from that of those giving luminous flames, but in general they are likely to behave in a similar way.

From the preceding discussion it is apparent that the 'effective thermal conductivity' approach is a useful and versatile means of interpreting the data obtained from a study of the factors affecting the rate of spread of flame across a liquid surface. It enables the effects of changes in conditions to be predicted and provides a means of assessing the relative importance of various factors. Mechanisms of heat transfer from the flame to the liquid and in the bulk of the liquid which are suggested by this approach are consistent with those which are suggested by other reasoning. A method of plotting the data, based on the prediction of the 'effective thermal conductivity' approach, enables the experimental measurements of rates of spread of thirteen different sets of circumstances to be represented by a single curve.

In view of the wide measure of agreement between the predictions based on the 'effective thermal conductivity' approach and the experimental results, it is concluded that the processes of convective heat transfer in a liquid, across the surface of which a flame is spreading, can be satisfactorily represented in terms of theequation for heat conduction and an effective thermal conductivity which has different values in the horizontal and vertical directions.

APPENDIX TO CHAPTER FIVE

The temperature variations in a solid associated with a moving heat source.

Part I Steady state conditions

Part II Conditions varying with time

PART I

Steady State Conditions

The differential equation for the unsteady state conduction of heat.

$$\frac{\partial^2\theta}{\partial x^2} + \frac{\partial^2\theta}{\partial y^2} + \frac{\partial^2\theta}{\partial z^2} = \frac{pc}{K} \cdot \frac{\partial\theta}{\partial t} \qquad -(5.1)$$

is satisfied by

$$\theta = \frac{Q}{8\left(\frac{\pi Kt}{pc}\right)^{3/2}} \exp\left[-\frac{(x-x')^2 + (y-y')^2 + (z-z')^2}{4 \cdot \frac{Kt}{pc}}\right] \qquad -(5.2)$$

This form of equation (5.2) gives the temperature at a point (x,y,z) in an infinite solid t seconds after the instantaneous generation of a quantity of heat Qpc at a point (x', y', z'). Thus equation 5.2 gives the temperature distribution due to an instantaneous point source of heat of strength Q at (x',y',z') at t=0.

It is required to know the temperature distribution in a solid when:-

i) The solid is bounded by two infinite parallel planes.

ii) The solid is heated by an infinite strip source of heat moving across one of its surfaces.

iii) The strip source of heat is moving in the direction perpendicular to itself across the surface of the solid.

iv) The other surface of the solid is maintained at its initial temperature.

v) Steady state conditions have been achieved.

The temperature distribution in a semi-infinite solid heated by a moving infinite strip source of heat has been given by Carslaw and Jaeger (37). It is:-

$$\theta = \frac{2Q}{\pi pcv} \int_{X-B}^{X+B} e^{u} \; K_0\left[Z^2 + u^2\right]^{\frac{1}{2}} du \qquad -(5.3)$$

where Q = heat flux

v = velocity of heat source

$X = \frac{vxpc}{2K}$; $Z = \frac{vzpc}{2K}$; $B = \frac{vbpc}{2K}$

2b = width of heat source

$K_o(u)$ = modified Bessel function of the second kind of order zero.

The direction of motion of the heat source is taken as the x negative direction.

Since this derivation has been given in full in reference (37) it will not be repeated here. The solution for a bounded solid (conditions (i) and (iv) above) is obtained by the Method of Images or by the use of Green's functions. Either of these methods gives the following extension of Equation 5.3 when conditions (i) and (iv) are incorporated.

$$\theta = \frac{2Q}{\pi pcv} \int_{X-B}^{X+B} \sum_{n=-\infty}^{\infty} e^{u} \; Ko\left[\left(u^2 + (Z\bar{n})^2\right)^{\frac{1}{2}}\right] - \sum_{n=-\infty}^{\infty} e^{u} \; Ko\left[\left(u^2 + (Z\bar{n})^2\right)^{\frac{1}{2}}\right] du \qquad - (5.4)$$

where

$$Z\overset{+}{n} = \frac{pcv}{2K}\left[(z - 1/_2)^2 + (2nl + 1/_2 - z)^2\right]^{\frac{1}{2}}$$

$$Z\bar{n} = \frac{pcv}{2K}\left[(z - 1/_2)^2 + (2nl - 1/_2 - z)^2\right]^{\frac{1}{2}}$$

$1/_2$ = distance between bounding planes.

The heat source is in the plane $z = 1/_2$

The other bounding plane is at z = o

Equation (5.4) is apparently original to the present work.

The solution for an anisotropic substance

Equations (5.3) and (5.4) were derived for an isotropic substance. If a substance is anisotropic with conductivities K_1, K_2, K_3 and its principal axes of conductivity parallel to the x,y, and z axes

the Equation (5.1) becomes

$$K_1 \frac{\partial^2\theta}{\partial x^2} + K_2 \frac{\partial^2\theta}{\partial y^2} + K_3 \frac{\partial^2\theta}{\partial z^2} = pc \frac{\partial\theta}{\partial t} \qquad -(5.5)$$

If the solutions analagous to equations (5.3) and (5.4) are derived for an anisotropic solid there is no change in the form of the equations. The only changes are in the values of the constants which become:-

$$X = \frac{vxpc}{2K_1} \quad ; \quad B = \frac{vbpc}{2K_1} \quad ; \quad Z = \frac{vzpc}{2(K_1K_3)^{\frac{1}{2}}} ; \quad \frac{2Q}{\pi pcv} = \frac{2Q}{\pi pcv} \left(\frac{K_1}{K_3}\right)^{\frac{1}{2}}$$

Similarly in the expressions for $Z\dot{n}$ and $Z\bar{n}$, K becomes $(K_1K_3)^{\frac{1}{2}}$.

Thus the solutions for an isotropic substance and for an anisotropic substance may both be written in the form $C_1V\theta = F[X,B,Z]$ but the significance of the constants is different in the different circumstances.

The numerical solution of Equation (5.4)

In reference (45) values of Ko(x) - p.737 - and e^x Ko(x) - p. 698 - are tabulated. Since only the solution for x negative was required (i.e. ahead of the flame front) values of e^{-x} Ko(x) were calculated. Values of e^u Ko$\left|(u^2+z^2)^{\frac{1}{2}}\right|$ were then calculated for values of u ranging from zero to minus two and of z ranging from zero to three. These ranges adequately covered the possible range of values of the above function for u negative. The values were then plotted and by graphical integration values of $\int_0^a e^u K_0\left|(u+Z)^{\frac{1}{2}}\right| du$ were found for values of a from zero to infinity and of z as before. This integral was plotted as a function of (a) and (z). From this graph solutions of Equation (5.4) may be obtained by substitution. In order to facilitate the use of Equation (5.4) further calculations were made for the special case where $z = 1/2$ i.e. at the liquid surface. The results of these calculations are shown in Fig. 5.1 for values of $1/2$ from zero to infinity. Values of

$\int_0^a e^u \, K_0/(u^2 + z^2)^{\frac{1}{2}}/ \, du$ are given in Table 5.2. These values may be used for the calculation of temperatures other than at the surface.

TABLE 5.2

z \ a	0.1	0.2	0.4	0.8	1.6	∞
0	0.33	0.50	0.71	0.89	0.98	1
0.1	0.215	0.376	0.575	0.753	0.844	0.856
0.3	0.130	0.245	0.409	0.571	0.656	0.668
0.5	0.086	0.159	0.273	0.405	0.480	0.493
0.9	0.046	0.085	0.151	0.233	0.293	0.305
1.5	0.020	0.038	0.067	0.105	0.135	0.140
2.0	0.011	0.020	0.036	0.058	0.080	0.084
3.0	0.003	0.006	0.011	0.018	0.027	0.029

PART II

Conditions varying with time

In reference (37) an equation is given for the temperature distribution in an infinite solid due to a stationary line source, before the attainment of steady state conditions. An extension to this equation gives the temperature distribution in a semi-infinite solid due to a strip source of heat. This is:-

$$\theta = \frac{q}{\pi}\sqrt{\frac{t}{k}} \int_{\bar{r}-\bar{b}}^{\bar{r}+\bar{b}} \left[\int_{z^2}^{\infty} \frac{e^u}{u} \, . \, du \right] dz \qquad - (5.6)$$

where $r^2 = x^2 + y^2$

$$\bar{r} = \frac{r}{2}\sqrt{\frac{pc}{Kt}} \qquad \bar{b} = \frac{b}{2}\sqrt{\frac{pc}{Kt}}$$

2 b = width of heat source

The exponential integral is defined by:-

$$-Ei\ (-x) = \int_{x}^{\infty} \frac{e^{u}}{u} \cdot du$$

This integral is tabulated in reference (46).

A numerical solution to Equation (5.6) is therefore obtained by solving $\int_{a}^{\infty} - Ei\ (-Z^2).dz$. Values of this integral are plotted against (a) in Fig. 5.13

CHAPTER 6

CONCLUSIONS

Before starting experimental work a review of the properties of inflammable liquids was made (Chapter 2) in order to decide which properties were likely to be of importance with respect to the spread of flame across a liquid surface. This review suggested that the closed flash point was the temperature of greatest significance since, in principle, at this temperature the composition of the vapour/air mixture at the liquid surface becomes equal to that of the lower limit mixture. Published values of open and closed flash points were shown to be consistent with the view that the open flash point is linked to the closed flash point in an arbitrary manner which depends on the way in which vapour diffuses from a liquid surface.

It follows that, the vapour above a point on a liquid surface can not be ignited unless the temperature at that point exceeds the closed flash point of the liquid. A distinction must therefore be made between two different situations. If the initial temperature of a liquid is less than the closed flash point, then before the flame can spread into a particular region the temperature of the surface in that region must have been raised to the closed flash point. The rate of spread of flame is therefore affected by the difference between the initial temperature and the closed flash point and by the presence of any heat sinks which affect the rate of temperature rise of the surface. If however the initial temperature of the liquid is greater than the closed flash point then an inflammable concentration of vapour is always present above the liquid surface and the rate of spread of flame becomes independent of heat transfer processes in the liquid. The effect of increasing the liquid temperature is to increase the concentration of vapour at the surface, which in turn, through the relationship between mixture strength and laminar burning velocity, increases the rate of spread of flame.

The existence of these two types of behaviour was confirmed experimentally. Measurements on butanol, amyl alcohol and hexanol at initial temperatures below their closed flash points showed that the rate of spread of flame was affected by the depth of the liquid and by the channel width. Temperature variations in the liquids were measured while flame was spreading across their surfaces. These measurements confirmed that a flame reaches a particular point on a liquid surface when the temperature there has been raised to the closed flash point of the liquid. In contrast to this, measurements showed that when the liquid temperature was greater than the closed flash point the effect of liquid depth and channel width disappeared.

In view of the importance of heat transfer processes in the liquid a theory was developed which related the rate of spread of flame to the initial temperature of the liquid, the liquid depth and the net heat flux from the flame to the surface. This theory was based on the expression of the effects of convective heat transfer in terms of an effective thermal conductivity. This approach predicted seven qualitative relationships between quantities which could be measured experimentally and these seven relationships were confirmed by the experimental work. A quantitative interpretation of the experimental data showed that in the circumstances of the experiments the effective thermal conductivity of the liquid is very much larger in the horizontal than in the vertical direction. This is consistent with the observation of slow surface currents established by the flame, which was made. The effect of these currents is to transfer heat along the surface of the liquid while heat is transferred downwards only by minor recirculation in the bulk of the liquid.

A method of correlating the data, which was suggested by this theory, enabled the experimental results for thirteen different sets of conditions to be represented in terms of a single curve.

Interpretation of the data suggested that while a spreading flame first enters a region when the temperature there has been raised to the closed flash point the progress of the flame is stabilised at a

point where the temperature is 4-7 °C higher than the closed flash point. Although over a period the flame advances at a constant average rate, under certain circumstances the flame advances with small scale fluctuations. This suggests that when a flame enters a region it is not necessarily stabilised there because the rate of consumption of vapour may exceed the rate of supply. Two sets of data give rise to the same critical temperature for flame propagation independently. For each liquid this temperature is 4-7° higher than the closed flash point and this difference of critical temperatures may be related to the fluctuating mechanism described above.

The products of combustion from the flame front are released near the liquid surface and it is concluded that, for the alcohols, the main mechanism by which heat is transferred from the flame to the liquid is through conduction and convection from these hot products. The possible effects of radiation from the flame are discussed.

When the liquid temperature is greater than the closed flash point the rate of spread of flame increases with liquid temperature at an increasing rate. When a temperature is reached which gives a stoichiometric vapour/air mixture at the surface a maximum rate of spread is attained. When this temperature was exceeded no appreciable decrease in the rate of spread was observed, in contrast to the findings of an earlier worker (25) whose results show a pronounced maximum.

The problem of the spread of flame through a homogeneous mixture of vapour and air enclosed in a tube has been studied extensively. If the flame were to spread through such a mixture as a plane flame front its rate of spread would be equal to the laminar burning velocity of the mixture. However in practice the flame front takes up a parabolic shape, not only because a plane flame front is an aerodynamically unstable phenomenon but also because viscous drag on the products of combustion at the walls of the tube causes an acceleration of the products at the axis of the tube; the resulting concentration of the streamlines near the axis of the tube also tends to displace the flame front from a plane. A flame spreading in a tube therefore moves at a rate greater than the burning velocity of the mixture; the definition of burning velocity then only applies to an element of flame front. Since at the axis of the

tube the flame front is normal to the direction of motion there must be a flow of unburned gases away from the flame front. At increasing distances from the axis the velocity of this flow decreases and then changes direction. The unburned gas ahead of the flame is therefore mixed.

The complications of the spread of flame in these circumstances make it impossible to predict the rate of spread of flame through a homogenous mixture of known burning velocity in a tube of known size. The spread of flame through an inflammable vapour/air mixture above a liquid surface is further complicated by the concentration gradient in the inflammable mixture and the absence of any solid boundary between the region where the mixture is inflammable and the region where it is not.

Certain aspects of the propagation of flame through a non homogeneous vapour/air mixture have been discussed elsewhere (43) but no detailed analysis of the situation appears possible at this stage.

Laminar burning velocities of propanol, butanol, and amyl alcohol have been measured (44) and each substance has a maximum burning velocity of about 45 cm/sec. which is close to that of the corresponding paraffin. To relate this value to the maximum observed rate of spread across an alcohol surface (200 cm/sec.) would require further detailed investigation. For a particular run it would be necessary to know the shape of the flame front, the concentration distribution of the mixture as burned (which because of the mixing effect described above would not be the same as the initial distribution), the local velocity of the unburned gas, and the burning velocity/composition relationship over the whole inflammable range. Only when such information has been obtained will it be possible to relate the rate of spread of flame across a liquid surface, for liquid temperatures greater than the closed flash point, to other properties of the substance concerned.

In addition to the study of steady state propagation the induction period, between the ignition of a liquid at a wick and the first spread of flame from the wick, was briefly studied. Sufficient experimental work was carried out to show that matters relating to the induction period were experimentally reproducible and measurements of temperature variations and induction times were made under different

conditions. No satisfactory criterion for the condition of first spread of flame from the wick was found however and this matter also would benefit from further investigation.

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