

UNIVERSITY OF THE WITWATERSRAND
DEPARTMENT OF MECHANICAL ENGINEERING

A CRITICAL EVALUATION
OF THE
SPHERICAL CONSTANT VOLUME VESSEL METHOD
FOR DETERMINING
LAMINAR BURNING VELOCITY

by

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A Thesis Presented in Fulfilment of the Requirements for the Degree of
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G25909

DECLARATION BY CANDIDATE

I, Costa John Rallis, hereby declare that this Thesis is my own work, and that the material forming the basis of this work has not been incorporated in any thesis submitted by me for any other degree.

C. J. Rallis

ABSTRACT

The objectives of combustion research are considered and attention directed to laminar flames, the burning velocity of which is recognised as a basic parameter in all combustion problems. Various methods of determining this property are critically reviewed and, as a result, it is concluded that the spherical constant volume vessel technique is potentially one of the most versatile and accurate. However this method does not appear to have been extensively used, probably because the available equations virtually relegate it to the status of a constant pressure technique.

The theory of the method is then examined and extended, particular attention being paid to the self-corroborative properties inherent in this technique. Two general forms of burning velocity equation are derived, which unlike previous burning velocity equations, are applicable throughout the entire combustion process. Combination of these two leads to a new form which is shown to yield more reliable results than either of the others. 'Exact' equations for the mass fraction burnt are presented, as is a treatment of the pressure distribution throughout the system at any instant. As a result of this theoretical study a method of directly determining both gas properties and burning velocities is proposed.

The results of a series of tests on a range of acetylene/air mixtures are used to compare the various equations proposed, both in the literature and in this thesis. This analysis leads to suggestions for improvements in the observations.

Both the apparatus and the experimental procedure used are described. The indications are that these lead to reproducible and hence accurate results.

Observations on two groups of tests on acetylene/air mixtures are presented: the first at ambient initial conditions but variable mixture strength, and the second on stoichiometric mixtures with different initial pressures.

The results of these experiments are used to illustrate the versatility of the method in providing extensive information from a limited number of tests. Incidentally the burning velocity versus pressure curves obtained show that the former passes through a minimum, the value of which is a function of temperature. The position of these minima moves to higher values of burning velocity and pressure as the temperature is increased. For the range of the results obtained burning velocity evidently varies linearly with temperature at any particular pressure.

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It is probably only when sitting down to write up a project of this nature that one becomes fully aware of the considerable contributions made by one's colleagues and friends. Inadequate though this may be, I would like to take this opportunity of expressing my appreciation to the following:

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LIST OF SYMBOLS

LATIN

A	Flame front area
E	Expansion ratio
M	Molecular weight
P	Absolute pressure
R	Radius of spherical vessel
$\mathcal{R}$	Specific gas constant
S	Velocity
T	Temperature
U	Gas velocity
c	Sonic velocity in unburnt mixture
k	γ_u / γ_b
m	Mass
n	Mass fraction burnt
r	Radius
t	Time

GREEK

α	Ratio of mean density of burnt gas to initial density of mixture ($\bar{\rho}_b / \rho_0$)
β	Ratio of density of unburnt gas at any instant to initial density of mixture (ρ_u / ρ_0)
γ	Ratio of specific heat capacities
ϵ	Pseudo Mach number
ρ	Density

Sub- and Superscripts

b and bg	Burnt gas
e	Final conditions
g	Gas
o	Initial conditions
s	Spatial
t	Transformation
u and ug	Unburnt gas

A bar over any symbol indicates a mean value.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND TO COMBUSTION PROGRAMME

The combustion programme of the Department of Mechanical Engineering at this University was conceived in 1948, following certain work on internal combustion engines by Dr E.A.Bunt and the author.

A study of the problem at that time indicated the desirability of obtaining reliable information of the ignition properties of combustible mixtures, as well as of the structure and burning velocities of the resultant flames.

In apportioning the work it was decided that Bunt would investigate the composition of flames using a mass spectroscopic technique, whilst the author would undertake studies on ignition and flame propagation.

To this end Bunt constructed a Nier-type mass spectrometer with which he did some preliminary studies of flames (Bu 59). However this instrument proved to be unsatisfactory and was subsequently dismantled. This aspect of the subject has in consequence not been followed up, although, as is indicated in Chapter 2, it is considered extremely important work which should, when possible, be continued.

The flame propagation and ignition studies were sub-divided into three stages:

- (1) Obtention of reliable data on laminar burning velocities.
- (2) Investigation of ignition temperatures and delay periods using an adiabatic compression machine.
- (3) Combination of knowledge gained from (1) and (2) above, together with the effects of turbulence and retained exhaust gas, to studies of comb-

ustion in engine cylinders, with particular reference to abnormal combustion, such as spark- and compression-ignition engine knock. To this end a special universal test engine, incorporating a glass cylinder head through which the flame could be observed, was designed and built, and a high speed Fastax camera purchased.

Due to a variety of difficulties and delays, only tests on item (1) have been carried out to date.

Various research students and members of staff have from time to time worked with the author on different aspects of this programme. Thus Mr T.O'D.Duggan was involved in the design of the single cylinder test engine mentioned above; K.H.O'Donovan worked on the early design of the spherical combustion vessel as well as on the optical calculations for the proposed schlieren system (O'D 59, OR 59); G.E.B.Tremeer joined the bomb programme in 1961 and helped to develop the apparatus and theory, as well as the initial data processing scheme (Tr 62, RP 62, RT 63); A.M.Garforth and J.A.Steinz are currently involved in extending the bomb instrumentation and other techniques in the light of suggestions made in this thesis. In particular Garforth has been responsible for the data processing scheme at present in use.

1.2 ORGANIZATION OF THIS THESIS

The main aim of the present study has been to critically review the constant volume method for the determination of laminar burning velocity, with particular reference to its application over a wider range of pressures and temperatures than it has hitherto been used for.

To this end, in Chapter 2, the objectives of combustion research are first considered and attention is directed to laminar flames, and in parti-

cular to the methods which have been used for determining laminar burning velocity.

Having concluded that the spherical vessel constant volume method is potentially one of the most reliable for burning velocity measurements, the previous work done in this field is reviewed in Chapter 3. The theory of the method is then examined and extended in Chapter 4, attention being paid to the self-corroborating properties inherent in this technique. Two basic forms of burning velocity equation are derived; it is shown that the majority of equations previously proposed are special cases of these two. Various new forms of 'exact' and 'approximate' equations are also presented, as is a treatment of the pressure distribution throughout the system at any instant. As a result of this theoretical study a method of directly determining both gas properties and burning velocities is proposed.

The results of a series of tests on a range of acetylene/air mixtures are then used to compare the various equations proposed both in the literature and in this thesis. This analysis leads to suggestions for improvements in the accuracy of the method.

The apparatus used is described in Chapter 6, and the experimental procedure and data processing in Chapter 7. Chapter 8 deals with all experimental results obtained to date. These are discussed in Chapter 9 and certain conclusions regarding both the theory and experiments are presented.

This thesis makes no pretence at being either comprehensive or definitive. Much developement work on the constant volume method still requires to be done if its rightfull status as the '... standard method against which the validity of other methods may be tested' (Le 54), is to be universally acknowledged.

References

Contrary to normal practice the list of cited references is given right at the end of the thesis rather than before the Appendices. This, it is felt, makes them easier to locate and in any event avoids the necessity of using footnote references in the Appendices.

The method used to designate references in the text is by two letters and two numerals. Where a paper or book has only one author, the first two letters of the surname are used, the second in lower case. This is followed by two numerals indicating the year of publication. Where there are two or more authors the initial letters of the surnames of the first two are used, both in higher case, followed by the year of publication.

CHAPTER 2

FORMULATION OF THE PROBLEM

2.1 INTRODUCTION

The primary aim of this chapter is the presentation of a brief review of the subject of combustion with particular reference to the formulation of one aspect of the research programme currently being pursued in the Department of Mechanical Engineering at this University.

To this end the objectives and methodology of combustion research are first considered and the conclusion arrived at that the most feasible approach, taking into account the facilities available in a mechanical engineering department, is via the physical rather than the chemical viewpoint.

Consideration is then given to the internal structure of pre-mixed laminar flames, and the methods used in studying this subject. Although flame front structure studies at present fall outside the scope of this work, a knowledge thereof is considered a pre-requisite to the correct understanding and interpretation of burning velocity measurements.

Various methods of determining laminar burning velocity are then critically reviewed. Of these the constant volume method, although little used previously, is acknowledged as one of the most accurate and versatile. Particularly is this the case in relation to the dependence of burning velocity on unburnt gas temperature, pressure and composition. However, it is concluded that before full advantage can be taken of the method the theory involved must be extended.

2.2 OBJECTIVES OF COMBUSTION RESEARCH

The ultimate objective of combustion research is the acquisition of a complete understanding of the mechanism of ignition, structure, and mode of propagation of flames. The practical results of such knowledge are evidently the control of the combustion process both from the point of view of safety and its utilization as a source of energy.

Ideally the approach would appear to be via chemical kinetics - the elementary chemical reactions between atoms, free radicals and molecules being used to predict the over-all rate of reaction as well as the conditions necessary for ignition. Unfortunately, due to the complexity of the problem, this method has met with only partial success. However the advent and eventual development of mass spectrometric and other techniques should materially assist such studies in the future.

The alternative approach of gradually accumulating knowledge via ad hoc experimentation is therefore generally favoured, the idea being that eventual correlation of such data will yield comprehensive theoretical explanations. To quote Lewis (Le 59) "...it is possible to develop new conceptual understandings from experimental observations and simple correlations whenever it is found that flame processes have some physical basis in common".

Adoption of the empirical approach calls for a decision between a microscopic or macroscopic study of the combustion process. Once again the inherent complexity of the underlying mechanism, as well as the rapidity with which it is carried out, are determining factors. Chemical analysis of the phenomenon requires measuring instruments of adequate resolution and a sufficiently short response time to permit the course of the intermediate reactions to be followed.

Techniques for doing this are only now becoming available. However the necessary equipment is expensive. In addition it is only applicable to the study of idealised low-pressure flames. Nevertheless there can be little doubt but that the results of such flame structure studies will eventually provide important information on high temperature chemical kinetics, thereby helping to unravel the more practical types of problem of interest to the engineer.

On the other hand measuring instruments with which instantaneous values of the macroscopic parameters may be followed are well advanced. The fundamental data of interest here are primarily of a mechanical or thermodynamic nature, such as temperature, pressure and velocity, all of which are amenable to relatively accurate measurement. This method of approach is therefore generally favoured.

It must be stressed however that these two methods of studying the problem are by no means incompatible. As microscopic techniques become available they can be incorporated into a research programme and used in conjunction with established methods.

2.2.1 Specific Objectives

In general, for any particular combustible mixture, the thermodynamic properties, both of the unburnt gas and of the equilibrium product, are known to an adequate degree of precision. What is lacking is a detailed understanding of the kinetics of the process, and thus of the actual mechanism leading to the propagation or stability of the subsequent flame.

In essence therefore combustion studies have as their aim one or more of the following :

- (1) The establishment of the limits of inflammability as functions of the concentration of the combustibles and of their thermodynamic state.

- (2) The determination of minimum ignition energies and quenching distances for various mixtures; also their ignition temperature and ignition delay.
- (3) The examination of the structure of laminar flames and the location and limits of the preheat and reaction zones. Also the measurement of temperature and concentration gradients and transport of active radicals in these zones.
- (4) The measurement of laminar burning velocity under various conditions, and its interrelation with other intrinsic properties of the mixture.
- (5) The investigation of instability phenomena, such as non-isotropy, flash-back and blow-off.
- (6) The behaviour of turbulent flames, with particular reference to their stabilization.
- (7) The study of abnormal conditions of burning, such as detonation in tubes and knock in spark ignition engines.
- (8) The integration of all the above into a comprehensive theory of the mechanism and propagation of all types of flame. (Some twenty different types can be distinguished.)

2.2.2 Laminar Flames

Basic to the whole subject of combustion research is a complete understanding of the internal structure and propagation of pre-mixed laminar flames (Li 54). Although formal equations for such systems - relating conservation of mass, energy and atomic species with the differential equations of conduction, diffusion and species production - can be formulated (HC 54), their solution, even in ideal cases, requires data which is not generally available. Recourse is therefore had to the experimental approach which is more tractable and in any event necessary for confirmation of theoretical findings.

The objects of such experiments are to determine inter alia ; (i) the variations in density, temperature and composition through such flames, with particular reference to the preheat and reaction zones, and (ii) their burning velocity as a function of the temperature, pressure and composition of the unburnt gas.

Although this thesis is concerned with the determination of laminar burning velocity, a brief discussion of the methods used in studying flame front structure, and particularly some of the results obtained, will not be out of place. In any event an understanding of this subject is an essential prerequisite to any reliable determination of burning velocity (Ge 53).

2.3 LAMINAR FLAME STRUCTURE

A flame is the result of a self-sustaining chemical reaction usually made visible by the luminosity of the burning gases. Associated with a flame is a flame front in which the unburnt gas is heated up and converted into products. Whether the flame is stationery or moving in space, the flame front (which is of finite thickness) is taken as an indication of the progress of the flame.

The flame front is generally considered to consist of two regions - referred to as the preheat and reaction zones. (Fig 2.1)

In the preheat zone the temperature of the unburnt gas is raised from T_u to its ignition value T_i , mainly by heat conduction from the reaction zone. Each element of gas in this region acts as a heat sink, gaining more heat than it loses. Hence the temperature profile is concave upwards ($\partial^2 T / \partial x^2 > 0$). Because of the temperature increase the unburnt gas expands and is accelerated (Fig 2.2). Little or no chemical reaction occurs in this region (DS 57).

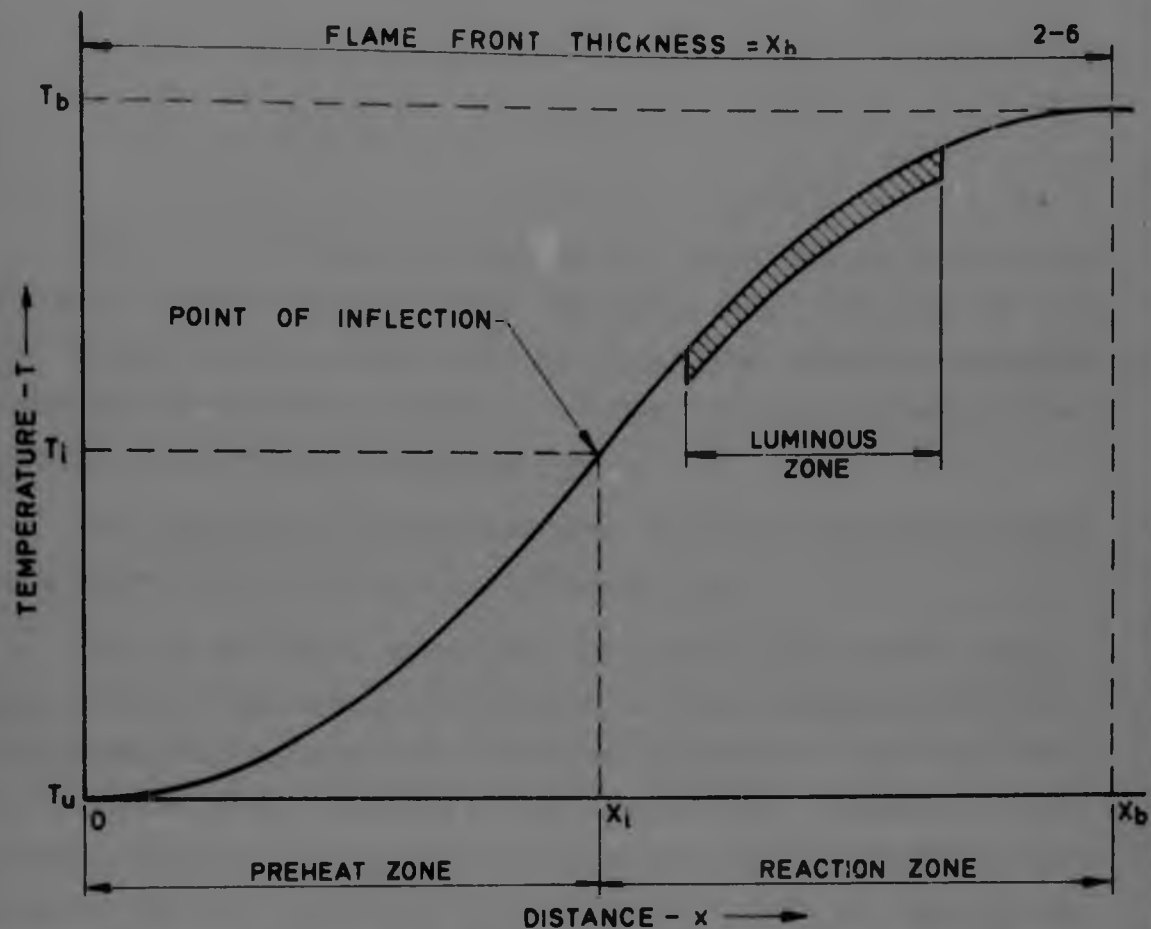


FIG. 2.1 TYPICAL TEMPERATURE PROFILE IN A FLAME FRONT

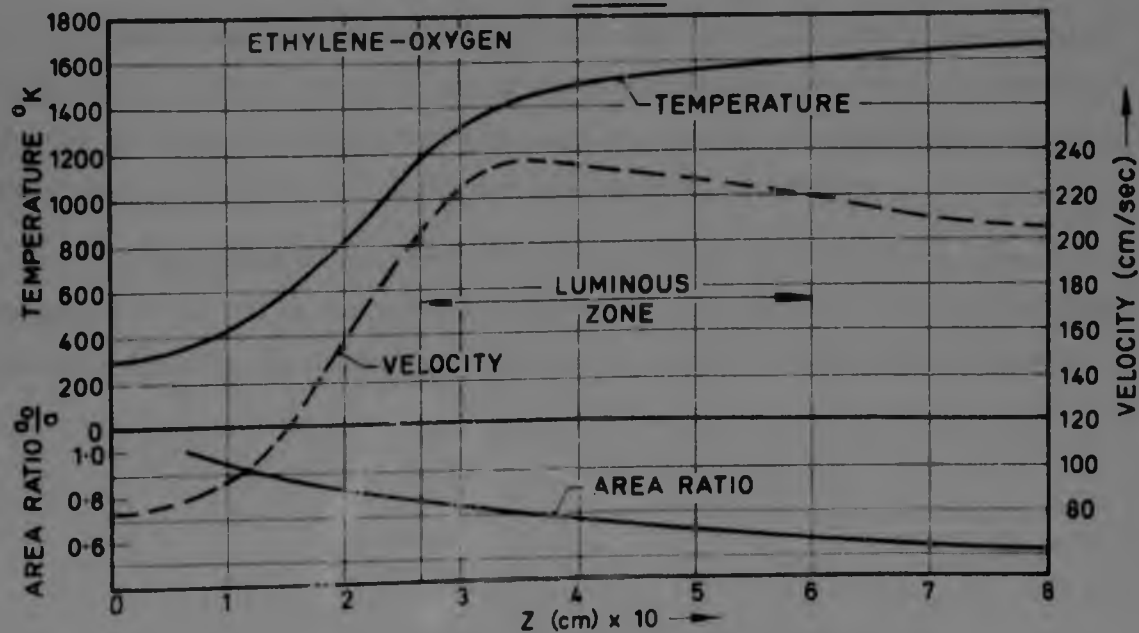


FIG. 2.2 TEMPERATURE, VELOCITY, AND STREAM TUBE AREA PROFILES (Fr 61)

On reaching its ignition temperature T_i , each element of gas starts undergoing chemical reaction with a consequent evolution of heat, the T - x curve being concave downwards ($\partial^2 T / \partial x^2 < 0$). The temperature continues to rise until its equilibrium value T_b is reached. The region between T_i and T_b is thus referred to as the reaction zone.

The luminous zone is contained within the reaction zone and generally starts somewhat beyond the point of inflection (T_i, x_i).

The whole region comprising the preheat and reaction zones - characterised by the term flame front - generally has a significant thickness. This is attributed to (a) thermal conduction, (b) diffusion, and (c) the finite time required for the reactions to reach equilibrium. Evidently, for any particular mixture, this characteristic thickness would be expected to vary inversely with the burning velocity and pressure. This trend, which is also predicted by chain theory (VD 56), has been confirmed experimentally (Fr 57).

Measurements of flame front structure fall into three interrelated categories: (i) fluid flow, (ii) temperature, and (iii) composition. In addition, due to the large concentration gradients existing in the flame front, data on the transport coefficients of the various species is essential.

In the interests of completeness, and since some of these ideas are required later, it is considered desirable to give a brief discussion of the various methods which have been proposed or used for these measurements.

2.3.1 Fluid Flow Measurements

The most versatile technique available for fluid flow measurements appears to be the particle track method. Here the paths followed by dust particles introduced into the gas stream are recorded photographically. With a steady source of illumination the resulting streamlines can be used to determine area variations of stream tubes; repetitive short duration flashes result in measurement of velocity profiles. This technique has been used by many investigators with excellent results (Sm 37, VL 43, AF 50, FP 53, Fr 57, FA 59). (See Figs 2.3 and 2.4).

Measurements of pressure drop in the flame can also lead to velocity profiles. However, the small pressure heads available and the disturbance of the flame by the probe renders this method unattractive.

2.3.2 Temperature Measurements

One of the first attempts to study the internal structure of stationary laminar flames was through the measurement of temperature profiles in the flame front (KW 48). In conjunction with density profiles these can lead to a knowledge of the average molecular composition at various points through the flame front, or, if all three are known, conclusion can be drawn about the most probable reaction mechanism.

Certain problems arise regarding the precise meaning of the term 'temperature' in such non-equilibrium conditions (GW 53, Fr 57). However, although these have not as yet been fully resolved the indications are that they do not appreciably influence the results (FP 53, FA 54).

The particle track technique, yielding density variations, may also be used for temperature measurements, provided average molecular weight profiles are known or can be estimated (AF 50, FO 53, FA 54, Fr 56). The reliability claimed is good particularly when flash illumination is used (Fr 57). However reduction of the data is apparently tedious.



2-9



Fig 2.4 Particle track photograph of a flat flame with sketch of direction of observed flow (LW 59)



Fig 2.3 Macroscopic flame structure - flame geometry (Fr 57)

Optical methods, which depend on variations in density or one of its derivatives, have the important advantage of not disturbing the flame. As with the particle track method a knowledge or estimate of the molecular weight profile is necessary. Several different methods have been used.

The use of interferometry, employing light of different wavelengths to determine both temperature and composition, has been proposed (OI 49). However because of experimental and interpretational difficulties it has not as yet been favoured for detailed profile studies (Fr 56).

Probably the most popular optical method (other than direct photography) of observing flames has been by the schlieren technique (GW 53). Here the deflection of a beam of light, proportional to $(1/\rho)d\rho/dx$, is measured. However, as a temperature measuring technique it is subject to the same interpretational limitations as interferometry. An additional complication is the necessity of integrating the above equation. Nevertheless it appears to have led to both reasonable and reproducible results (DV 51, Di 53, BW 53, BW 54).

Thermocouples and resistance thermometers have the merit of yielding direct readings, that is, they do not depend on a knowledge of either the density or composition profiles. They are however subject to certain limitations which must be guarded against. These are; (i) disturbance of the flame, (ii) catalytic action, (iii) radiation losses, (iv) relatively low melting points, and (v) thermal equilibrium. The method is nevertheless well developed and has led to good results (KW 48, Fr 53, GL 53, FB 54, LC 55).

Spectroscopic methods, in common with other optical techniques, need not disturb the flame, even when it is found necessary to introduce minute quantities of foreign matter into it (VL 43, GW 53, LC 53, Si 49, BC 55). Either spectral emission or absorption techniques may be used (GW 48, GW 53). Even though there is no upper limit to the temperature which may be measured, these methods suffer from a lack of spatial reso-

lution and interference from colder portions of the flame. They have been fairly successfully used in high temperature regions where resolution is not of vital importance (VL 43, AV 53, WW 55, AA 55).

Clearly any method of temperature measurement may in principle be used for determining temperature profiles, provided it can be adapted to yield satisfactory spatial resolution and is capable of measuring high temperatures. The following have been used or suggested for flame temperatures, and it may be possible to adapt them for profile measurements: (i) α -particle range (Sh 33), (ii) X-ray absorption (WK 51, KK 55), (iii) electrical conductivity or attenuation by radio-waves (AA 48), and (iv) velocity of sound (MN 49).

2.3.3 Composition Measurements

The composition of the gases in a flame changes continuously through the flame front, from unburnt gases through intermediates to burnt products. The species present in these regions include molecules, radicals and atoms. A knowledge of the relative concentrations and concentration gradients of these species provides information as to the course of the reaction as well as data against which the chemical kineticist can test various reaction schemes.

Whilst the initial composition of the reactants is generally known, and the final equilibrium concentrations can usually be calculated, the intermediates must be studied experimentally. Two categories of intermediates are recognised; (i) stable species, which constitute the majority of the molecules present, and (ii) free radicals, which initiate the reactions.

A knowledge of the types and relative abundance of free radicals and atoms in flames is of importance since these give an indication of the probable reaction scheme (Fr 61). In particular, information on their build-up in the pre-luminous region would be of considerable interest and might

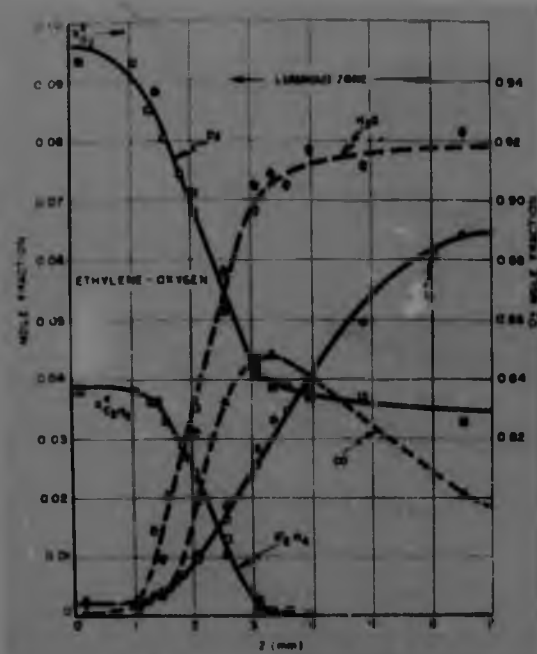
serve to explain many combustion problems (viz. inflammability limits, ignition delay, SI-engine knock, etc.). Unfortunately satisfactory measurements in this region have not as yet proved possible.

Two general techniques have been used for studying local concentrations in flames - spectroscopic analysis and direct sampling (Fr 57, Fr 61).

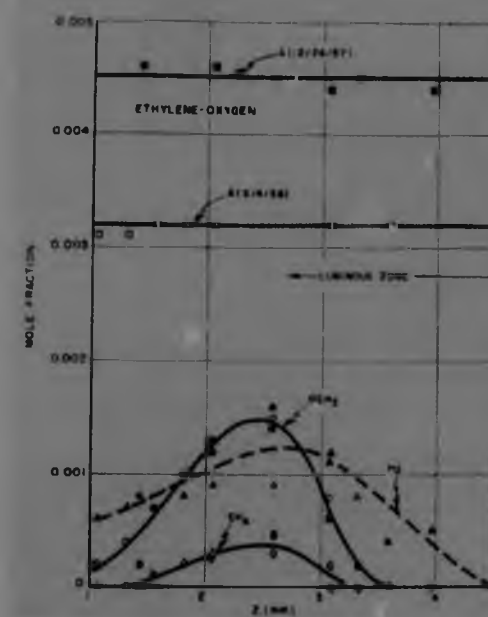
Spectroscopic methods have no temperature limitations and do not disturb the flame. However their spatial resolution is poor, they can only be used in homogeneous regions and the interpretation of the results is difficult. For these reasons they have mainly been used to study the post-luminous region where spatial resolution is not important (AA 55, CM 57).

Direct sampling, followed by one of a variety of techniques for analysing the quenched mixture, is the most generally favoured method at present (FC 55, FP 57, FW 57, FA 59, Ma 59, Fr 61). It appears to be limited only by the softening temperature of the probe. Four methods of analysing the samples have been used; (i) manometric analysis (FC 55), (ii) infra-red analysis (AP 58), (iii) gas chromatography (YF 58, BD 59), and (iv) mass spectrometry (FP 57, Wi 57). The latter is probably the most direct and accurate, and has the further advantage that the sample size required is very small. Gas chromatographic methods hold great promise and have the advantage that the apparatus required is relatively inexpensive.

Quantitative interpretation of composition profiles requires a knowledge of the diffusion coefficients of the various species in the flame. Until recently such information as was available was for temperatures below about 100°C (We 57). Extrapolation techniques, based on statistical mechanics had therefore to be used (HC 54). Latterly however a method has been developed which permits of measurements at temperatures up to about 1400°K (WW 58). More reliable calculations should therefore now become possible.

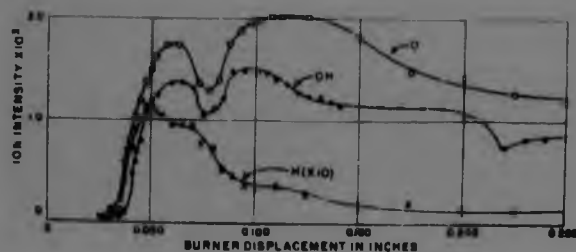


(a) Major constituents

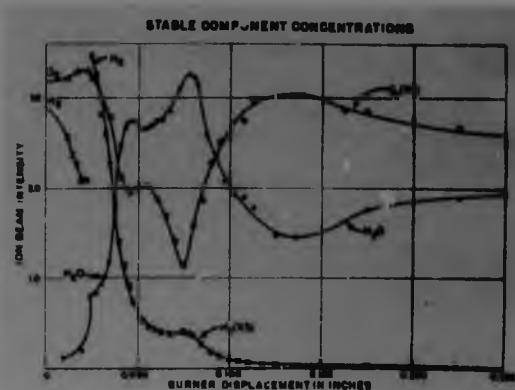


(b) Minor constituents

Composition profiles of lean ethylene/oxygen flame



(e) Stable component concentration



(d) Atom and free radical concentration

Hydrogen/oxygen diffusion flame

Fig 2.5 (Fr 61)

2.3.4 Interpretation of Flame Structure Studies

A knowledge of the fluid flow, temperature and composition profiles, together with the transport coefficients of the various species present, provides a complete description of the intensive properties of a flame. Such data should permit conclusions to be drawn regarding: (i) the relative effects of diffusion, heat conduction and reaction on the mechanism of flame propagation, and (ii) the probable reaction scheme and associated reaction rates.

All flame structure studies to date have been carried out on low-burning velocity, low-pressure, stationary flames. Low burning velocity since this is the only type of flame that can be rendered stable on flat flame or bunsen type burners; low pressure to ensure thick flame fronts in which adequate spatial resolution can be achieved; and stationary since with the low response-rate instruments available this is the only type that can be studied. Whether the results so obtained (as well as any inferred reaction schemes) can be extrapolated to high velocity, high pressure, propagating flames still remains to be established. Essential to such studies is the existence of reliable values of laminar burning velocities over a range of initial mixture compositions, temperatures and pressures. One of the aims of the programme of research to be discussed in this thesis is the obtention of such data.

A result of flame structure investigations of immediate interest to the present study is the rate of heat release in the flame front (Fig 2.6) and its relation to the luminous zone. As will be discussed in Section 2.4.1, the determination of burning velocity in experiments in which the flame front is not plane, is critically dependent on the decision taken regarding the location of this front (Li 53). It appears to be generally agreed that for burner flames the slope of the schlieren cone gives the most reliable results

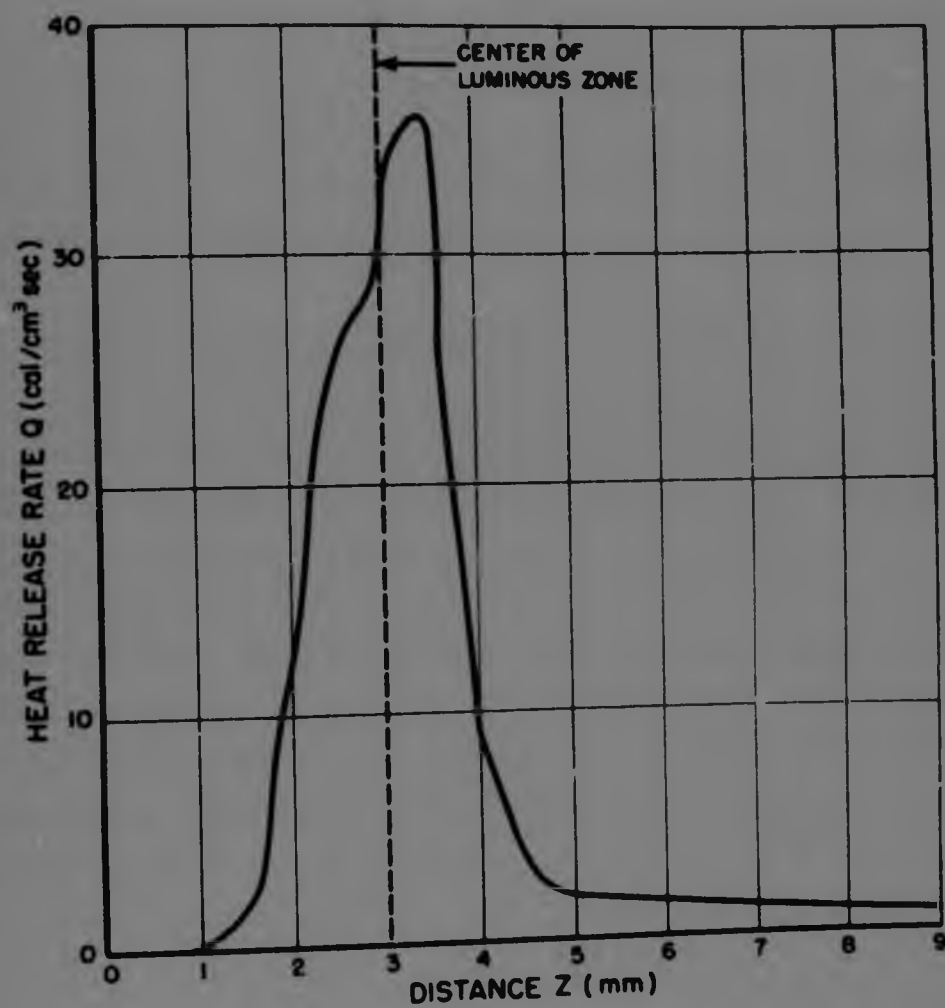


Fig .26 Heat release in : propane/air flame front
(Fr 57)

(GW 53). The maximum intensity of the schlieren image in such flames would seem to occur at about 200°C (KW 48). Thus this technique sets the flame front very near to the beginning of the preheat region - particularly when account is taken of the variation of intensity contour due to curvature of the flame front. Whether such a technique is necessary or justified in rapidly propagating spherical flames, such as occur with soap bubble and constant volume bomb methods, requires careful assessment. This aspect will be dealt with in the sections to follow.

2.4 LAMINAR BURNING VELOCITY

One of the most important intrinsic properties of any combustible mixture is its laminar burning velocity. On reflection this may appear surprising, particularly in relation to such topics as ignition energy and turbulent flames. However there is a wealth of experimental evidence in support of this contention. Thus, for example, correlation equations for flash-back and flame tilt in burners, minimum ignition energy of an electric spark, and turbulent flame velocity, to mention but a few, all contain laminar burning velocity as an important variable. Evidently therefore an accurate knowledge of this property, together with the influence of other variables on it, are essential to any combustion study. Unfortunately many of the methods available for its determination leave much to be desired.

The ignition of a combustible homogeneous mixture from some point within it results in the propagation of a flame. The velocity of spread of such a flame relative to the point of ignition is readily measurable. However this spatial velocity (S_s) is not a unique property of such a mixture. It can be shown to be the sum of two velocities, namely the burning or transformation velocity (S_t) and the unburnt gas velocity immediately adjacent to the flame front (S_{ug}): that is

$$S_s = S_t + S_{ug} \dots\dots\dots (2.1)$$

The second and generally larger component (S_{ug}) of the spatial velocity evidently will be a function of the relative densities of the burnt and unburnt gas at any instant.

The burning velocity (S_t) is defined as the relative velocity, normal to the flame front, with which the unburnt gases move into this front and are transformed (V_n in Fig 2.3). It is considered to be a thermodynamic property of the specific combustible mixture. Symbolically it can be expressed as (RP §2);

$$S_t = -(1/A\rho_u)(dm_u/dt) \dots\dots\dots (2. 2)$$

where A is the flame front area, ρ_u is the unburnt gas density immediately adjacent to the area A , and dm_u/dt is the mass rate of flow of unburnt gas into the flame front.

The methods used for determining laminar burning velocity fall into two categories; those in which the flame front remains stationary in space, that is,

$$S_s = 0, \text{ or } S_t = -S_{ug} \dots\dots\dots (2. 3)$$

and those in which it moves with respect to some fixed point - usually the point of ignition.

The first category can be sub-divided into two classes, namely diffusion flames and pre-mixed flames. Examples of the former are the burning of candles, oil wicks, wood or coal. In these the rate-controlling process is the transport of combustible constituents into the flame front. They cannot therefore be used to determine burning velocity. The best example of the latter type of flame is that obtained in a Bunsen burner. When the combustible gases are pre-mixed and the flow is laminar, this yields the characteristic inner cone and mantle of all burner flames. The experimental difficulties associated with the use of this type of flame for determining burning velocity, centre around the measurement of the flame front area A .

These may be overcome for laminar burning velocity studies of slow flames, by designing special burners yielding plane flame fronts. (See Fig 2.4).

Propagating flames may also conveniently be subdivided into two classes, namely constant volume and constant pressure. Examples here are the spherical constant volume vessel, soap bubble and cylindrical tube methods. Their study requires a means of measuring the velocity of propagation relative to the fixed point of ignition. This may be achieved either photographically using direct, schlieren, shadow or interferometric methods, or by the use of ionization gaps, fusing wires, temperature probes or similar devices. In the constant volume technique an additional desirable observation, if full advantage is to be taken of the method, is the change in pressure in the vessel during the course of the flame.

Each of the methods mentioned above has certain advantages and disadvantages. These will be discussed in greater detail below.

2.4.1 Determination of Burning Velocity

As was mentioned in the foregoing, many of the experimental difficulties associated with the determination of burning velocity centre around the precise meaning to be given to the flame front area A (eqn 2.2).

The case of an infinite plane flame, in which the flame front is normal to the direction of flow of unburnt gas, is the only one in which this difficulty does not arise. In all other systems "...no definition free from all possible objections can be formulated" (Li 53). Unfortunately the closest approximation to an infinite plane flame, that is the flat flame burner of Egerton and Powling (Po 49, Po 61), is limited to very slow flames - with maximum burning velocities of from 15 to 20 cm/s (Po 61). Alternative methods must therefore be considered.

Before these can be used however a satisfactory answer must be found to the following question: Which part of the flame should be selected as a measure of the flame front area? Evidently from eqn(2.2) any surface within the flame front at which the corresponding values of density (ρ_u) and mass rate of flow (dm_u/dt) can be accurately and reproducibly determined would be satisfactory. Undoubtedly the best surface is that at which the temperature just starts increasing above the unburnt gas value. Unfortunately, due to the asymptotic nature of the temperature profile this position is unmeasurable.

2.4.2 Methods of Observing the Flame Front

Various methods of locating the position of the flame front have been proposed and used (DS 57). These include:

- (a) Direct photography of the luminous flame (LP 51, GW 53, Se 59).
- (b) Shadow photography using a point source of light (SL 48, GL 49, AF 50).
- (c) Schlieren photography using either a coarse grating illuminated from behind (GW 53, Gi 57) or an optical system using lenses or mirrors (CL 51, DL 51, PL 51, BW 53, Di 53, BW 54, Se 61).
- (d) Interferometry (Ol 49, GW 53).
- (e) Particle track measurements (Sm 37, VL 43, AF 50, FA 54, Fr 56).
- (f) Ionization gaps (Es 57, SA 57, EA 58, Gr 59, AG 61).
- (g) Temperature measurements (KW 48, Fr 53, GL 53, GW 53, FB 54).

Since the intensity of the luminous zone is generally sufficiently high, particularly for hydrocarbon mixtures, direct photography is possible and has frequently been used. However as was discussed in Section 2.3, this zone is located some distance behind the initial temperature rise and hence does not represent the start of the interaction between the unburnt gas and the combustion wave. (See Figs 2.1, 2.2 and 2.3). In burner flames the

thickness of the preheat region ahead of the luminous front is found to vary from about 1 mm at atmospheric pressure (AF 50), to about 10 mm at 1/20 atmosphere (KW 48). This surface would therefore appear to be unsuitable for determining burning velocity (for low pressure burner flames at any rate) unless the corresponding unburnt gas density can be estimated.

Shadow photography has been studied fairly extensively (SL 48, Wo 49, AF 50, GH 50), and it has been established that the sharp inner shadowgraph edge is dependent on the distance between the flame and the screen or photographic plate. Further, this edge is located ahead of the preheat region and approaches the start of this region as the distance between flame and screen is decreased. This well defined edge may therefore only be used if suitable corrections can be made. On the other hand the outer shadowgraph edge, which is coincident with the schlieren edge and is not dependent on distance, is not well defined and is hence difficult to measure. For these and other reasons shadow photography is considered unreliable, and Gaydon and Wolfhard recommend that it be abandoned (GW 53).

Of the optical methods the best measurements of the start of the preheat zone are afforded by the schlieren, interferometric and particle track methods. Interferometry, although possessing many attractive features, is expensive and complicated to use. In any case it is doubtful whether it can provide much additional information as compared with schlieren or particle track techniques.

Schlieren methods yield a focused image of the flame enabling the position of maximum intensity, given approximately by $(-1/T^2)(dT/dx)$, to be easily located. In burner flames this apparently occurs at about 200°C (KW 48). It has however been pointed out that "...because of the optical arrangement for photography the schlieren in a conical flame may be at much lower temperature, and this displacement will depend on the thickness of the pre-heating zone, and therefore on the burning velocity.

The schlieren thus may serve to locate the position of the first temperature increase which is required for measurement of burning velocity" (GW 53, p 67). Smoke (Br 49) and particle track (AF 50, CL 51, Ge 53) measurements in burner flames, confirm that the flow lines remain parallel to the burner axis until the schlieren image is reached. There seems little doubt therefore that wherever possible the schlieren edge should be used for burning velocity studies (GH 50). (See Fig 2.7).

The particle track method is an extremely versatile technique for the study of flames (See Section 2.3.1 and 2.3.2). By its use von Elbe and Lewis (VL 43) were able to show that burning velocity is a 'genuine physical constant' (GW 53). However it is apt to be rather tedious as a means of determining burning velocities per se. Care has to be exercised that the particles used do not have any catalytic effects on the flame and also that they are small enough to accurately indicate any changes in direction of the stream tubes. Nevertheless it is one of the most powerful techniques available.

It has long been known that the electrical conductivity of flame gases is high as compared with the unburnt gas. A method of detecting the position of the flame front as a result of such changes in conductivity (by means of ionization gaps) has been used by Agnew and his co-workers in their studies of flame propagation in spherical constant volume vessels (Es 57, Sa 57, Ea 58, Gr 59, AG 61). Evidently such ionization gaps will trigger at some point within the luminous zone (CK 55, KN 59). If the flame front thickness is variable, as it might well be in constant volume experiments, this technique may introduce significant error. Further, unless care is exercised regarding the probe dimensions, there is a possibility of deforming the flame front due to cooling and/or quenching effects (PB 59).

Since it appears that the best surface at which to locate the flame front is that at which the temperature just starts to deviate from the unburnt

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Since it appears that the best surface at which to locate the flame front is that at which the temperature just starts to deviate from the unburnt

gas value, evidently the most direct determination would be via some form of temperature measuring device of high spatial resolution and sensitivity. This method does not appear to have been considered for burning velocity measurements, probably because of the labour involved in probing for such a temperature contour in burner flames, as well as a fear of disturbing the flame. There seems little doubt however that for propagating flames this might prove quite an attractive method, provided devices of small size, adequate sensitivity and sufficiently short response time can be developed. Any temperature dependent property such as melting point, thermoelectric effect, electrical resistance, conductivity, permittivity, permeability, etc., could in principle be used.

To summarize therefore it would appear that: (i) if an optical method of observing the flame front is to be used then either schlieren or particle track techniques are indicated; if non-optical methods are necessary, a temperature sensing device of small size, high sensitivity and short response time would seem to be preferable.

It must be stressed however that the bulk of the experimental evidence relating to flame front structure has been obtained on low velocity, low pressure, stationary flames. For such flames the thickness of the preheat region is given approximately by (GW 53);

$$\delta_{pr} = (4.6k) / (\bar{c}_p \rho_u S_t) \dots\dots\dots (2.12)$$

If this equation is equally applicable to high velocity, high pressure propagating flames, such as are to be reported in this study, the thickness of the preheat zone may not be significant. Any of the above methods would then be equally effective. However there is a probability that the controlling mechanism and reaction schemes deduced from stationary flames may not be applicable to propagating flames (GW 53 p.81). Wherever possible therefore, alternative methods of observing the flame front would appear to be desirable as a check on each other.

2.4.3 Methods of Measuring Laminar Burning Velocity

Following Linnett (Li 53, Li 54), the five main methods which have been used to determine laminar burning velocity will be presented in order of increasing complexity of the flame front shape. These are :

- (a) Flat flame method (Po 49, BS 54, Po 61, La 62).
- (b) Soap bubble or constant pressure method (St 23, FR 35, La 62).
- (c) Spherical constant volume vessel method (LV 34, FM 40, LV 51, Co 62, RP 62).
- (d) Cylindrical tube method (Jo 46, LV 51, Co 62).
- (e) Burner methods (GW 53, La 62).

Here (a) approximates closest to the ideal infinite plane flame; (b) and (c) ideally yield spherical and hence one-dimensional combustion waves; (d) and (e) result in pseudo-spherical and complex conical flame fronts respectively, making it virtually impossible to attach a precise meaning to the term 'flame front area'. They are also subject to wall interaction effects.

(a) Flat flame method

This method, due to Powling and Egerton (Po 61) provides a close approximation to the ideal one-dimensional infinite plane flame, but is unfortunately limited to low burning velocities (15 to 20 cm/s). The apparatus used is shown in Fig 2.8. Here the pre-mixed combustible gases enter a wide cylindrical burner tube (A), of approximately 6 cm diameter, from below. After being evenly distributed across the whole diameter of the tube by a matrix (E), glass bead packing (B) and fine diffusion screens (C), the mixture enters the vertical channels of the matrix D. These matrices are built up of alternate layers of plain and corrugated metal tape, as shown, resulting in units of high porosity and low pressure drop. In passing through the channels of D any turbulence in the gas is eliminated and Poiseuille flow set up in each channel. The distance of the top of D below

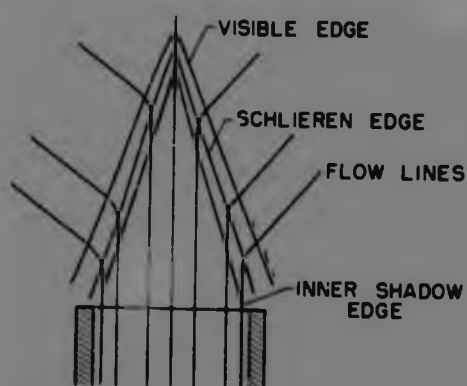


Fig 2.7 Relation of flow lines to flame images.

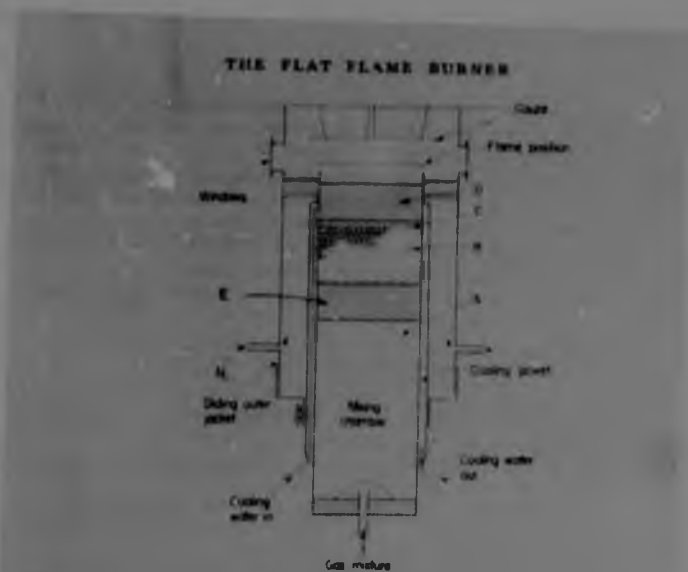


Fig. 1. Flat flame burner.



Fig. 2. Burner matrix material.

Fig 2.8 Flat flame burner



Fig 2.9 Typical record of an explosion in a soap bubble.

the burner port is adjusted to a value (usually 0.5 to 1.0 cm) such that these irregularities in velocity are eliminated, but parabolic flow has not begun to be established in the main burner tube. A wire gauze or perforated asbestos board placed above the flame serves to stabilize it by causing a slight divergence at the burner port (see Fig 2.4). The resulting flame has the appearance of a flat disk with a slightly curled up edge. The area of this disk divided into the volumetric flow rate of the mixture yields the burning velocity.

Since flow rates can generally be accurately determined, the accuracy of the method depends on the measurement of the disk diameter. Because of mixing and cooling by the surrounding nitrogen, the exact position of the flame edge is uncertain. However provided the burner diameter is large the error from this cause is apparently small. But for flame stability reasons large diameters may only be used with slow burning mixtures. Faster flames require narrower burners. Alternatively concentric nozzle burners may be used. Powling (Po 61) claims that with such an arrangement essentially flat flames can be obtained up to burning velocities of about 100 cm/s.

Another disadvantage of the method is that the matrix D becomes heated, sometimes to as high as 200°C , thus resulting in pre-heating of the unburnt mixture. Provided such pre-heating is uniform across the whole diameter of the burner this need not be a very serious limitation. In fact additional pre-heating by external heaters has been used to study high temperature kinetics (LW 59).

Botha and Spalding (BS 54) have used a porous sintered bronze plate for stabilizing the mixture. They measured the heat transferred to this plate at various flow rates. By extrapolating the ratio of the volumetric flow rate to flame disk area ('apparent burning velocity') to zero heat transfer, it is claimed that true adiabatic burning velocity is obtained. Comparison with reliable values obtained by other methods appear to substantiate this claim.

Mainly because of the low velocity restriction the flat flame method has not found much favour for burning velocity measurements. It has however been extensively used for flame structure studies and the determination of the limits of inflammability.

(b) Soap bubble method

Of the techniques which are independent of burner surfaces possibly the simplest is the soap bubble or constant pressure method devised by Stevens (St 23) and developed by Fiock and Roeder (FR 35). Here the combustible mixture to be tested is used to blow a spherical soap bubble around a central spark gap. Since such a bubble offers no significant resistance to thermal expansion, ignition of the mixture results in the propagation of a spherical combustion wave at virtually constant pressure. (For relatively low velocity flames the pressure field across the flame front is generally ignored. Significant errors will however be introduced in high velocity flames if the pressure is assumed constant.) For purposes of analysis the bubble is photographed through a narrow horizontal slit using a drum camera. A typical record is shown in Fig 2.9, from which it is seen that the spatial velocity (S_s) is essentially constant for the majority of the process.

Now from our definition of burning velocity (eqn 2.2), since $(dm_u/dt) = (-dm_b/dt)$, it follows that

$$S_t = (1/A\rho_u)(dm_b/dt) \dots \dots \dots (2.13)$$

But for a spherical flame front

$$A = 4\pi r_b^2 \quad \text{and} \quad m_b = 4\pi r_b^3 \rho_b^0 / 3$$

$$\text{Thus } (dm_b/dt) = 4\pi r_b^2 \rho_b^0 (dr_b/dt)$$

since ρ_b^0 is assumed constant.

Also $\rho_u = \text{constant} = \rho_o$

$$\text{Hence } S_t = (\rho_b^o / \rho_o) (dr_b / dt) = \alpha_o S_s^o \dots \dots \dots (2.14)$$

Thus provided the density ratio α_o can be measured or calculated and S_s^o determined from the photographic trace, then S_t follows. Generally α_o is obtained from measurements of the initial diameter of the spherical bubble ($2r_o$) and the final diameter of the burnt gas ($2r_f$), since for conservation of mass,

$$\alpha_o = (V_o / V_f) = (r_o / r_f)^3 \dots \dots \dots (2.15)$$

However although it is possible to measure both S_s^o and r_o accurately, the determination of r_f can present difficulties, particularly when it is noted that any errors in r_f are cubed. As a result of afterburning it may not be possible to establish a precise value for the final diameter (Li 53). Inertia effects should also become significant at higher velocities. Surface irregularities certainly then become apparent (SW 53). Also for low velocity flames buoyancy effects introduce distortion of the burning sphere.

An alternative method of determining α_o is via the general gas equation. Thus provided the burnt gas temperature T_b^o can be calculated or measured and the molecular weights determined, then,

$$\alpha_o = \rho_b^o / \rho_o = (M_b^o / M_o) (T_o / T_b^o) \dots \dots \dots (2.16)$$

Evidently thermodynamic calculations of the adiabatic flame temperature T_b^o and molecular weight M_b^o yield results in very close agreement with observed values and are thus in general to be preferred (SW 53, SE 59).

A decision as to the use of schlieren or direct photography for observing the flame front does not arise here since, because of the constancy of S_s^o , both techniques should yield the same results (LP 51, PL 51).

A disadvantage of the method is that if water-based soap solutions are used dry mixtures cannot be tested (SW 54). However non-aqueous soap solutions based on glycerol (SS 53, SE 59) have been developed which

have proved quite successful. Also it has been suggested that diffusion of the mixture through the bubble wall may be sufficiently great to alter its composition (LV 51). No evidence of this has been found with either acetylene/air mixtures (LP 51) or with ethylene/oxygen/helium mixtures (ML 53). In any event the use of transparent latex rubber balloons should obviate this difficulty (PP 53, SE 59).

Two important advantages of the soap bubble method are, (i) the use of small quantities of combustible mixture, and (ii) the ability to vary both the initial temperature (within narrow limits) and pressure (within wide limits). Hence studies of the effects of these important parameters can be easily carried out.

(c) Spherical bomb method

The spherical constant volume combustion vessel method has not been used extensively, but is described by Linnett (Li 53) as '..potentially a powerful method for determining burning velocities'. Its main limitations to date appear to have been the lack of (i) suitable equations for deriving burning velocities over the full range of the process, and (ii) inadequate instrumentation for observing the progress of the flame, particularly the variations of pressure with time. These problems are now well on the way to being solved. (See Chapter 4, et seq ; also RP 62, RT 63, RT 63a)

Explosions in closed vessels were used in the early days for determining the mean heat capacities of gases at high temperatures (Ho 06). However the initial development of the spherical constant volume bomb technique for determining burning velocities appears to have been due to Lewis and von Elbe, and Flock and his associates (LV 34, LV 51, FK 35, FM 37, FM 40). In this method the combustible mixture is contained in a thick-walled spherical vessel which is fired at the centre. Provided the differences in concentration and diffusivity between the various constituents of the mixture are not too large (LV 51, p.310), and the spatial velocity is not

too low (LV 51, p.449), the resulting combustion wave is generally isotropic. The propagation of the flame towards the wall of the vessel is attended by a pressure rise which results in a temperature increase of the unburnt gas. If these changes in pressure and temperature, as well as the position of the flame front, can be accurately determined the method becomes extremely versatile. This since their combined effects on burning velocity can then in principle be studied in a single experiment. Unfortunately the majority of equations which have been developed are only applicable to the early stages of the process when the pressure rise is small (Chapter 3; also RP 63). This has seriously restricted the value of the method, virtually relegating it to the status of a constant pressure technique, albeit with several advantages over the soap bubble method. New forms of equation which should in large measure overcome these limitations are developed in Chapter 4, (see also RT 63), as is also a new method for directly determining burning velocities in both constant pressure and constant volume experiments.

As currently used (RT 63a), the constant volume method has the following important advantages (see also Tr 62) :

- (i) Only small quantities of combustible mixture are required.
- (ii) The mixture composition - including humidity - can be accurately controlled.
- (iii) Only a few experiments at different initial pressures, or temperatures, are required in order to establish the separate effects of these parameters on the burning velocity of any particular mixture.
- (iv) As with the soap bubble method, true free-space adiabatic burning velocities can be determined. That is, there are no surface interaction effects and the radiant heat transfer can be made negligible. The latter can in any case be allowed for.
- (v) Since the radius of curvature of the flame front is large (for all but the initial stages) as compared with the anticipated flame front thickness, and the system is essentially one-dimensional, any errors in locating this surface should not be too serious, provided suitable

burning velocity equations are used, that is, equations that do not magnify observational errors.

The disadvantages of the method are :

- (i) If full advantage is to be taken of its potentialities, the associated apparatus is complex and expensive, and the time required to do a test is long (up to one hour for tests in which the initial pressure is not atmospheric) .
- (ii) Transcription of the observations and calculation of the results is tedious even with the aid of a digital computer.

(d) Cylindrical tube method

The early literature contains many values of flame speeds measured in tubes (BT 27). It is doubtful however whether these results are of any significance in determining burning velocity since this method is subject to serious wall interaction effects, such as friction and heat loss. Thus the spatial velocity of any given mixture may increase many times, as a result of less wall interaction, as the tube diameter is increased (Fi 43). However the flame front shape then tends to become irregular and difficult to measure. Also different values are obtained depending on whether the flame propagates in an upwards, downwards or horizontal direction. Finally it appears to be difficult to avoid flame front vibrations, particularly if the mixture is ignited by means of a spark rather than an open flame. The excellent set of photographs given by Fiock (Fi 43) illustrate some of these points (Fig 2.10).

In essence the method as used by Coward and Hartwell (CH 32), consists of a long cylindrical tube closed at one end and filled with the gas mixture under test. Ignition at the open end results in an initial uniform flame travel towards the closed end (F in Fig 2.10). Measurement of this uniform velocity (S_m) together with the area (A) of the pseudo-hemispherical



All photographs for a stoichiometric mixture of CO/O_2 in a tube about 1-in diameter and 20-in long.

- A,B,C - Tube closed at both ends, initial pressure 1, $2/3$ and $1/3$ atmosphere respectively.
- D - Tube closed at both ends, initial pressure 1 atmosphere, fired simultaneously at both ends.
- E - Top end of tube opened, pressure 1 atmosphere, fired at closed end.
- F - Top end of tube opened, pressure 1 atmosphere, fired at open end.

Fig 2.10 Typical record of explosions in a closed and open ended tube.

(FI 43)



(a)



(b)

Fig 2.11 (a)&(b) Symmetrical and asymmetrical flame fronts in the tube method (Co 62)

flame front (Fig 2.11) yields the burning velocity (S_t) via the following equation,

$$S_t = (\pi R^2 / A) S_m \dots\dots\dots (2.17)$$

where R is the tube radius. Evidently due to wall cooling the method can at best result only in an average value of burning velocity over the flame surface (Li 53).

The provision of a small hole at the end of the tube towards which the flame travels, and a larger one at the other end, apparently renders the flame movement uniform, stable and reproducible (GM 48, GL 51). However even with such refinements it is doubtful whether the wall interaction effect can ever be adequately corrected for. On the whole therefore the method appears to be intrinsically unsatisfactory.

(e) Burner methods

Most of the burning velocity values available in the literature have been obtained by burner methods (Jo 46, LV 51, GW 53). Doubtless the main reasons for this are that in its rudimentary form the apparatus required is cheap and easy to use. The results obtained with such simple apparatus however are notoriously unreliable (Li 53, GW 53).

Various types of burner have been tried, including common bunsen burners, shaped nozzles and slot burners. In essence the method entails establishing laminar flow in a vertical tube or nozzle, the flame being held stationary at the top end by the flow of combustible gas. Since the spatial velocity (S_s) is then zero, the average burning velocity (S_t) is numerically equal to the gas velocity, which can be obtained by dividing the volumetric flow rate by the 'flame front' area. Alternatively, since the local burning velocity must be equal and opposite to the component of the gas flow normal to the flame front, it follows that

$$S_t = S_{ug} \sin \theta \dots\dots\dots (2.18)$$

where θ is the angle of the flame front with respect to the gas velocity S_{ug} - generally the vertical axis of the burner.

Many techniques for locating and measuring the area of the flame front have been developed (LV 51, GW 53, Li 53), the most satisfactory of which appear to be based on schlieren or particle track methods. However because of the surface effects associated with the burner port, the complex-conical shape of the flame front and variations in S_t over this surface (probably as a result of temperature changes of the unburnt gas) this method is inherently unsatisfactory.

Comprehensive reviews of the burner method are to be found in references Jo 46, LV 51, GW 53 and Li 53.

2.5 DEPENDENCE OF BURNING VELOCITY ON TEMPERATURE, PRESSURE AND COMPOSITION.

Although the literature abounds with burning velocity data (LV 51, Jo 46), most of the earlier values must be considered of doubtful reliability since they were determined from burner or tube methods. In consequence of the limitations of these methods they have also yielded few results on the effects of temperature and pressure on burning velocity. Where they have been used to study pressure dependence, tests have generally been confined to the sub-atmospheric region - with one notable exception (EL 54).

Relatively few experiments appear to have been made to date on the effect of temperature on burning velocity, although both from a theoretical and practical viewpoint this would seem to be an important variable. On the other hand some attention has recently been directed towards the pressure dependency of S_t to the extent that there is at least agreement as to whether increasing or decreasing the pressure of a particular mixture produces corresponding changes in burning velocity. Quantitative agreement as between different methods is however still lacking. Clearly if reliable values

of burning velocity are to be obtained, any method of determining this property should permit accurate control and measurement of unburnt gas temperature, pressure and composition immediately ahead of the flame front. Also, if possible, each of these parameters should be capable of variation over reasonably wide limits. These requirements would seem to be self-evident, yet many investigators frequently do not even report the initial pressure or temperature of their mixtures.

Consider some of the more recent results of the effect of these variables on burning velocity.

2.5.1 Temperature Dependence

Possibly the first measurements of the effect of temperature on burning velocity were carried out by Ubbelohde and Hofsaes (UH 13) who found little or no dependence. Sachse (Sa 37) came to much the same conclusion, but as pointed out by Gaydon and Wolfhard (GW 53) when appropriately corrected his results show a marked temperature dependence. This has been confirmed by Sherratt and Linnett (SL 48) and by Johnston (Jo 47).

More recently Dugger and co-workers (Du 50, Du 52, DH 52, GD 53, DS 57), using a burner method, have shown that S_t varies appreciably with temperature. They suggest an equation of the form (DG 53),

$$S_t(\max) = AT^n(\kappa - \lambda) \dots\dots\dots (2.19)$$

where A , κ and n are constants for a particular fuel and λ is the mole fraction of oxygen in the mixture. Heimeel and Weast (HW 57), also using a burner method with burning velocities determined from schlieren photographs by a total area method, propose an equation which they claim fits the experimental results better. This is of the form

$$S_t(\max) = B + CT^m \dots\dots\dots (2.20)$$

where B , C and m are constants for a particular mixture. The results of these two equations for different fuels are shown in Fig 2.12.

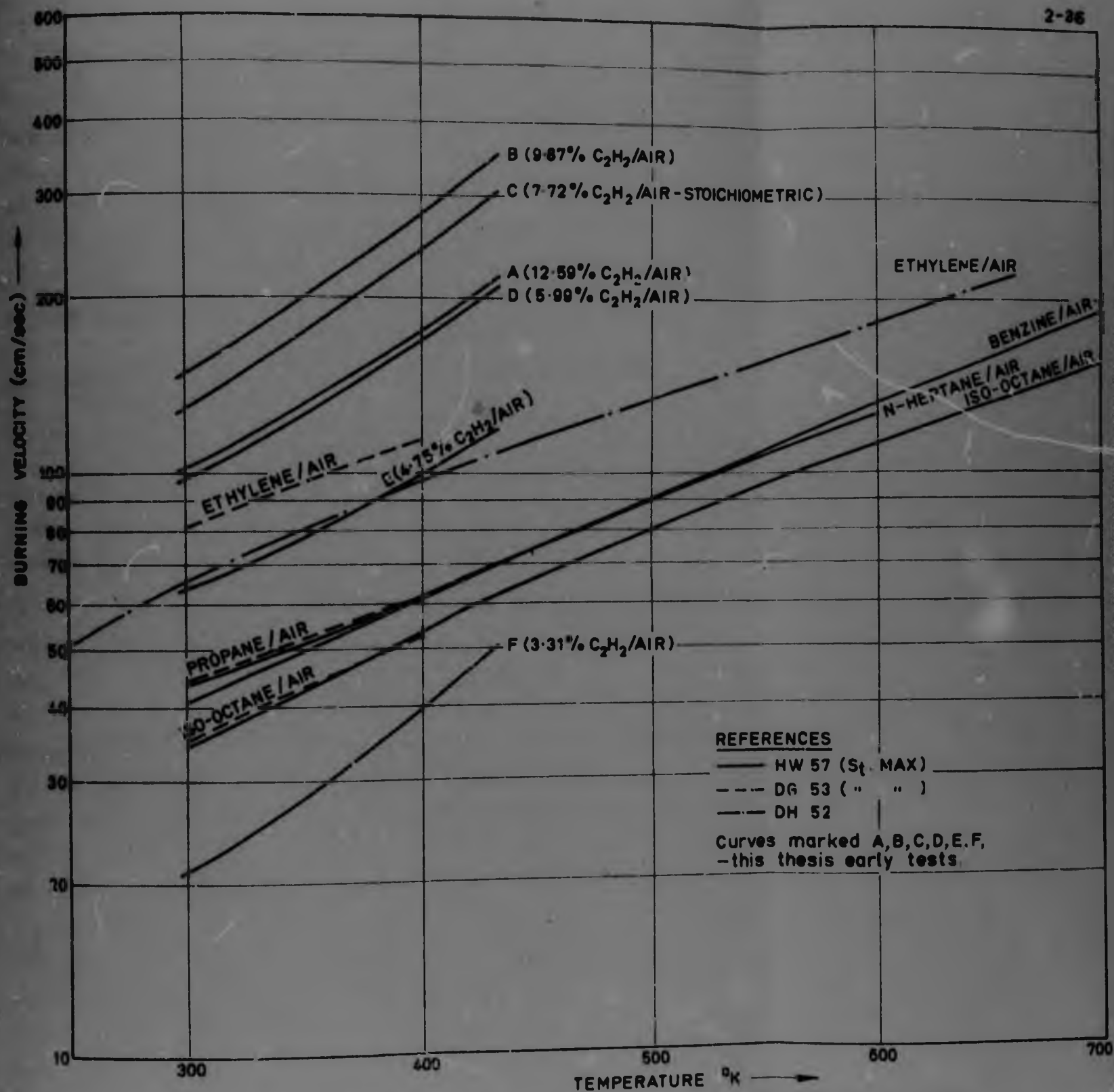


FIG. 2-12 EFFECT OF TEMPERATURE ON LAMINAR BURNING VELOCITY

This figure also includes some of the results of tests to be described later in this thesis (Chapter 5). These plots are based on the assumption that the C_2H_2 /air mixtures tested are not pressure dependent. Each of the curves A through F are for different mixture strengths ranging from rich to lean, C being the stoichiometric. In general these results confirm the form of the above two empirical equations. However more work is clearly required to unambiguously settle the separate effects of temperature and pressure suggested by these tests.

2.5.2 Pressure Dependence

Considerably more work has been done on the effects of pressure than on temperature. No doubt this is to some extent due to the greater ease with which pressures can be varied and controlled in many of the methods used.

The earlier results on pressure dependence were the subject of much controversy, particularly as regards fuel/air mixtures. Thus Culshaw and Garside (CG 49) found no change for ethylene/air between 30 and 70 cm Hg. Garner *et al* (GL 51a) observed an increase with lower pressures for benzene/air over the range 40 to 76 cm. Linnett and co-workers (WL 49, PL 51) found conflicting results with soap bubble and burner methods for acetylene/air mixtures; the soap bubble method, which was considered more reliable, giving practically constant results. Badin, Stuart and Pease (BS 49) found considerable increases in burning velocity for hydrocarbon/air flames at lower pressures over the range 18 to 76 cm Hg. Gaydon and Wolfhard (GW 50) found a slight increase at lower pressures for acetylene/air flames, rising to a maximum at about 20 cm Hg before decreasing again. Others who have found a negative pressure dependence are Ubbelohde and Koelliker (UK 16) using a burner method between 0.5 and 2 atmospheres,

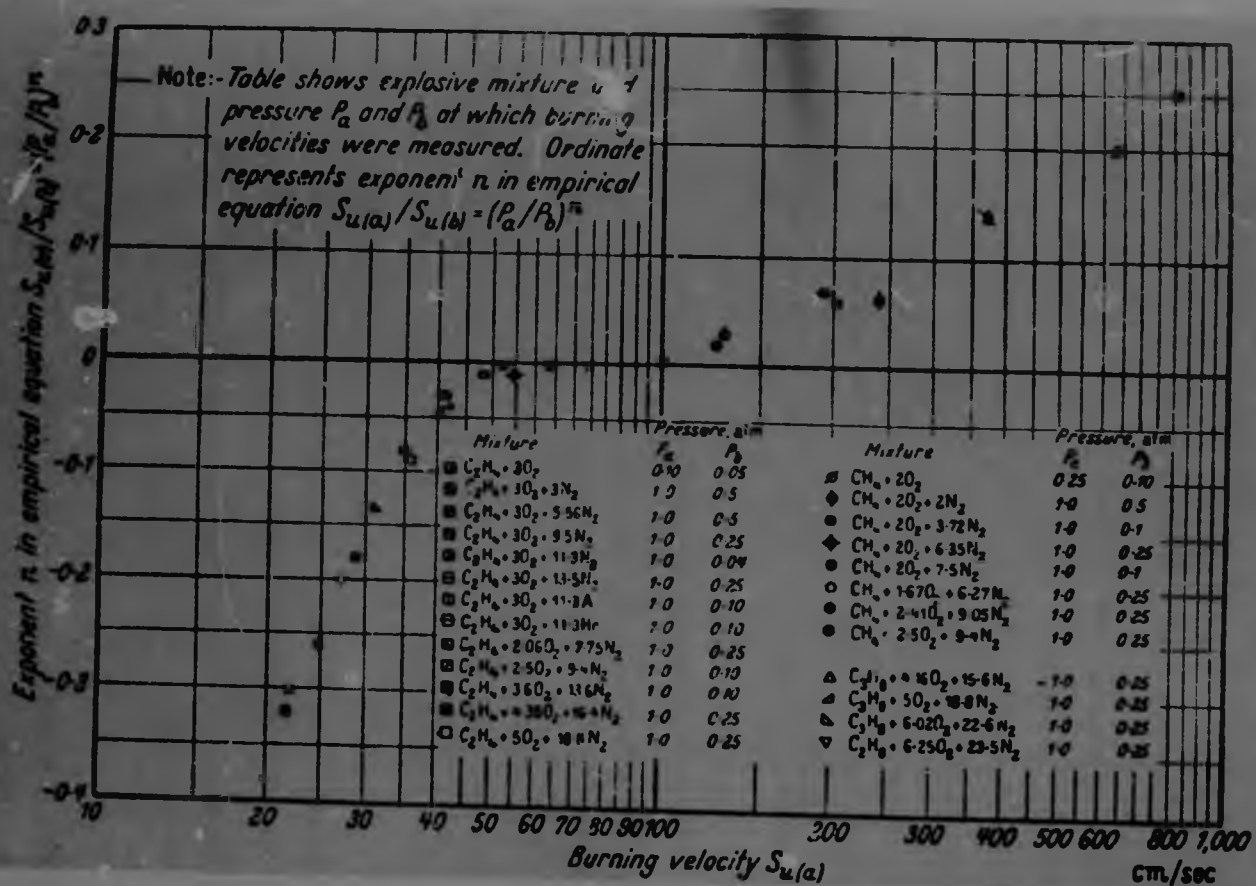


Fig 2.13 Pressure exponent of burning velocity (Le 54)

and Egerton and co-workers (ES 53, ET 52) using the flat flame method at 20 and 50 cm Hg.

Kolodtzev and Khitrin (KK 36) used a soap bubble method to study CO/O_2 flames up to 40 atmospheres and found no change with pressure. Wolfhard (Wo 43) using the total area method on acetylene/oxygen flames between 1.0 and 76 cm Hg also found no change.

An extensive study by Manton, using a constant volume vessel, at the U.S. Bureau of Mines (cited by Lewis, Le 54) has provided some extremely interesting results (see Fig 2.13). These were obtained over the range 1.0 to 0.04 atmospheres using a large variety of fuels and fuel mixtures, and show that pressure dependence is a function of the absolute value of burning velocity. Thus at velocities below about 50 cm/s an increase in pressure reduces S_t , whilst above about 100 cm/s increasing pressure has the opposite effect.

These findings have been confirmed by more recent work at both higher and lower pressures, obtained by various methods. Thus Egerton and Lefebvre (EL 54) used a refined tube method with schlieren photography; Gilbert (Gi 57) used a cylindrical burner and wire shadow technique (sub-atmospheric pressures only); Strauss and Edse (SE 59) used a constant pressure rubber balloon method (soap bubble); and Graiff (Gr 59) and Grumer et al (GC 61) used a constant volume vessel. All these results have been converted to the same units and replotted on Fig 2.14, on the assumption that the unburnt gas temperatures were the same throughout. This figure show that there is at least qualitative if not quantitative agreement between these various results and in general appear to support Mantons findings (Fig 2.13).

However the suggestion that the pressure dependence of burning velocity is connected with the absolute value of S_t would be far more convincingly demonstrated if the mixture composition and pressure for a particular

fuel could be held constant while the initial burning velocity was altered to bring it above 100 cm/s or below 50 cm/s. Evidently this could be done by varying the initial temperature of the mixture. Thus for a stoichiometric ethylene/air mixture for example (Fig 2.12) varying the initial temperature over the range 250 to 600°K should apparently vary the initial burning velocity from about 50 to 180 cm/s.

Alternatively if the composition can be shown not to have too large an effect on the nature of the pressure dependence, then clearly this could provide a large change in S_t with only slight differences in the percentage of the fuel present, viz. 150 cm/s with 9.87 percent C_2H_2 down to 22 cm/s with 3.31 per cent C_2H_2 in air at 300°K (Tests B and F in Fig 2.10).

However the use of a constant volume method over the whole or even part of the full process, rather than for the initial stages only as has previously been done, can afford a much more elegant solution to this problem as will be illustrated in Section 2.6.1.

2.5.3 Influence of Fuel Structure and Mixture Composition

Some not very successful attempts have been made to relate burning velocity with the structure of hydrocarbon fuels. One of these (HP 51) is based on the number and types of chemical bond in the fuel; another on the diffusion rates of OH, H and O in the equilibrium products (Si 51).

Possibly the best results have been obtained by comparing burning velocities with the concentration of hydrogen atoms in the flame (Fig 2.15) (GW 60). Evidently for carbon monoxide and hydrogen flames a definite correlation exists. However even though there is clearly some correlation for hydrocarbons there seems little doubt that this represents an over-simplification, since other atoms and radicals must evidently also contribute.

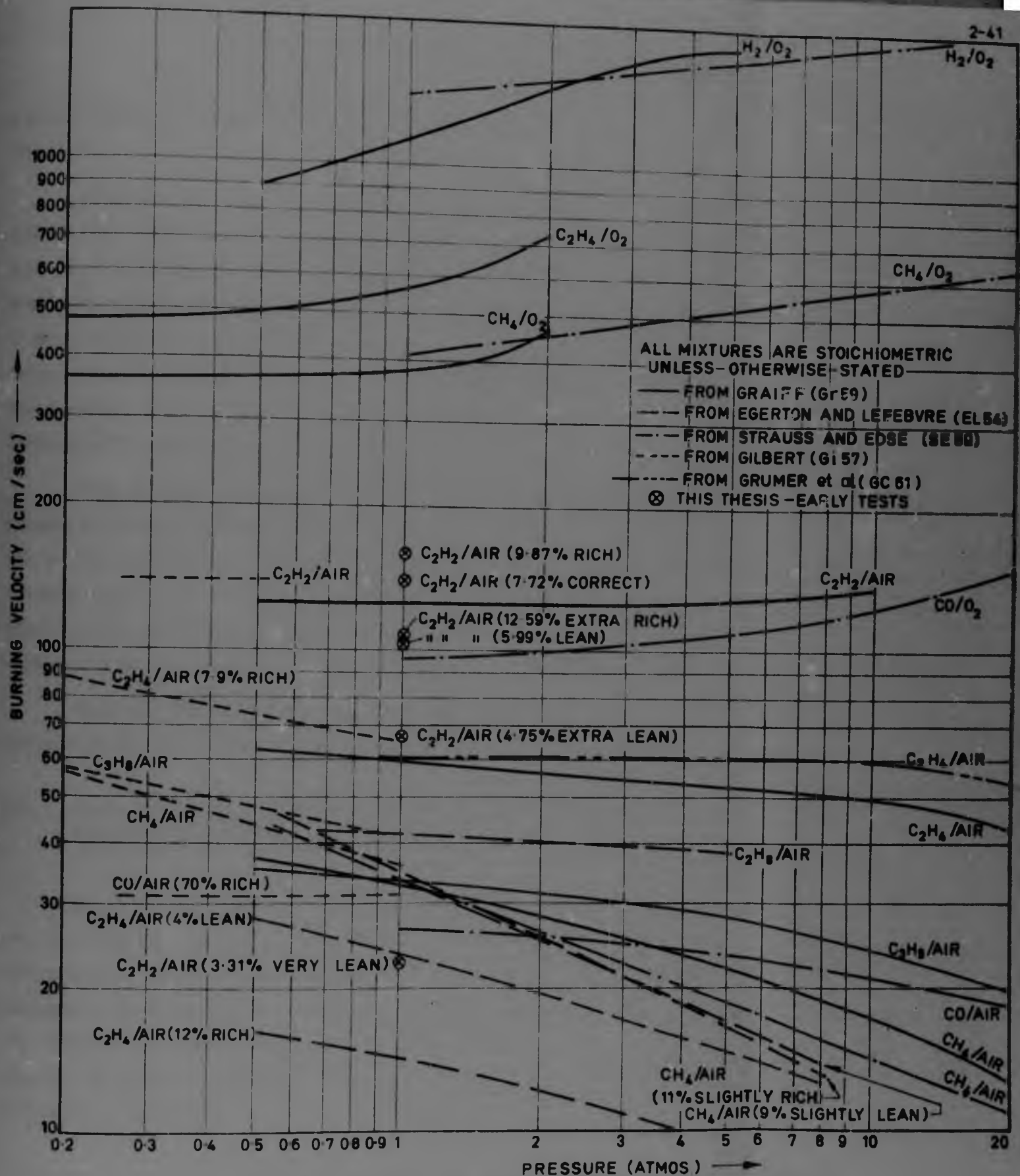


FIG 2-14 EFFECT OF PRESSURE ON BURNING VELOCITY

(Notice particularly that acetylene mixtures fall on the hydrogen curve - Fig 2.15) .

Consider next the effects of mixture composition. It is well established that burning velocities vary with mixture strength (Fig 2.16 and 2.17), maximum velocity generally occurring on the fuel rich side. This position of the maximum is also affected by dilution. Thus in hydrogen mixtures it moves towards richer mixtures with increasing dilution (Fig 2.16), whereas the opposite effect is observed with acetylene flames (Fig 2.17). Evidently the pressure and temperature dependence of burning velocity will also be influenced by mixture strength (Jo 47, Gi 57).

The introduction of certain additives can also exert considerable influence on burning velocity. Thus dry mixtures of CO/O_2 burn slowly if at all, yet the addition of very small traces of water vapour can increase the burning velocity by a factor of seven or more (GW 60). Other additives reduce burning velocity - notably the organic halides - whilst there is some evidence that metallic particles may assist flame propagation (GW 60).

From the above it is evident that considerable care has to be exercised in preparing mixtures for study, as well as in reporting findings.

2.6 EVALUATION OF METHODS FOR DETERMINING LAMINAR BURNING VELOCITY

Since burning velocity is known to be dependent on the temperature, pressure and composition of the unburnt mixture, any experiments for its determination should ensure accurate control or measurement of these parameters. Further, the flame front should ideally be plane and well removed from any surface which could cause heating, quenching or catalytic effects. If a plane surface is unattainable then the flame front should at least have a large radius of curvature compared with the anticipated flame

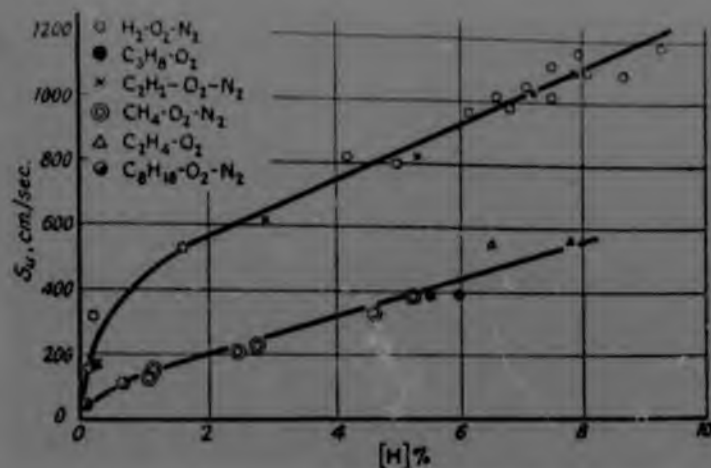


Fig 2.15 Burning velocity against concentration of H atoms (GW 53).

Fig 2.16-Hydrogen/oxygen/nitrogen

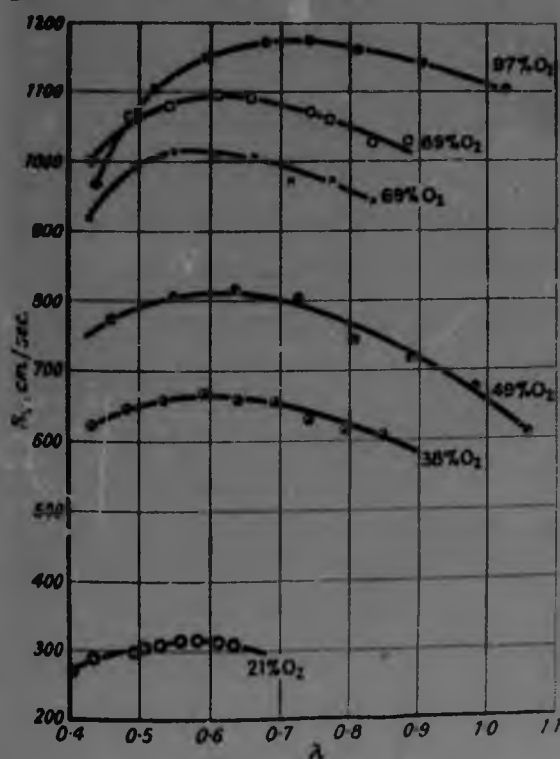
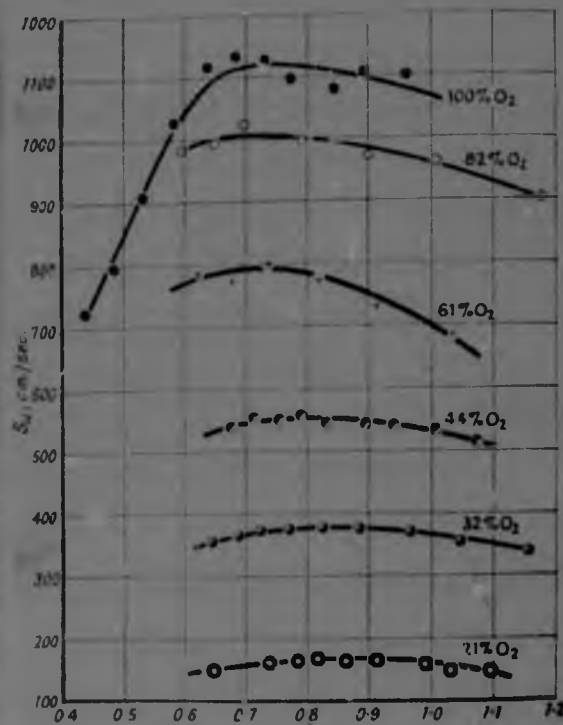


Fig 2.17-Acetylene/oxygen/nitrogen



Variation of burning velocity with mixture strength (GW 53)

front thickness. Also the system should preferably be one-dimensional so that it is amenable to rigorous mathematical description.

On the experimental side the method should, (i) be as economical as possible on fuel, (ii) permit of wide variations in initial temperature, pressure and composition, (iii) yield reproducible results, and (iv) be simple to use.

2.6.1 Comparison of Various Methods

Of the five essentially different methods which have been described in Section 2.4.3, the burner and tube methods appear to be inherently unreliable. Burner methods are cheap, versatile and superficially easy to use, but yield large differences in results under apparently similar conditions. Tube methods, even when considerable care is exercised to produce smooth combustion, and the flame front area is carefully measured, at best lead to some sort of average value of burning velocity.

The flat flame method although attractive, is restricted to slow flames and is hence mainly of value in flame structure studies. However at low velocities it is probably preferable to either the soap bubble or constant volume methods, both of which are subject to interpretational difficulties due to buoyancy and heat loss effects. On the other hand, there can be little doubt that these spherical flame methods are the most reliable at intermediate velocities; also provided an adequate understanding of the phenomena associated with high velocity flames can be obtained, they should be possible of development for this range as well.

Of the soap bubble and constant volume methods, the latter appears to be more powerful since, if its full potentialities are taken advantage of, it can yield considerably more information from a single experiment than can the soap bubble method. Also, to quote Lewis (Le 54) '....the method is

self-corroborating, and since the experimental precision is very high, it must be regarded as a precision method and at the same time a standard method against which the validity of other methods may be tested.' Its main disadvantages are that the associated equipment is expensive and the calculations involved tedious. Also because of a lack of understanding of the processes involved and consequently of the adequacy of the resulting equations, research workers in general have been somewhat hesitant to adopt the method. However it possesses so many obvious advantages (some of which are outlined below) that it would appear to warrant closer investigation.

2.6.2 The Constant Volume Method

It is only proposed here to give some indication of the scope of this method. Detailed consideration of the theory involved will be deferred until later.

If it is assumed that the unburnt gas in a constant volume vessel is compressed adiabatically, then for the case of (say) a stoichiometric acetylene/air mixture initially at 300°K and 1.0 atmosphere, the temperature-pressure variations of the unburnt gas would be as shown in Fig 2.18 - curve OA. (For such a mixture observed values of $P_{\text{max}}/P_{\text{initial}} \approx 8.35$). The resulting burning velocity would thus be expected to vary throughout such an experiment as a function of both temperature and pressure. Clearly the separate effects of these variables cannot be isolated from the results of a single experiment. However by varying the initial pressure over the range (say) 1 to 3 atmospheres the whole region between curves OA and BC can be studied. Similarly by changing the initial temperature to say 400°K and varying the initial pressure over the same range of 1 to 3 atmospheres the region FEHG can be studied. Thus with a small number of tests at different

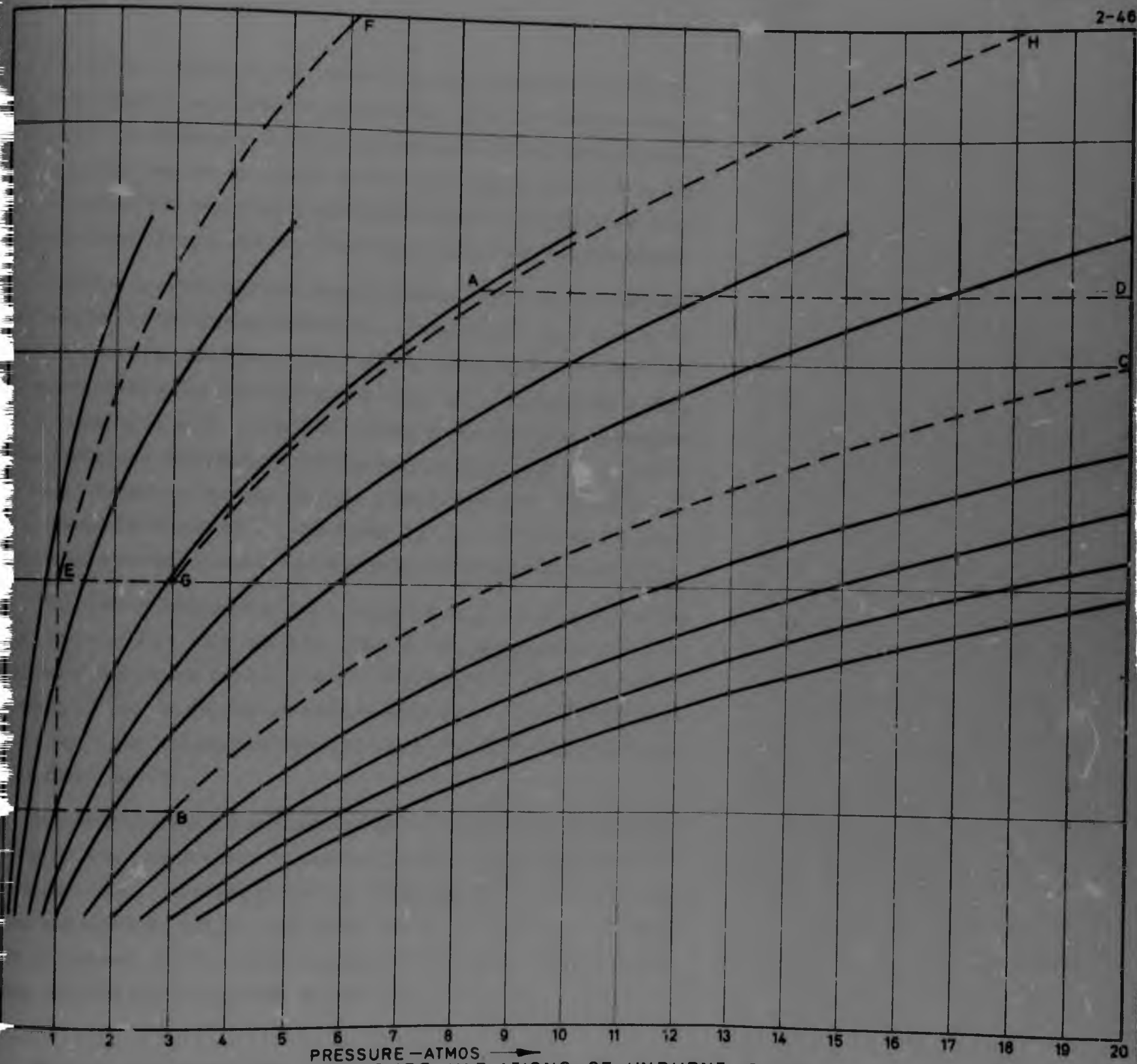


FIG.2.18 TEMPERATURE—PRESSURE VARIATIONS OF UNBURNT GASES

initial conditions a wide range of values of S_t can be obtained provided the testing procedure is accurate and reproducible. Even if reliable information can only be obtained from such tests over half the available pressure rise (due to heat loss or vibrations as the flame approaches close to the wall) the method can still yield a considerable amount of information from a limited number of tests - far more than is possible by any other technique.

Consider now the problem posed in Section 2.5.2, that is, of obtaining information on the burning velocity of a mixture of given composition at various values of the absolute burning velocity. An example of a typical set of six hypothetical temperature-pressure curves for a stoichiometric ethylene/air mixture is given in Fig 2.19. These are based on the assumption that the results are reliable up to half the total pressure rise ($P_e/P_o \approx 9$ in this case). Values of burning velocity, interpolated from Figs 2.12 and 2.14, (curves DH 52 and Gr 59) have been filled in next to each curve. (These would normally of course be obtained from the experimental results).

The type of information which would normally result from such a test is shown in Figs 2.20 and 2.21. Thus if any anomalous pressure or temperature dependence occurs it would be qualitatively determined from the results of such tests. (No anomalous behaviour is evident in Figs 2.20 and 2.21 since the results have been extrapolated from low initial burning velocity data - Gr 59).

Similar results to those illustrated could be obtained by maintaining the initial mixture temperature constant but by varying the initial pressure over a wider range. However at very low initial pressures the results may then be untrustworthy due to thick flame fronts. These results could of course be ignored, but the maximum unburnt gas temperatures at which readings could be taken would then be lower than that shown.

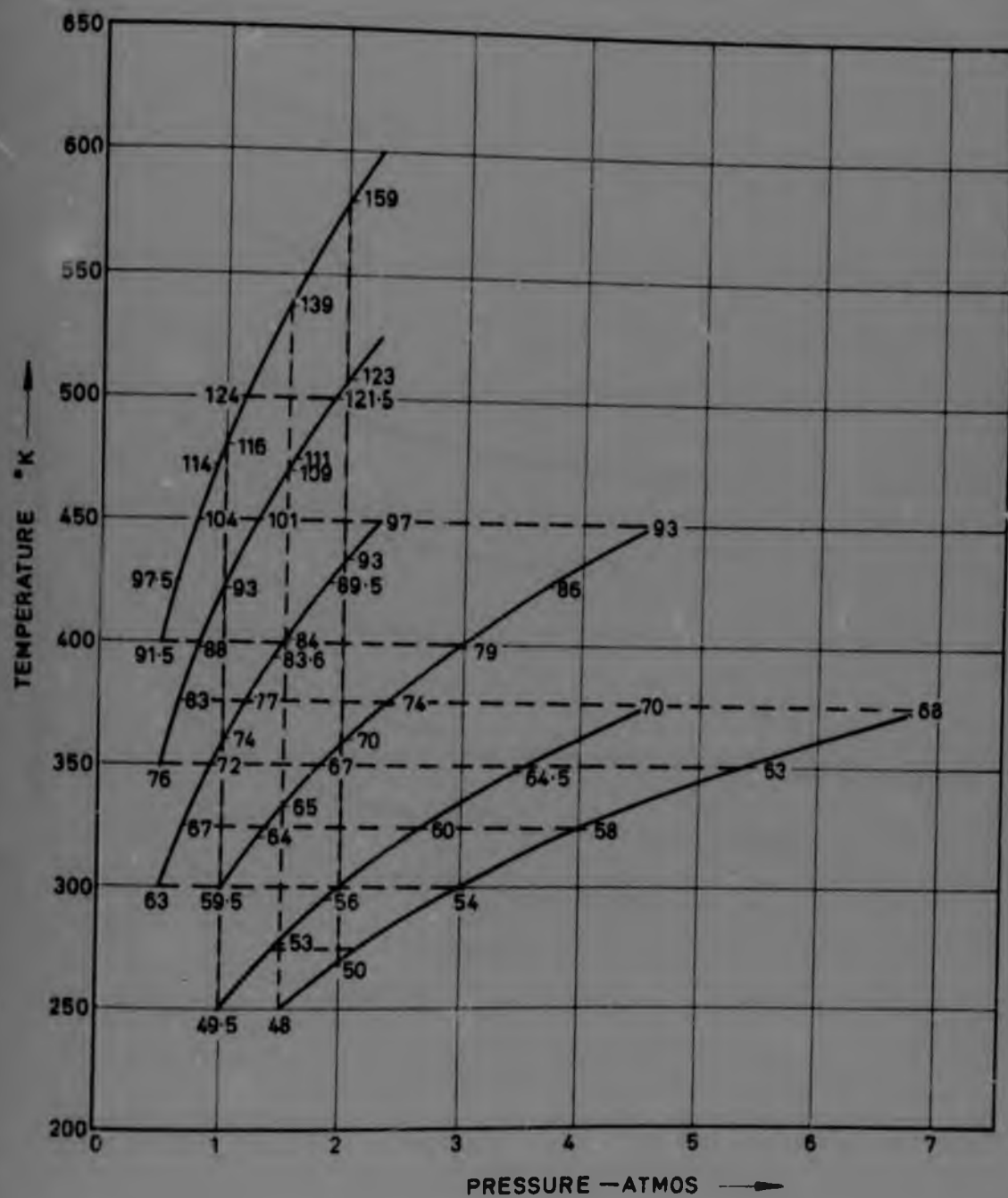


FIG 2-19

HYPOTHETICAL TEMPERATURE-PRESSURE CURVES FOR
A STOICHIOMETRIC ETHYLENE/AIR MIXTURE IN A
CONSTANT VOLUME VESSEL

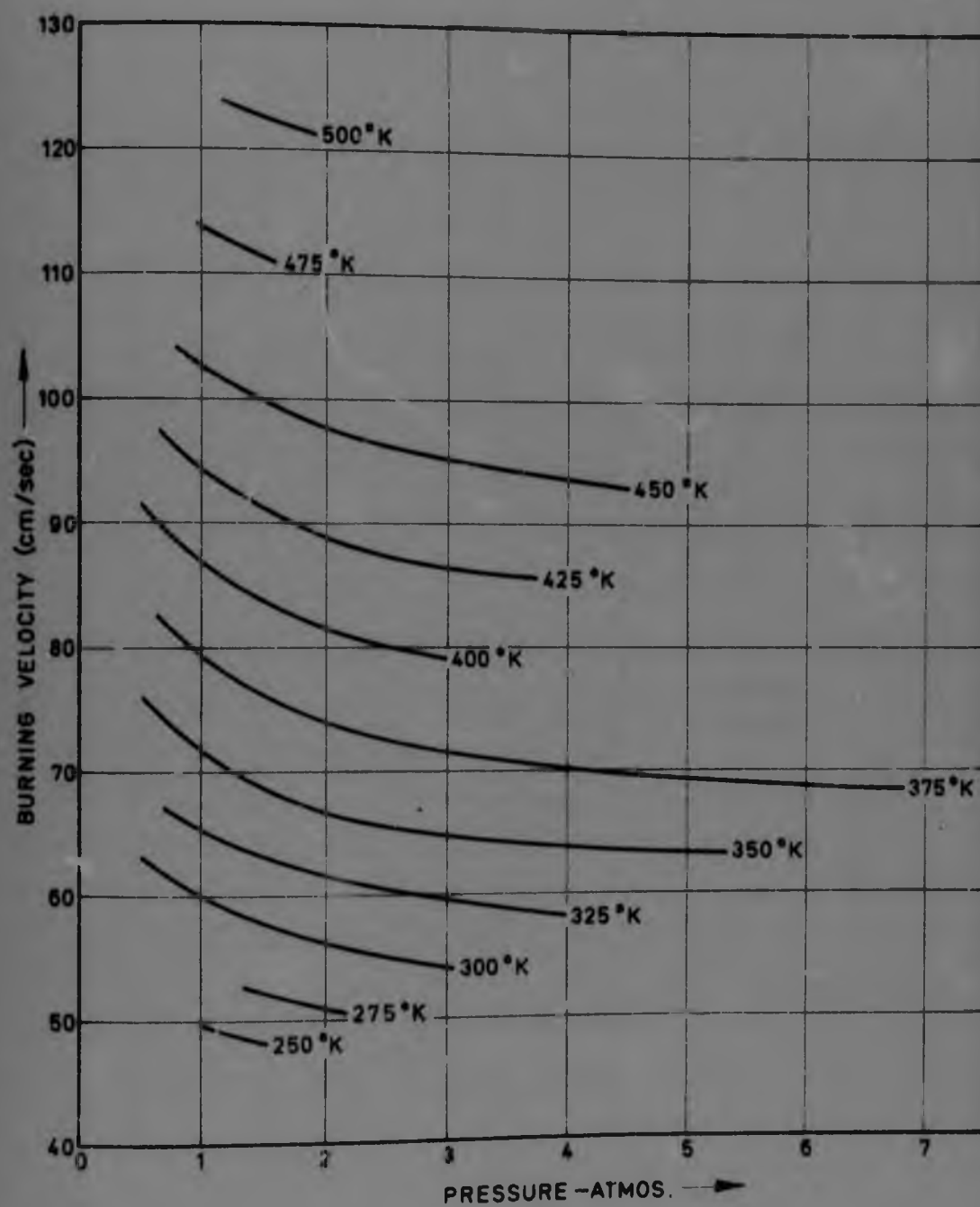


FIG. 2 20
HYPOTHETICAL BURNING VELOCITY-PRESSURE
CURVES

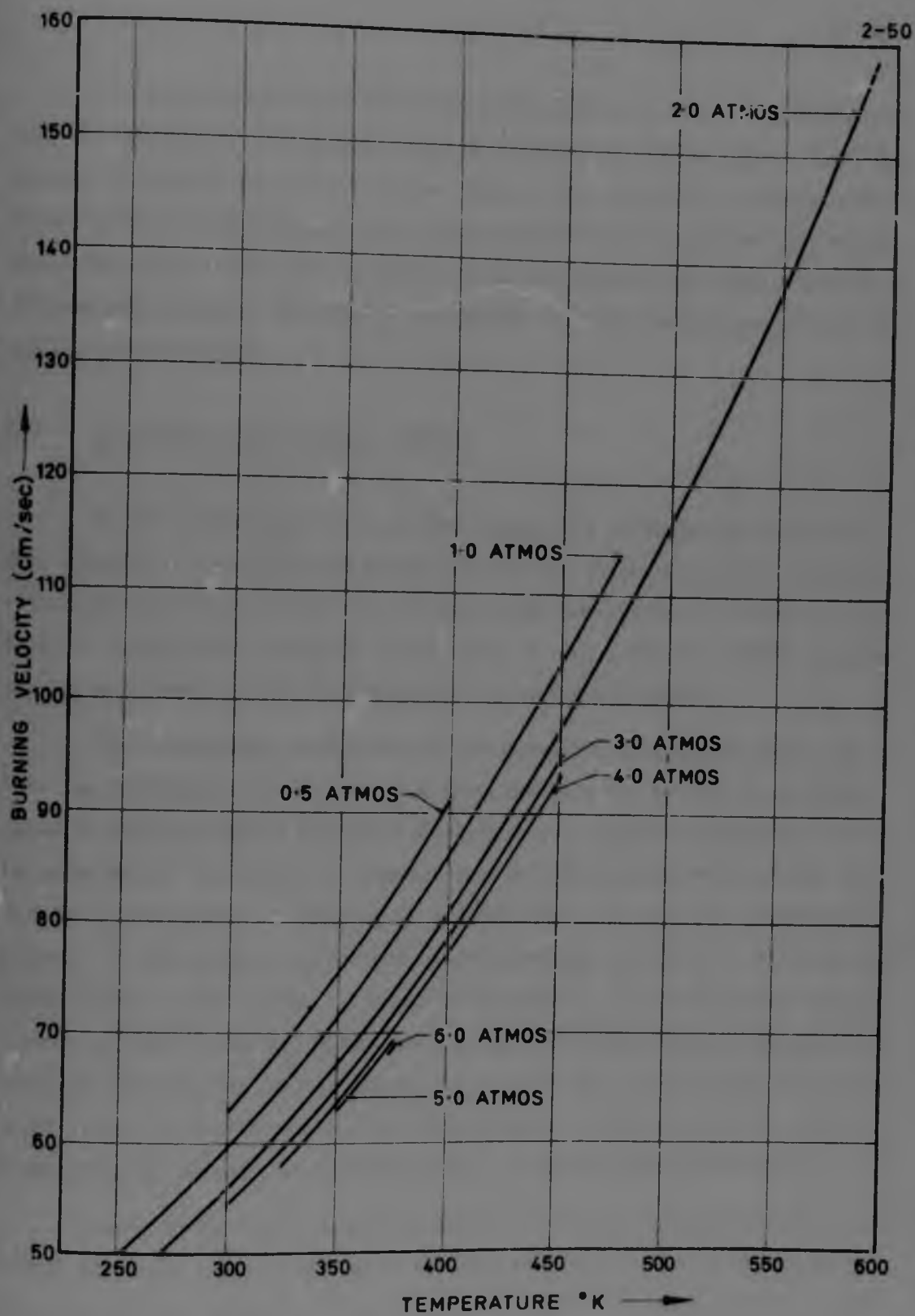


FIG 2-21
HYPOTHETICAL BURNING VELOCITY-TEMPERATURE
CURVES

From these hypothetical results (Figs 2.20 and 2.21), it would appear that the amount of information that it is possible to obtain from a limited number of tests in a constant volume vessel is considerable, even when interpretation is restricted to half the available maximum pressure rise. For these and other reasons it is felt that of all the methods previously used for determining burning velocities, the constant volume method seems to hold out the most promise.

2.7 SUMMARY AND CONCLUSIONS

In the earlier sections of this chapter the methodology of combustion research was discussed and the conclusion reached that experimental investigations from the physical rather than the chemical viewpoint are likely to prove more tractable at this stage. In any event the results of such studies are required for confirmation of theoretical findings.

The information necessary for the complete description of the ignition and propagation of flames was then listed with the object of finding some basic parameters in terms of which more complex phenomena could be understood. In essence it appears that the information required for the practical utilization of flames in engineering falls into two categories, namely (i) the ignition properties of combustible mixtures, and (ii) their flame speed - both under all types of condition. A research programme embracing both these areas has been under way in the Department of Mechanical Engineering at this University (under the writers direction) for some years. In this thesis it is only proposed to treat one aspect of the second category, namely the determination of laminar burning velocity.

Basic to the whole subject of flames is an understanding of the internal structure and propagation of pre-mixed laminar flames. Further, an intrinsic physical property of such flames is their burning velocity, which

appears to bear directly on such complex phenomena as minimum ignition energy, isotropicity, inflammability limits and turbulent flame speed. However the burning velocity of laminar flames apparently has no direct bearing on topics such as ignition temperature and delay, although, for example, it is generally conceded that it is the comparative value of the above and turbulent flame speed which determines the onset of knock in spark-ignition engines.

Necessary to the measurement of the macroscopic property of burning velocity is an understanding of the microscopic structure of the flame front. The data required for the complete description of the flame front and the various methods used to obtain these have been discussed in relation to the location and measurement of the flame front position in burning velocity measurements. Evidently the flame front thickness is a function of pressure so that for high pressure tests no significant error should arise by assuming that the start of this front coincides with the edge of the luminous zone. However for low pressure work more refined means of locating its position are necessary. In any event it would be as well always to use two independent means of locating flame front position so as to provide a cross-check.

Five different methods have been used to date to measure the burning velocity of pre-mixed laminar flames. Of these the flat flame method seems to be the most satisfactory for low velocity flames, whilst the constant volume method appears to hold out the greatest promise for both intermediate and high velocity flames. However the equations involved require extension so that greater advantage can be taken of its potentialities.

Conclusions

1. Data on the flame front structure and laminar burning velocity of homogeneous combustible mixtures, under various conditions of temperature, pressure and composition, are basic to any combustion research programme.
2. Due to the specialised technique involved and the cost of the associated equipment, flame structure studies must for the present be considered outside the scope of this investigation.
3. Of the five main methods which have been used to determine laminar burning velocity, the spherical constant volume vessel technique appears to be potentially the most accurate and versatile.
4. To date it has only been used to measure burning velocities during the early stages of the combustion process when the pressure rise is small. This unnecessarily restricts its value, virtually reducing it to a constant pressure technique.
5. Before the method can be used to determine burning velocities at higher pressure ratios the theory involved must be extended.

CHAPTER 3

THE SPHERICAL CONSTANT VOLUME BOMB METHOD

REVIEW OF PREVIOUS WORK

The spherical vessel, constant volume combustion method for determining burning velocities is generally acknowledged as being potentially one of the most versatile and accurate: versatile, because the results of a single test can yield values of burning velocity over a range of temperatures and pressures; and accurate, because the combustion wave is spherical and so amenable to a rigorous mathematical description.

There are however two main problems associated with the method. Firstly, burning velocities cannot be measured directly. Thus an understanding of the phenomenon is necessary if satisfactory equations are to be derived from which the burning velocity can be calculated. Secondly, it necessitates accurate measurements, in particular of the propagation of the flame and of the pressure rise.

Some theoretical and experimental work has been done over recent years towards improving the accuracy of the method. On the theoretical side this has resulted in a plethora of equations, in the main applicable only to the early stages of combustion, during which the pressure and temperature of the unburnt gas has not changed significantly. This has seriously restricted the value of the method, virtually relegating it to the status of a constant pressure technique, albeit with several advantages over the soap bubble method.

The analysis involved is inevitably more complicated than in other techniques because of the variations in pressure and temperature during the process, which lead to changes in burning velocity. In addition the movement of both the unburnt and burnt gas is generally more complicated than in other methods. (See Section 4.4).

Before proceeding to a review of the literature on this subject it will be as well to consider the various phenomena associated with the propagation of a flame in a closed spherical vessel.

3.1 CONSTANT VOLUME COMBUSTION

Consider a homogeneous combustible gas mixture contained in a closed spherical vessel and ignited at the centre (Fig 3.1). If the flame propagates isotropically then at any time t after ignition the flame front will be spherical and have a radius r_b . Imagine an element of gas which before ignition was at a radius r_x . After ignition, and as a result of the expansion of the hot gases behind the flame front, this element will be driven outwards. However, because the system is closed, immediately it is overtaken by the flame it will change direction and move back towards the centre. Ideally if there are no temperature gradients in either the burnt or unburnt gas, and no vibrations or inertia effects, all elements will come back to their original positions when the flame eventually reaches the wall of the vessel.

In practice even if there is no uneven cooling of the unburnt gas, and no oscillations occur, a temperature gradient is always set up in the burnt gas (LV 34a, LV 51); that portion of the gas which burns first being hotter than that which burns last. Thus an element which started off at r_x finally ends up at some new position $r_x + \Delta r_x$.

For the purpose of analysis which is to follow it is desirable to determine the mean temperature of the burnt gas at any instant. Because of the gas movement described above, and other reasons, theoretical evaluation of this mean proves difficult. (Experimental determination of the mean burnt gas temperature appears to present no serious problem.) However it

seems possible to establish a reasonably good estimate. In order to do this though, it is necessary to make certain assumptions. Many of these are in any case required for the development of burning velocity equations for the constant volume method.

3.1.1 Usual Assumptions Made

The combustion process in a closed vessel involves compression of the unburnt gas ahead of the flame front, expansion within this front, and compression of the burnt gas behind it. Flock *et al* (FM 40) have listed the assumption which they made and justified them by the fact that they were consistent with physical observations of the behaviour of the gas mixture during combustion. Lewis and von Elbe (LV 51 p. 448) added two more, being satisfied that the errors involved in Flocks are negligible. These assumptions are :

- (1) At any instant during combustion the pressure is uniform throughout the whole vessel, i.e. any effects due to the finite velocity of sound are ignored.
- (2) The whole process is adiabatic, i.e. no heat is lost to the walls during combustion.
- (3) The temperature of the unburnt gas is related to the pressure by the usual gas law, a mean value for the ratio of heat capacities being used.
- (4) The flame propagates isotropically, i.e. in this case it remains spherical throughout the process.
- (5) The flame front is a surface of discontinuity across which the change from the unburnt to the burnt state takes place.
- (6) The total mass of gas and the number of moles present remain constant.

Lewis and von Elbe made the following additional assumptions, which are tantamount to specifying a functional relation between pressure and flame front radius. Only one of these variables need then be observed in order to calculate burning velocities.

- (7) The temperature of the burnt gas is related to the pressure by the usual gas law, the ratio of heat capacities used being the mean value between the beginning and end of combustion.
- (8) The mass fraction (n) of burnt gas is related to the pressure (P) at any instant by the equation

$$n = (P - P_0) / (P'_e - P_0)$$

where P_0 is the initial pressure of the mixture and P'_e is a fictitious maximum pressure at the end of the process.

It will be shown later that in any well designed experiment the majority of these assumptions can be dispensed with. Thus, for example;

- (i) the pressure need not be considered uniform throughout the vessel; suitable corrections for pressure gradients and the finite velocity of sound can be made when necessary.
- (ii) the instantaneous and mean densities and temperatures of both the burnt and unburnt gas can be measured directly.
- (iii) the total number of molecules need not be considered constant.
- (iv) the equilibrium temperature of the burnt gases can be determined from combustion charts, thus making allowance for dissociation and variable heat capacity.
- (v) more accurate equations can be derived for the mass fraction burnt.
- (vi) burning velocities can be measured directly, using a particle track method, with the minimum of assumptions.

For the purposes of our present discussion however let us accept the above assumptions.

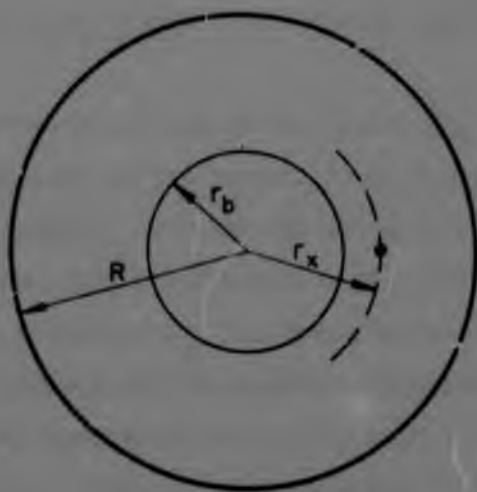


FIG 3-1 GAS MOVEMENT IN
SPHERICAL CONSTANT VOLUME
COMBUSTION

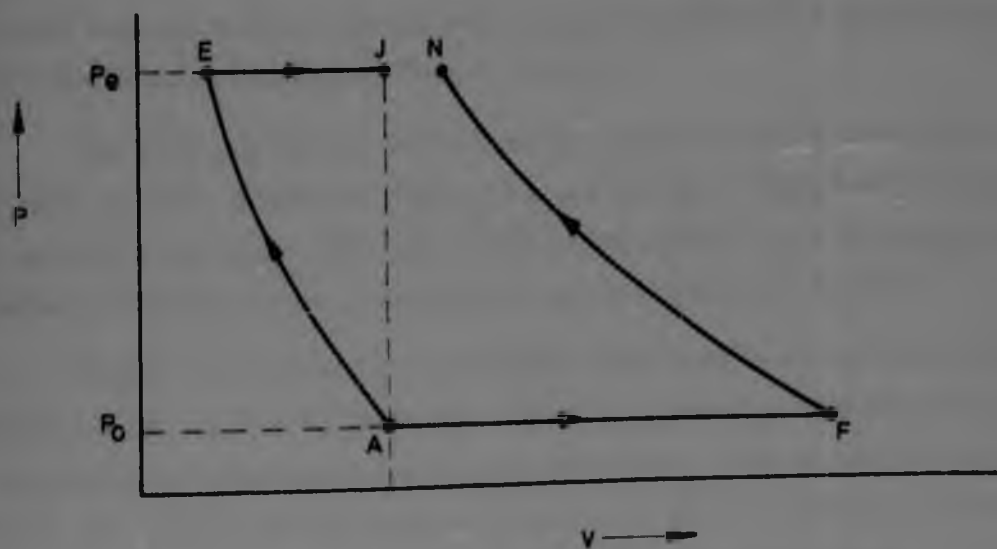


FIG 3-2 FIRST AND LAST GAS ELEMENTS
TO BURN - TEMPERATURE GRADIENT

3.1.2 Mean Temperature of Burnt Gas (OR 59, Ra 59)

Consider an element of gas at the centre of a spherical vessel. Immediately before ignition let the pressure and temperature throughout the whole system be P_0 and T_0 respectively (Point A Fig 3.2). After ignition the temperature of this element will rise to $T_b^0 (= T_F)$ while it expands at essentially constant pressure P_0 , thus doing work on its surroundings. Subsequently its temperature will be further increased due to adiabatic compression as the flame progresses beyond it, until at the end of the process it will have attained a value T_N corresponding to the pressure P_e at that instant. (See also Fig 3.3, path AFN). Evidently more work will be done on this element in recompressing it back to practically its initial volume than was delivered by it during expansion.

Consider next an element of gas adjacent to the wall of the vessel. This will be first compressed adiabatically from P_0 to P_e (A to E, Fig 3.2) and will then, on burning, expand back to approximately its original volume, thus clearly doing more work than it received.

The first part of the gas to burn thus gains energy at the expense of the last to burn. Evidently this must apply during the intermediate stages as well (see Fig 3.3). The net result is the setting up of a temperature gradient in the burnt gas. (First observed by Hopkinson - Ho 06).

Figure 3.3 shows the temperature-time history of the burnt gas at different radii in space. Here the curves (γ_b) and (γ_u) indicate adiabatic compression of burnt and unburnt gas respectively. Thus an element at radius r_0 (the spark radius) burns to temperature T_b^0 and is then compressed to T_N . Elements at radii r_1 , r_2 and r_3 are compressed as unburnt gas, then burned, and then compressed further as burnt gas to temperatures T_M , T_L and T_K respectively. The wall element is compressed as unburnt gas before burning at essentially constant pressure P_e . It is also worth noting

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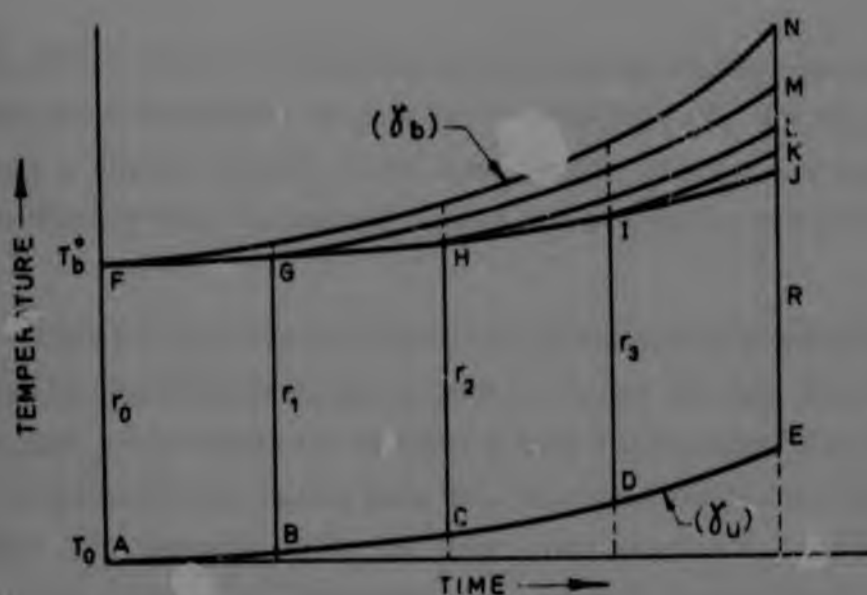


FIG. 3'3
TEMPERATURE-TIME PROFILES IN CONSTANT
VOLUME COMBUSTION

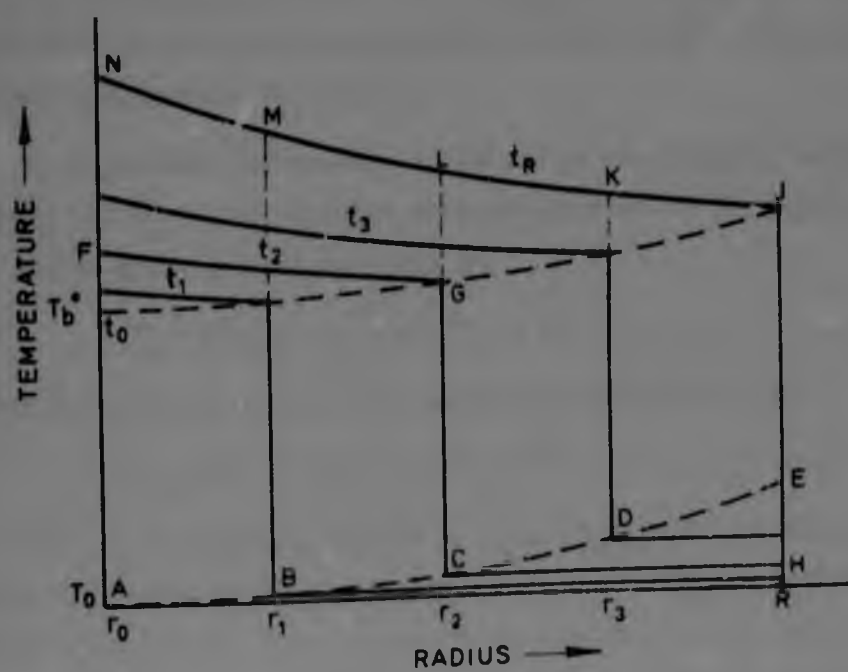


FIG 3-4
TEMPERATURE-RADIUS PROFILES IN CONSTANT
VOLUME COMBUSTION

that the temperature rise during burning decreases slightly with increase in unburnt gas temperature, so that $EJ < DI < CH < BG < AF$. The curve FGHLJ thus has a slightly smaller slope than ABCDE. Further, any heat loss of the unburnt gas near the wall will accentuate any such gradient in the burnt gas.

A family of curves of temperature versus radius at different times t can thus be plotted using points on the (γ_b) curves FN, GM, etc. (Fig 3.4). In this case t represents the interval of time that has elapsed from the instant of ignition to the instant when the flame front reaches the radius considered. For example, when the flame front reaches r_2 , a time t_2 has elapsed since ignition and the temperature gradient throughout the vessel is given by the curve FGCH.

The temperature of the burnt gas at the instant t_2 varies from radius r_0 to radius r_2 according to the curve FG. In particular, the curve NMLKJ gives the temperature distribution in the whole vessel at the instant the flame front reaches the wall.

If, in general, curves such as FG can be expressed as some function of radius, i.e. $T_b = T(r)$, then the mean temperature of the burnt gas at any time t will be given by (see Appendix A),

$$\bar{T}_b = (\bar{M}_b r_b^3 / 3) / \int_0^{r_b} (M_b / T_b) r^2 dr \dots \dots \dots (3. 1)$$

whilst at the end of the process the mean temperature will be,

$$\bar{T}_e = (\bar{M}_e R^3 / 3) / \int_0^R (M_b / T_b) r^2 dr \dots \dots \dots (3. 2)$$

Due to the interdependence of mass movement and burnt gas temperature, the exact functional relation between M_b / T_b and r is difficult to establish theoretically. (Apparently it is possible to determine the functional relation between ρ_b and r experimentally - see Section 4.4). However in deriving any burning velocity equations, errors from this cause can be

reduced by working in terms of the temperature ratio T_b/T_e (OR 59), or preferably in terms of the density ratio ρ_b/ρ_e (HP 62, RT 63).

3.2 REVIEW OF PREVIOUS WORK

This review will, as far as is possible, follow a chronological presentation of previous work.

3.2.1 Nagel, Flamm and Mache, and Ellis

Although Hopkinson (Ho 06) used the constant volume method for determining heat capacities at elevated temperatures, Nagel (Na 07) and Flamm and Mache (FM 17) appear to have been the first to derive equations relating the pressure at any instant to the volume of gas burnt. Thus these latter authors showed that (see LV 51, p.455; Jo 46, p.153):

$$1 - (v_i/V) = \frac{R_o T_o (P_e - P)}{P_o \left[R_o T_u (\gamma_b - \gamma_u) / (\gamma_u - 1) + (\gamma_b - 1)K \right]} \dots\dots\dots (3.3)$$

where K is a constant given by

$$K = (N_e/N_o) C_{vb} T_b^0 - C_{vu} T_o \dots\dots\dots (3.4)$$

Here (v_i/V) = n = mass fraction of total charge burnt

(N_e/N_o) = -ratio of moles after complete combustion to moles before ignition.

C_{vb} = average constant volume molal heat capacity of burnt gas between T_b^0 and T_b .

and C_{vu} = average constant volume molal heat capacity of unburnt mixture between T_o and T_u .

The remaining symbols have been defined previously.

The use of these equations thus makes possible the determination of burning velocity and temperature distribution in the burnt gas at any instant.

Ellis and Wheeler (EW 27, E1 28), with their classical photographs of combustion in a glass sphere, showed that, provided the spatial velocity was not too low, the flame propagates isotropically. Their photographs also show the re-illumination which takes place at the centre of the vessel after the flame has reached the wall, which Lewis and von Elbe (LV 51, p.451) have attributed to the existence of a temperature gradient.

3.2.2 Lewis and von Elbe

Using the Flamm and Mache expression (eqn 3.34) for mass fraction burnt, Lewis and von Elbe (LV 34) derived equations with which they determined the burning velocities of a range of ozone/oxygen mixtures from pressure-time records of the process. These equations are (see also LV51):

$$S_t = (r_i/r_b)^2 (T_u/T_o) (P_o/P) (dr_i/dt) \dots\dots\dots (3.5)$$

where r_i is the radius which the burnt gas would occupy at conditions before ignition, and is given by

$$r_i = R(v_i/V)^{1/3} \dots\dots\dots (3.6)$$

$$\text{and } r_b = R \left[1 - (P_o/P)(T_u/T_o) \{ 1 - (v_i/V) \} \right]^{1/3} \dots\dots (3.7)$$

These authors subsequently simplified the Flamm and Mache expression (eqn 3.3) by restricting it to the earlier stages of combustion where the pressure rise is small. Thus by setting $T_u = T_o$ in eqn (3.3) they showed that the mass fraction burnt could be expressed as

$$n = (P - P_o)/(P'_e - P_o) \dots\dots\dots (3.8)$$

Using this equation the burning velocity was determined from

$$S_t = (R^3/3r_b^2)(\rho_o/\rho_u)(dn/dt) \dots\dots\dots (3.9)$$

where r_b is given by eqn (3.7) with (v_i/V) replaced by n from eqn (3.8). (Clearly, using eqn 3.9, S_t is indeterminate at the beginning of the process).

As a check on the validity of their assumptions they compared values of r_b calculated from eqn (3.7) with observed values (MV 53). However in order to do this they used a thermodynamically calculated maximum pressure P_e' rather than the observed value P_e . The agreement which they found for carbon monoxide/oxygen mixtures was excellent. Whether such good results would be obtained with hydrocarbon/air mixtures seems doubtful (Li 53). (See Section 5.4).

3.2.3 Fiock et al

At about the same time as Lewis and von Elbe were engaged on this work a team, headed by E.F. Fiock, was also studying the movement of flames in closed spherical vessels. Thus in 1935 Fiock and King (FK 35), using a pyrex glass vessel, measured the spatial velocities of stoichiometric carbon monoxide/oxygen mixtures containing various proportions of water vapour. They used a drum camera, similar to that used by Stevens (St 23), to record the movement of the flame.

Fiock and Marvin (FM 37) extended this early work to the determination of burning velocities. They used a spherical stainless steel vessel fitted with slit windows through which streak photographs of the flame were obtained. In addition six pre-set balanced diaphragm indicators were used for obtaining a pressure-time record. With this apparatus they once again studied carbon monoxide oxygen mixtures containing various amounts of water vapour.

In this paper they derived two forms of burning velocity equation.

These are:

$$S_u = S_s - \left[(R^3 - r_b^3) / (3r_b^2 \gamma_u P) \right] (dP/dt) \dots\dots\dots (3.10)$$

and

$$S_b = (1/E) \left[S_s + (r_b / 3\gamma_b P) (dP/dt) \right] \dots\dots\dots (3.11)$$

The expansion ratio E being defined as the ratio of the volume of burnt gas to the volume of the same mass of unburnt gas both at pressure P (FM 40). It is thus given by (see Appendix B).

$$E = r_b^3 / \left[R^3 (\rho_o / \rho_u) - (R^3 - r_b^3) \right] \dots\dots\dots (3.12)$$

$$\text{where } (\rho_o / \rho_u) = (P_o / P)^{1/\gamma_u} \dots\dots\dots (3.13)$$

Equation (3.10) is based on the properties of the unburnt gas, whilst (3.11) involves in addition the burnt gas properties. Since ideally these two equations should yield the same results we can set $S_b = S_u$ and eliminate $(1/P) (dP/dt)$ to give

$$S_t = \left[(1 + X) / (E + X) \right] \cdot S_s \dots\dots\dots (3.14)$$

$$\text{where } X = \left[r_b^3 / (R^3 - r_b^3) \right] (\gamma_u / \gamma_b) \dots\dots\dots (3.15)$$

This equation has the advantage of requiring differentiation of r_b only. Evidently for constant pressure combustion, since R is infinite and hence $X = 0$, $S_b^o = S_s^o / E_o$ - as is to be expected. (Note however that E_o may then not be determined from eqn 3.12. Equation B-2, Appendix B must then be used).

Fiock et al (FM 40), in 1940, published a comprehensive report on the constant volume method, in which they used the unburnt gas equation (3.10) to determine the burning velocities of a wide range of fuels. Results were calculated from both pressure- and flame radius-time records for all but the initial stages of the process, during which the flame occupied less than 25 per cent of the bomb radius and the pressure rise was negligible.

The unsatisfactory form of eqn (3.10), in that it magnifies observational errors, precluded their obtaining satisfactory results in this region. They made no attempt to use the burnt gas equation (3.11), due to the difficulty of evaluating the properties of the burnt gas during the progress of the flame.

This work of Fiock et al (FM 40) appears to have been one of the two attempts (the first being that of Lewis and von Elbe - LV 34) to use the full potentialities of the constant volume bomb method. Unfortunately by using an unburnt gas equation they limited the scope of their work. All subsequent workers appear to have restricted the bomb method to essentially a constant pressure technique, thus seriously curtailing its value. It is doubtful whether under these conditions, and in view of the considerably costlier equipment required, there is merit in preferring it to a constant pressure method using say rubber balloons. However as will be shown later such a restriction of its scope is unnecessary.

3.2.4 Dery's Equation

Manton, von Elbe and Lewis (MV 53) showed that a particularly simple form of burning velocity equation could be derived in which the only time derivative required is that of flame radius. This equation (see Appendix C), attributed to R.J. Dery, is

$$S_t = S_s / \left[1 + (1/\gamma_u) \{ (P'_e/P) - 1 \} \right] \dots\dots\dots (3.16)$$

and is claimed to be valid only when the mass fraction burnt is less than 0.01. Here P'_e is the same fictitious thermodynamically calculated maximum pressure referred to in the previous section. (See LV 61 and Tr 62 for method of calculating P'_e).

Equation (3.16) has been used to determine the burning velocities of stoichiometric propane, butane and ethylene/air mixtures (MV 53). As a check on the consistency of the constant volume method these authors com-

pared the results of this equation with those obtained from eqn (3.9) and found close agreement.

Smith and Agnew (SA 57) also used this equation to determine the burning velocity of various methane/oxygen/nitrogen mixtures. They timed the flame travel over the initial stages of the process when the flame speed was essentially constant and the pressure rise negligible. The effect of pressure on burning velocity was studied by changing the initial pressure of the mixtures.

Since $S_t^0 = \alpha_o S_s^0 = S_s^0/E_o$ the use of eqn (3.16) in this way is tantamount to assuming that

$$1 + (1/\gamma_u) \left\{ (P_e/P_o) - 1 \right\} = E_o \approx (P_e/P_o) \\ \text{i.e. } P_e' \approx \gamma_u (P_e - P_o) + P_o \dots\dots\dots (3.17)$$

where P_e is the observed maximum combustion pressure. The exact physical significance of P_e' is thus difficult to see. However we are told (LV 61) that P_e' '.... represents an extrapolation of the initial part of the pressure rise under the assumption that the thermodynamic properties of the mixture do not change in the later stages of the process'.

Under these conditions it would seem preferable to determine burning velocities from the equation

$$S_t^0 = \alpha_o S_s^0 = S_s^0/E_o \dots\dots\dots (3.18)$$

where E_o is obtained from thermodynamic calculations assuming chemical equilibrium behind the flame front. This technique has the merit of having been confirmed by soap bubble experiments (SW 53, SE 59). It has been used by Watermeier (Wa 57) to investigate the influence of hydrogen and deuterium on the burning velocities of dry carbon monoxide/oxygen mixtures. He used schlieren photography to record the passage of the flame.

3.2.5 Eschenbach and Agnew

These authors have proposed several equations for the calculation of burning velocity (Es 57, EA 58). They have shown that effects due to the pressure gradient across the flame front can lead to errors in the burning velocities of fast burning mixtures determined from the previous equations. The influence of the finite velocity of sound is shown to be significant if the spatial velocity of the flame is greater than about one-tenth of the velocity of sound in the unburnt gas. Several equations have been developed which apparently allow for the effects of a non-uniform pressure distribution. The basic equation which they propose is,

$$S_t = (M_b T_u P_b / M_u T_b P_u) \left[S_s + (r_b / 3P_b) (dP_b / dt) \right] \dots \dots \dots (3.19)$$

$$\text{where } P_b / P_u = 1 + \gamma_u \epsilon^2 T_o' / T_u \dots \dots \dots (3.20)$$

$$\epsilon = (S_s - S_t) / c = \text{pseudo Mach number} \dots \dots \dots (3.21)$$

$$\text{and } C = (g_c \gamma_u P_u / \rho_u)^{1/2} \dots \dots \dots (3.22)$$

= velocity of sound in unburnt mixture

Here P_b refers to the pressure behind the flame front and P_u to the pressure immediately ahead of it.

The propagation of a spherical combustion wave has been discussed by Courant and Friedrichs (CF 48). The above allowance for compressibility effects is based on Taylors' solution (Ta 46) for the pressure and velocity distribution of a compressible fluid outside an impenetrable sphere which is expanding at a constant radial velocity in an infinite medium. Conditions outside the flame front are assumed to correspond to the above if the velocity of the expanding sphere is taken as $(S_s - S_t)$ (Es 57). (This assumes that the spatial velocity of the burnt gas behind the flame front is zero - which is not the case).

The term outside the bracket in eqn(3.10) is the inverse of what may be called an 'effective expansion ratio' (compare eqn 3.11). That is,

$$(M_b T_u P_b / M_u T_b P_u) = (1/E)(P_b/P_u) = (\rho_b/\rho_u)(P_b/P_u) \dots\dots\dots (3.23)$$

Evidently P_b can be set equal to P_u for relatively slow burning mixtures. (For the tests described in this thesis $1 < P_b/P_o < 1.001$). However for such cases these authors have derived alternative equations as follows:

$$S_t = \left[1 + \gamma_u (r_b/R)^3 \left\{ 1 - (1/E) \right\} \right] (S_s/E) \dots\dots\dots (3.24)$$

$$S_t = (P/P_o)(S_s/E) \dots\dots\dots (3.25)$$

or for use with pressure-time records only,

$$S_t = (R/AE_o)(P/P_o)^B (dF/dt) \dots\dots\dots (3.26)$$

where $A = \left[\gamma_u \left\{ 1 - (1/E_o) \right\} \right]^{1/3}$

$$B = (2/3) - (1/\gamma_u)$$

and $F^3 = (P/P_o) - 1$

Details of the procedure to be followed when the flame speed is an appreciable fraction of the velocity of sound in the unburnt mixture are given in reference Es 57 and EA 58. The analysis is then claimed to be applicable only when the pressure rise is less than about 7 per cent of the initial pressure in the vessel, and is only valid during the period which elapses before the first pressure wave, reflected from the wall of the vessel, intersects the advancing flame front.

It is to be noted that implicit in eqn (3.19) is the assumption that the ratio of heat capacities of the unburnt gas (γ_b) is unity. This does not appear to have been noted by the authors. Admittedly since they have used the constant volume bomb method essentially as a constant pressure technique (when dP_b/dt is in any case either zero or negligible) this assumption is of no great consequence. However attention is drawn to it here since their analysis gives the impression of being general.

Using two forms of the above equation Agnew and his co-workers (Gr 59, AG 61) examined the pressure dependence of a wide range of mixtures. Equation (3.25) (with $E = E_o$) was used for fuel/air mixtures, whilst for fuel/oxygen mixtures the following modified form was employed;

$$S_t = (S_s/E_o)(T_o/T_u) \left[1 + \gamma_u \epsilon^2 (T_o/T_u) \right] \dots \dots \dots (3.27)$$

As before no attempt was made to measure transient pressure during combustion, the pressure dependence of burning velocity being determined by varying the initial pressure of the system.

3.2.6 O'Donovan and Rallis

In an attempt to take advantage of the scope offered by the constant volume method these authors derived an equation for the mass fraction burnt (n) which is claimed to be valid throughout the combustion process (OR 59, Ra 59). It may be written in the form (see Appendix D),

$$n = \left[P - (P_o T_u / T_o) \right] / \left[(P_e \bar{T}_b / \bar{T}_e) - (P_o T_u / T_o) \right] \dots \dots \dots (3.28)$$

and since

$$(r_b/R)^2 = \left[1 - (1-n)(P_o/P)(T_u/T_o) \right]^{2/3},$$

burning velocities may be calculated from eqn (3.9). Thus,

$$S_t = (R/3)(P_o/P)(T_u/T_o)(dn/dt)/(r_b/R)^2 \dots\dots\dots(3.29)$$

These authors appear to have been the first to use the fact that the mean density of the system remains constant throughout the process. Their equation for n thus incorporates the boundary condition $\rho_o = \bar{\rho}_e$. They have however assumed that $M_b = M_e$, which for most practical cases introduces no significant error.

Included in this paper (OR 59) are equations for determining burning velocity from either radius- or pressure-time records alone. No experimental work is reported.

3.2.7 Grumer et al

Grumer and co-workers (GC 59, GC 61) have used the constant volume method to investigate the pressure dependence of a wide range of mixtures. They have shown that the Flamm and Mache relation for the mass fraction burnt (eqn 3.3) can be reduced to,

$$n = (P - P_o)/\gamma_u P_o (E-1) \dots\dots\dots(3.30)$$

provided $P \leq 1.1 P_o$. By substituting this value for n , and its derivative with respect to time, into eqn (3.9) they show that,

$$S_t = (P/P_o)(S_s/E) \dots\dots\dots(3.31)$$

which corresponds to eqn (3.25) derived independently from other considerations by Eschenbach and Agnew (Es 57).

By re-arranging the Fiock unburnt gas equation (3.10) into the form,

$$S_t/S_s = 1 + d[\ln(P)^{1/\gamma_u}] / d[\ln(R^3 - r_b^3)] \dots\dots\dots(3.32)$$

they were able to determine experimental expansion ratios based on pressure- and radius-time records. These they compared with values of E obtained from eqn (3.31) and the Dery equation (3.16), both over the period during which the pressure rise was insignificant. Average deviations of about 14 per cent were noted, with maximum values lying within the range - 28 per cent.

As usual pressure dependence was studied by varying the initial pressure of the mixture.

3.2.8 Raezer's Equation

By assuming equilibrium conditions in the burnt gas Raezer (Ra 61) derived an equation involving the ratio of the burning to the spatial velocity. Thus, in its corrected form (private communication) it can be expressed as

$$(r_b/R)^3 = 1 - \left[(S-1)/(\Theta-1) \right] \left[\left\{ \gamma_u^{(\Theta-1)+1} \right\} / \left\{ \gamma_u^{(S-1)+1} \right\} \right]^{(\gamma_u-1)/\gamma_u} \dots\dots\dots(3.33)$$

where $S = S_s/S_b$

and $\Theta = T_b/T_o$

No experimental results are reported.

3.2.9 Rallis et al

Rallis, Posel and Tremeer (RP 62) have recently determined the burning velocities of a stoichiometric acetylene/air mixture over a range of pressures and temperatures from simultaneous radius- and pressure-time records. Results were calculated from both the unburnt gas equation (3.10) and a new form of burnt gas equation (RT 63), the derivation of which will be presented later (Section 4.1.1). Their results appear to correlate well with reliable values obtained by other methods.

3.3 DISCUSSION AND CONCLUSIONS

As has been stressed by Lewis (Le 54) the closed vessel technique '...must be regarded as a precision method and at the same time as a standard method against which the validity of other methods may be tested'. However it appears that '...there still exists an unawareness of the fact that the method yields accurate and reliable values of burning velocities if the proper procedure is followed' (Le 54) (The underlining is mine). Lewis is referring here to the self-corroborating properties of the method, which in his case is done by comparing observed and calculated flame front radii as a check on the validity of the thermodynamic assumptions made. Following on the approximate form of the equations which he and his co-workers use however, this check is only applicable to the early stages of combustion. It will be shown later (Chapter 4) that the basic equations applicable to the method can be generalised to a far greater extent than has hitherto been

done, whilst at the same time providing checks which are applicable over the whole range of the process, thus retaining the precision of the method whilst extending its scope and value. It seems rather surprising how few of the workers in this field (other than Lewis *et al*) have attempted to take advantage of this self-corroborating nature of the method.

Due to the suspicion of a lack of chemical equilibrium in the burnt gas, some doubt has been cast (EA 58) on the values obtained by this method. If this criticism is applicable to the constant volume method (which has heretofore only been used as a constant pressure technique) it must be equally applicable to the soap bubble method. Surely though this does not invalidate these methods, but rather calls for a better understanding of the phenomena involved. In both cases it is possible to compare experimentally determined expansion ratios with thermodynamically calculated values (SW 53, SE 59). Thus the extent of any lack of equilibrium during the early stages can be determined and allowed for.

In any event provided the velocity vectors can be directly determined at the flame front, then such a lack of equilibrium does not enter into the argument. In essence the problem of determining burning velocities then reduces to finding the difference between the unburnt gas velocity at the flame front and the spatial velocity. Alternatively, the spatial velocity can be considered as being the result of the velocity of free expansion of the burnt gases, under the conditions prevailing at any instant, reduced by the inward velocity of these gases immediately adjacent to the flame front. Thus provided the spatial velocity of the flame front as well as either one of these gas velocity vectors can be directly observed, the burning velocity follows. If both can be determined then a cross-check is provided. A method whereby these velocities can be determined directly is discussed in Section 4.4. Further, with this method it is possible to obtain instantaneous

values of density and hence density gradients at any instant. Detailed analysis of the process should thus be possible, the results of which could be of considerable value in establishing the existence of temperature and pressure gradients as well as providing information of value to the chemical kineticist.

As has been observed throughout this review, other than the originators of the method (LV 34, FM 40) all subsequent workers have used it essentially as a constant pressure technique. However if present theories regarding flame front thickness are valid then there seems to be no good reason why the method cannot be used at other than the early stages of the process. In fact indications are that, if anything, results based on observations of these early stages might be less reliable, due to spark interaction, initial acceleration, and similar effects. Before the method can be thus extended however, more reliable equations than have heretofore been available must be developed. In particular the restricting assumption of adiabatic combustion should if possible be eliminated. Further, as many cross-checking observations as possible should be undertaken for obvious reasons. To suggest - as has been done - that, for example, because it is difficult to interpret either radius- or pressure-time records, one or other of these need not be observed surely avoids the issue.

Finally, at the risk of stating the obvious, any attempts at analysis should start off with as few assumptions as possible, consistent with keeping the analysis tractable. In this way if restricting assumptions become necessary because of experimental difficulties, their full implications can be examined.

Such a general set of equations is developed in the next chapter. Equations previously derived are then shown to follow as special cases of these.

CHAPTER 4

DERIVATION OF EQUATIONS FOR THE DETERMINATION OF BURNING VELOCITY IN A CLOSED SPHERICAL VESSEL

As far as can be determined the various equations proposed from time to time in the literature (Chapter 3) have never been satisfactorily compared, either theoretically to see whether they are particular cases of a more general set of equations, or practically by applying them to the results of a particular set of experiments.

In essence all have been based on the same assumptions. Evidently therefore they should be derivable from the same fundamental definition and, depending on the subsequent approximations made, should yield essentially the same results.

Thus it would appear that some basic analysis, as well as a comparison of the results obtained with the better known of these equations, would be useful. This and the following chapter are contributions in this direction.

In terms of the continuity equation a fundamental definition of burning velocity is presented, the use of which leads to two basic forms of equation for the determination of laminar burning velocities in constant volume vessels. Strictly these two equations should yield the same results when applied to any given set of experimental data. However, due to systematic and other errors inherent in the observations, they are found to lead to different values over different ranges of the combustion process. This can be used to advantage for providing an indication of the probable source and extent of such errors.

All of the previously proposed equations are shown to be special cases of the set presented here. These new equations involve a dimensionless density ratio α and incorporate known boundary conditions. They thus

claim to be valid throughout the combustion process. Also they partly allow for any lack of chemical equilibrium in the burnt gas, which tests show exists.

Burning velocities, determined for a stoichiometric acetylene/air mixture using various forms of equation, are compared in Chapter 5.

4.1 BURNING VELOCITY EQUATIONS

In the analysis which follows it will be assumed that:

- (1) The total mass of gas in the system remains constant.
- (2) The flame propagates isotropically, that is, in this case it remains spherical throughout the process. (The analysis is equally applicable if the flame propagates anisotropically - for example as a prolate or oblate spheroid - provided the geometry of the burning gas is known or can be determined. However it is obviously more convenient to try and arrange that the flame propagates spherically.)
- (3) The flame front is a surface of discontinuity across which the change from the unburnt to the burnt state takes place. This implies that the mass of gas undergoing reaction in the flame front at any instant is negligibly small as compared with the mass of burnt and unburnt gas. Clearly this assumption breaks down at the start and end of the process.

4.1.1 Basic Equations

From the equation of continuity, the mass rate of transfer of unburnt gas, of density ρ_u , across a flame front of area A , is evidently,

$$\frac{dm_u}{dt} = -A\rho_u S_u \dots\dots\dots(4.1)$$

where S_u is the normal velocity with which the unburnt gas crosses such a front and is transformed. In this context the word 'normal' implies that the velocity is measured perpendicular to the flame front.

Now for combustion in a constant volume spherical vessel the mass of unburnt gas at any instant (assuming isotropic flame propagation) is given by,

$$m_u = (4\pi/3)(R^3 - r_b^3) \bar{\rho}_u \dots\dots\dots(4.2)$$

where $\bar{\rho}_u$, the mean density of the unburnt gas, is introduced to allow for non-uniform properties on the unburnt gas due to pressure gradients, heat loss at the wall, etc. Its value will evidently be given by

$$\bar{\rho}_u = \left[3/(R^3 - r_b^3) \right] \int_{r_b}^R \rho_u(r) r^2 dr \dots\dots\dots(4.3)$$

where $\rho_u(r)$ is some function of r ($r_b \leq r \leq R$).

Thus

$$dm_u/dt = (4\pi/3) \left[(R^3 - r_b^3) (d\bar{\rho}_u/dt) - 3r_b^2 \bar{\rho}_u (dr_b/dt) \right] \dots\dots\dots(4.4)$$

hence, from (4.1) and (4.3) remembering that $A = 4\pi r_b^2$,

$$S_u = (\bar{\rho}_u/\rho_u) \left[(dr_b/dt) - \left\{ (R^3 - r_b^3)/(3r_b^2 \bar{\rho}_u) \right\} (d\bar{\rho}_u/dt) \right] \dots\dots\dots(4.5)$$

Thus if the flame front radius r_b , the unburnt gas density immediately ahead of the flame front ρ_u , and the mean unburnt gas density $\bar{\rho}_u$ can be measured as functions of time, then S_u follows. Clearly values of S_u should be reported at the flame front density ρ_u .

Alternatively if the mean unburnt gas pressure and temperature be measured, then from the equation of state

$$\bar{P}_u M_u = \mathcal{R} \bar{\rho}_u \bar{T}_u$$

hence

$$(1/\bar{\rho}_u)(d\bar{\rho}_u/dt) = (1/\bar{P}_u)(d\bar{P}_u/dt) - (1/\bar{T}_u)(d\bar{T}_u/dt) \dots\dots\dots (4.6)$$

since $M_u = M_o = \text{constant}$.

If on the other hand the unburnt gas can be considered to undergo adiabatic compression for which

$$\bar{P}_u = C \bar{\rho}_u^{\gamma_u}$$

then

$$(d\bar{\rho}_u/dt) = (d\bar{\rho}_u/d\bar{P}_u)(d\bar{P}_u/dt) - (\bar{\rho}_u/\gamma_u \bar{P}_u)(d\bar{P}_u/dt) \dots\dots\dots (4.7)$$

Hence (4.5) can be rewritten as,

$$S_u = (\bar{\rho}_u/\rho_u) \left[(dr_b/dt) - \left\{ (R^3 - r_b^3)/(3r_b^2 \gamma_u \bar{P}_u) \right\} (d\bar{P}_u/dt) \right] \dots\dots (4.8)$$

For low velocity flames ρ_u can be set equal to $\bar{\rho}_u$ without significant error.

If the process is not adiabatic, γ_u can be replaced by the appropriate polytropic index if this can be determined. However equations (4.5) or (4.6) are then to be preferred.

Equation (4.8) requires measurements of r_b , $\bar{P}_u$ and $\bar{\rho}_u/\rho_u$ as functions of time, in addition to evaluation of γ_u (see Appendix E). A

similar form, with $\bar{\rho}_u = \rho_u$, was originally developed by Fiock and Marvin (FM 37), using a somewhat different approach. Equations (4.5) and (4.8) will be referred to here as the unburnt gas equations for burning velocity.

Alternative forms of these equations can be obtained by considering the burnt gas behind the flame front. Thus, since for combustion in a constant volume vessel,

$$m_u = m_o - m_b \dots\dots\dots (4.9)$$

and consequently,

$$(dm_u/dt) = - (dm_b/dt) \dots\dots\dots (4.10)$$

it follows from (4.1) and (4.10) that

$$S_b = (1/A \rho_u) (dm_b/dt) \dots\dots\dots (4.11)$$

where S_u has been changed to S_b to indicate that the burning velocity is expressed in terms of the properties of the burnt gas.

Now for a spherical flame front

$$m_b = (4\pi/3) r_b^3 \bar{\rho}_b \dots\dots\dots (4.12)$$

where $\bar{\rho}_b$, the mean density of the burnt gas, is introduced to allow for non-uniform properties of the gas behind the flame front due to recompression, pressure gradients, and other possible effects. It is given by (Appendix A)

$$\bar{\rho}_b = (3/r_b^3) \int_0^{r_b} \rho_b(r) r^2 dr \dots\dots\dots (4.13)$$

where $\rho_b(r)$ is some function of r ($0 \leq r \leq r_b$). Clearly when $r_b = R$, $\bar{\rho}_b = \bar{\rho}_e = \rho_o$, since the total volume and mass of gas in the vessel does not change. This fact provides an important check on the calculations.

Now from eqn (4.12),

$$(dm_b/dt) = (4\pi/3) \left[r_b^3 (d\bar{\rho}_b/dt) + 3r_b^2 \bar{\rho}_b (dr_b/dt) \right] \dots \dots \dots (4.14)$$

hence from (4.11) and (4.14),

$$S_b = (\bar{\rho}_b/\rho_u)(dr_b/dt) + (r_b/3\rho_u)(d\bar{\rho}_u/dt) \dots \dots \dots (4.15)$$

Use of the above equations for determining burning velocity requires a knowledge of r_b , ρ_u and $\bar{\rho}_b$ as functions of time.

Alternatively if the mean burnt gas temperature and pressure can be measured, then from the equation of state,

$$\bar{P}_b \bar{M}_b = \bar{R} \bar{\rho}_b \bar{T}_b$$

hence

$$(1/\bar{\rho}_b)(d\bar{\rho}_b/dt) = (1/\bar{P}_b)(d\bar{P}_b/dt) - (1/\bar{T}_b)(d\bar{T}_b/dt) + (1/\bar{M}_b)(d\bar{M}_b/dt) \dots (4.16)$$

If the unburnt gas can be considered to undergo adiabatic compression (with $\bar{M}_b$ constant - see Appendix F), then

$$(d\bar{\rho}_b/dt) = (\bar{\rho}_b/\gamma_b \bar{P}_b)(d\bar{P}_b/dt) \dots \dots \dots (4.17)$$

and eqn (4.15) can be rewritten as

$$S_b = (\bar{\rho}_b / \rho_u) \left[(dr_b/dt) + (r_b/3\gamma_b P_b)(dP_b/dt) \right] \dots\dots\dots (4.18)$$

or with the appropriate polytropic index if the process is not adiabatic. Evaluation of this equation requires a knowledge of r_b , ρ_u , $\bar{\rho}_b$, P_b and γ_b as functions of time.

Equations (4.15) and (4.18) will be referred to here as the burnt gas equations for burning velocity. Equation (4.18) is similar to one derived by Flock and Marvin (FM 37)(see eqn 3.11). Eschenbach and Agnew (Es 57) have also derived an equation (3.19) similar to this, but have inadvertently neglected the variation in the flame front temperature during the process, that is, they have tacitly assumed that $\gamma_b = 1$. Their equation is thus strictly only applicable to the early stages of combustion.

4.1.2 The Density Ratio α

Before equations (4.15) or (4.18) can be applied it is necessary to evaluate the mean density of the burnt gas ($\bar{\rho}_b$) from eqn (4.13), as well as the unburnt gas flame front density ρ_u . Discussion of the latter will be deferred until the next section.

The nature of the radial density distribution in the burnt region at any instant, expressed by $\rho_b = \rho_b(r)$, is fairly complex. Attempts at its accurate determination have in the past proved unsuccessful. (However a simple method whereby this can be done has recently been evolved and is described in Section 4.4.1).

In practice it has been found convenient (RP 62) to modify eqn (4.15) as follows:

Define $\bar{\rho}_b = \alpha \rho_o$ (4.19)

then $(d\bar{\rho}_b/dt) = \rho_o (d\alpha/dt) = \rho_o (d\alpha/d\bar{P}_b)(d\bar{P}_b/dt)$ (4.20)

hence

$$S_b = (\rho_o/\rho_u) \left[\alpha (dr_b/dt) + (r_b/3)(d\alpha/d\bar{P}_b)(d\bar{P}_b/dt) \right] \dots\dots\dots (4.21)$$

This equation has the important advantage of incorporating the boundary condition

$$\left[\bar{\rho}_b \right]_{r_b=R} = \bar{\rho}_e = \rho_o \dots\dots\dots (4.22)$$

that is $\left[\alpha \right]_{r_b=R} = \alpha_e = 1$

From eqn (4.19) above and the equation of state it follows that the dimensionless density ratio

$$\alpha = \bar{\rho}_b/\rho_o = (\bar{M}_b/M_o)(T_o/\bar{T}_b)(\bar{P}_b/P_o) \dots\dots\dots (4.23)$$

or since from (4.22)

$$\rho_o = \bar{\rho}_e = (\bar{M}_e \bar{P}_e / R \bar{T}_e) \dots\dots\dots (4.24)$$

an alternative form of eqn (4.23) is

$$\alpha = (\bar{M}_b/\bar{M}_e)(\bar{T}_e/\bar{T}_b)(\bar{P}_b/\bar{P}_e) \dots\dots\dots (4.25)$$

In practice the variations in $\bar{M}_b$ and $\bar{T}_b$ are relatively small; hence

from equations (4.23) and (4.25) it follows that α is practically proportional to $\bar{P}_b$, that is, $d\alpha/d\bar{P}_b \approx 1/\bar{P}_e$.

Comparing equations (4.23) and (4.25), it is apparent that, even if the absolute values of $\bar{M}_b$, $\bar{T}_b$ and $\bar{P}_b$ are in error, eqn (4.25) must yield the correct value of α (that is $\alpha_e = 1$) at the end of the process. The magnitude of any such errors can be estimated by evaluating α_e from eqn (4.23), which in general will not yield a value of unity. Evidently the use of eqn (4.25) is to be preferred, since errors in the determination of $\bar{M}_b$, $\bar{T}_b$ and $\bar{P}_b$ tend to be cancelled out. In fact it should, in general, be unnecessary to calculate mean values of the burnt gas temperature, pressure and molecular weight. Values immediately behind the flame front, calculated on the basis of chemical equilibrium in this region, may then be used in place of the mean values, without causing significant error in α .

4.2 RELATION BETWEEN LOCAL AND MEAN VALUES OF PRESSURE TEMPERATURE AND DENSITY

The derivation of the foregoing equations is general to the extent that no restricting assumptions were placed on the uniformity or otherwise of the thermodynamic properties within the burnt and unburnt gas respectively. In general, due to changes of momentum across the flame front the burnt gas pressure immediately adjacent to this front (P_b) will be higher than the corresponding pressure on the unburnt gas side (P_u). Also due to spatial velocity distributions in both the burnt and unburnt gas, the pressure at the centre of the vessel- (P_c) will be less than P_b , whilst that at the wall (P_w) will be less than P_u . Further, due to these pressure gradients as well as temperature gradients in both the burnt and unburnt gas (arising mainly from recompression and conduction heat loss at the wall) the densities will not be uniform throughout either the burnt or unburnt gas. Solution of the

foregoing equations therefore requires that we find functional relations between these various properties. (Except where $\bar{\rho}_u$, $\bar{\rho}_b$ and ρ_u are measured directly - Section 4.4). It must be stressed that values of burning velocity should be reported for the pressures and temperatures existing in the unburnt gas immediately ahead of the flame front, that is, just ahead of the pre-heat zone.

4.2.1 Pressure Relations

Consider firstly the pressure difference across the flame front. This must equal the change in momentum across this front. Thus at any instant, treating this as a quasi steady-state process, we have that

$$\Delta F = -\rho_u U_u \Delta U$$

that is

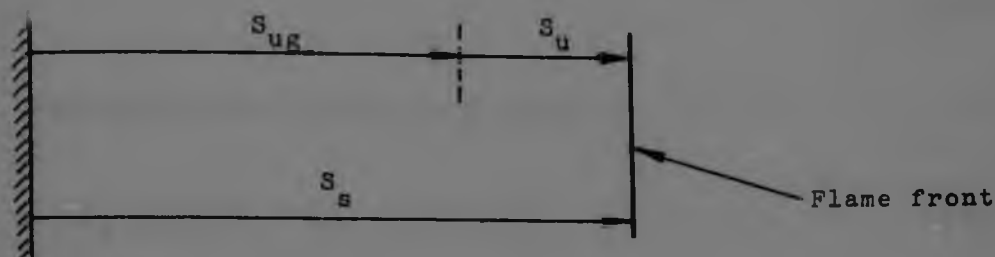
$$\Delta P_F = P_b - P_u = \rho_u U_u (U_u - U_b) \dots\dots\dots (4.26)$$

where U_b and U_u are the spatial velocities of the burnt and unburnt gas respectively.

Now according to eqn (4.5), assuming in the first instance that $\bar{\rho}_u = \rho_u$

$$S_s = S_u + S_{ug} \dots\dots\dots (4.27)$$

where S_{ug} is the spatial velocity of the unburnt gas immediately adjacent to the flame front, S_u is the burning velocity relative to the unburnt gas, and S_s is the spatial velocity of the flame front. That is,



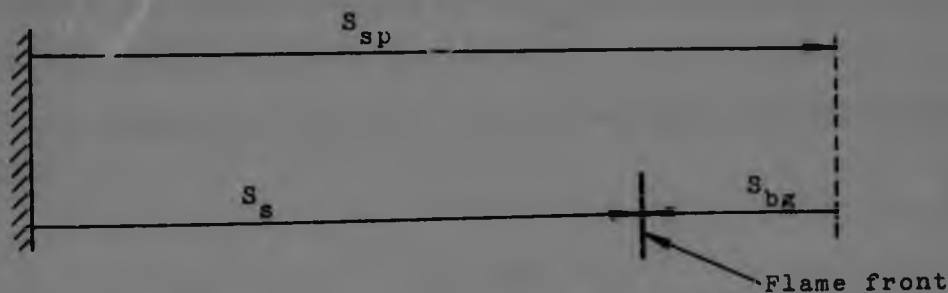
But from (4.15),

$$S_s = (\rho_u / \bar{\rho}_b) S_b - (r_b / 3 \bar{\rho}_b) (d\bar{\rho}_b / dt)$$

that is

$$S_s = S_{sp} - S_{bg} \dots \dots \dots (4.28)$$

or



Here $S_{sp} = (\rho_u / \bar{\rho}_b) S_b$, is evidently the spatial velocity which the flame front would have at constant pressure under the prevailing conditions (see eqn 2.14). Thus $S_{bg} = (r_b / 3 \bar{\rho}_b) (d\bar{\rho}_b / dt)$, must be the effective spatial velocity of the burnt gas at the flame front.

Hence from (4.27) and (4.28), setting $S_b = S_u = S_t$, we have that

$$U_u = S_{ug} = S_s - S_t$$

and

$$U_b = -S_{bg} = S_s - (\rho_u / \bar{\rho}_b) S_t$$

Substituting these values into (4.26) gives

$$\Delta P_F = \rho_u S_t (S_s - S_t) \left[(\rho_u / \bar{\rho}_b) - 1 \right] \dots \dots \dots (4.29)$$

or

$$P_b / P_u = 1 + (\rho_u S_t / P_u) (S_s - S_t) \left[(\rho_u / \bar{\rho}_b) - 1 \right] \dots \dots \dots (4.30)$$

At the start of the process, or for constant pressure combustion, eqn (4.29) reduces to

$$P_b^0 - P_o = \rho_o (S_s^0 - S_t^0)^2 \dots \dots \dots (4.31)$$

which is the equation derived by Eschenbach (Es 57) and by Graiff (Gr 59) following the suggestion of Courant and Friedrichs (CF 48) that the burnt gas comes to rest behind the flame front ($S_{bg} = 0$), which should be approximately the case at the start of the process.

Now since $\rho_u = P_u M_u / RT_u$, and sonic velocity in the unburnt gas is given by

$$c_u = (g_c \gamma_u P_u / \rho_u)^{1/2} = (g_c \gamma_u RT_u / M_u)^{1/2}$$

equation (4.30) can be expressed as

$$P_b / P_u = 1 + g_c \gamma_u (S_s - S_t) (S_t / c_u^2) \left[(\rho_u / \bar{\rho}_b) - 1 \right]$$

or

$$P_b / P_u = 1 + g_c \gamma_u (S_s - S_t) (S_t / c_o^2) (T_o / T_u) \left[(\rho_u / \bar{\rho}_b) - 1 \right] \dots \dots \dots (4.32)$$

since

$$c_u^2 = (T_u / T_o) c_o^2$$

Substituting these values into (4.26) gives

$$\Delta P_F = \rho_u S_t (S_s - S_t) \left[(\rho_u / \bar{\rho}_b) - 1 \right] \dots \dots \dots (4.29)$$

or

$$P_b / P_u = 1 + (\rho_u S_t / P_u) (S_s - S_t) \left[(\rho_u / \bar{\rho}_b) - 1 \right] \dots \dots \dots (4.30)$$

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Now since $\rho_u = P_u M_u / RT_u$, and sonic velocity in the unburnt gas is given by

$$c_u = (g_c \gamma_u P_u / \rho_u)^{1/2} = (g_c \gamma_u RT_u / M_u)^{1/2}$$

equation (4.30) can be expressed as

$$P_b / P_u = 1 + g_c \gamma_u (S_s - S_t) (S_t / c_u^2) \left[(\rho_u / \bar{\rho}_b) - 1 \right]$$

or

$$P_b / P_u = 1 + g_c \gamma_u (S_s - S_t) (S_t / c_o^2) (T_o / T_u) \left[(\rho_u / \bar{\rho}_b) - 1 \right] \dots \dots \dots (4.32)$$

since

$$c_u^2 = (T_u / T_o) c_o^2$$

At the start of the process this reduces to Eschenbach and Graiff's equation (Es 57, Gr 59)

$$P_b/P_o = 1 + \gamma_c \gamma_u \left[(S_s^o - S_t^o)/c_o \right]^2$$

(It should be noted that these authors imply that their equation has a greater generality than is the case. It is only valid at the start of the process.)

Consider next the pressure distribution between the flame front (P_u) and the wall of the vessel (P_w). Silsbee (cited by St 23, Rept. 176 - see LV 51, p.241) has developed an equation for the pressure P as a function of the distance r from the flame origin in a soap bubble. (Assuming an incompressible fluid, that is, for burning velocities that are small as compared with sonic velocity in the unburnt gas). Thus he obtains

$$P = P_o + \rho_u S_s^2 \left[1 - (\rho_b/\rho_u) \right] \left[(2r_b/r) - \left\{ 1 - (\rho_b/\rho_u) \right\} r_b^4/2r^4 \right]$$

where $r \approx r_b$. At the flame front therefore

$$P_u = P_o + 0.5 \rho_u S_s^2 \left[1 - (\rho_b/\rho_u) \right] \left[3 - (\rho_b/\rho_u) \right]$$

or since for constant pressure combustion $S_s = (\rho_u/\rho_b) S_t$ this reduces to

$$P_u/P_o = 1 + 0.5(\rho_u/\rho_o)(S_s - S_t)(3S_s - S_t) \dots\dots\dots (4.31)$$

where P_o is the pressure at infinite distance from the wave.

For the early stages of the process in a constant volume vessel, eqn (4.31) could probably be used without significant error where now $P_o = P_w$, the pressure measured at the wall of the vessel. Evidently at the end of the

process, since then $S_s = S_t$, $P_u/P_w = 1$ as is required. However, use of this equation throughout the entire process probably over-emphasises this effect. A more suitable equation, based on the momentum change between the flame front and the wall is

$$P - P_w = \rho_u (S'_{ug})^2 = \rho_u \left[(R^3 - r^3)/3r^2 \rho_u \right] (d\rho_u/dt)^2 \dots\dots\dots (4.32)$$

for $r_b \leq r \leq R$. Thus the pressure difference between the unburnt gas immediately ahead of the flame front and the wall will be

$$\Delta P_u = P_u - P_w = \rho_u (S_s - S_t)^2 \dots\dots\dots (4.33)$$

Evidently the mean unburnt gas pressure can be obtained from eqn (4.32) by integrating over the appropriate limits, keeping in mind that the system has a spherical geometry.

An alternative method of estimating P_u from the observed pressure-time records is to apply a correction for the time required for information from the flame front to reach the wall of the vessel. Thus, since a pressure pulse received by the transducer at a time t must have originated at the flame front at a time $(t - \Delta t)$, where

$$\Delta t = (R - r_b)/c_u, \dots\dots\dots (4.34)$$

the P - t records may be corrected as indicated in Fig 4.1.

The pressure distribution in the burnt gas follows as before from the momentum equation. Thus

$$P_b - P = \rho_b (S'_{bg})^2 = \rho_b \left[(r/3 \rho_b) (d\rho_b/dt) \right]^2 \dots\dots\dots (4.35)$$

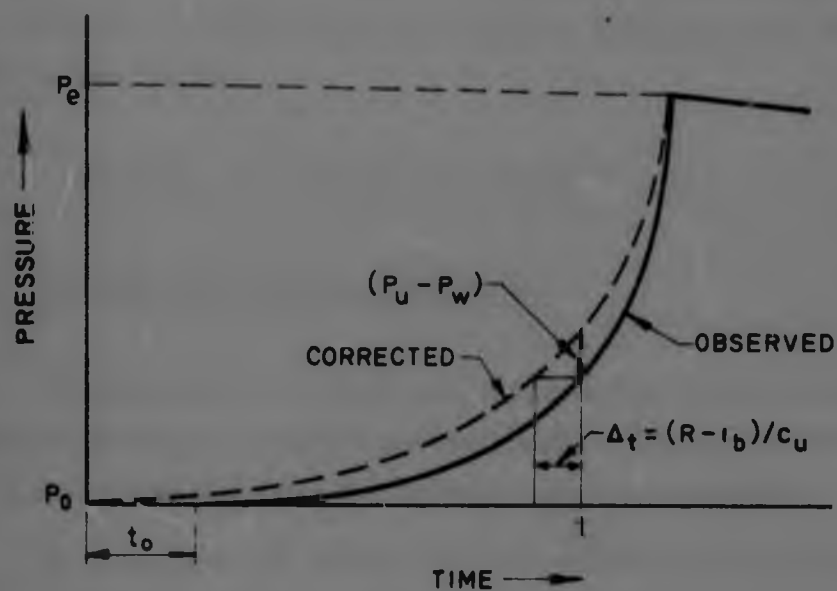


FIG. 4-1

EFFECT OF TIME LAG DUE TO FINITE VELOCITY
OF SOUND

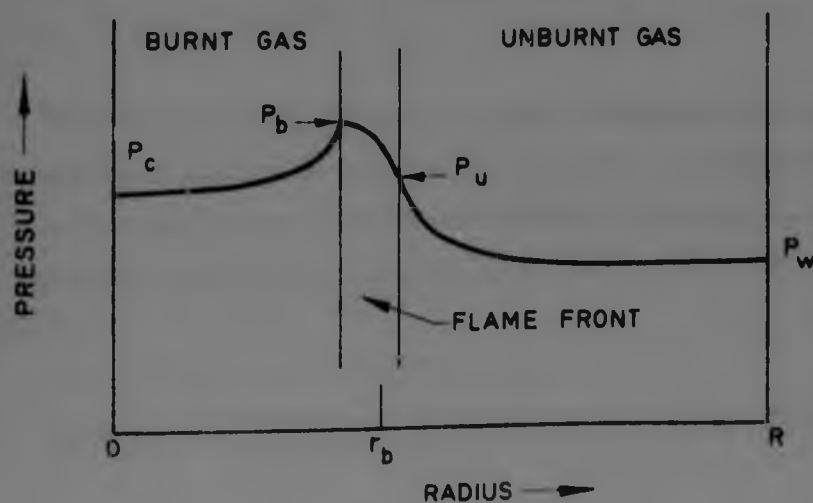


FIG. 4-2

PRESSURE PROFILE DURING FLAME PROP-
AGATION

for $0 \leq r \leq r_b$, from which the mean burnt gas pressure can be calculated. The maximum pressure difference, between the flame front and the centre of the vessel, is thus

$$\Delta P_b = P_b - P_c = \rho_b \left[S_s - (\rho_u / \rho_b) S_t \right]^2 \dots\dots\dots (4.36)$$

4.2.2 Temperature and Density Relations

Temperatures corresponding to the various instantaneous pressures indicated above may be determined with sufficient accuracy on the assumption that compression from the boundary values is adiabatic.

In particular the unburnt gas temperature and density immediately ahead of the flame front will be approximately given, for most of the process, by

$$T_u = T_o \left[(P_w + \Delta P_u) / P_o \right]^{(1-1/\gamma_u)} \dots\dots\dots (4.37)$$

and

$$\rho_u = \rho_o \left[(P_w + \Delta P_u) / P_o \right]^{1/\gamma_u} \dots\dots\dots (4.38)$$

The use of such equations is considered adequate on the grounds that the foregoing analysis for determining pressure gradients throughout the system is in any case approximate, since quasi steady-state conditions have been assumed, that is, acceleration and deceleration effects have been neglected.

4.2.3 Application of Pressure, Temperature and Density Relations

If it is assumed that compressibility effects at the flame front are negligible then P_b can be set equal to P_u in the foregoing equations. This

is essentially the situation in relatively slow burning mixtures, that is, with S_s^0 less than about one-tenth of the initial sonic velocity (c_0) (Es 57, Gr 59). When this is not the case then the corrections indicated above must be taken into account in calculating mean densities, temperatures or pressures (Fig 4.2), and for determining the pressure and temperature dependence of burning velocity (flame front values being required here). Evidently with such fast burning mixtures at high initial pressure, evaluation of burning velocity will have to be done via some form of iterative procedure.

(NOTE: For all the tests reported in ^{this} thesis the differences between P_b , P_u and P_w are negligible for the purpose of determining burning velocities. For example, near the start (1.0 ms) of combustion in Test C (Appendix J) from eqn (4.30), $P_b^0/P_0 \approx 1.0029$, that is, $P_b^0 - P_0 \approx 0.035$ psi, since $P_0 = 12.09$ psia. Near the end of the process (9.0 ms), $P_b - P_u \approx 0.026$ psi. Also at the start, from eqn (4.34), the time required for information to reach the wall was about 0.22 ms, by which time the pressure had not risen sufficiently to affect the burning velocity. At 9.0 ms the time delay was about 0.01 ms; thus a pressure correction of about 0.47 psi is required (in 57.03 psia).

On the other hand for a mixture having a burning velocity of say 1000 cm/s, and at the same initial temperature, P_b^0/P_0 would be about 1.187, that is, $P_b^0 - P_0 \approx 2.26$ psi - or 22.6 psi if the initial pressure were ten times higher.)

4.3 REDUCTION TO SPECIAL CASES

Many of the various forms of burning velocity equation proposed in the literature, and based on similar assumptions to the foregoing, follow directly from equation (4.1). Some examples have already been given;

others follow. (See also Section 4.3.1).

For constant pressure combustion with relatively slow flames, $d\bar{p}_b/dt$ (eqn 4.15) is essentially zero. Thus in the soap bubble method, or during the early stages of combustion in a constant volume vessel, eqn (4.15) reduces to

$$S_t = (\rho_b^0/\rho_o)(dr_b/dt) = \alpha_o S_s^0 = S_s^0/E_o \quad \dots\dots\dots (4.39)$$

or if compressibility effects are significant suitable corrections, as suggested in Section 4.1.3, must be included.

Consider next the equations proposed by Lewis and von Elbe (LV 51, pp. 455-9) (Section 3.2.2, eqns 3.7, 3.8 and 3.9).

They define

$$n = m_b/m_o$$

from which

$$dn/dt = (1/m_o)(dm_b/dt)$$

Substituting for dm_b/dt in (4.11) yields

$$\begin{aligned} S_t &= (m_o/A \rho_u)(dn/dt) \\ &= (R^3/3r_b^2)(\rho_o/\rho_u)(dn/dt) \quad \dots\dots\dots (4.40) \end{aligned}$$

Also these authors assume that during the early stages of combustion, with P uniform throughout the vessel,

$$n = (P - P_o)/(P_e' - P_o) \quad \dots\dots\dots (4.41)$$

hence

$$dn/dt = [1/(P_e' - P_o)](dP/dt) \quad \dots\dots\dots (4.42)$$

Clearly r_b can be eliminated from eqn (4.40) since from eqn (4.9)

$$m_u/m_o = 1 - n = \rho_u(R^3 - r_b^3)/R^3 \rho_o$$

hence

$$r_b = R \left[1 - (1-n)(\rho_o/\rho_u) \right]^{1/3} \dots\dots\dots(4.43)$$

Their equation for n (eqn 4.41) is an approximation. Its exact value is given by

$$n = (r_b^3 \bar{\rho}_b)/(R^3 \rho_o) = \alpha r_b^3/R^3 \dots\dots\dots(4.44)$$

but

$$\alpha = (\bar{M}_b/\bar{M}_e)(\bar{T}_e/\bar{T}_b)(P/P_e) \approx P/P_e$$

hence

$$n \approx (r_b^3/R^3)(P/P_e) = [P - (\rho_o/\rho_u)P]/[P_e - (\rho_o/\rho_u)P] \dots\dots(4.45)$$

which during the early stages of combustion since $\rho_u \approx \rho_o$ and $P \approx P_o$ reduces to the approximate equation of Lewis and von Elbe (eqn 4.41), except that they compensate by using a fictitious maximum pressure P'_e .

On substituting (4.44) in (4.43) and solving for r_b , we obtain,

$$r_b = R \left[\left\{ (\rho_u/\rho_o) - 1 \right\} / \left\{ (\rho_u/\rho_o) - \alpha \right\} \right]^{1/3} \dots\dots\dots(4.46)$$

Hence

$$n = \alpha \left[(\rho_u/\rho_o) - 1 \right] / \left[(\rho_u/\rho_o) - \alpha \right] \dots\dots\dots(4.47)$$

Values of r_b calculated from this equation may be compared with the observed values to indicate the validity or otherwise of assumptions made in determining α and the density ratio ρ_o/ρ_u . This technique was used by Manton et al (MV 53) to check the thermodynamic assumptions implicit in equation (4.41).

4.3.1 Alternative New Equations

Since we are in possession of two basis forms of burning velocity equation (burnt and unburnt) their combination can yield a third which may prove of some value.

Thus from equations (4.15) and (4.16), with $\bar{P}_b = \bar{P}_u = P$,

$$(\rho_u / \bar{\rho}_b) S_b = S_s + (r_b/3) \left[(1/P)(dP/dt) - (1/\bar{T}_b)(d\bar{T}_b/dt) + (1/\bar{M}_b)(d\bar{M}_b/dt) \right] \quad \dots\dots\dots (4.48)$$

but from equations (4.5) and (4.6), with $\rho_u = \bar{\rho}_u$,

$$S_u = S_s - \left[(R^3 - r_b^3)/(3r_b^2) \right] \left[(1/P)(dP/dt) - (1/T_u)(dT_u/dt) \right] \quad \dots\dots\dots (4.49)$$

Setting $S_u = S_b = S_t$ since strictly these are all the same, and substituting (4.49) into (4.48) yields,

$$(\rho_u / \bar{\rho}_b) S_t = S_s + r_b^3 (S_s - S_t) / (R^3 - r_b^3) + (r_b/3) \left[(1/T_u)(dT_u/dt) - (1/\bar{T}_b)(d\bar{T}_b/dt) + (1/\bar{M}_b)(d\bar{M}_b/dt) \right] \quad \dots\dots\dots (4.50)$$

But

$$\begin{aligned} & (1/T_u)(dT_u/dt) - (1/\bar{T}_b)(d\bar{T}_b/dt) + (1/\bar{M}_b)(d\bar{M}_b/dt) \\ &= (\bar{T}_b/\bar{M}_b T_u)(d/dt)(\bar{M}_b T_u/\bar{T}_b) = (\rho_u/\bar{\rho}_b)(d/dt)(\bar{\rho}_b/\rho_u) \\ &= (\rho_u/\alpha \rho_0)(d/dt)(\alpha \rho_0/\rho_u) = (\beta/\alpha)(d/dt)(\alpha/\beta) \end{aligned}$$

where $\beta = (\rho_u/\rho_0)$ and $\alpha = (\bar{\rho}_b/\rho_0)$

Also from equation (4.46)

$$r_b^3 / (R^3 - r_b^3) = (\beta - 1) / (1 - \alpha)$$

Hence eqn (4.50) reduces to

$$S_t = \alpha S_s + \left[\frac{r_b^3 (1 - \alpha)}{3(\beta - \alpha)} \right] (d/dt)(\alpha/\beta) \quad \dots\dots\dots (4.51)$$

Consider the values yielded by this equation at the two limits of the process. Immediately after ignition in a constant volume vessel (or for constant pressure combustion as in a soap bubble), $\beta = 1$ and $\alpha = \alpha_0 = a$ constant. Therefore,

$$S_t^0 = \alpha_0 S_s^0 = (\rho_b^0 / \rho_0) S_s^0 \quad \text{as it should be.}$$

Also at the end of constant volume combustion $\alpha = \alpha_e = 1$, hence $S_t^e = S_s^e$, which is correct.

Consider now the case where both the unburnt and burnt gas can be assumed to be compressed adiabatically.

Equation (4.51) may be rewritten as

$$S_t = \alpha S_s + \left[\frac{\alpha r_b^3 (1 - \alpha)}{3(\beta - \alpha)} \right] \left[(1/\alpha)(d\alpha/dt) - (1/\beta)(d\beta/dt) \right] \quad \dots\dots\dots (4.52)$$

but for adiabatic compression

$$(1/\alpha)(d\alpha/dt) = (1/\bar{\rho}_b)(d\bar{\rho}_b/dt) = (1/\gamma_b P)(dP/dt)$$

and

$$(1/\beta)(d\beta/dt) = (1/\rho_u)(d\rho_u/dt) = (1/\gamma_u P)(dP/dt)$$

Now from (4.49) for adiabatic compression of the unburnt gas

$$(1/P)(dP/dt) = 3r_b^2 \gamma_u (S_s - S_t) / (R^3 - r_b^3)$$

hence (4.50) reduces to

$$S_t = \alpha S_s + \left[(\gamma_u / \gamma_b) - 1 \right] \left[(\beta - 1) / (\beta - \alpha) \right] \alpha (S_s - S_t)$$

and on rearranging

$$S_t = \alpha S_s \left[(1 - \alpha) + k(\beta - 1) \right] / \left[\alpha(1 - \alpha) + \alpha k(\beta - 1) \right] \dots \dots (4.53)$$

where

$$\left. \begin{aligned} \alpha &= \bar{\rho}_b / \rho_o = (\bar{M}_b / \bar{M}_e) (\bar{T}_e / \bar{T}_b) (P / P_e) \\ \beta &= \rho_u / \rho_o = (P / P_o)^{1/\gamma_u} \\ k &= \gamma_u / \gamma_b \\ S_s &= dr_b / dt \end{aligned} \right\} \dots \dots \dots (4.54)$$

This equation (4.53) has the important advantage of requiring only one of the observations (r_b) to be differentiated with respect to time, thus reducing computation time and possible errors. The only additional assumption made as compared with eqn (4.51) is that of adiabatic compression of both the unburnt and burnt gas.

If it is assumed that $\gamma_u = \gamma_b$, that is, $k = 1$, then eqn (4.53) reduces to (using α from eqn 4.23)

$$S_t = \alpha S_s = (\bar{M}_b / M_o) (T_o / \bar{T}_b) (P / P_o) S_s \approx (P / P_o) (S_s / E_o) \dots (4.55)$$

which is one of the equations derived by Eschenbach and Agnew (EA 58) and independently by Grumer, Cook and Kubala (GC 59). This will give correct values of S_t ($= S_s^o / E_o$) at the beginning of the process. The value at the end should be somewhat high, whilst in the middle of the process it should be low during the early stages becoming high later.

An alternative form of eqn (4.55) can be obtained by using eqn (4.25)

for α thus,

$$S_t = (\bar{M}_b / \bar{M}_e)(\bar{T}_e / \bar{T}_b)(P/P_e) S_s \approx (P/P_e) S_s \dots (4.56)$$

Finally, if it is assumed that $\gamma_b = 1$ then

$$S_t = \alpha S_s \left[(1 - \alpha) + \gamma_u (\beta - 1) \right] / \left[\beta (1 - \alpha) + \alpha \gamma_u (\beta - 1) \right] \dots (4.57)$$

4.3.2 Equations Involving Pressure- or Radius-Time Observations Only

The necessity of observing both the pressure-time and radius-time variations during the combustion process complicates the experimental and computational procedure and thus increases the probability of error. Reliable equations for evaluating burning velocity over the whole process, using either one or other of these variables would thus be advantageous.

In particular for high pressure work the use of windows for observing the propagation of the flame can introduce difficulties, both in the design of the apparatus and in the interpretation of the flame radii. Thus although for relatively low pressures slit windows giving an uninterrupted view of the flame across a diameter have been used (FM 40, RP 62), higher pressures apparently require arrays of closely spaced small windows (GC 61) (Fig 4.3).

Windowless bombs have been used to determine burning velocities via either radius-time records using ionized gaps (Es 57) or pressure-time records (LV 34). However practically all of these attempts have been restricted to the early stages of the process during which the pressure rise was small (generally with $P < 1.1P_0$). If the method is to be used in this restricted way it is almost trivial to spend time deriving various forms of burning velocity equation. Such analysis only has merit if the technique is

to be used to its full extent, that is, for obtaining burning velocities over a range of pressures and temperatures from the results of a single experiment.

Since we possess an equation relating r_b and P , it is possible to derive equations in terms of either one or other of these variables. This is done in Appendices G and H.

Thus if radius-time records only are available, we may use the following equation to solve for P ,

$$(P/P_o)^{1/\gamma_u} [1 - (r_b/R)^3] + (P/P_e)(r_b/R)^3 \approx 1 \quad \dots\dots\dots(5.58)$$

Hence α and β can be determined from eqn (4.54); S_t then follows from (4.53)

Alternatively, where pressure-time records alone are to be used the burning velocity can be obtained from either,

$$S_t = (R^3/3r_b^2\beta)(dn/dt) \quad \dots\dots\dots(4.59)$$

or by substituting for r_b and n from (4.46) and (4.47) respectively,

$$S_t = \left[\frac{\{(1-\alpha) + k(\beta-1)\}}{(\beta-\alpha)^{4/3}(\beta-1)^{2/3}} \right] (\alpha R/3\gamma_u P)(dP/dt) \quad \dots(4.60)$$

However as will be noted, both of these approaches require measurements or estimates of the complimentary variable at at least one point of the process. Thus if r_b - t records are to be used, P_e is required; if P - t records are to be used S_s^o must either be measured or obtained by extrapolation.

Pressure-time records have the following advantages:

(a) Pressures can be continuously and accurately measured, at the wall of

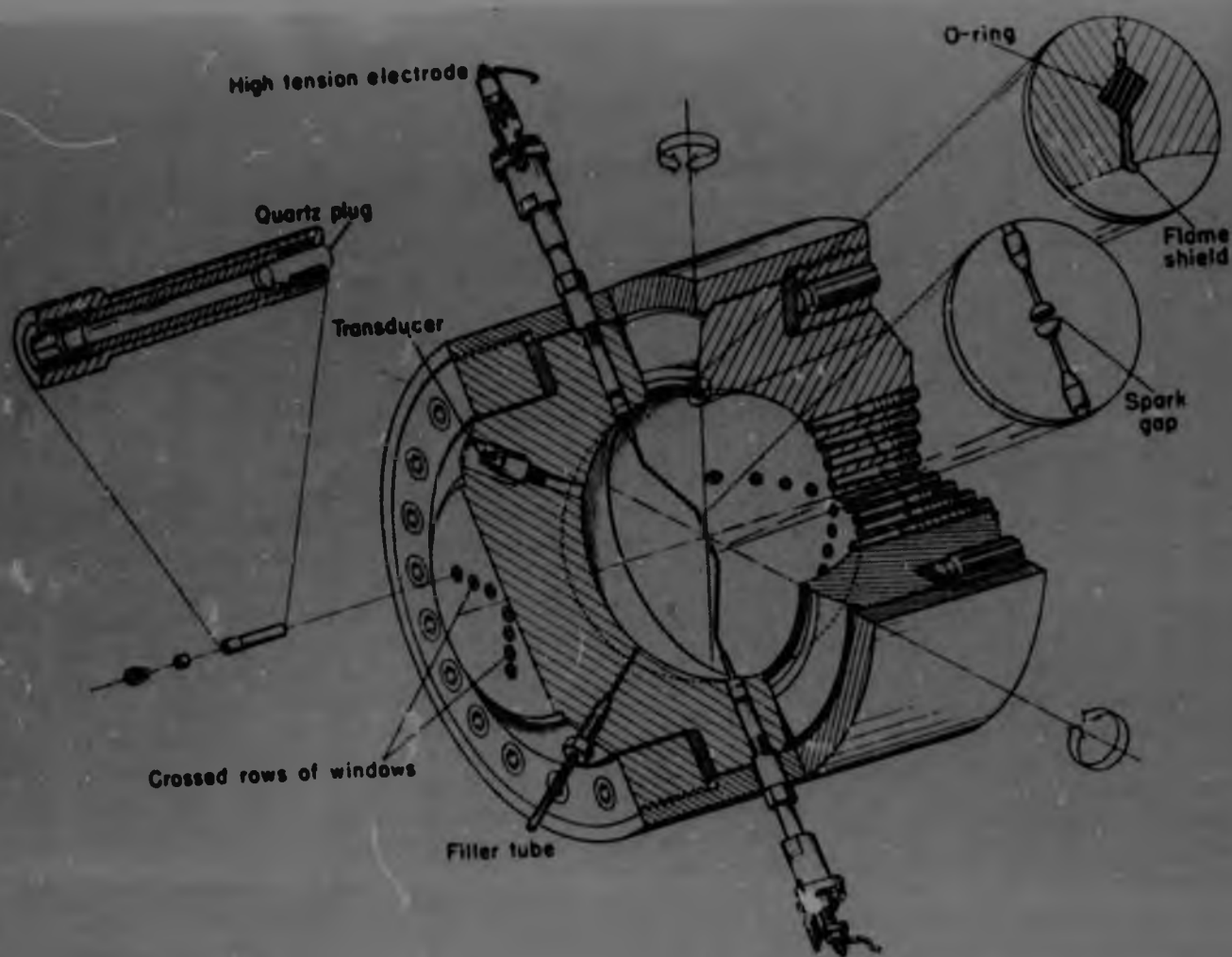


Fig 4.3 Spherical vessel for high pressure combustion studies (GC 61)

the vessel, throughout the entire combustion process with, if necessary, one or more records covering different ranges.

- (b) For slower flames pressure can be considered as a property of the system as a whole. Thus local irregularities of the flame front will, in general, be averaged out.
- (c) The design of a suitable vessel is considerably simplified.
- (d) The equations for burning velocity (4.59, 4.60) are simple to use.

However they have the following disadvantages:

- (i) Satisfactory pressure instrumentation is expensive.
- (ii) Non-isotropy due to buoyancy or other flame irregularities cannot be observed directly but must be inferred.
- (iii) Tedious corrections for time-lag must be applied with high velocity flames.
- (iv) Due to the rapid rate of change of dP/dt , particularly during the later stages of combustion, accurate determination of this rate can be difficult.

Radius-time records on the other hand have the following advantages:

- (a) Satisfactory equipment for photographing the flame is simple and inexpensive.
- (b) Non-isotropy due to buoyancy or other causes can generally be detected.
- (c) Due to the relatively slow rate of change of dr_b/dt determination of this variable is not subject to large errors.

But they have the following disadvantages:

- (i) At best - using slit windows - they only allow continuous viewing of the flame across a diameter. The use of such windows, or what is even worse closely spaced small windows or ionization gaps, can lead to serious errors if flame front irregularities exist.

- (ii) If the flame front is thick its location can present difficulties.
- (iii) As usually applied only luminous flames can be studied.
- (iv) Optical errors due to distortion of the windows or effects of the unburnt gas have to be guarded against.

Thus it appears that if a choice is to be made between one or other of these methods of observation, pressure-time records appear to have a slight advantage. However if a particle track technique is used in conjunction with radius-time records (Section 4.4.2) this method becomes extremely powerful. On the whole however it would appear that wherever possible both types of record should be taken, if for no other reason than that they can provide corroboration or indicate discrepancies in the results. In any case if radius-time records, with or without a particle track technique, are used to determine burning velocities over a range of pressures and temperatures from a single experiment, then it would seem highly desirable to determine pressure directly.

4.4 DIRECT DETERMINATION OF GAS PROPERTIES AND BURNING VELOCITIES

4.4.1 Theory

It has been shown earlier (Section 4.1.1, eqn 4.5) that for isotropic flame propagation in a constant volume spherical vessel, the burning velocity, expressed in terms of the properties of the unburnt gas, is given by:

$$S_u = (dr_b/dt) - (R^3 - r_b^3)(d\rho_u/dt)/(3r_b^2\rho_u) \dots\dots\dots (4.61)$$

when $\delta_u = \rho_u$. That is

$$S_s = S_u + S_{ug} \dots\dots\dots(4.62)$$

Here S_s ($= dr_b/dt$) is the spatial velocity of the flame front, S_u is the burning velocity relative to the unburnt gas, and $S_{ug} \left[-(R^3 - r_b^3)(d\rho_u/dt)/(3r_b^2 \rho_u) \right]$ is the spatial velocity of the unburnt gas immediately adjacent to the flame front (Fig 4.4 a).

Alternatively, in terms of the properties of the burnt gas, from eqn (5.15) ;

$$(\rho_u/\bar{\rho}_b) S_b = (dr_b/dt) + (r_b/3\bar{\rho}_b)(d\bar{\rho}_b/dt) \dots\dots\dots(4.63)$$

or

$$S_s = S_{sp} - S_{bg} \dots\dots\dots(4.64)$$

where

$$\left. \begin{aligned} S_{sp} &= (\rho_u/\bar{\rho}_b) S_b \\ S_{bg} &= (r_b/3\bar{\rho}_b)(d\bar{\rho}_b/dt) \end{aligned} \right] \dots\dots\dots(4.65)$$

Evidently S_{sp} is the spatial velocity which the flame front would have at constant pressure under the conditions prevailing at any instant (compare with eqn 4.39). Thus S_{bg} must be the spatial velocity of the burnt gas immediately adjacent to the flame front. (Fig 4.4 b).

Apparently therefore the spatial velocity of any element of unburnt gas at radius r and time t is given by

$$S'_{ug} = (R^3 - r^3)(d\rho_u/dt)/(3r^2 \rho_u) \dots\dots\dots(4.66)$$

where $r_b < r < R$, and will be a maximum at $r = r_b$ and zero at $r = R$.

Similarly, the spatial velocity of any element of burnt gas at radius r and time t is given by

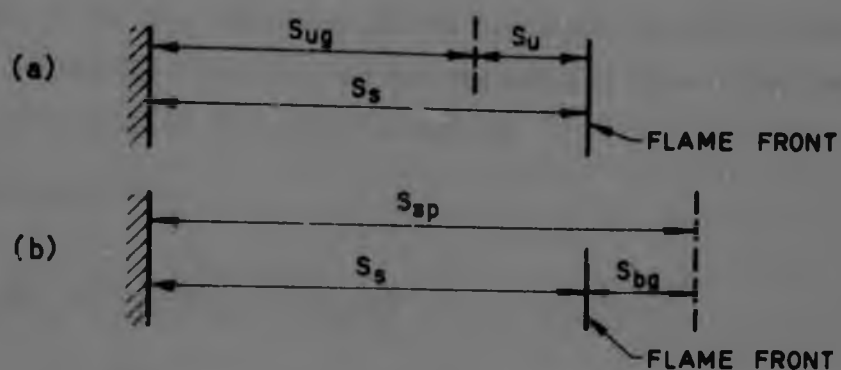


FIG. 4-4
VECTOR DIAGRAMS FOR UNBURNT AND
BURNT GAS

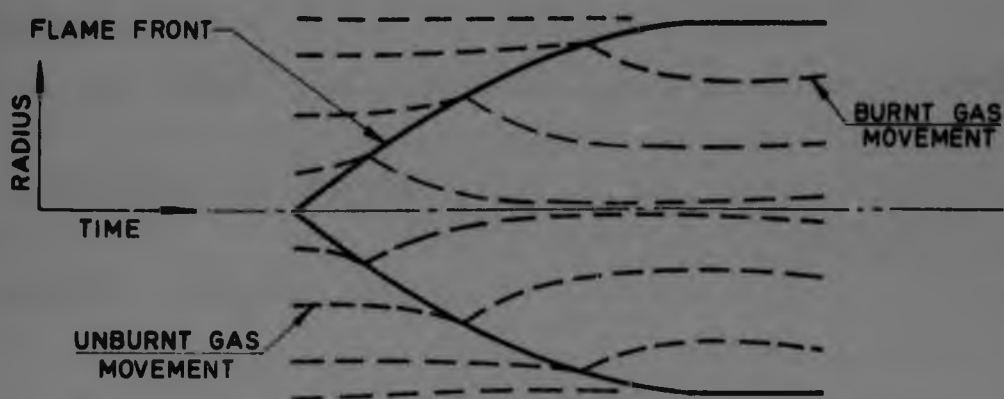


FIG. 4-5
PARTICLE TRACK RECORD FOR
CONSTANT VOLUME COMBUSTION
-DIAGRAMMATIC

$$S'_{bg} = (r/3 \rho_b)(d\rho_b/dt) \dots\dots\dots (6.67)$$

where $0 < r < r_b$, and will be a maximum at $r = r_b$ and zero at $r = 0$.

Hence if the gas velocities can be measured directly at various radii at any particular time then the gas densities at these radii can be determined by integrating eqn's (4.66) and (4.67).

Thus from (4.66),

$$(d\rho_u/dt) - [3r^2 S'_{ug}/(R^3 - r^3)] \rho_u = 0$$

or

$$\rho_u = C_1 e^{At}$$

$$\text{where } A = (3r^2 S'_{ug})/(R^3 - r^3)$$

and since at $t = 0$, $\rho_u = \rho_0$, $C_1 = \rho_0$.

Therefore

$$\rho_u = \rho_0 e^{At} \dots\dots\dots (4.68)$$

Similarly from eqn (4.67)

$$(d\rho_b/dt) - (3S'_{bg}/r)\rho_b = 0$$

or

$$\rho_b = C_2 e^{Bt}$$

where

$$B = 3S'_{bg}/r$$

and since at $t = 0$, $\rho_b = \rho_b^0$, $C_2 = \rho_b^0$.

Therefore

$$\rho_b = \rho_b^0 e^{Bt} \dots\dots\dots (4.69)$$

Solution of eqn's (4.68) and (4.69) at various radii at any time t thus yields density profiles in both the unburnt and burnt gas. Hence the mass densities of the unburnt and burnt gas follow from eqn's (4.3) and (4.13). Thus if the pressure throughout the system at time t is known then from the general gas equation the temperature profiles may be determined provided molecular weight profiles are known or can be estimated. For high velocity flames suitable corrections for pressure gradients would have to be applied. (See Section 4.2.1).

If the main purpose of any constant volume experiment is to determine burning velocity per se then evidently this can be obtained directly from either eqn (4.62) or (4.64) by measuring the spatial velocity of the flame front as well as either of the gas velocities adjacent to this front. (Eqn 4.64 requires in addition that the densities ρ_u and ρ_b immediately adjacent to this flame front be determined.)

The foregoing equations are general to the extent that no restricting assumptions regarding heat loss, temperature and pressure uniformity, etc. have been introduced. Also if eqn's (4.62) or (4.64) are used for determining burning velocity any an-isotropicity of the flame should not seriously affect the results.

If both S_{ug} and S_{bg} are determined then the method is self-corroborative since for unit area of flame front, at each instant of time, from continuity

$$\rho_u S_u = \rho_b S_{sp}$$

that is

$$\rho_u(S_s - S_{ug}) = \rho_b(S_s + S_{bg}) \quad \dots\dots\dots (4.70)$$

Clearly the method is equally applicable to constant pressure (soap bubble) as well as tube experiments. Thus for constant pressure combustion as in a soap bubble it can be shown (Appendix I) that, for relatively low velocity flames and neglecting inertia effects, the spatial velocity of the burnt gas S_{bg} is everywhere zero. Thus

$$S_u = (\rho_b^0 / \rho_u^0) S_s \quad \dots\dots\dots (4.71)$$

or

$$S_u = S_s - S_{ug} \quad \dots\dots\dots (4.72)$$

For high velocity flames or where inertia effects are not negligible S_{bg} will not be zero nor will ρ_u^0 and ρ_b^0 be constant. Thus although eqn (4.72) will still be applicable at each instant of the process, S_u will not be constant. Results should then be reported in terms of the prevailing variable density of the unburnt gas immediately adjacent to the flame front.

4.4.2 Particle Track Method

Evidently one of the most direct techniques of determining the various velocities required above is by the particle track method, preferably using intermittent illumination. In essence Flock et al (FM 40) used such a method, but with the equivalent of continuous illumination, in an attempt to settle the afterburning argument. By attaching minute particles of black gunpowder to human hairs suspended in a spherical vessel the burnt gas movement could be observed.

The use of the particle track method for stationary flames is well established and has yielded excellent results (VL 43, Fr 57, LW 59). Its application to propagating flames should therefore present no serious difficulties. If a streak camera is used it should yield the type of record shown in Fig 4.5.

Incidentally it should also be possible using this method to get some indication of the flame front thickness and also to study flames of low actinic value.

CHAPTER 5

COMPARISON OF BURNING VELOCITY EQUATIONS

One of the early disadvantages of the constant volume method was the inaccuracy resulting from the use of the unburnt gas equation (3.10) developed by Fiock and Marvin (FM 37). Since this entails finding a small difference between two large quantities, errors in observation are magnified, particularly during the early stages of the process. Lewis and von Elbe (LV 34, LV 51) overcame this difficulty by introducing a burnt gas form of equation (3.9) requiring two additional assumptions (OR 59). However, the range of this equation was thereby limited to the early stages of combustion during which the pressure rise is small, besides being admittedly approximate (but adequate) even over this range.

Many attempts have since been made (Chapter 3) to derive more reliable equations, generally with limited success. Most of these have been based on a burnt gas form of equation but are mainly applicable to the early stages of the process. As such therefore they do not represent any significant contribution, particularly since they frequently turn out to be less reliable than the Lewis and von Elbe equation.

In this chapter we will first illustrate the relative effects of observational errors on the unburnt and burnt gas forms of equation. This will be followed by a comparison of values of ; (i) density ratio α , (ii) mass fraction burnt n , (iii) calculated and observed radii, (iv) calculated and observed pressures, (v) burning velocities using different equations developed in this thesis, and (vi) burning velocities from various equations proposed in the literature. The data used for these comparisons will be that obtained from tests on acetylene/air mixtures fired in a spherical vessel of 6.306-in (16.02 cm) internal diameter. (RP 62, RT 63, Appendix J).

These observations represent the mean of three tests under nearly identical conditions. Due to the low rate of pressure rise during the early stages of combustion two pressure traces were recorded. One covered the full range 0 - 100 psig - whilst the other recorded a range of about 0 - 4 psig.

5.1 UNBURNT VERSUS BURNT GAS EQUATION

Here the relative effects of observational errors on burning velocities obtained by using an unburnt and a burnt gas form of equation will be compared (RP 62).

Thus from eqn (4.8), with $\bar{p}_u = p_u$

$$S_u = dr_b/dt - [(R^3 - r_b^3)/(3r_b^2 \gamma_u P)] (dP/dt) \dots\dots\dots(5.1)$$

and from eqn(4.21), with $\bar{P}_b = P$

$$S_b = (\rho_o/\rho_u) \left[\alpha(dr_b/dt) - (r_b/3)(d\alpha/dP)(dP/dt) \right] \dots\dots\dots(5.2)$$

Figure 5.1 shows burning velocities for a stoichiometric acetylene/air mixture, calculated from each of these two equations, plotted against flame front radius.

At radii below about 2-in (≈ 5 cm) the values of S_u are uncertain (compare S_u and S'_u obtained from the high and low pressure records respectively). In addition S_u is consistently greater than S_b over this region. Two parameters appear to be mainly responsible for these discrepancies. Firstly, values of dP/P are apparently too low over the early stages of combustion due to insufficient sensitivity in the measurement of P . Thus the initial steep portion of the curve marked S_u (calculated from data obtained on the high-range pressure record) is immediately eliminated by

calculating values of S'_u based on data from the more sensitive low pressure record. As it becomes more and more difficult to discriminate small pressure changes from this latter record, values of S'_u in turn are found to be considerably in excess of S_b .

The second contributory factor for the discrepancy between S_u and S_b over the initial stages, is the term r_b . If values of the flame radius are consistently high due to a systematic error, values of S_u will also be high - becoming progressively larger towards the instant of ignition. On the other hand the effect of such an error on S_b will be insignificant over the initial stages, since the second term in eqn (5.2) is then very small. (It is assumed here that, since the burning velocity is then relatively constant, values of dr_b/dt are not much affected by a constant systematic error in r_b . Even if the derivative were affected S_u and S_b would change in the same direction, the effect on S_u being more pronounced.)

A reliable assessment of the errors in flame front radius and pressure over the intermediate and final stages of combustion is difficult. However, an indication of the errors in S_u and S_b likely to arise from assumed systematic errors r_b and P can be obtained if it is assumed that the first derivatives dr_b/dt and dP/dt are unaffected by these errors. A standard technique is employed (GS 41, Wi 52, Tr 62) in which the total differentials dS_u and dS_b are used as approximations to the total increments ΔS_u and ΔS_b . In equations (5.1) and (5.2) the partial derivatives of S_u and S_b with respect to both r_b and P were calculated and the total differentials determined at various stages of the process, using systematic errors Δr_b and ΔP based on estimates of the resolution and accuracy attainable in practice. The results of this error analysis are given in Fig 5.2, from which it is seen that greater reliance must be placed on the values of burning velocity determined from the burnt gas equation over all stages of the

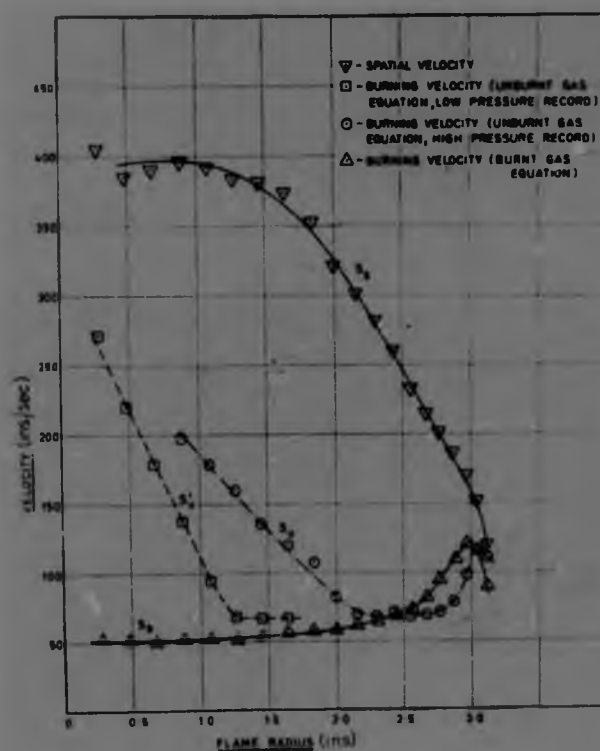


Fig 5.1 Flame velocity versus flame front radius for stoichiometric acetylene/air mixture (RP 62)

I	r_b	P	% ERRORS			
			Δr_b	ΔP	S_u	S_b
ms	ins	psia	ins	psia		
1	0.48	12.1	± 0.01	± 0.1	± 100	± 0.4
2	0.87	12.2	± 0.01	± 0.1	± 75	± 0.9
4	1.64	13.6	± 0.01	± 0.5	± 43	± 3.5
6	2.30	19.0	± 0.01	± 1.0	± 28	± 4.0
8	2.77	35.3	± 0.01	± 1.0	± 8	± 2.6
9	2.96	55.9	± 0.01	± 1.0	± 8	± 0.7

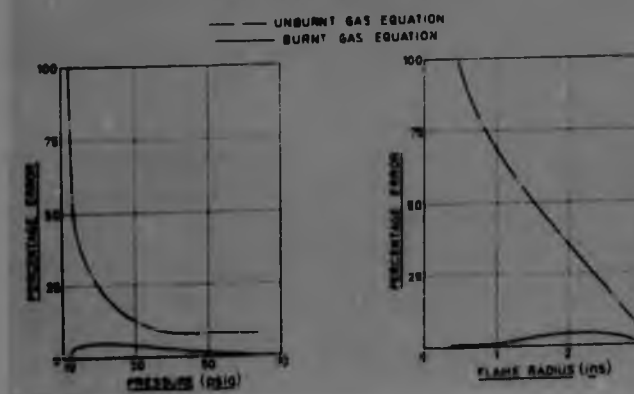


Fig 5.2 Effect of errors in radius and pressure on S_u and S_b (RP 62)

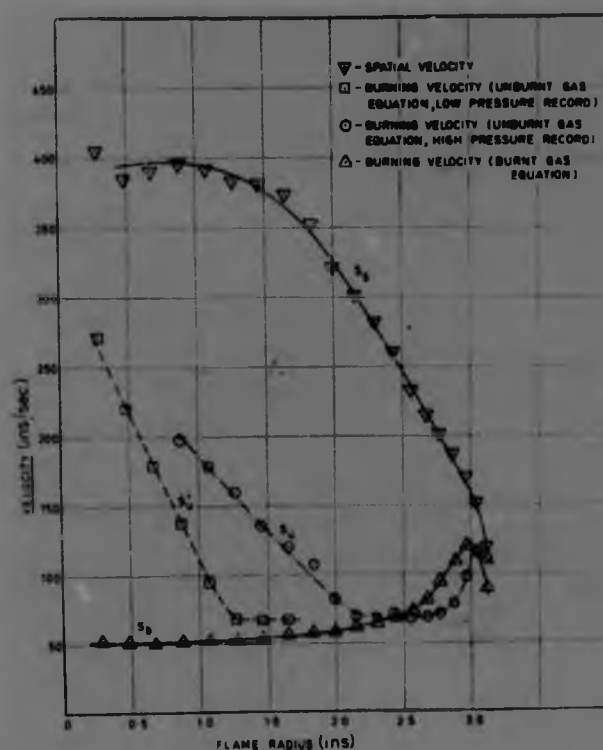


Fig 5.1 Flame velocity versus flame front radius for stoichiometric acetylene/air mixture (RP 62)

t	r _b	P	Δr_b	ΔP	% ERRORS	
					S _u	S _b
1	0.48	12.1	±0.01	±0.1	±100	±0.4
2	0.87	12.2	±0.01	±0.1	±75	±0.8
4	1.64	13.8	±0.01	±0.5	±43	±3.8
8	2.30	18.0	±0.01	±1.0	±28	±4.0
8	2.77	35.3	±0.01	±1.0	±9	±2.8
9	2.86	85.9	±0.01	±1.0	±8	±0.7

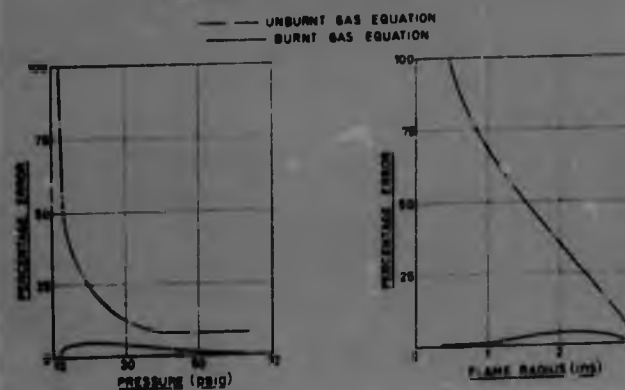


Fig 5.2 Effect of errors in radius and pressure on S_u and S_b (RP 62)

combustion process.

5.2 DENSITY RATIO α

Because of the radial density distribution in the burnt gas region it has been found convenient, in the burning velocity equations derived earlier, to introduce a dimensionless density ratio α . Thus with $\bar{P}_b = P$, is given by (Section 4.1.2):

$$\alpha = \bar{\rho}_b / \rho_o = (\bar{M}_b / M_o) (\bar{T}_o / \bar{T}_b) (P / P_o) \dots\dots\dots (5.3)$$

or since at the end of the process $\bar{\rho}_e = \rho_o$

$$\alpha = \bar{\rho}_b / \bar{\rho}_e = (\bar{M}_b / \bar{M}_e) (\bar{T}_e / \bar{T}_b) (P / P_e) \dots\dots\dots (5.4)$$

Evidently, provided $\bar{M}_b / \bar{T}_b$ can be accurately determined, both these equations should yield the same results. However, due to a variety of reasons, exact evaluation of $\bar{M}_b / \bar{T}_b$ is difficult. Fortunately in practice the use of flame front values in place of means, appears to provide a reasonable compromise. In any event comparison of the results obtained from equations (5.3) and (5.4) using flame front values gives an indication of the probable source and extent of any errors in $\bar{M}_b / \bar{T}_b$.

5.2.1 Initial and Final Values of α

For comparative purposes a good indication of any discrepancy in the calculated values of $\bar{M}_b / \bar{T}_b$ can be obtained by comparing values of α from the above equations for the initial and final stages of the process. Thus for any given mixture composition and initial conditions, together

with observed maximum pressures, values of M_b and T_b corresponding to equilibrium conditions at the flame front may be determined from combustion charts. (Appendix K). Table 5.1 below lists values of α_o and α_e calculated from the results of a series of tests covering a range of acetylene/air mixtures. Clearly α_e from eqn(5.4) must be equal to unity.

Table 5.1
Initial and Final Values of α

Mixture	Rich		Correct	Lean		
	A	B	C	D	E	F
%Acetylene	12.59	9.87	7.72	5.99	4.75	3.31
eqn 5.3	0.1085	0.1115	0.1161	0.1255	0.1455	0.1814
α_o eqn 5.4	0.1169	0.1224	0.1248	0.1313	0.1500	0.1865
α_e eqn 5.3	0.9281	0.9120	0.9301	0.9559	0.9684	0.9727

In all cases eqn (5.3) yields lower values than eqn (5.4). In particular α_e from eqn (5.3) is seen to be less than the correct terminal value of unity. Each of the terms in the expression for α_e (eqn 5.3) must thus be examined if the cause of this discrepancy is to be found.

The quantities M_o , T_o and P_o are accurately known and can be immediately exonerated. The discrepancy must therefore be attributed to P_e and/or M_e/T_e being too low. Consider P_e : An error here could arise either from (i) incorrect calibration of the pressure measuring system, or (ii) inadequate transient response of the pressure transducer. The possible error due to (i) is insufficient to account for the observed discrepancy (RP 62, Tr 62). The effect of any error arising from (ii) would be to overestimate P_e , due to overshoot at the end of the process. Use of the correct value would thus lower α_e still further.

Consider next the error which may arise from using flame front values of M_e/T_e instead of mean values $\bar{M}_e/\bar{T}_e$. It has been shown (Section 3.12) that the temperature at the flame front is less than that at the centre of the vessel. Thus T_e must be less than $\bar{T}_e$. Hence under equilibrium conditions M_e may be slightly larger or smaller than $\bar{M}_e$, depending on the mixture strength (Fig 5.3). However the difference between M_e and $\bar{M}_e$ is small as compared with the difference between T_e and $\bar{T}_e$. The use of mean equilibrium temperatures to calculate α_e would thus in general yield even lower values than those obtained by using flame front temperatures.

Since the difference between the molecular weight of the burnt and unburnt gas in this case is small ($M_e/M_o \approx 1$) errors from this source are unlikely. The only term left to account for the discrepancy between the calculated and required values of α_e is the temperature of the burnt gas. Thus it appears that the calculated equilibrium value of flame front temperature is too high. However the method (HW 49) used for determining T_b has been checked against three other methods* none of which give low enough values. (Temperatures and molecular weights calculated from HW 49 are shown in Fig 5.3. The required values of $\bar{T}_e$ and α_e - eqn 5.3 - to be unity is also plotted.)

* For example, at the initial pressure of 12 psia, calculated values of T_b^o were;

- (a) from generalised thermodynamic charts (HW 49) - 4622°R ,
- (b) by direct calculation taking only water-gas and CO_2 reactions into account - 4628°R ,
- (c) from acetylene/air charts (KT 60) - 4480°R ,
- (d) from reference GW 48 - 4540°R .

There are two factors which may account for the calculated value of T_b being too high. Firstly, combustion may not occur adiabatically due to heat loss. Calculations suggest that even under the worst realistically possible conditions, the quantity of heat lost by radiation up to the time the flame reaches the bomb wall is negligible. Conductive heat loss, due to buoyancy, is likely to be larger for slow burning mixtures, and should thus lead to lower values α_e for the rich and lean mixtures tested. This is contrary to what has been found (Table 5.1). Heat loss cannot therefore explain the discrepancy.

Secondly, the assumption that equilibrium is attained immediately behind the flame front may not be justified: insufficient time may be available for the reaction to go to completion. If this is the case then at any air/fuel ratio the thickness of such a reaction zone should increase with flame speed. Moreover, there is likely to be an additional effect due to air/fuel ratio, very rich and lean mixtures attaining equilibrium more rapidly.

These predictions may be checked by plotting values of α_e against spatial velocity and air/fuel ratio (Fig 5.4 a and b). As a representative spatial velocity for each mixture that occurring during the constant flame speed period after ignition has been chosen.

These graphs reveal definite correlations between α_e and initial spatial velocity and air/fuel ratio. The lowest value of α_e (corresponding to the maximum error in the burnt gas temperature and hence greatest departure from equilibrium) coincides with the highest observed spatial velocity. Thus if there is a lack of equilibrium at the end of the process ($\alpha_e < 1$) this is probably also the case over the initial stages, where its effects may be even more pronounced due to higher spatial velocity - and hence a thicker reaction zone. The value of α_0 from eqn (5.3) is thus likely to be too low.

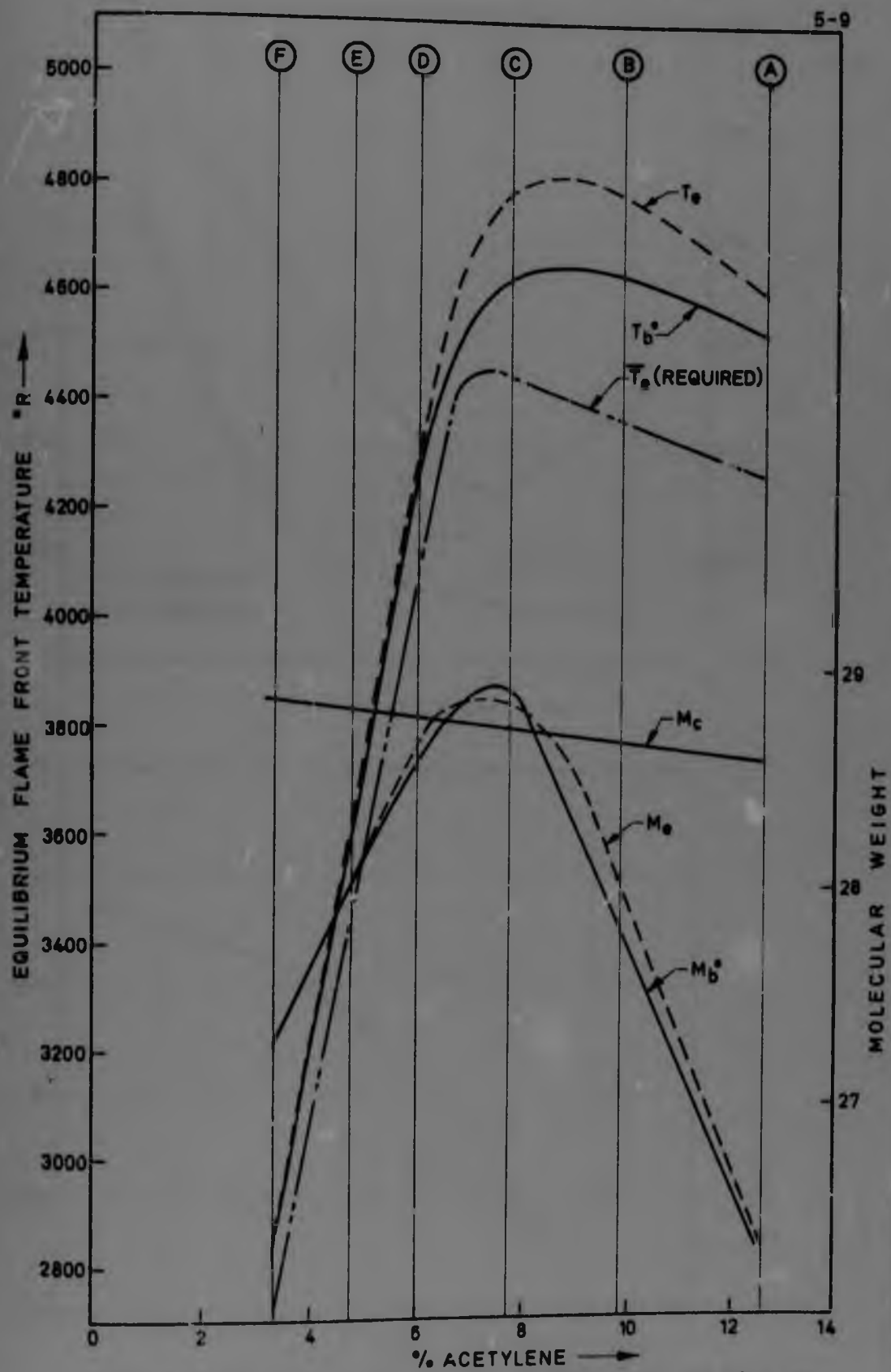


FIG. 5-3 FLAME FRONT TEMPERATURES AND MOLECULAR WEIGHTS FOR ACETYLENE/AIR MIXTURES

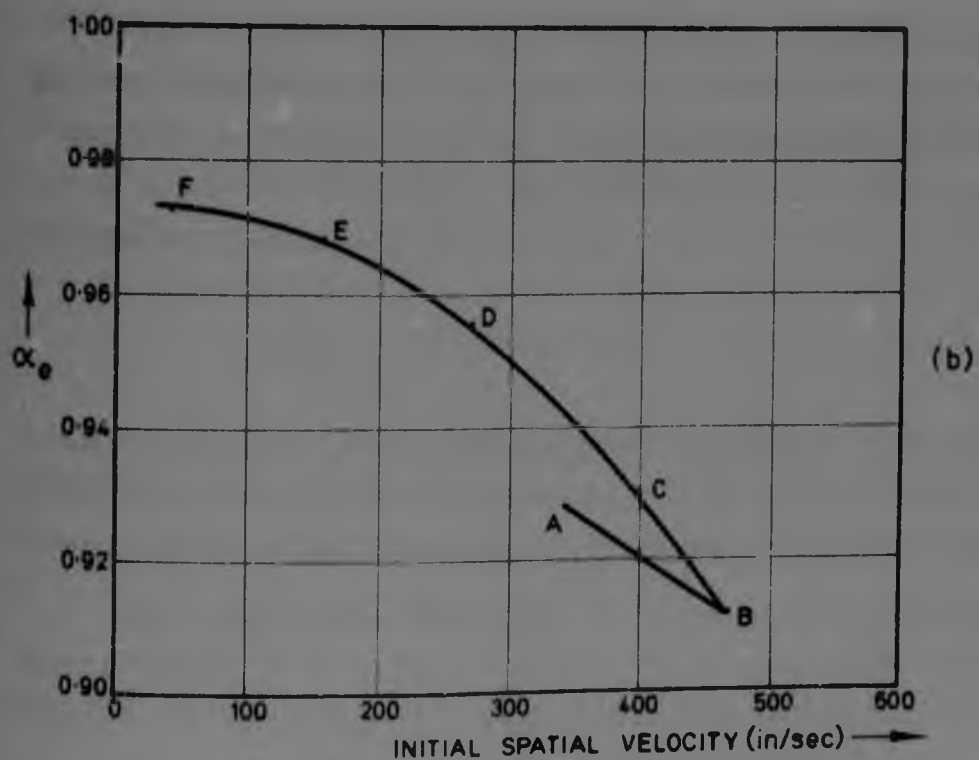
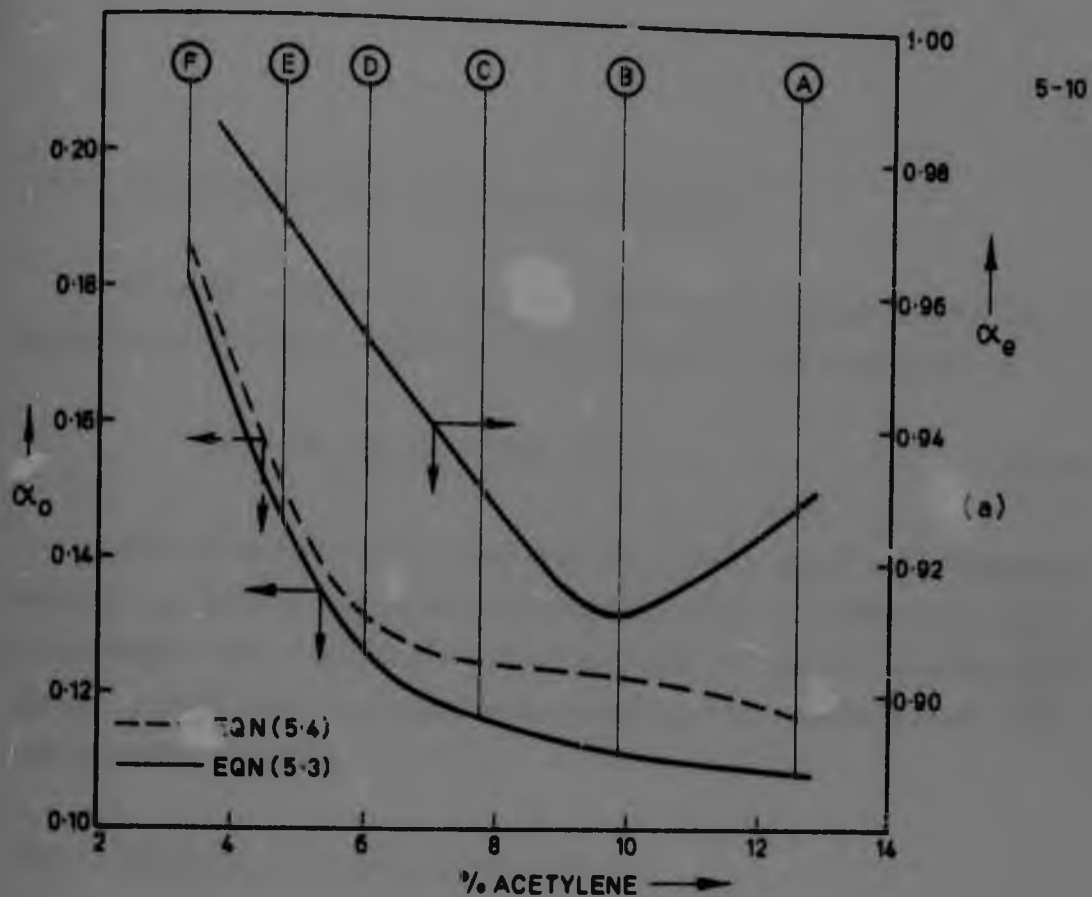


FIG 5.4 VARIATIONS OF α WITH MIXTURE STRENGTH AND INITIAL SPATIAL VELOCITY

5.2.2 Recommended Equation for Determining α

In order to allow for any lack of equilibrium we may use the alternative expression for α - eqn (5.4) - but with flame front values, that is,

$$\alpha = (M_b/M_e)(T_e/T_b)(P/P_e) \dots\dots\dots(5.5)$$

This must yield the correct value of α_e (unity) at the end of the process irrespective of any systematic errors in the calculation of the molecular weight and temperature of the burnt gas. In fact the use of eqn (5.5) should be justified even if under some conditions the departure from equilibrium were negligible.

5.2.3 Variation of α During the Process

The evaluation of α throughout the process requires determination of the interrelated parameters M_b/T_b and P . In this report the former is obtained from generalised combustion charts (HW 49)(Appendix K) and tabulated as a function of pressure. For convenience in the digital computer calculations an equation of the form

$$\mu = M_b/T_b = A - B \log P \dots\dots\dots(5.6)$$

is fitted to this data over the pressure range of each experiment. The maximum error resulting from this is always less than 0.25 per cent, which is in any event better than the accuracy to which the charts can be read.

Since the terminal value of P can be accurately established in any particular test, and α is directly proportional to the pressure ratio P/P_0 (Fig 5.5), the evaluation of α during the process presents no difficulty.

In fact for the tests shown in Fig 5.5, the slopes of all the α versus P/P_0 curves are essentially the same*. Apparently therefore all that is required here (in order to establish the slopes of these curves) is a knowledge of M_b/T_b and P at the two end points for any particular test. The curves for any other air/fuel ratio can then be drawn once the values of P_0 and P_e for such tests are known.

Evidently the accuracy with which α can be determined at any particular stage of the process is directly dependent upon the accuracy of measurement of the pressure P . Care must therefore be taken in any experiment to ensure accurate and sensitive measurement of this variable.

5.3 MASS FRACTION BURNT

One of the most reliable techniques which has been used to evaluate burning velocities in a spherical constant volume vessel involves the determination of the mass fraction burnt (n). Various attempts have from time to time been made to obtain simple approximations to the Flamm and Mache expression (eqn 3.3) applicable to the early stages of the process. It will be shown here that the most convenient of these - for pressure ratios P/P_0 up to about 1.1 - are those due to Lewis and von Elbe (eqn 3.8) and Grumer et al (eqn 3.30). However where it is desired to determine burning velocities at higher pressure ratios, either the approximate expression due to O'Donovan and Rallis (eqn 3.28) or one of the exact forms developed in this thesis must be used. These latter equations yield essentially the same results throughout the whole process and have the advantage that they incorporate known boundary conditions. Further any lack of equilibrium in the burnt gas is effectively accounted for.

*Actually from eqn (5.5)

$$d\alpha/dP = (\alpha/P) - (\alpha M_b/T_b) \left[(1/M_b)(dM_b/dP) - (1/T_b)(dT_b/dP) \right]$$

or if the second term is small, $d\alpha/dP \approx \alpha/P$.

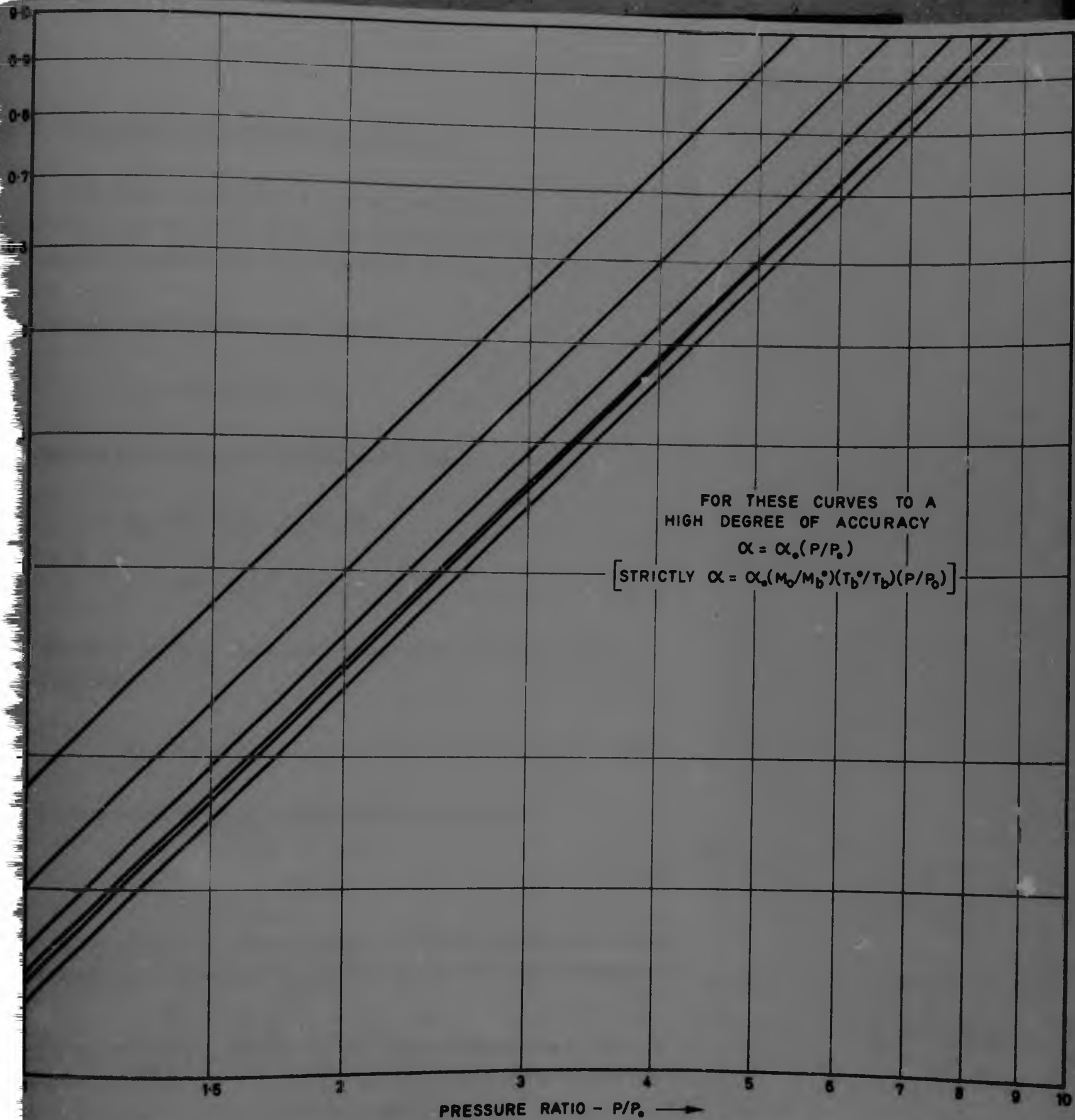


FIG. 5.5 VARIATION OF α WITH PRESSURE RATIO

5.3.1 Comparison of Various Expressions for n

Only four equations for n will be considered here. These will be compared by applying them to the data obtained from the combustion of a stoichiometric acetylene/air mixture (Test C). The equations to be compared are:

- (i) That due to Lewis and von Elbe (LV 51);

$$n_L = (P - P_0)/(P_e - P_0) \dots\dots\dots(5.7)$$

- (ii) That due to Grumer, Cook and Kubala (GC 59);

$$\begin{aligned} n_G &= (P - P_0)/\gamma_u P_0 (E - 1) \\ &= \alpha(P - P_0)/\gamma_u P_0 (\beta - \alpha) \dots\dots\dots(5.8) \end{aligned}$$

- (iii) The exact equation expressed in terms of the flame front radius (eqn 4.44);

$$n_R = \alpha r_b^3 / R^3 \dots\dots\dots(5.9)$$

- (iv) The equivalent equation in terms of pressure (eqn 4.47);

$$n_P = \alpha(\beta - 1)/(\beta - \alpha) \dots\dots\dots(5.10)$$

The equation developed by O'Donovan and Rallis yields results which are insignificantly different from eqn(5.10) and will thus not be considered here.

Clearly any expression for n must yield a zero value at the start of the process and unity at the end. However as is seen from Fig 5.6 only equation (5.9) and (5.10) satisfy both these conditions.

The equation due to Lewis and von Elbe is evidently quite adequate for pressure ratios up to about 1.1 (Fig 5.7). Thereafter the deviation from the exact value of n becomes progressively larger, until at the end of the process the error for this particular mixture is about 23 per cent (Fig 5.6).

Grumer, Cook and Kubala's equation also gives acceptable results up to a pressure ratio of about 1.1 (Fig 5.7) after which it σ rapidly from the exact value, the error at the end of the process being about 37 per cent.

The two 'exact' forms of equation are seen to yield similar results. However values from eqn (5.9) - involving the observed flame front radius - are somewhat high during the early stages and low later, as compared with eqn (5.10). This discrepancy gives an indication of the consistency achieved as between pressure and radius observations.

At first glance it would appear that the 'radius' equation (5.9) should be more reliable. Yet the fact that it gives results which are high during the initial stages as compared with the Lewis and von Elbe equation - which can be shown to be correct at the start of the process - suggests that it is probably in error over the early stages of the process.

In order to discuss the possible source of these discrepancies in greater detail it is necessary to consider a comparison of the observed flame front radii with those obtained from the pressure data.

5.4 OBSERVED VERSUS CALCULATED FLAME FRONT RADII

From eqn (4.43) the flame front radius is given by

$$r_b = R \left[1 - (1 - n)/\beta \right]^{1/3} \dots\dots\dots (5.11)$$

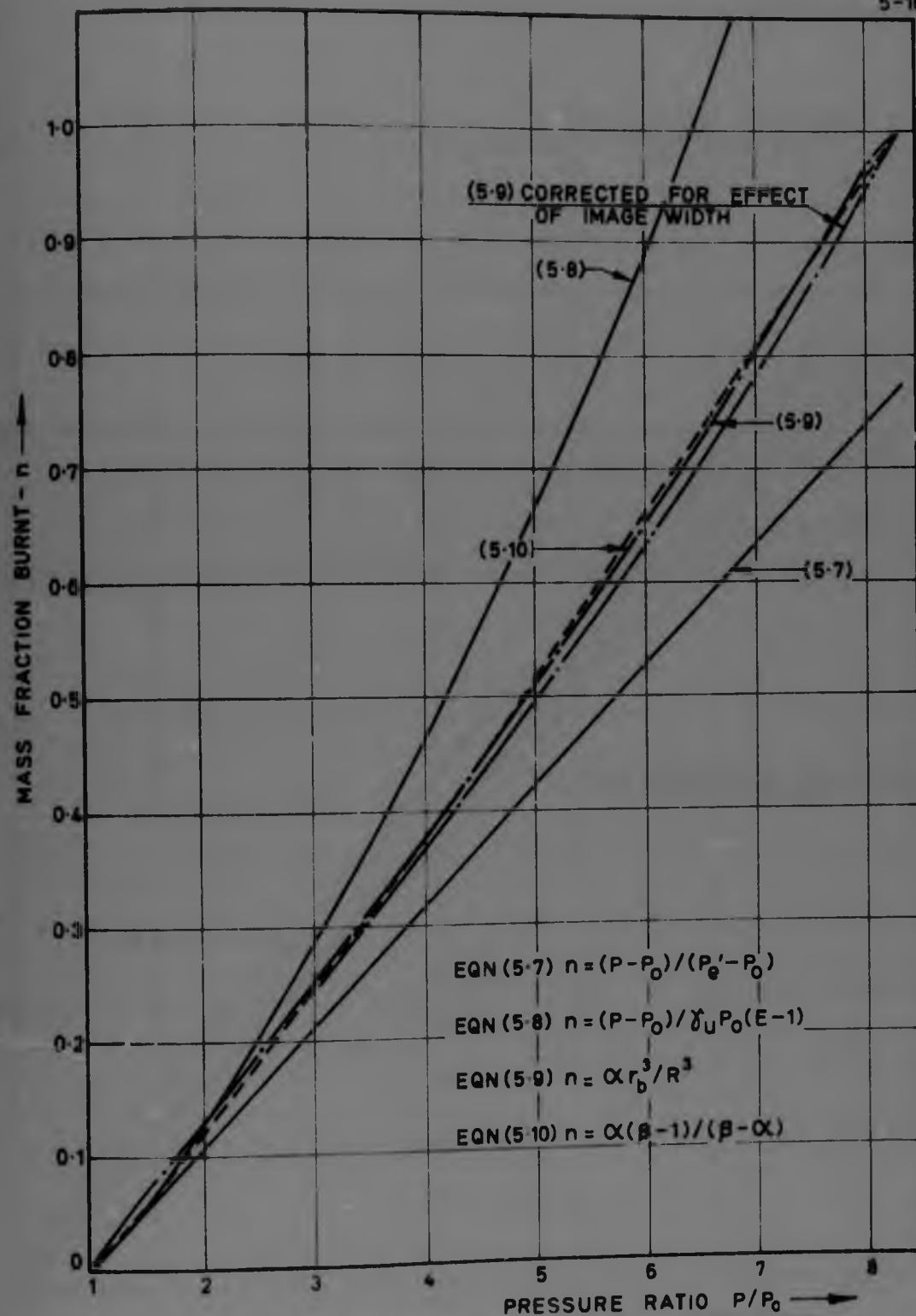


FIG 5-6 MASS FRACTION BURNT VERSUS PRESSURE RATIO (HIGH-RANGE PRESSURE RECORD - TEST C)

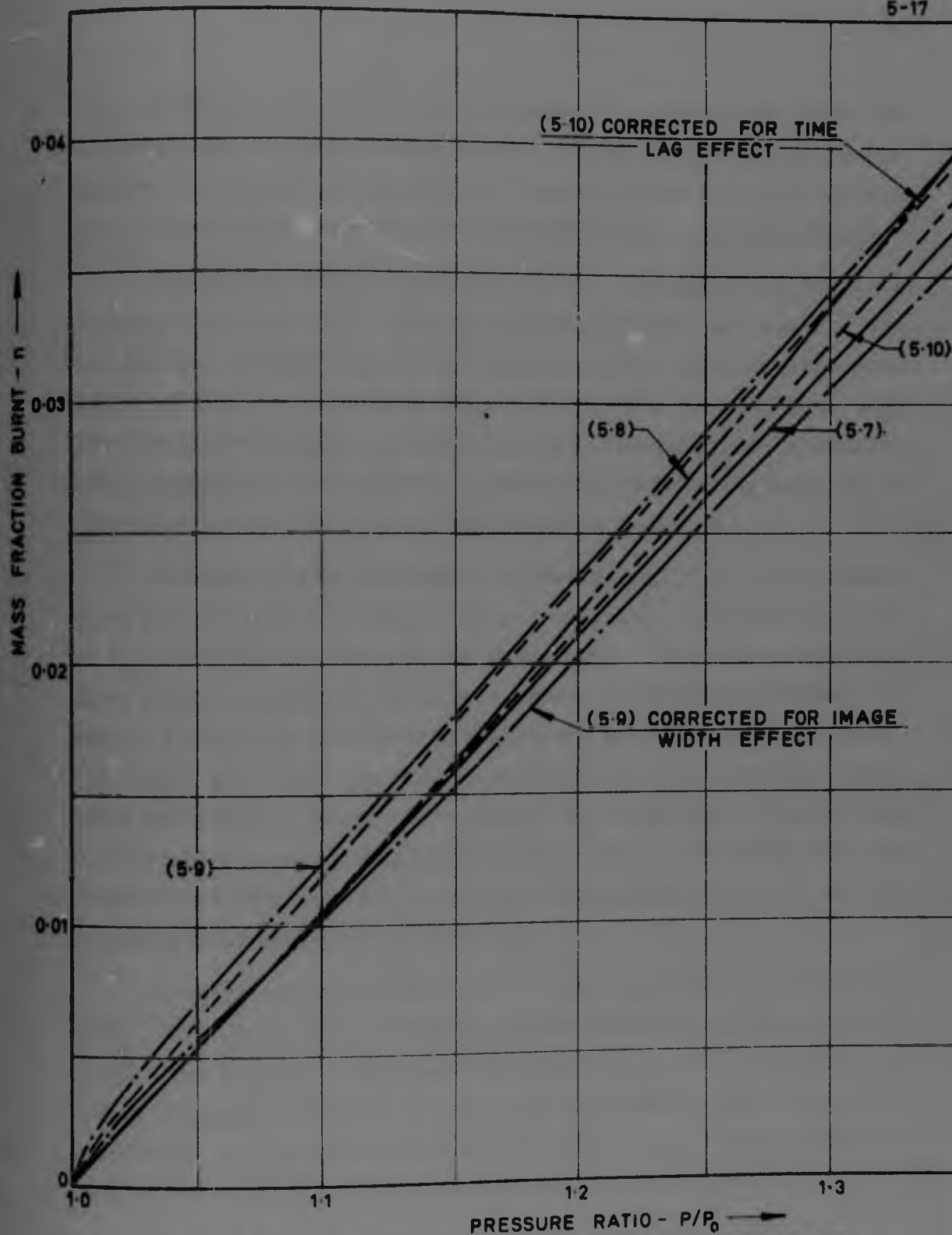


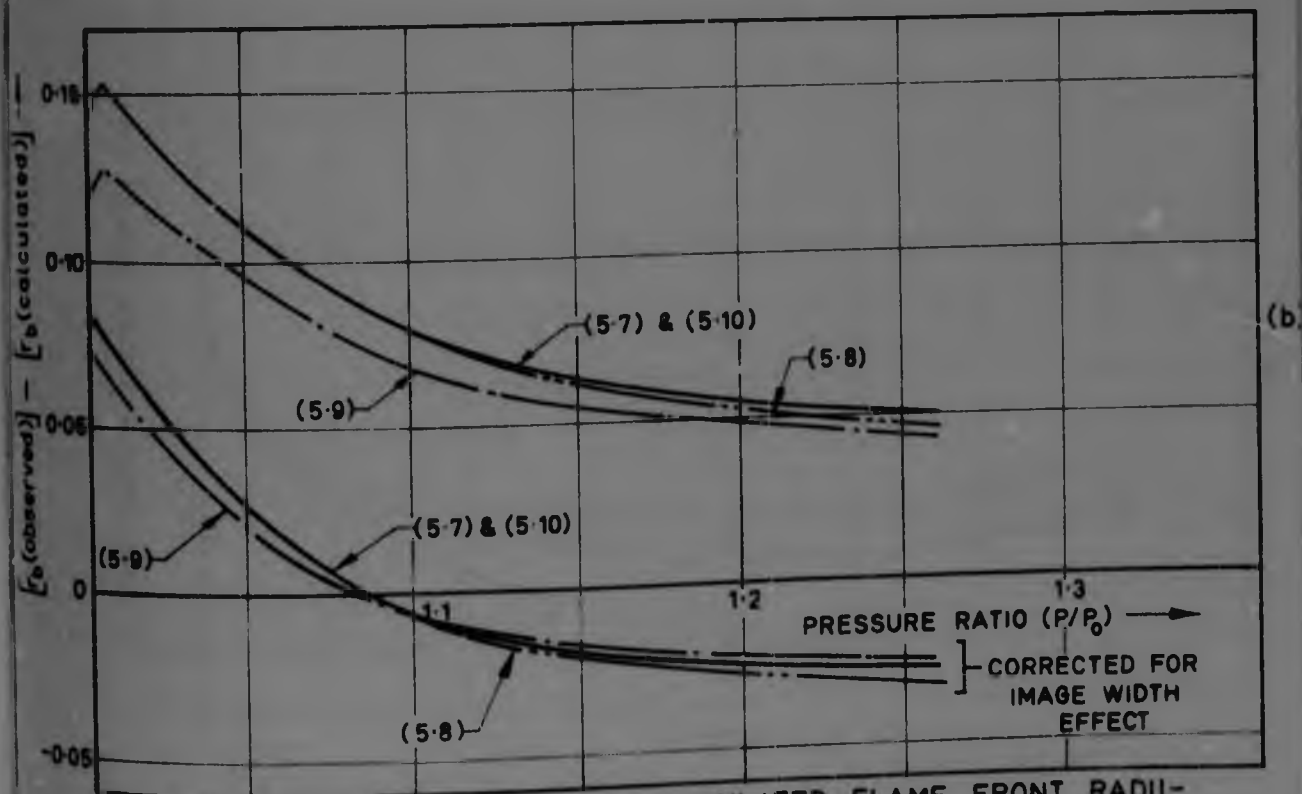
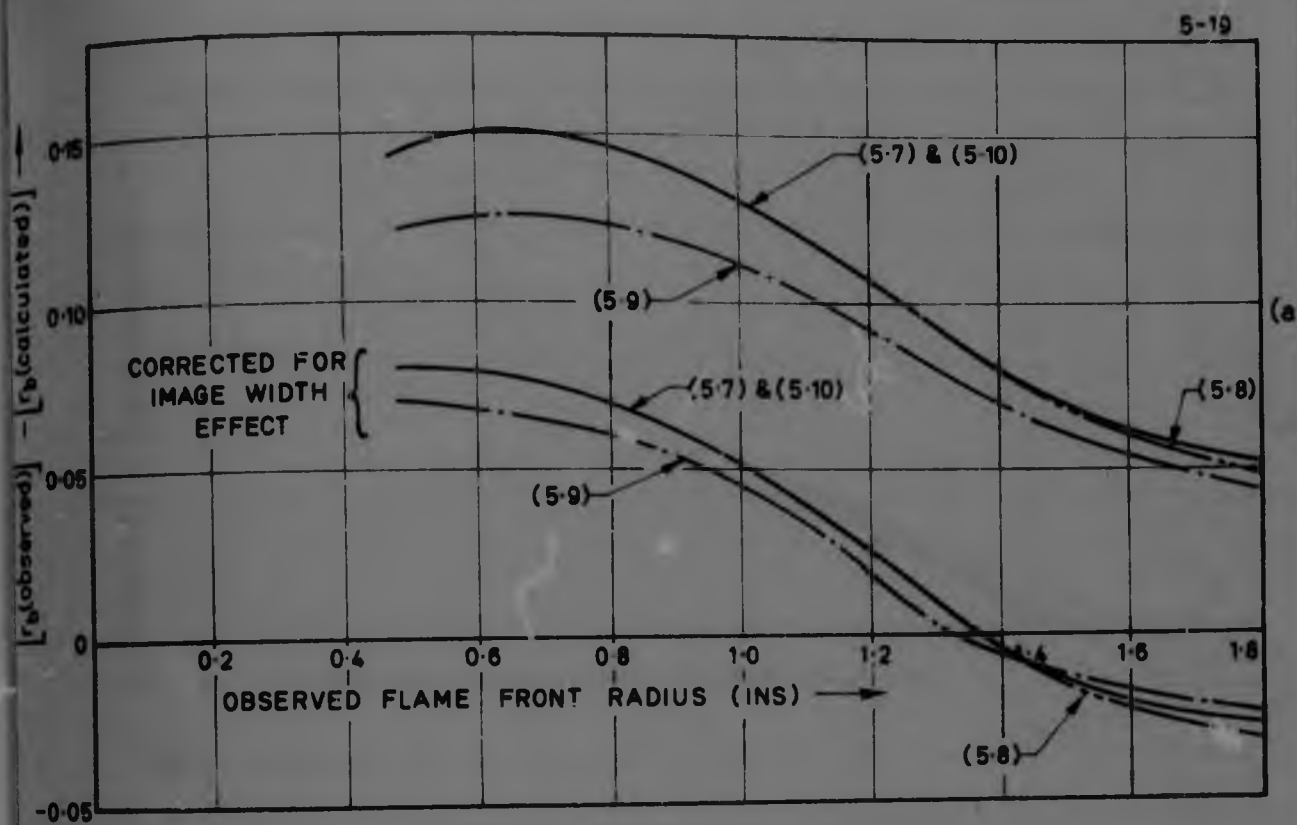
FIG. 5.7 MASS FRACTION BURNT VERSUS PRESSURE RATIO (LOW-RANGE PRESSURE RECORD-TEST C)

Thus knowing β ($= \rho_u / \rho_o$), R and n , values of r_b may be calculated and compared with the corresponding observed values. This technique, used by Manton, von Elbe and Lewis, provides a sensitive indication of the consistency of the results and validity of the thermodynamic assumptions made.

Differences between r_b -observed and r_b -calculated from the above equation, using values of n given by eqn (5.7) and (5.10), are shown in Figs 5.8 and 5.9. Results from the low-range pressure records (abbreviated LRPR) of Test C are plotted in Fig 5.8, whilst those from the high-range pressure record (HRPR) are shown in Fig 5.9. The differences between the observed and calculated values of r_b are seen to be relatively large, and to correspond to those between n_R (eqn 5.9) and n_P (eqn 5.10).

Consider now the discrepancy between n_R and n_P in terms of these observed and calculated values of flame front radius. Evidently the values of n_R ($= \alpha r_b^3 / R^3$) are high over the initial stages. There are clearly only three possible sources of error here: either r_b and/or α are initially too high or R is too low, or both. It is unlikely that R is in error to any significant extent since care was taken to measure its value accurately. In any event correcting n_R so as to correspond to n_P would require R to be about 3.57-in at $P/P_o = 1.033$, dropping to 3.20-in at $P/P_o = 1.38$ (LRPR), whereas its measured value was 3.153-in. At worst therefore any error in R can only produce a small systematic error in n_R .

Consider next the density ratio α . For n_R to equal n_P then at say $P/P_o = 1.033$, α should be 0.0889 as compared with the calculated value of 0.1289 - that is, about 65 per cent of this latter value. This difference becomes progressively worse at lower pressure ratios. Such a change in α would however produce an even greater reduction in n_P . For this and other reasons therefore α cannot be held responsible for this discrepancy.



**FIG. 5-8 OBSERVED VERSUS CALCULATED FLAME FRONT RADII-
LOW PRESSURE RECORD**

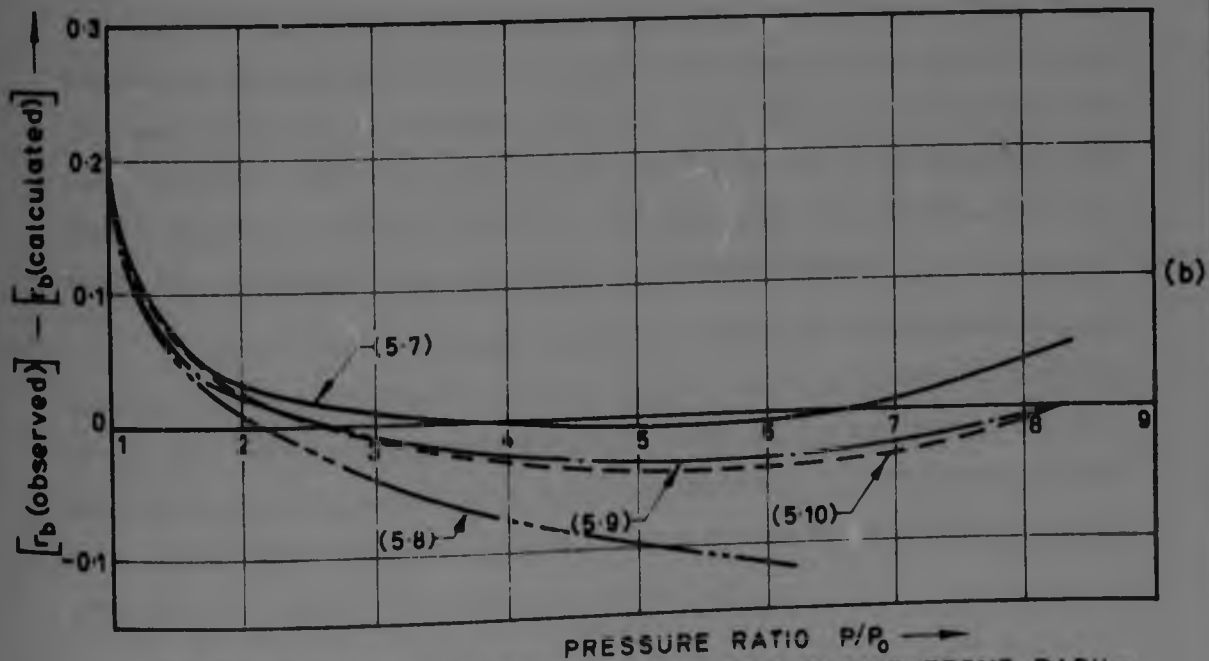
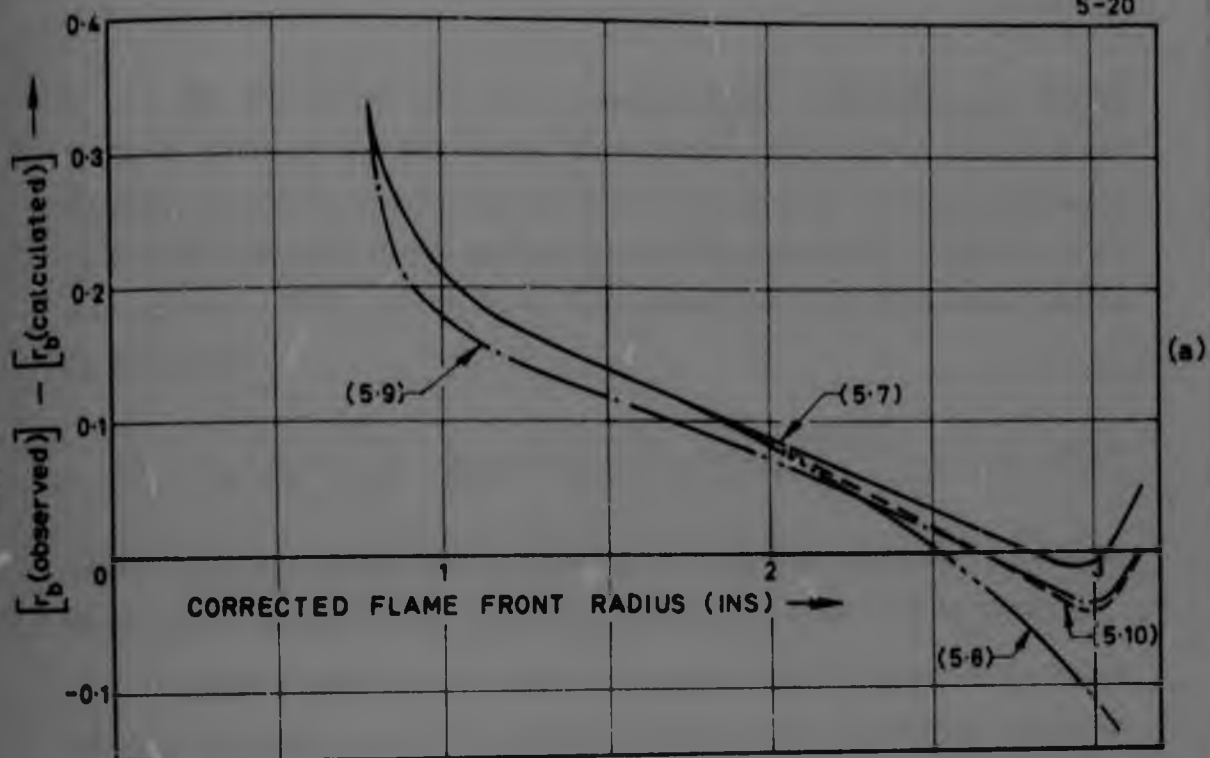


FIG. 5.9 OBSERVED VERSUS CALCULATED FLAME FRONT RADII—
HIGH PRESSURE RECORD

The only factor left is the observed flame front radius r_b . Due to the finite width of the slit window through which the flame is observed and the finite velocity of the film in the drum camera, it can be shown (Appendix L) that the resulting streak photographs will be bounded by a region of partial exposure. This results in an overestimation of the flame front radius by an amount

$$\Delta r_b = r'_b - r_b = r'_b \left[1 + (S_s w / 2v r'_b) - \left\{ 1 + (w / 2r'_b)^2 \right\}^{1/2} \right] \dots\dots\dots(5.12)$$

where r'_b is the flame radius determined from the maximum trace width of the streak photographs. The other symbols are defined in Appendix L.

Unfortunately for the tests analysed in Fig 5.8 and 5.9 the image width of the slit was not measured. However from the radius calibration photographs (see Section 7.1.1) of these earlier tests it is estimated that the equivalent slit width in the plane of the flame front was of the order of 0.36 in. Also the equivalent film speed in this plane was 725 in/s. From these figures and the tabulated values of apparent flame radius and spatial velocity (Appendix J) the corrected flame radii have been determined from eqn (5.12) and compared with the values calculated from eqn (5.11) (Appendix M). These results are shown in Fig 5.8. Fig 5.9 shows only the difference between the corrected flame radius and its calculated value.

Evidently this correction serves to reduce the discrepancy between the observed and calculated values of r_b , but not to eliminate it. Because of the lack of accurate knowledge of slit width and the fact that no particular effort was taken to measure maximum flame trace widths in these tests firm conclusions cannot be drawn. Nevertheless these findings indicate what precautions have to be taken in future tests.

However the remaining discrepancy still requires to be explained. A possible reason might be the asphericity of the flame. If this were the sole cause then the difference between n_R and n_P requires that the flame initially propagates as a prolate spheroid, changing to an oblate spheroid (at $P/P_0 > 2.7$ - HRPR) and back to a sphere at the end of the process (Fig 5.9 b). Thus the required eccentricity (σ) at 1.0 ms (LRPR) would be 0.715, whilst at 4.5 ms it would be 0.951 (see Appendix N). Similarly from the high-range pressure record at 3.0 ms $\sigma = 0.785$ and at 9.5 ms $\sigma = 0.957$. Unfortunately no independent check of these figures is possible for these tests. However these results indicate that some check on asphericity is necessary if reliable results of burning velocity are to be achieved. (See Section 6.4.3).

Finally it is necessary to check on the accuracy of the pressure measurements. From eqn (5.11) it is evident that any errors in the measurement of transient pressure will have a significant effect on the calculated value of r_b - via the density ratios α and β . Thus at 1.0 ms (LRPR - Test C) the required value of β for no discrepancy between r_b -observed and r_b -calculated (using eqn 5.10 for n) works out at 1.0021, as compared with the experimentally determined value of 1.001 - an error of minus 0.11 per cent. Similarly at 4.5 ms (LRPR) β should be 1.172 as compared with the observed value of 1.184, that is, an error of 1.0 per cent. From the high-range pressure record at 9.5 ms the required value of β is 2.83, whereas the observed value is 3.693 - an error of 30.5 per cent! This requires that the pressure at 9.5 ms be 50.1 psia as against 72.3 psia. Pressure-wise such an error is clearly impossible.

Consider firstly the time required for information from the flame front to reach the pressure transducer. Following the method described in Section 4.2.1, both the high- and low-pressure records for Test C have been

corrected (Fig 5.10 and 5.11). With these corrected pressures, values of flame front radius have been re-calculated (using n_p - eqn 5.10) and compared with the observed values of r_b in Fig 5.12.

Evidently this correction serves to completely account for the discrepancy between r_b -observed and r_b -calculated from the more sensitive low-range pressure record. Results from the high-range pressure record however still show a significant difference. Much of this must, at this stage, be attributed to the lower sensitivity and hence accuracy of this record, particularly at lower pressure ratios. On the other hand the region (r_b = 2.5 to 3.153-in) over which the difference between the observed and calculated radii, is negative, may be due to either ; (i) asphericity of the flame (max. eccentricity = 0.95), (ii) distortion of the time base on the oscilloscope, or (iii) heating of the unburnt gas to above its adiabatic compression temperature. (A temperature of about 260°R above the adiabatic value of 862°R at 9.5 ms would yield $\beta = 2.83$ as required). Of these possible causes (i) and (iii) appear to be most likely.

From all the foregoing it seems desirable in future tests to; (i) improve on the sensitivity and accuracy of the pressure measurements, particularly the high-range pressure record, (ii) provide a check on the asphericity of the flame, and (iii) incorporate some means of measuring unburnt gas temperature.

5.5 OBSERVED VERSUS CALCULATED PRESSURE

In Appendix G it is shown that the pressure P and isotropic flame front radius r_b are related by the equation,

$$(P/P_o)^{1/\gamma} \left[1 - (r_b^3/R^3) \right] + (P/P_e)(r_b^3/R^3) \approx 1 \dots\dots\dots (5.13)$$

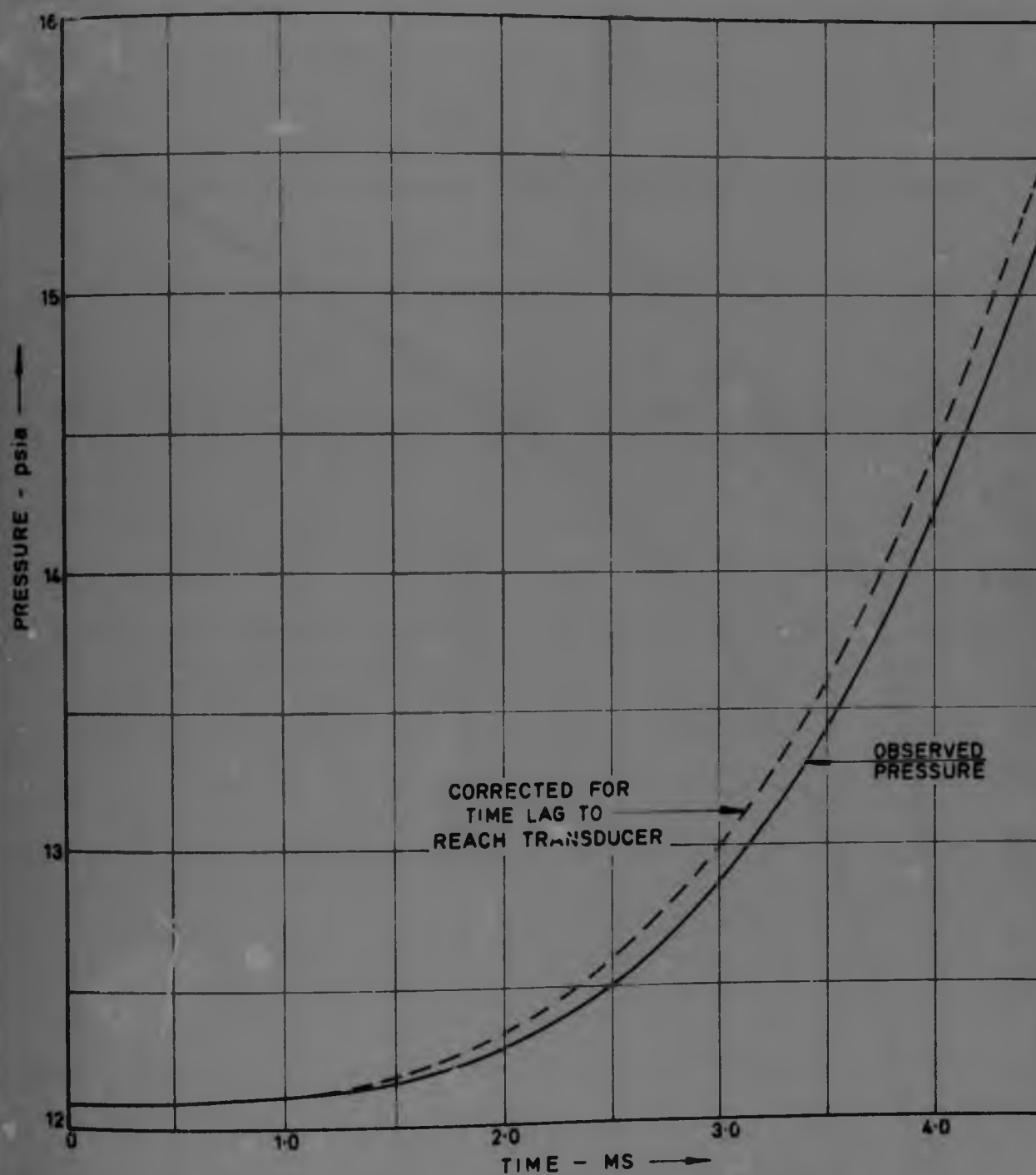


FIG. 5-10 LOW-RANGE PRESSURE RECORD (TEST C)
CORRECTED FOR TIME LAG

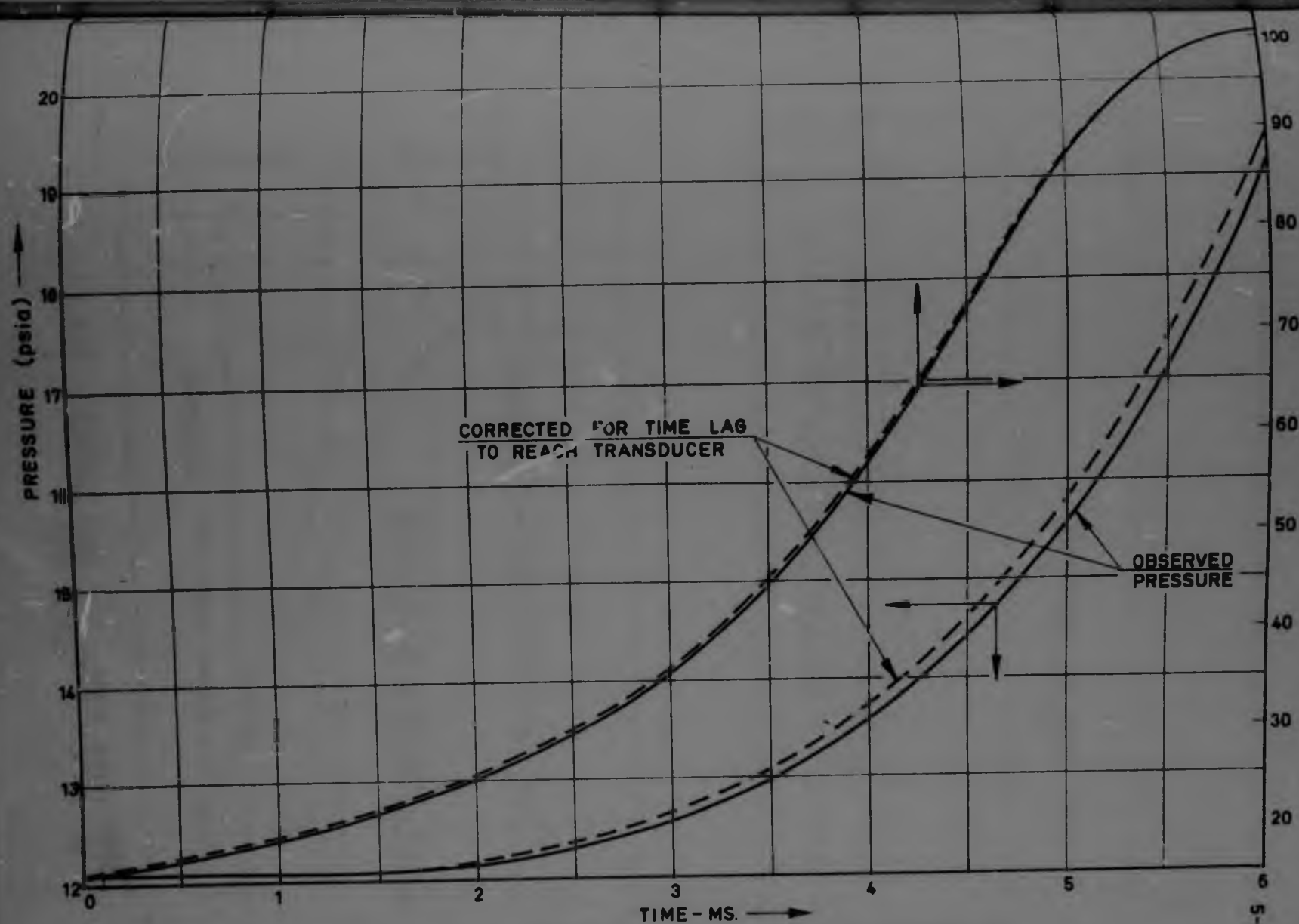


FIG. 5-11 HIGH PRESSURE RECORD (TEST C) CORRECTED FOR TIME LAG

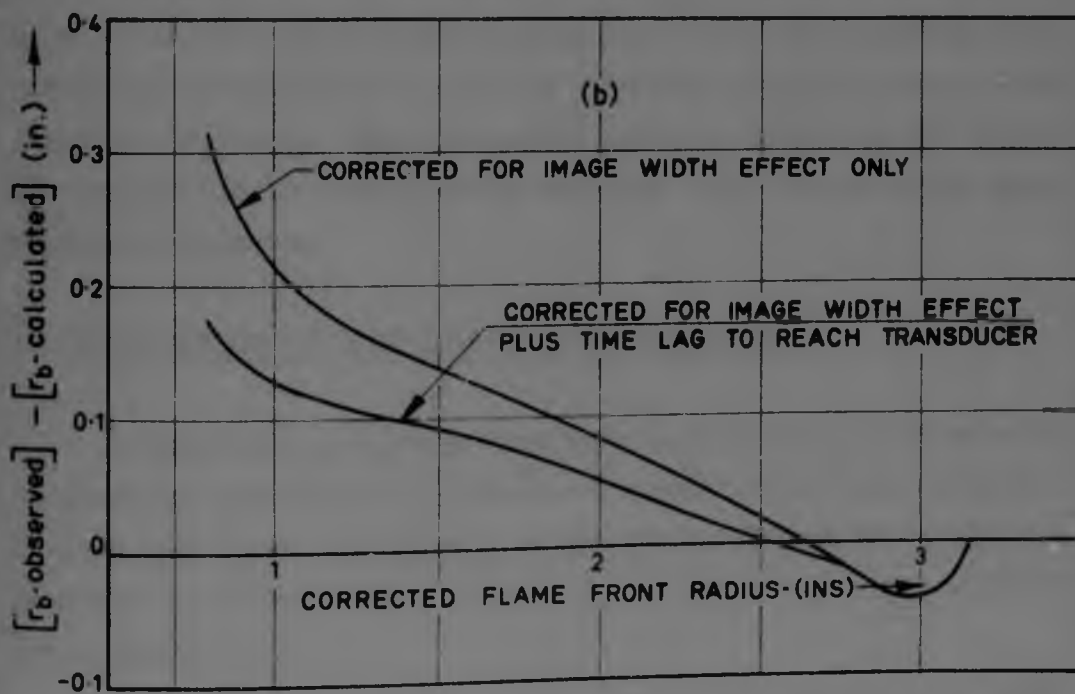
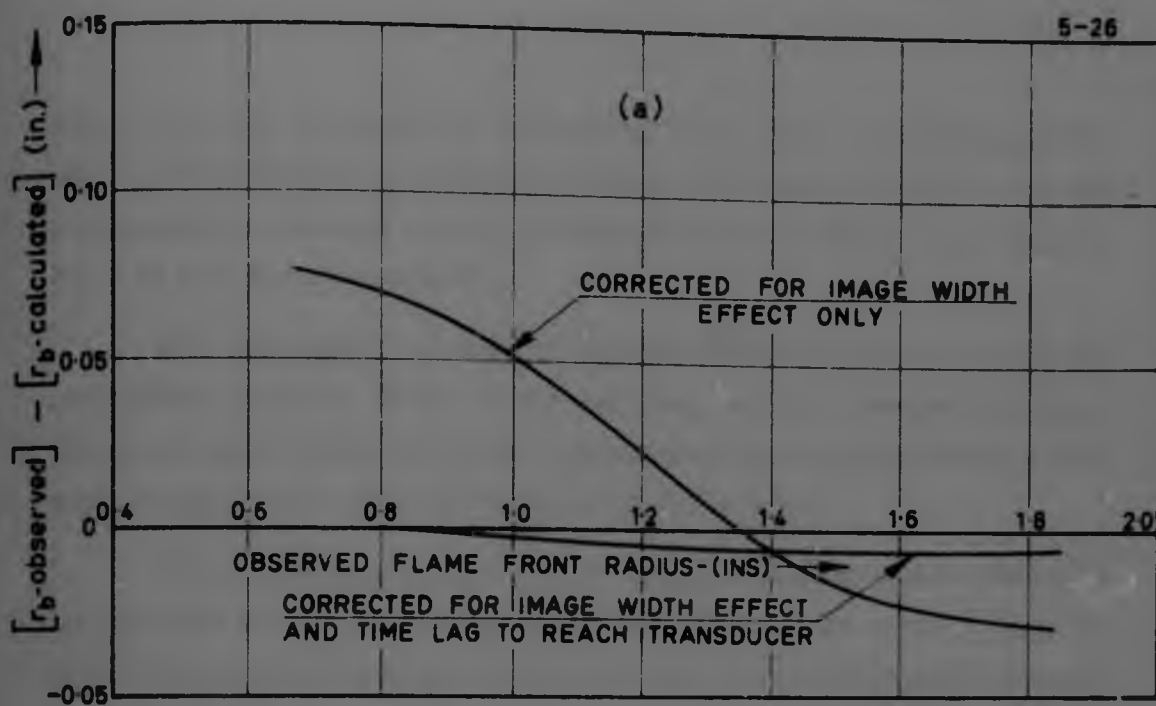


FIG. 5-12 OBSERVED AND CALCULATED RADII CORRECTED FOR TIME LAG

Hence since for any particular experiment R , P_o and γ_u are known, and P_e and r_b are measured, pressures can be calculated and compared with the corresponding observed values. Results obtained for Test C are shown in Fig 5.13 (see also Appendix P).

The discrepancy is seen to be remarkably small during most of the combustion process. Towards the end however the observed pressure increases significantly above the calculated value, dropping to zero - as it must by eqn (5.13) - when the flame reaches the wall.

These results simply serve to confirm the conclusions reached in the previous section, that is, that at the later stages of the process the mass of gas actually burnt is larger than is indicated by the radius measurements. Thus either the flame propagates as an oblate spheroid during this period, or the density of the unburnt gas is lower than on the assumption of adiabatic compression, or both. When the flame ($T_b \approx 4700^\circ R$) is at a distance from the highly reflective wall of less than 0.4-in, the possibility of the unburnt gas being heated to above its adiabatic compression temperature cannot be discounted. Thus independent means of measuring the unburnt gas temperature, as well as flame front radii near the wall of the vessel seem most desirable.

5.6 COMPARISON OF BURNING VELOCITY EQUATIONS

Although many equations have from time to time been proposed in the literature (see Chapter 3), they do not appear to have been satisfactorily compared, either theoretically or by applying them to the results of a particular set of experiments (RT 63). The present section is a contribution in this direction.

For convenience in presentation, the various equations to be tested

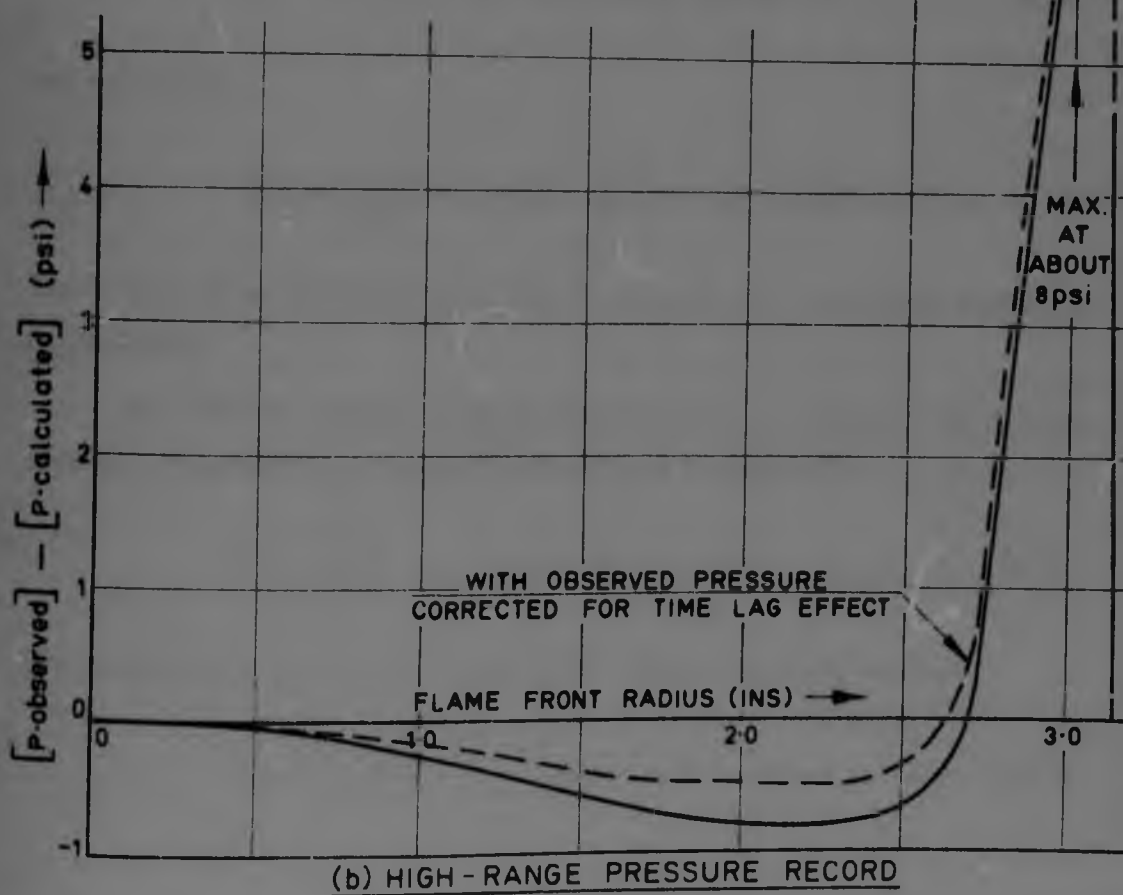
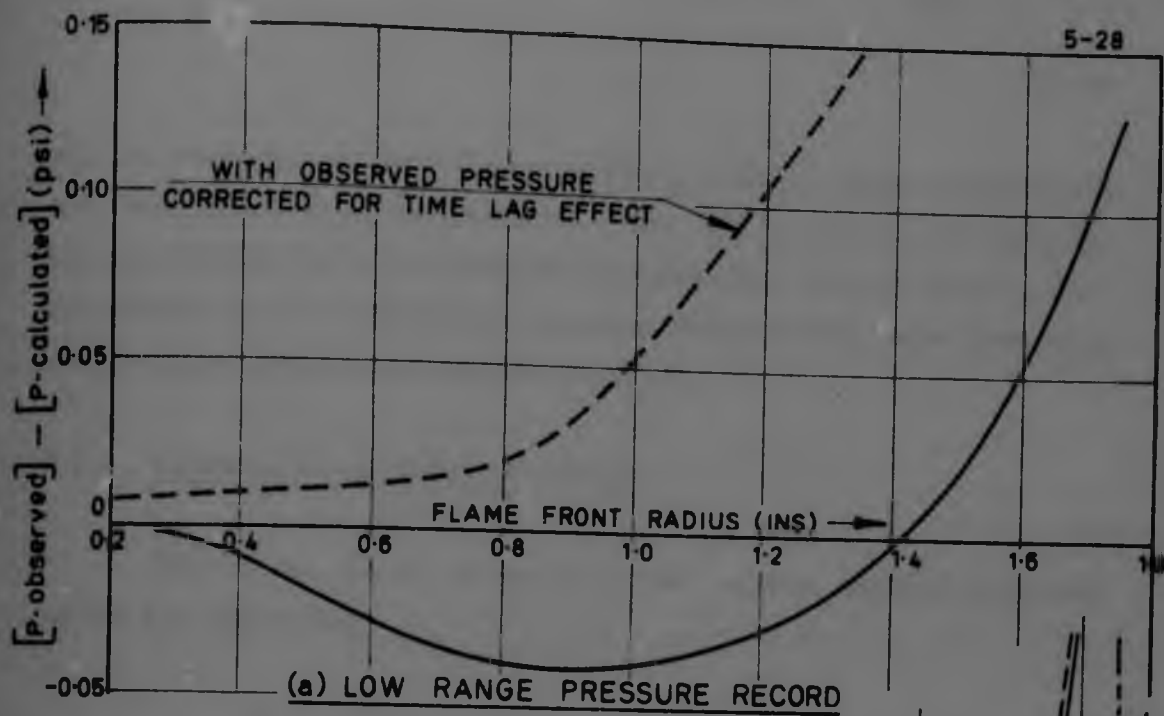


FIG. 5.13
OBSERVED VERSUS CALCULATED PRESSURE

will be considered under two main headings: those developed in this thesis and those proposed in the literature. They will be used to determine the burning velocities of a stoichiometric acetylene/air mixture (Test C). For the purpose of this comparison corrected values of both flame front radii and pressures will be used (see Section 5.4).

5.6.1 Equations Developed in this Thesis

Two of the 'exact' forms of burning velocity equation developed herein are (eqn 4.21),

$$S_b = (\alpha/\beta) \left[(dr_b/dt) + (r_b/3\alpha)(dx/dP)(dP/dt) \right] \dots\dots\dots (5.14)$$

and (eqn 4.53)

$$S_t = \alpha S_s \left[\frac{(1 - \alpha) + k(\beta - 1)}{\beta(1 - \alpha) + \alpha k(\beta - 1)} \right] \dots (5.15)$$

These have been referred to as the 'burnt gas' and 'combined' equations respectively.

In addition various 'approximate' forms of equation have been derived. Thus with $\gamma_b = 1$, eqn (5.15) reduces to (eqn 4.57),

$$S_t = \alpha S_s \left[\frac{(1 - \alpha) + \gamma_u(\beta - 1)}{\beta(1 - \alpha) + \alpha\gamma_u(\beta - 1)} \right] \dots (5.16)$$

Whilst with $\gamma_b = \gamma_u$ (i.e. $k = 1$) eqn (5.15) yields (eqn 4.55 and 4.56)

$$S_t = \alpha S_s (P/P_o) \dots\dots\dots (5.17)$$

or

$$S_t = S_s (P/P_e) \dots\dots\dots (5.18)$$

If either pressure-time or radius-time records only are available, then the following equations may be used:

For pressure-time observations alone (eqn 4.60),

$$S_t = (\alpha R/3 \gamma_u P) (dP/dt) \left[(1 - \alpha) + k(\beta - 1) \right] / (\beta - \alpha)^{4/3} (\beta - 1)^{2/3} \dots (5.19)$$

whilst for radius-time observations, the combustion pressure can be calculated from

$$(P/P_o)^{1/\gamma} \left[1 - (r_b^3/R^3) \right] + (P/P_e)(r_b^3/R^3) \approx 1 \dots\dots\dots (5.20)$$

and the burning velocity then obtained using either eqn (5.14) or (5.15), the latter being preferable since it does not require dP/dt to be determined, although this follows quite easily from eqn (5.20) above.

Burning velocities, for Test C, calculated from the above equations are shown in Fig 5.14 and 5.15 (see Appendix Q for tabulated values).

5.6.2 Equations Proposed in the Literature

The following equations proposed in the literature will be compared:

Lewis and von Elbe

Here	$S_b = (R^3/3\beta r_b^2)(dn/dt)$
where	$r_b^2 = R^2 \left[1 - (1-n)/\beta \right]^{2/3}$
and	$n = (P - P_o)/(P_e' - P_o)$

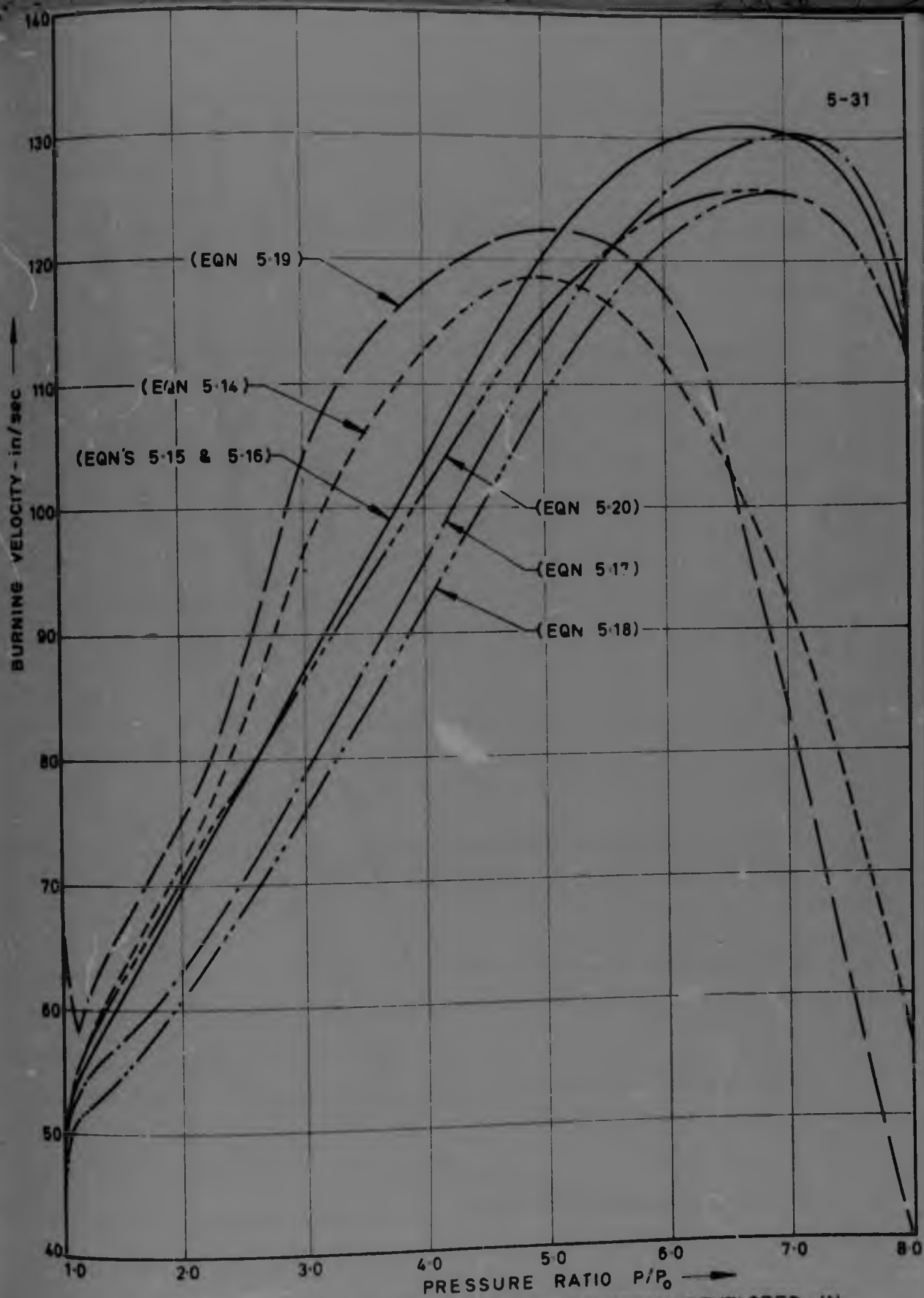


FIG. 5-14 BURNING VELOCITIES FROM EQUATIONS DEVELOPED IN
THIS THESIS (HIGH-RANGE PRESSURE RECORD-TEST C)

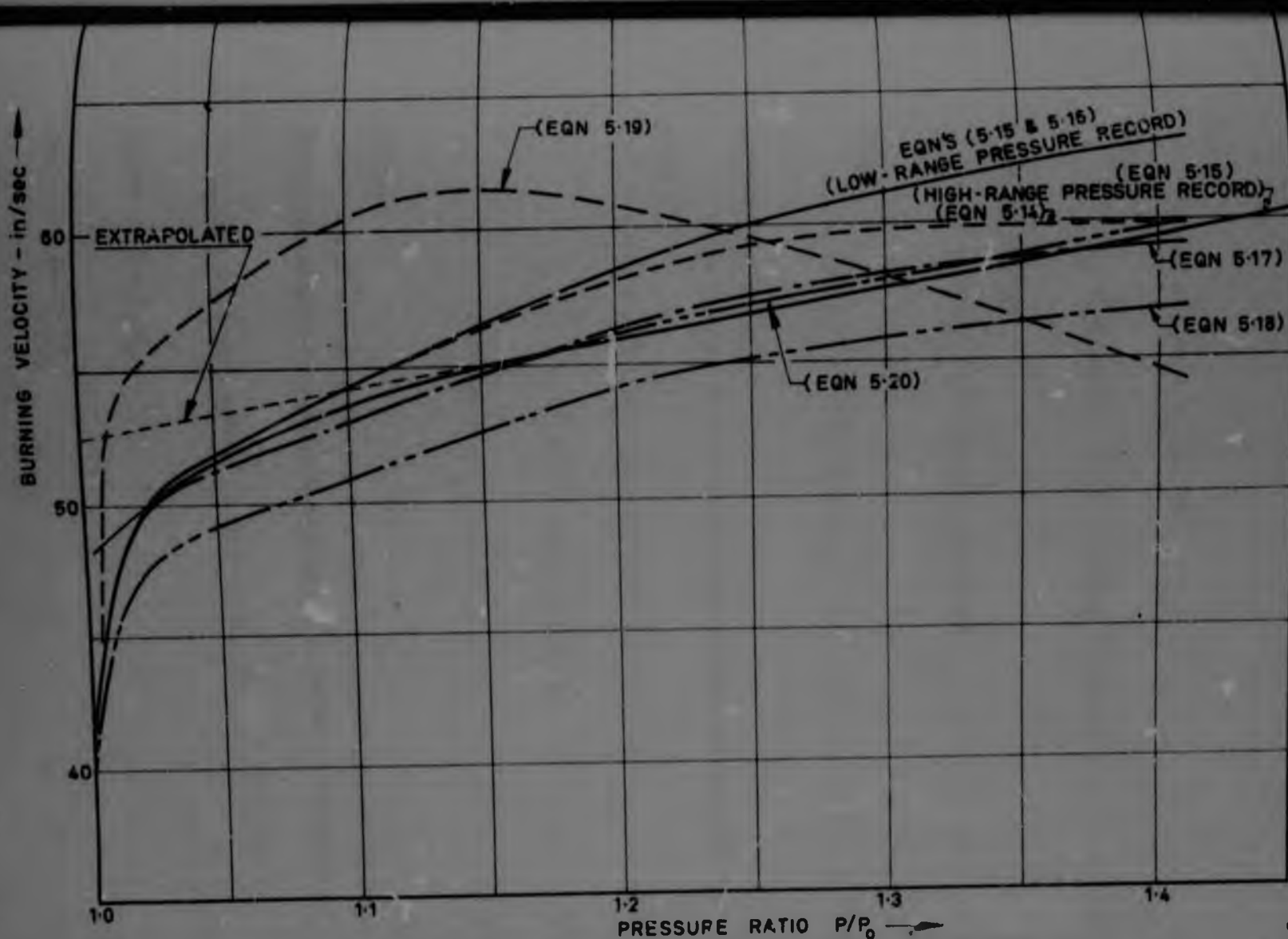


FIG. 5-15 BURNING VELOCITIES FROM EQUATIONS DEVELOPED IN
THIS THESIS (LOW-RANGE PRESSURE RECORD)
TEST C

that is

$$(dn/dt) = \left[1/(P'_e - P_o) \right] (dP/dt)$$

therefore

$$S_b = \left[R/3\beta(P'_e - P_o) \left\{ 1 - (1-n)/\beta \right\}^{2/3} \right] (dP/dt) \dots\dots\dots(5.21)$$

Flock and Marvin

$$S_u = S_s - \left[(R^3 - r_b^3)/2r_b^2 \gamma_u P \right] (dP/dt) \dots\dots\dots(5.22)$$

Dery

$$S_t = S_s / \left[1 + \left\{ (P'_e/P) - 1 \right\} \gamma_u \right] \dots\dots\dots(5.23)$$

Eschenbach and Agnew

These authors have proposed various forms of equation, three of which are;

$$S_b = (\alpha/\beta) \left[S_s + (r_b/3P)(dP/dt) \right] \dots\dots\dots(5.24)$$

$$S_u = \left[1 + \gamma_u (r_b^3/R^3) \left\{ 1 - (\alpha/\beta) \right\} \right] (\alpha S_s/\beta) \dots\dots\dots(5.25)$$

$$S_u = (\alpha/\beta)(P/P_o) S_s \dots\dots\dots(5.26)$$

Raezer

As originally published this authors equation contained an error. In its corrected form (private communication) it can be expressed as

$$(r_b^3/R^3) = 1 - \left[(S-1)/(\Theta-1) \right] \left[\left\{ \gamma_u(\Theta-1) + 1 \right\} \left\{ \gamma_u(S-1) + 1 \right\} \right]^{(\gamma_u-1)/\gamma_u} \dots\dots\dots(5.27)$$

where $S = S_s/S_b$

and $\Theta = T_b/T_o$

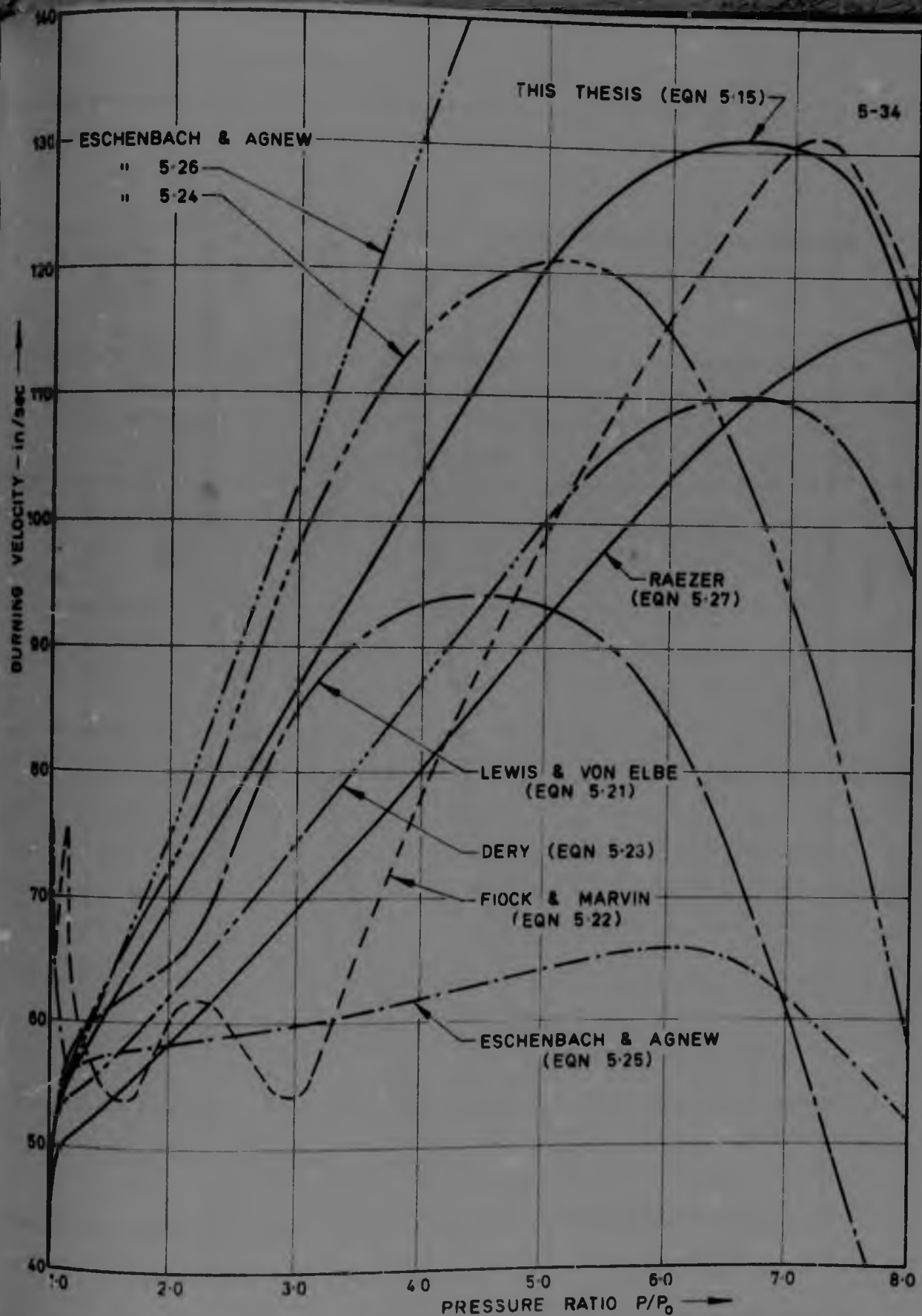


FIG. 5.16 BURNING VELOCITIES FROM EQUATIONS DEVELOPED IN THE LITERATURE (HIGH-RANGE PRESSURE RECORD TEST C)

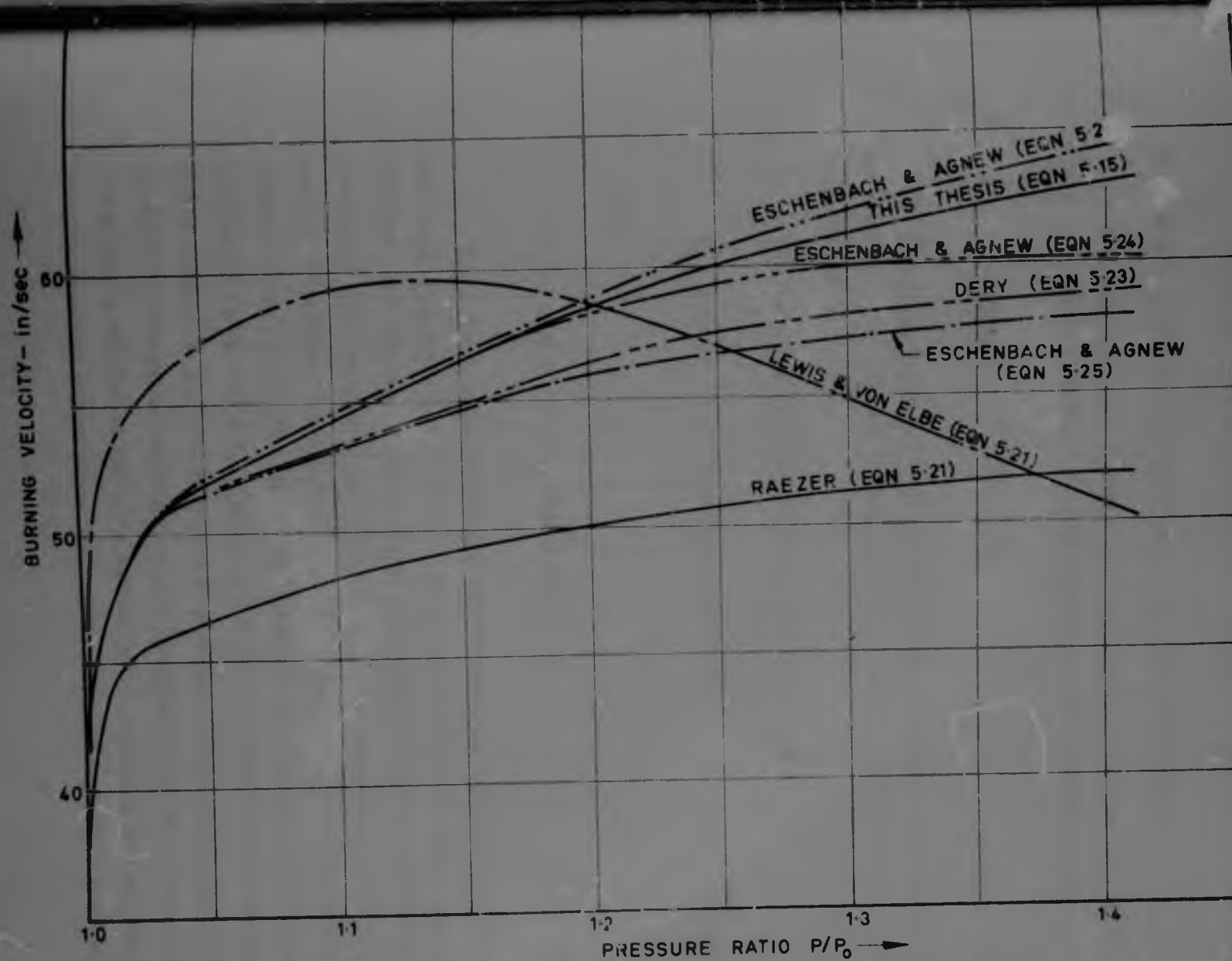


FIG. 5-17 BURNING VELOCITIES FROM EQUATIONS DEVELOPED IN THE LITERATURE (LOW-RANGE PRESSURE RECORD TEST C)

From which, by a trial and error method, S_b can be determined.

Burning velocities, for Test C, calculated from the above equations are shown in Figs 5.16 and 5.17. (See Appendix S for tabulated values).

5.6.3 Discussion

Equations developed in this thesis. It is convenient, in comparing the results of the various burning velocity equations, to start with those developed in this thesis.

The burnt gas equation (5.14) can be re-arranged as

$$S_b = (\alpha/\beta) S_s \left[1 + (r_b/3\alpha S_s)(d\alpha/dP)(dP/dt) \right] \dots\dots\dots (5.28)$$

That is,

$$S_b = (\alpha/\beta) S_s \left[1 + (r_b/3\alpha)(d\alpha/dr_b) \right] \dots\dots\dots (5.29)$$

The second terms in the squared brackets of both these equations have been evaluated, for Test C, and are shown in Fig 5.18. When used in the form given by eqn (5.29) the burnt gas equation yields almost identical results as the combined equation (5.15) up to a pressure ratio (P/P_0) of about 5. Thereafter the values fall off but not at as fast a rate as in its original form (eqn 5.28). Evidently therefore the 'hump' in the curve marked eqn (5.14) on Fig 5.15 is not real but is caused by undue sensitivity of this equation to the time derivative of pressure (dP/dt), which apparently has been overestimated between the pressure ratios of 2 to 5:1. Confirmation of this is afforded by the curve marked eqn (5.19) which was calculated from the pressure record alone, and which is directly dependent on dP/dt .

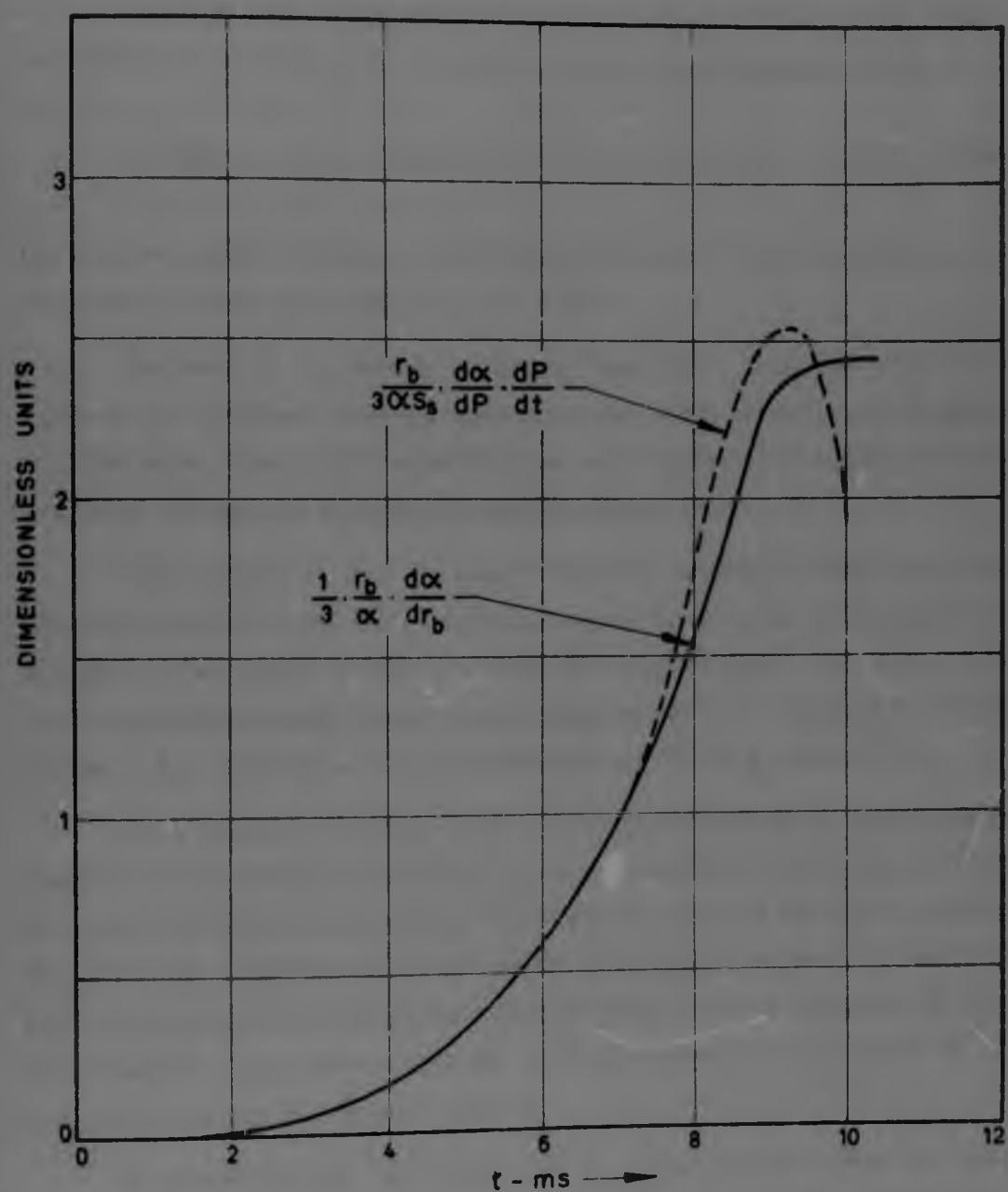


FIG. 5-18 DISCREPANCY BETWEEN TWO FORMS OF
BURNT GAS EQUATION

Consider next the 'approximate' equations (5.17) and (5.18). These are derived by setting $\gamma_u = \gamma_b$ in eqn (5.15), and are alternative forms of

$$S_t = \alpha S_s \dots\dots\dots(5.30)$$

the former (eqn 5.17) being a better approximation to eqn (5.30), which in any case is better than either (5.17) or (5.18).

However it can readily be shown that with $\gamma_u > \gamma_b$ (as is the case for Test C) the term in squared brackets in eqn (5.15) must always be greater than unity. Hence both eqn (5.30) as well as its approximations (5.17) and (5.18) will always yield lower values than eqn (5.15).

Thus it appears that any improvement in accuracy of the remaining equations tends to bring their results closer to those given by the combined equation (5.15), which is thus probably the most reliable. Incidentally, it is worth noting that, unlike the burnt gas equation, eqn (5.15) yields the correct values of S_t at both ends of the process, that is, $S_t^0 = \alpha_0 S_s$ and $S_t^e = S_s$.

Next consider equation (5.20). Although depending on radius measurements alone (since in any event P_e can be calculated thermodynamically) it yields surprisingly good results. However the effect of the approximation $\alpha P_0/P = P_0/P_e$ (Appendix G) as well as the discrepancy between the observed and calculated pressures towards the end of the process (Section 5.5, (Fig 5.13) causes a progressive fall-off in S_t at pressure ratios above 3, as compared with eqn (5.15) (see Fig 5.15).

It should be noted that with all the equations (except 5.10 at the start of the process when in any event it is unreliable) the burning velocity falls off at both the start and end of the process. This is no fault of the equations but rather of the accuracy attainable in the measurement of pressure rise and spatial velocity - particular the latter. Thus the value of S_t at P/P_0

equals unity is best obtained by extrapolating the straight portion of the curve (5.15) backwards towards the axis (Fig 5.15). (Corroboration of this is provided by plotting S_t versus T_u - see Fig 5.19). The value towards the end of the process could similarly be obtained by extrapolation, but this is considered unwise since there is some doubt as to the values of unburnt gas temperature when the flame front is close to the wall of the vessel.

Finally consider a brief comparison between the results of the high- and low-range pressure records (Figs 5.14 and 5.15). In general the latter gives results which are about 3-in/s lower than the former. Strictly the low-range record should be more accurate. However the shape of the S_t versus P/P_0 curves (Fig 5.15) suggests that this may not be the case in this instance, probably as a result of a time-base error in the low-range pressure record (of the order of about 0.25 ms). In consequence of this the method of recording pressure has been modified (Section 6.6.4).

Equations proposed in the literature. The Fiock and Marvine equation (5.22) is the only one which does not depend on a knowledge of the properties of the burnt gas. However, as has been shown earlier (Section 5.1), it has the disadvantage of magnifying small errors in the observations. This is apparent in the erratic behaviour of curve (5.22) (Fig 5.16), particularly at low pressure ratios. (Equation 5.22 has not been plotted in Fig 5.17 since the values it yields lie outside the range of the scale chosen - see Appendix S).

The Lewis and von Elbe equation (5.21) and the Dery equation (5.23) are derived using an approximate equation for the mass fraction burnt, which has been shown to apply only during the early stages of the process (Section 5.3). Thus little reliance can be placed on most of the range of values calculated from the high-range pressure record (Fig 5.16), most of which will be too low. A discrepancy between the results from these

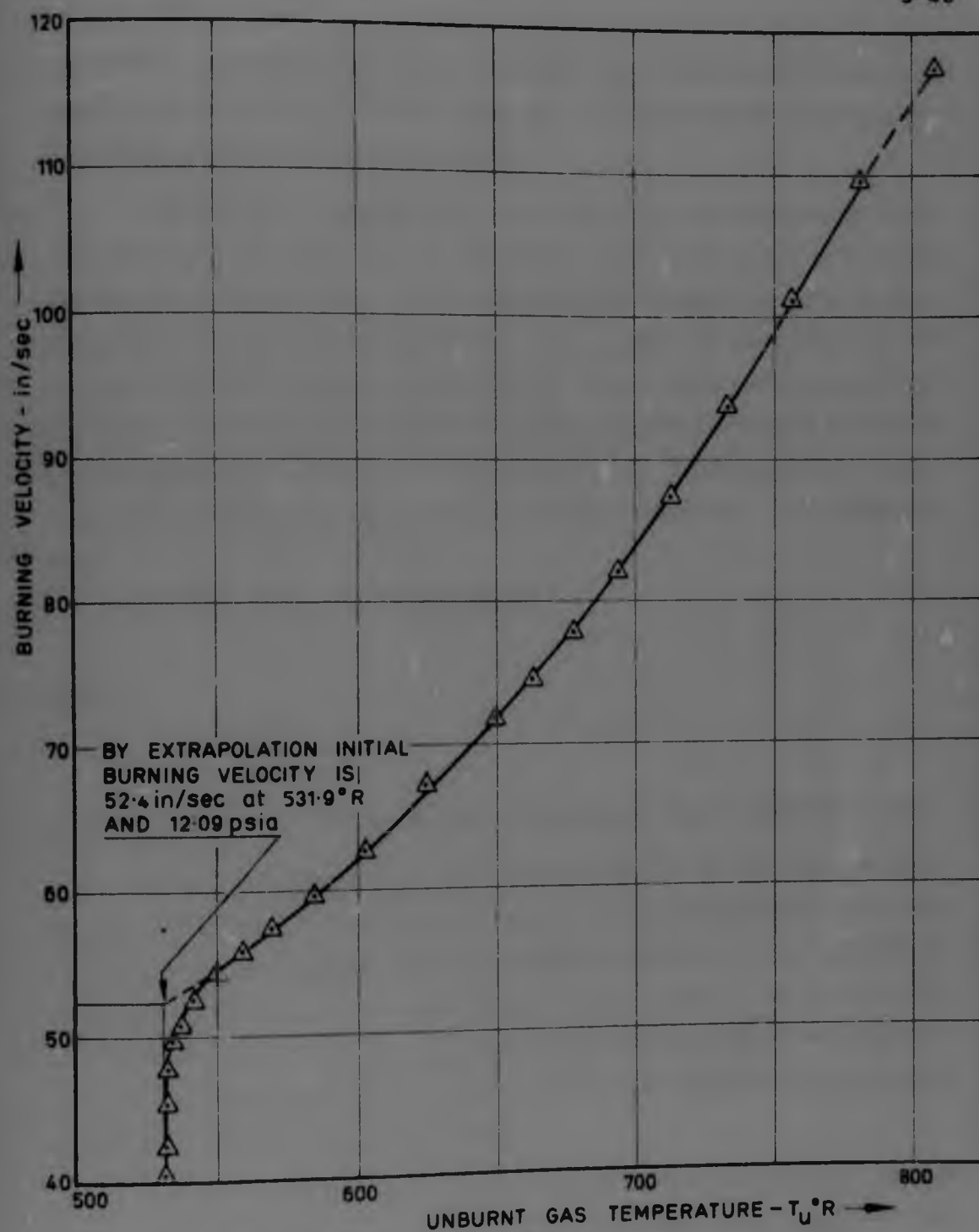


FIG. 5-19 BURNING VELOCITY VERSUS UNBURNT
GAS TEMPERATURE (TEST C)

equations is evident at low pressures (Fig 5.17). Equation (5.21) is most likely to be in error over this region, due to a probable error in the time base of the low-range pressure record.

Eschenbach and Agnew's equation (5.25) gives reasonable results up to a pressure ratio of about 1.3, but values from most of the high-range record seem to be too low. Their equation (5.24) is based on similar considerations to eqn (5.14), from which it can be derived by setting $d\alpha/dP$ equal to α/P (see footnote in Section 5.2.3). Hence since for these particular tests $\gamma_b \approx 1$ (which the above assumption implies) the results it yields are essentially the same as those from eqn (5.14). Equation (5.26) is approximate and should be valid only at low pressure ratios. It is equivalent to

$$S_u = \alpha S_s (P/P_0)^{(\gamma_u - 1)/\gamma_u} = \alpha S_s (T_u/T_0)$$

since

$$\beta = (P/P_0)^{1/\gamma_u}$$

and evidently overestimates burning velocities at higher pressure ratios.

Finally consider the Raezer equation (5.27). In its original form (Ra 61, RT 63) it contained an error which has subsequently been corrected (private communication). However, probably because of the simplifying assumptions made, it now yields values which appear to be low over the whole range of the process. It seems likely that with these assumptions removed it would yield results much more in conformity with the combined equation (5.15) developed in this thesis.

All in all therefore, it seems that the equations developed in the literature are strictly valid only during the very early stages of the process. Unfortunately reliable measurements of spatial velocity are

difficult to obtain during this period, either due to initial acceleration or asphericity of the flame. The general applicability of these equations is thus questionable.

5.7 CONCLUSIONS

1. A comparison between unburnt and burnt gas forms of burning velocity equations indicates that the latter are to be preferred since they do not magnify observational errors to anything like the same extent as the former.
2. From the two forms of equation for the dimensionless density ratio α , it is concluded that, for the range of acetylene/air mixtures tested, chemical equilibrium is not attained in the flame front. The degree of lack of equilibrium appears to be influenced both by the spatial velocity and mixture ratio.
3. Of the four equations for the mass fraction burnt which have been compared, that due to Lewis and von Elbe underestimates the mass burnt at the later stages of the process, whilst that due to Grumer *et al* overestimates this value. However, either of these equations are adequate up to pressure ratios (P/P_0) of about 1.1 to 1.
4. Slight discrepancies in the mass fraction burnt, as calculated using two forms of equation developed in this thesis, lead to corrections being made both in the observations of flame radius and pressure.
5. Even after the corrections indicated above, have been made however, a small discrepancy still exists between the observed and calculated values of radius and pressure, particularly during the later stages of the process. Further experimental evidence is required before these differences can be resolved.

6. A comparison between various burning velocity equations developed in the literature and in this thesis, suggests the so-called combined equation (5.15) as the most reliable.
7. Without exception all the burning velocity equations developed in the literature contain unnecessary assumptions which restricts their use to the early stages of the process. However it appears difficult to obtain reliable values of burning velocity over this region, either because of initial acceleration of the flame or asphericity.

CHAPTER 6

APPARATUS

6.1 GENERAL REQUIREMENTS

The experimental determination of burning velocities by the spherical constant volume method, using one or other of the equations developed in Chapter 4, requires some or all of the following:

- (1) A rigid spherical combustion vessel, preferably fitted with windows through which the progress of the flame can be observed.
- (2) Means for accurately introducing predetermined quantities of fuel, oxidant and inert gas into the system.
- (3) Apparatus for varying and measuring the initial temperature and pressure of such mixtures.
- (4) A method of reproducibly igniting the combustible charge at the centre of the vessel.
- (5) Suitable photographic or other equipment for observing and recording the gas and flame movements.
- (6) Fast-response, high-sensitivity transducers, together with their associated apparatus for detecting and recording density and/or pressure and temperature variations both in the burnt and unburnt gas during the combustion process.
- (7) A control system to ensure the correct sequence of events and to synchronize the operation of the various recording instruments.

Although the above are not all essential requirements, their inclusion in any constant volume combustion set-up makes for greater accuracy by permitting corroborative data to be obtained

Consider each of the foregoing items in turn.

6.2 COMBUSTION BOMB

6.2.1 Requirements

The mechanical design of a combustion bomb calls for a rigid spherical vessel, having a smooth and polished inner surface, and capable of withstanding a specified maximum internal pressure without distortion or leakage. In addition such a vessel should be provided with some or all of the following: windows for viewing the progress of the flame; central spark terminals for igniting the mixture; valves for supplying the different components of mixtures and for exhausting the system; suitable holes for inserting such devices as pressure transducers, temperature or density probes, ionization gap electrodes, and the like; means for introducing and illuminating dust particles along a diameter - all the foregoing designed in such a way as to have the minimum possible effect on the progress of the flame. Also, if possible, the system should be provided with means for varying and controlling its initial temperature over a fairly wide range.

Finally, such a combustion vessel should be capable of being dismantled easily for cleaning purposes so as to preserve the quality of the inner surface and to ensure that each test is performed under controlled and reproducible conditions.

Once again it may not be convenient or necessary to provide all the above facilities in one unit. However from the point of view of versatility in determining the best approach to this type of test, as many as possible should be included.

6.2.2 General Design (O'D 59, RP 62, Tr 62)

In essence the combustion vessel used consists of two flanged hemi-

spherical sections which when clamped together over a central ring form a spherical cavity of 6.306-in (16.02 cm) internal diameter (Fig 6.1). The central ring, clamped and sealed with rubber O-rings between the two main sections, is provided with slit windows on opposite sides through which an unrestricted view of the flame across a diameter can be obtained - the width of these slits being slightly less than 0.5-in (1.27 cm). This arrangement ensures that the windows are adequately protected at all times, and obviates the necessity of resealing them each time the bomb is dismantled and re-assembled. The transparent window material used in all tests to date has been 'Perspex'. This appears to be quite satisfactory for the pressures which have been used - the only result of firing over one-hundred mixtures being a slight crazing of the inner surface. Glass lens-windows have been designed (OD 59) and are available for use with external plano-convex lenses (forming a doublet system) so that schlieren photography can be undertaken as well. However in all the tests reported herein direct photography has been used. Only one window is thus required, the other being masked out.

When the windows are not required for observation of the flame, a solid 'dummy' ring having the same overall dimensions as the window ring is used.

The bomb assembly, consisting of the two main hemispherical sections with the window or dummy ring sandwiched between them, is held together by two rigid clamping rings and four bolts (Fig 6.1).

The three main sections of the bomb were machined from a nickel-chrome steel, the whole arrangement being designed for a maximum internal pressure of 1000 psi ($\approx$ 70 atmospheres). Since the bomb is eventually intended to form part of a schlieren system, the design criterion was rigidity and freedom from distortion rather than strength. Thus for tests in

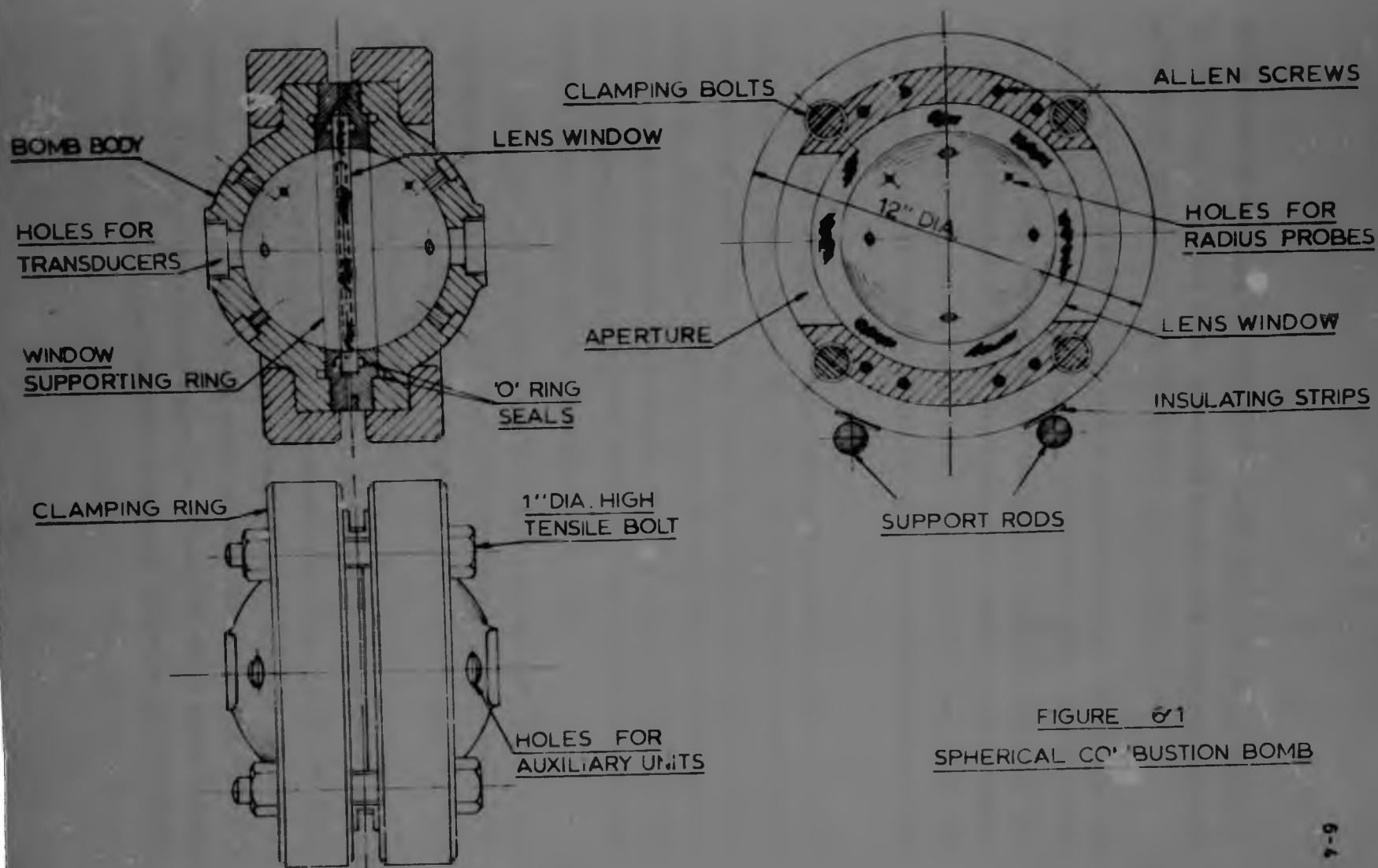


FIGURE 61
 SPHERICAL CO₂ BUSTION BOMB

which direct photography, or some method other than schlieren, is employed for observing the flame front, pressures in excess of 70 atmospheres are permissible, particularly when the dummy ring is used.

For convenience during certain preliminary work the vessel was mounted with the observation windows in a horizontal plane. However, tests with relatively slow burning propane/butane/air mixtures indicated that buoyancy of the hot gases during the combustion process could introduce serious errors. In consequence the bomb has since always been used with the windows in a vertical plane so that the extent of any buoyancy effects can be observed.

For ease of handling, each hemispherical section of the bomb is bolted onto its clamping ring, the latter being supported on a pair of horizontal ground steel bars. This allows the vessel to be opened and closed merely by sliding one section back and forth relative to the other, which is rigidly fixed to the workbench, and onto which the window ring is attached. This arrangement ensures that the bomb is always in the same position relative to the camera used for photographing the flame.

The inner surface of the vessel has been hard-chrome plated to protect the base metal against corrosion by the products of combustion. In addition the chrome surface is kept polished so as to reduce radiative heat transfer during the combustion process.

The vessel is provided with a total of ten threaded holes - five in each half. These are intended to accommodate three gas valves, two spark electrodes, two variable-capacitance transducers, one transient temperature measuring probe and one thermocouple probe. The remaining hole is a spare. Provision has also been made for introducing either three mutually perpendicular temperature sensitive probes, or ionization gap electrodes,

for checking on the flame front radius. In addition, in the latest version of the window ring, the 'Perspex' window material has a small hole at its highest point through which dust particles can be injected for particle track studies. A small hole - through the metal portion but not the Perspex - at the base of the window ring is provided for illuminating these dust particles.

Needle-type gas valves are used, with their sealing points close to the inner surface of the vessel to keep the 'dead' volume as small as possible.

6.2.3 Lens Windows - Schlieren System

Although for all the tests reported in this thesis direct photography of the flame has been used, it is the intention at some later date to undertake studies of pre-flame zone thickness by comparing direct with schlieren traces of the flame front. To this end various optical designs have been analysed (see OD 59). The system finally decided upon as representing the best compromise between cost and optical aberration is shown in Fig 6.2.

Here each of the windows, which are made of glass, have been designed as part of a doublet lens system, their inner radius being approximately equal to that of the bomb. As indicated the resulting optical path through the bomb is essentially parallel. However due to internal reflection in the concentric lens windows the flame front cannot, with such a system, be viewed across a full diameter.

6.3 INITIAL MIXTURE COMPOSITION

6.3.1 Requirements

An essential pre-requisite to any reliable measurement of burning

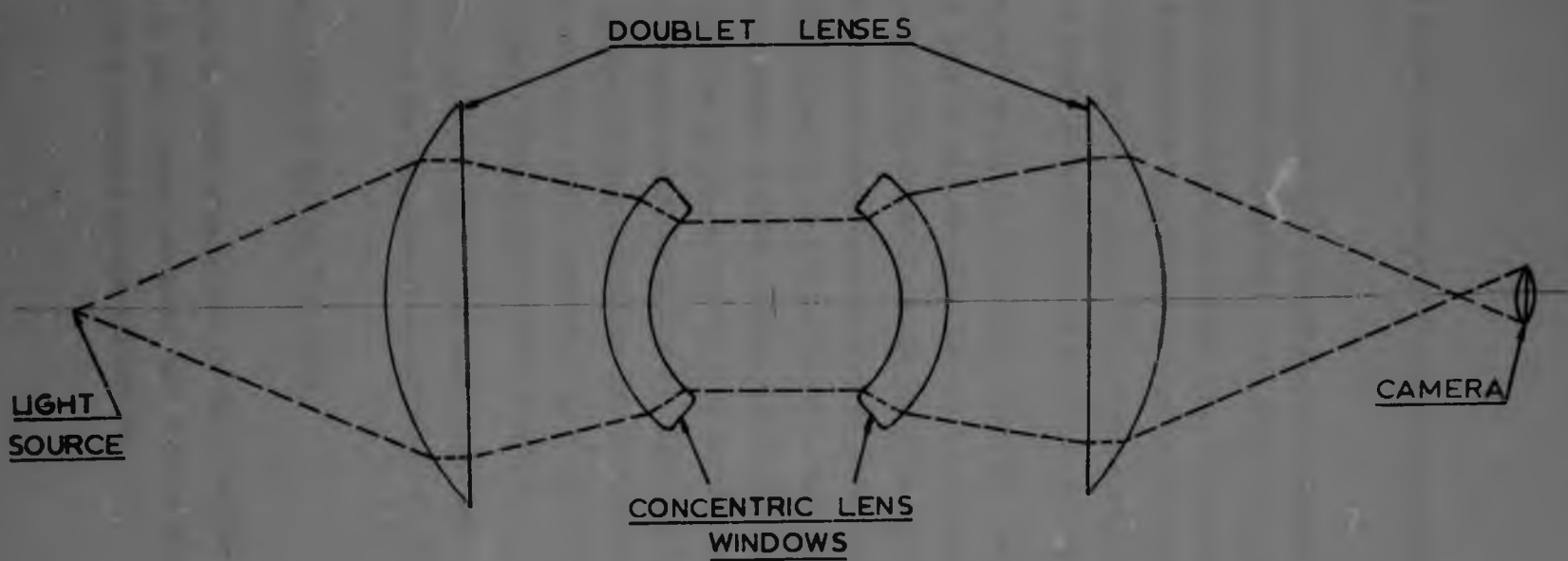


FIGURE 6.2
SCHLIEREN SYSTEM

velocity is an accurate knowledge of the initial composition and state of the unburnt mixture.

There are two possible procedures for filling the bomb with a mixture of predetermined composition. The first is to prepare and store a quantity of gas containing known proportions of fuel, oxidant and inert gas. This method is attractive in that thorough mixing of the various components is assured. Consistent results can thus be expected over a series of tests. For reasons of safety however it must be ruled out in this case.

The second technique is to mix, within the combustion vessel, only sufficient fuel, oxidant and inert gas for one test. Due to the smaller mass of mixture involved this method is basically not as accurate as the former. However, with suitable instrumentation adequate accuracy can be achieved. Either a partial volume or partial pressure method may be used. Analysis shows that an ordinary U-tube manometer is not satisfactory since the 'dead' volume of the pipes connecting it to the bomb can lead to serious errors due to thermal and diffusion effects. Because of this a partial pressure method of determining component concentration is favoured. Clearly the partial pressure of each component must be set so as to provide both the required initial pressure and mixture strength.

Variation of the initial temperature is preferably achieved by varying and controlling the temperature of the massive containing vessel.

6.3.2 Measurement of Partial Pressures

In order to avoid effects due to 'dead' volume mentioned above, it was decided to use a balanced-diaphragm type of pressure transducer in conjunction with a standard U-tube manometer.

The balanced-diaphragm transducer (Fig 6.3) finally adopted was a variable-capacitance unit having an ^{clamped} integral diaphragm of 1.125" diameter, resulting in a standing capacitance of 140 pF. This was incorporated into a parallel-T bridge (Po 60 and 61a), operating at a carrier frequency of 200 Kc/s, the output of which was displayed on a Tektronix 545A oscilloscope. (For reasons of convenience the frequency used was the same as that for the transient pressure measuring system to be described in Section 6.6).

This unit fits into the wall of the combustion vessel so that one side of the diaphragm is exposed to the internal pressure. A balancing pressure is provided on the opposite side, the magnitude of which is measured on a conventional U-tube manometer. Initially the bridge circuit is brought to balance with atmospheric pressure on both sides of the diaphragm. Other pressure within the vessel, either above or below atmospheric, are then readily measured on the manometer by adjusting the back pressure until the bridge returns to balance. Near balance a pressure change of less than 0.01-in (0.25 mm) of water can be detected.

6.3.3 Initial Mixture Temperature

Two chromel-alumel thermocouples are provided for the measurement of gas temperature. These are mounted within the bomb, one near the wall and the other near the centre. Their output is continually plotted on a potentiometer recorder. Switching is provided for either individual or series connection of the thermocouples. To protect the recorder when a mixture is fired, a shunt is arranged to be brought into circuit automatically when the motor of the flame trace camera is switched on.

No attempt was made, in this series of tests, to vary the initial temperature of the mixture which was thus always approximately equal to the ambient air temperature.

6.3.4 Miscellaneous

A supply and exhaust manifold is connected to one of the gas valves on the bomb. This provided access to a compressed air supply (also used for calibrating the transient pressure transducer). Connections to atmosphere and to a vacuum pump provided exhaust facilities.

All atmospheric air used for the tests was dried, before entering the bomb, by being passed through a U-tube filled with silica gel.

A cold trap, consisting of a copper spiral immersed in a freezing mixture, was connected into the fuel supply line. In the tests reported here (all of which were performed on acetylene/air mixtures) the cold trap was maintained at a temperature of -20°C and was intended to remove any acetone and water vapour that might have been carried over from the fuel cylinder containing dissolved acetylene. The acetylene used was obtained from a commercial cylinder and had a guaranteed purity of 97.5 per cent, the remainder being mainly air.

6.4 IGNITION SYSTEM

6.4.1 Requirements

The spark electrodes should be arranged so that the mixture may be ignited at the centre of the vessel. The spark gap and electrode dimensions

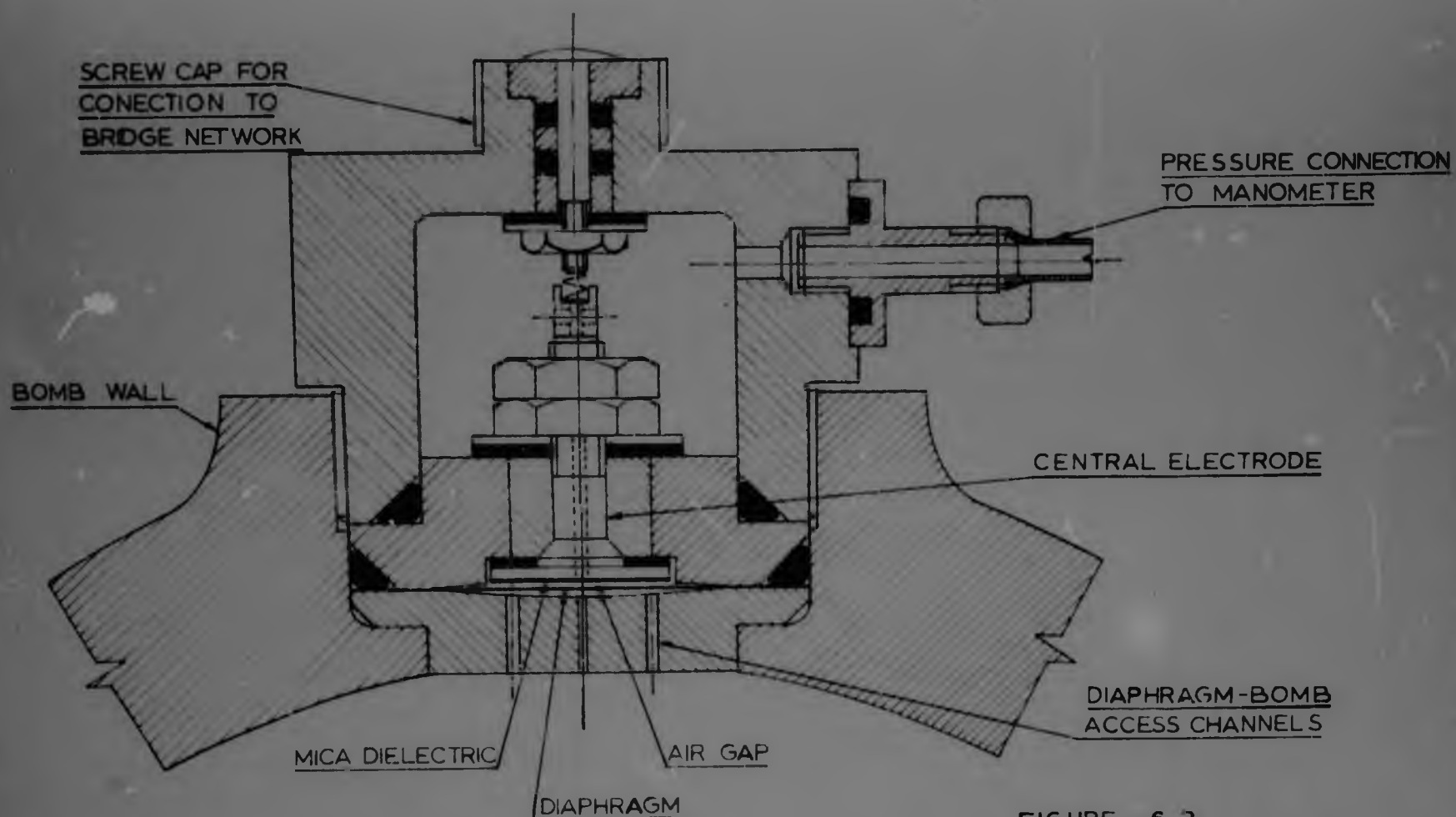


FIGURE 6.3
SECTIONED ASSEMBLY VIEW OF
BALANCED DIAPHRAGM TRANSDUCER

should be adjustable so as to provide a spherical core of burning gas. Further, the electrodes should be as thin as possible to reduce any possible interference with the propagation of the flame. They need not be insulated inside the bomb.

The ignition circuit should be such as to provide a reproducible spark of known maximum voltage and energy, and of as short a duration as possible. Both the spark voltage and energy should be capable of independent variation. Also, since the spark initiates the whole sequence of events, some means of triggering the various recording devices should be incorporated into the circuitry.

6.4.2 Spark Circuit

Originally an induction coil system was used to ignite the gas mixture. Besides the difficulty of measuring spark energy, this proved unsatisfactory for a variety of reasons. Firstly, the long duration of the spark (up to about 2 ms) made determination of the exact instant of ignition uncertain. Secondly, the even longer duration of the interference picked up by the transient pressure measuring circuitry, and displayed on the oscilloscopes, effectively obliterated the initial portion of the pressure traces.

As a consequence it was decided to adopt a capacitative type of ignition system. In addition to the short duration of the spark, such a system has the advantage that the spark energy can be varied independently of the spark voltage by merely altering the value of the storage condenser.

The circuit adopted (designed by J.J.Kritzinger) is shown on Fig 6.4. An oscillator built around an EL 34 valve, produces a low voltage, at a frequency of about 500 kc/s, which is stepped up to several kilovolts through

an air-cored transformer $L_1 - L_2$. This high voltage, after being rectified by the 1B3 diode, is then used to charge condenser C through a $75\text{ M}\Omega$ resistor. Variation of the condenser potential - between 3.0 and 8.4 KV - is achieved by controlling the screen potential on the EL 34 valve using a $100\text{ K}\Omega$ potentiometer. If desired higher values of output voltage can be obtained by using a different coil assembly. Coil L4 consists of a single turn placed around the high voltage winding and serves to provide the filament voltage for the diode rectifier. The charging time of the condenser C, determined by the high series resistance, was chosen to be in excess of the operating time of the control relays to prevent repetitive sparking after ignition. In these tests C had a value of $0.001\text{ }\mu\text{F}$.

The function of the switches D1 and E1 will be described in Section 6.7.2.

6.3.3 Spark Electrodes

The spark electrodes used were each $1/8\text{-in}$ ($\approx 3.2\text{ mm}$) in diameter and projected radially from the inner surface of the vessel for about 2.5-in (6.35 cm) (Fig 6.5). The final portion of each electrode consisted of a length of 0.036-in ($\approx 0.9\text{ mm}$) diameter high-carbon steel wire bent twice so that the final $1/2\text{-in}$ (1.27 cm) lay along the line of vision of the camera. One electrode was earthed to the body of the vessel while the other was insulated and terminated in a screwed cap for connection to the spark supply voltage. The spark gap was positioned at the exact centre of the bomb. In the present series of tests the gap was set at 0.04-in (1.016 mm).

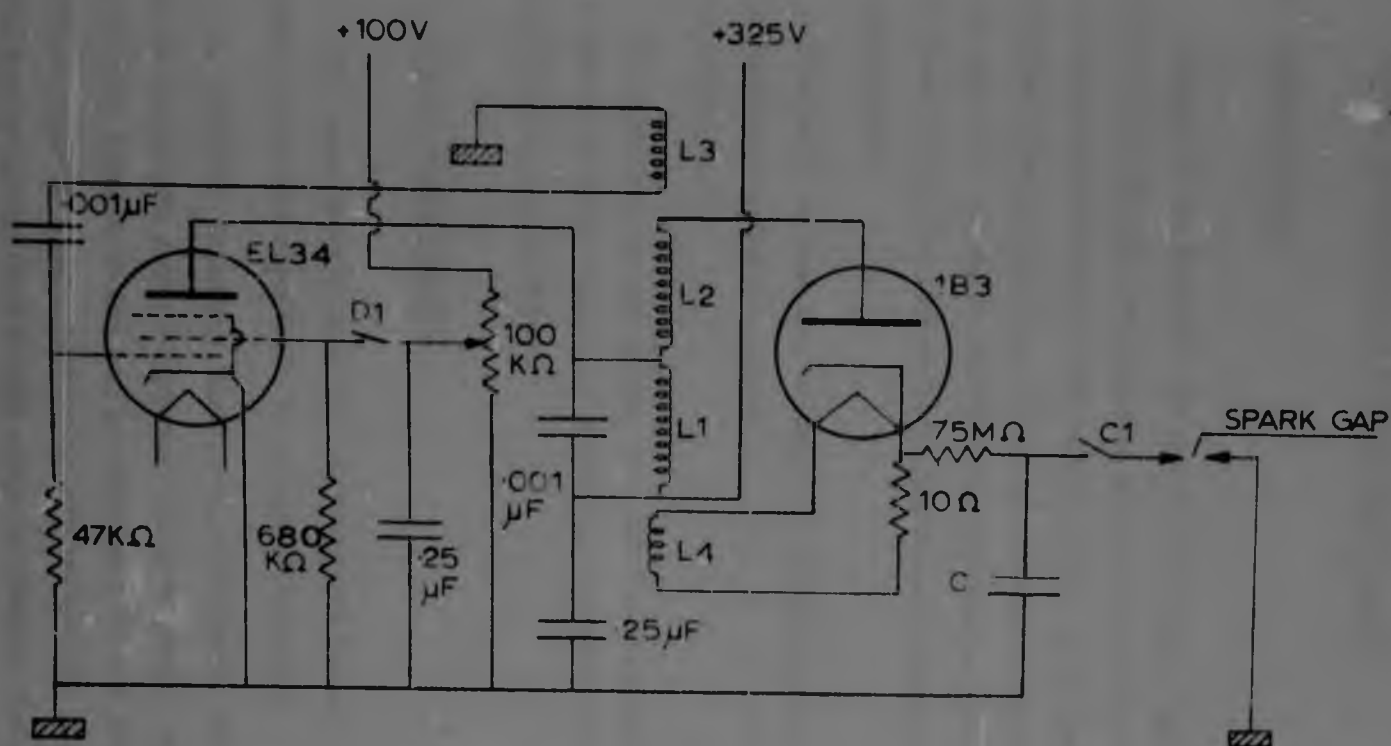


FIGURE 6.4 — HIGH VOLTAGE SUPPLY

6.5 MEASUREMENTS OF FLAME MOVEMENT

6.5.1 Requirements

Ideally it is desirable to observe the whole flame front from three mutually perpendicular directions so as to check on its isotropicity, and enable reliable measurements of burnt gas volume to be made. Any method of observation should, if possible, locate the radius at which the temperature of the mixture just starts to deviate from the unburnt gas value. As a check on the latter, more than one method of locating the flame front position would be advantageous.

Provision should also be made for the introduction and illumination of dust particles so that gas movement ahead, at, and behind the flame front may be determined.

Irrespective of the means used for observing the flame front position - that is, whether optical or electrical - suitable photographic recording devices must be provided.

6.5.2 Flame-Trace Camera

The main method used for recording and measuring the position of the flame across the vessel was via streak photography.

A modified Southern Instruments Universal Recording Camera (Model M 731), fitted with a Dallmeyer f1.9 anastigmatic lens, was used. The drum of this camera, which can be loaded with 70 mm film on its circumference, is rotated about a vertical axis by an electric motor. Its speed of rotation can be varied over a wide range by changing the drive pulleys and

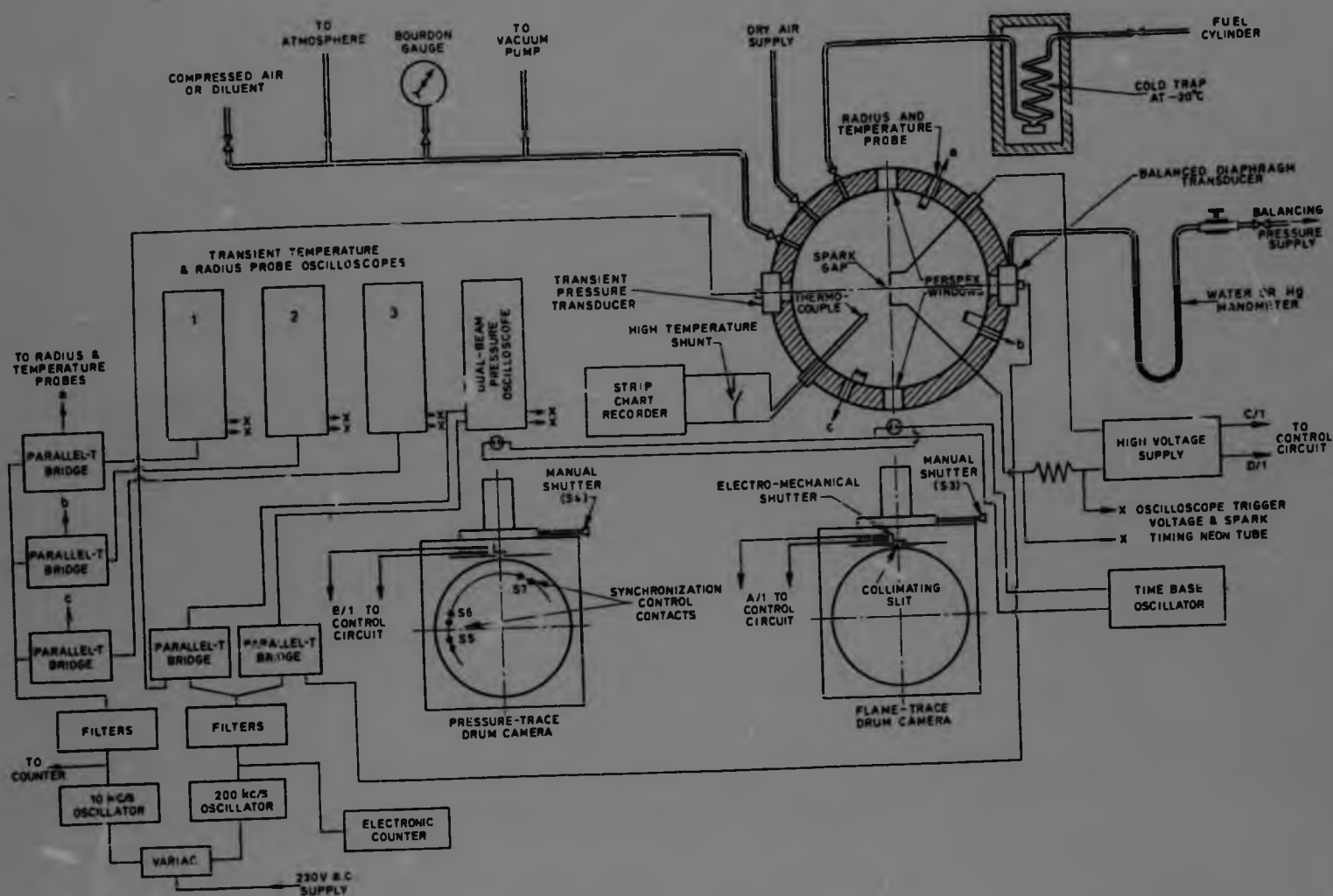


FIG 6-5 SCHEMATIC LAYOUT OF APPARATUS

gear ratios, as well as the armature and field voltages supplied to the motor.

A plane, about one-half inch (1.27 cm) in front of the vertical centre line of the bomb, sighted through the front window, was brought to focus on the film. As the spherical flame front increases in radius, the camera sights along a tangent to this front, thus recording an edge which progressively moves nearer to the camera. Focusing on a plane in front of the vertical centre line of the bomb thus reduces the effect of the restricted depth of focus associated with the aperture and focal length of the lens used. The plane chosen provided the best compromise on focus throughout the process.

The linear velocity of the film during each test was determined by recording timing marks on it (Fig 6.6). These were provided by a miniature neon glow lamp connected to the rectified output of a high voltage square wave oscillator. The lamp was brought to focus at the surface of the drum via a small strip mirror mounted slightly above the front window of the bomb. The duration of the flashes was measured immediately before each test by a crystal calibrated electronic timer (Advance Components Transistorised Measuring Counter - Type TC1).

As supplied by the manufacturers the drum camera was provided with only a manually operated sliding shutter situated between the lens and the film. This was found to be inadequate for flame-trace work since, due to the relatively long actinic persistence of the burnt gases, superimposition of images occurred if the shutter was left open for more than one revolution of the drum. The camera was therefore modified by the addition of an electro-mechanical focal-plane shutter built from a standard post-office type relay. This was controlled by a set of timing contacts so as to remain open for slightly less than one revolution of the drum. These timing contacts

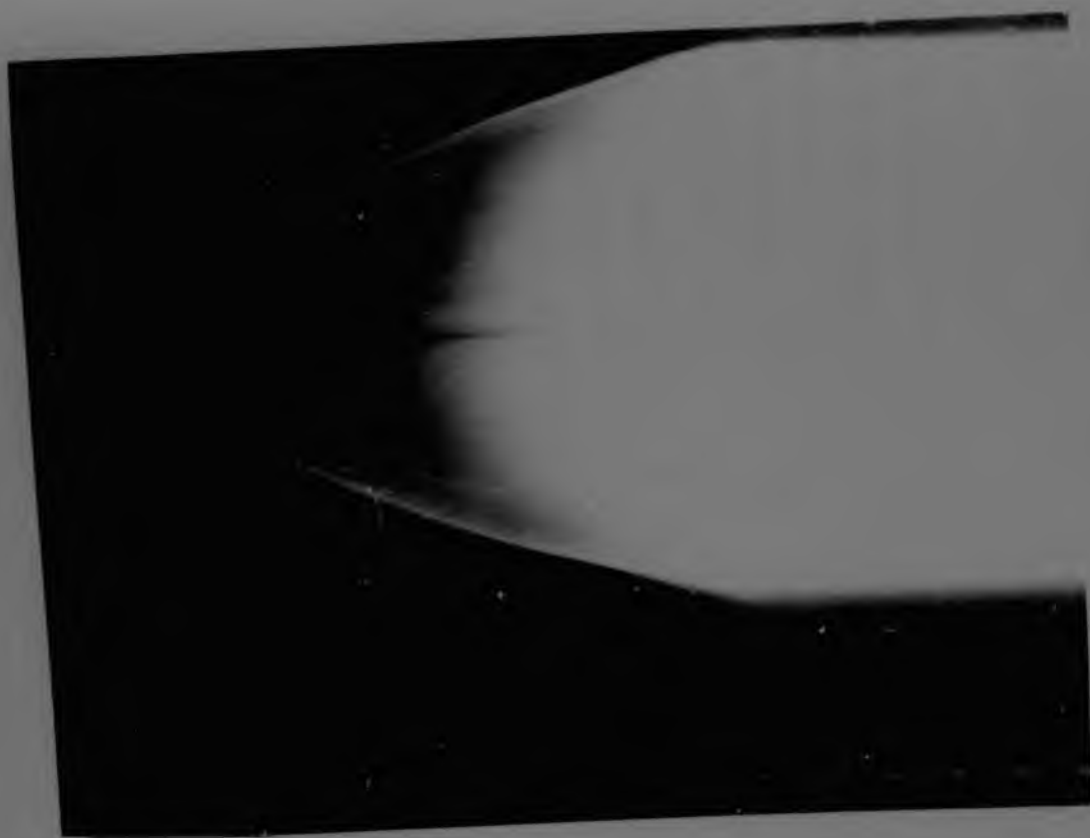


Fig 6.6 Typical flame trace



Fig 6.6 Typical flame trace

form part of the basic camera unit and are intended to synchronise the phenomenon with the loading slot on the rotating drum. Operation is through a cam which can be engaged when required by a manually operated mechanical trip-switch on the camera.

In an attempt to reduce the image width effect discussed in Section 5.4, a brass-shim mask, provided with a 1/8-in (3.175 mm) slot, was introduced immediately in front of the bomb window. The width used was decided upon as a result of experiments conducted with different slit widths, films and film processing techniques, so as to obtain a clear image with maximum contrast (Ga 63).

The whole camera unit was rigidly fixed in position in front of the window of the bomb. A suitable cowl was provided between the lens and the bomb window to exclude stray light. Care was taken to eliminate stray reflections by painting all metallic parts in the neighbourhood of the optical path matt-black.

Calibration of the flame-trace records is discussed in Section 7.1.1.

6.4.3 Alternative Flame Radius Measurements

Various alternative methods of measuring the position of the flame front were considered. The ionization gap technique, although easy to apply, was not favoured because of the suspicion that triggering may only occur well behind the flame front. Low melting-point fusing-wire probes were investigated, but were eventually ruled out because of the difficulty of making foils of reproducible thickness. In any event experiments indicated that the thermal lag from even the thinnest foils which could be used (obtained by electro-polishing) would probably be too high.

In the circumstances it was decided to attempt to use a resistance thermometer type of temperature measurement technique. Provided probes having a sufficiently low thermal lag can be designed then, in principle, they can be used to measure both the flame front radius and the temperature of the unburnt and burnt gas.

With normal circuitry it appears unlikely that a sufficiently fast response can be obtained from wires having adequate mechanical strength. However, provided a sufficiently high carrier frequency (of the order of 5 to 10 Mc/s) can be used in the bridge circuit, then it should be possible to confine the flow of electric current to the skin of the measurement element. In this way the effects of thermal lag should be considerably reduced.

Unfortunately although suitable probes have been constructed and installed in the bomb (see Fig 6.7), at the time of writing development work was still in progress.

6.4.4 Particle Track Method

As indicated in Section 4.4, it appears possible to obtain information of both gas properties and burning velocities through the use of a particle track method.

The window ring of the bomb has been modified so as permit the introduction and illumination of a suitable aerosol. This work has however been held up due to the lack of an intermittent light source of sufficiently high flashing rate. In the interim it is proposed to use minute particles of gunpowder or magnesium attached to fine hairs suspended in the vessel as was done by Flock *et al* (FM 40). Clearly this will only give an indication of the movement of the burnt gas.

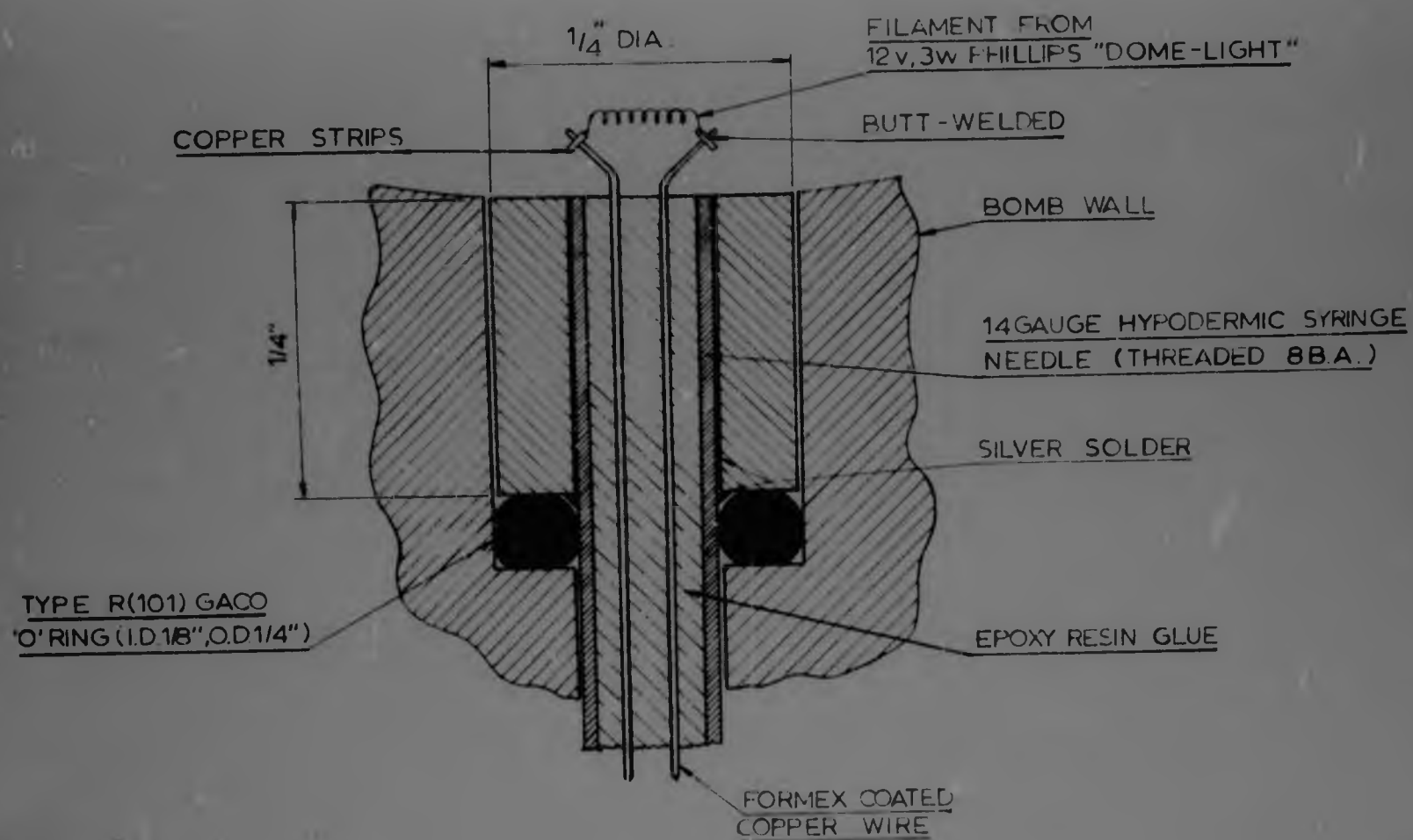


FIGURE 6.7 RESISTANCE THERMOMETER
TYPE RADIUS PROBE

Unfortunately once again this work is still under development - no results being as yet available.

6.6 TRANSIENT PRESSURE MEASUREMENTS

6.6.1 Requirements

The pressure rise during combustion is approximately proportional to the mass fraction burnt. Because of the spherical nature of the flame, the initial rate of pressure rise in a spherical constant volume vessel with central ignition, is therefore small, rising to a maximum at the end of the process.

Thus if transient pressures are to be accurately measured throughout the whole process, the pressure should be recorded over two or more ranges of sensitivity. This can be achieved either by using more than one transducer or by splitting the output from a single transducer and magnifying each by different amounts.

If possible the transducer should be designed so that its sensing element has the same curvature and is flush with the inside of the vessel, thus avoiding distortion of the flame and spurious vibrations due to gas resonance in connecting passages.

The natural frequency of the whole system should be as high as possible consistent with adequate sensitivity. The transducer design should be such that clamping forces or temperature gradients do not affect its calibration or sensitivity to any significant extent.

The system should be capable of being statically calibrated.

6.6.2 System Adopted

The design and development of the pressure measuring system adopted in this study is in the main due to Dr K. Posel (Po 60,61 a & b, 63 a & b).

In essence this consists of a pressure transducer clamped into the wall of the vessel, a transfer bridge, a high frequency oscillator, one or more oscilloscopes and a suitable means for recording the oscilloscope traces. The design provides for at least two pressure traces - one covering the early stages of the combustion process and the other the full range.

6.6.3 Transducer Design

The pressure transducer used was of the variable capacitance type (Po 60) having an integral clamped diaphragm and a composite dielectric consisting of mica and air (Fig 6.8). The relative proportions of the mica and air were chosen so as to achieve a substantially linear relationship between bridge output voltage and applied pressure. The dimensions of the stainless steel diaphragm finally adopted were: diameter 0.375 (~ 1 cm) ; thickness .015-in (.04 cm). The unit used (Fig 6.8) was initially designed for an effective diaphragm diameter of 1½-in (~2.9cm), but subsequent analysis by Posel (Po 63 a & b) showed that, for a given natural frequency the sensitivity of the system increases as the diaphragm diameter (and hence also its thickness) decreases. The transducer was thus modified as shown (Fig 6.8) to provide the the minimum diameter possible. Under these conditions the natural frequency of the unit, given by (Po 61a),

$$f_o = 9.82 \times 10^4 T/R_d^2 = 42 \text{ kcps}$$

The standing capacitance of the transducer alone was measured at 50 pF. This data, together with the capacitance of the pick-up leads (15 pF) and the decision to operate the transfer bridge at a frequency of 200 Kc/s permitted a suitable parallel-T bridge to be designed (Po 61b).

6.6.4 Circuitry (Fig 6.9)

A 200 Kc/s carrier was provided by a Hewlett-Packard wide range oscillator (Model 200CD). The output from this oscillator was taken through a number of series connected filters so as to reduce unwanted frequencies from the signal entering the bridge. Since the parallel-T network can be balanced for zero output at only a single frequency, any spurious signals at frequencies other than the design value pass through unimpeded. Undesirable frequencies in the oscillator output are of two types: (i) Hum from the mains - consisting of a relatively strong 50 c/s fundamental and numerous harmonics of this; (ii) The 400 Kc/s and 600 Kc/s harmonics of the 200 Kc/s carrier.

The first of these was reduced by two cascaded high-pass RC filters with cut-off's at 100 Kc/s. The second was reduced by using two LC filters, tuned to reject each of the harmonics mentioned in (ii) above. By this means the bridge output at balance was reduced to less than 0.2 mV for a 19 V rms input. This was negligible at the required sensitivity.

Due to the frequency dependence of the bridge, stability of the carrier frequency was of prime importance. Continuous monitoring of the oscillator frequency indicated a significant variation with the normal drift of the mains supply voltage and frequency. The resultant changes in oscillator frequency were sufficient to unbalance the bridge, this being observed as an increase in thickness of the oscilloscope traces. This was overcome

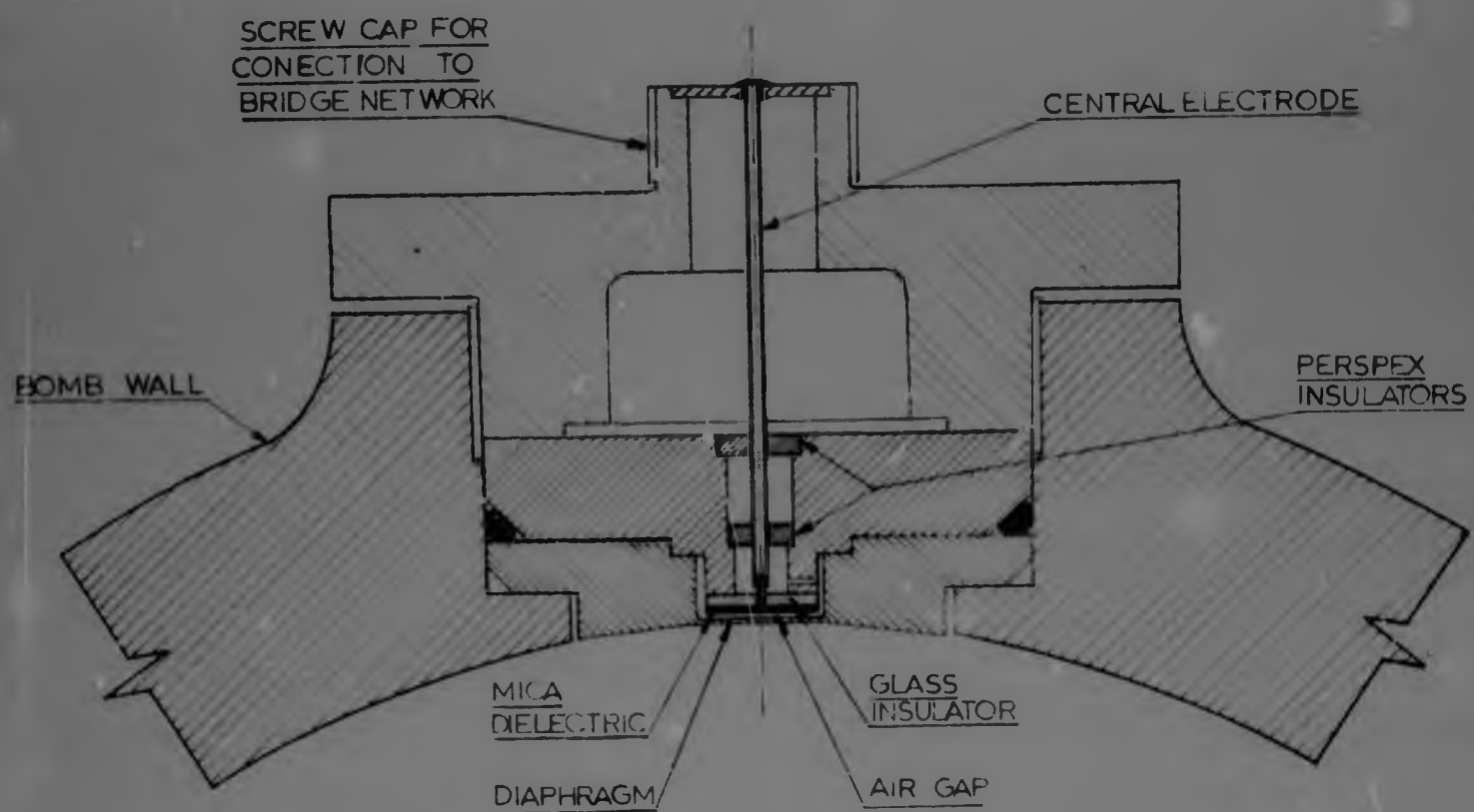


FIGURE 6.7 — SECTIONED ASSEMBLY VIEW
OF PRESSURE TRANSDUCER

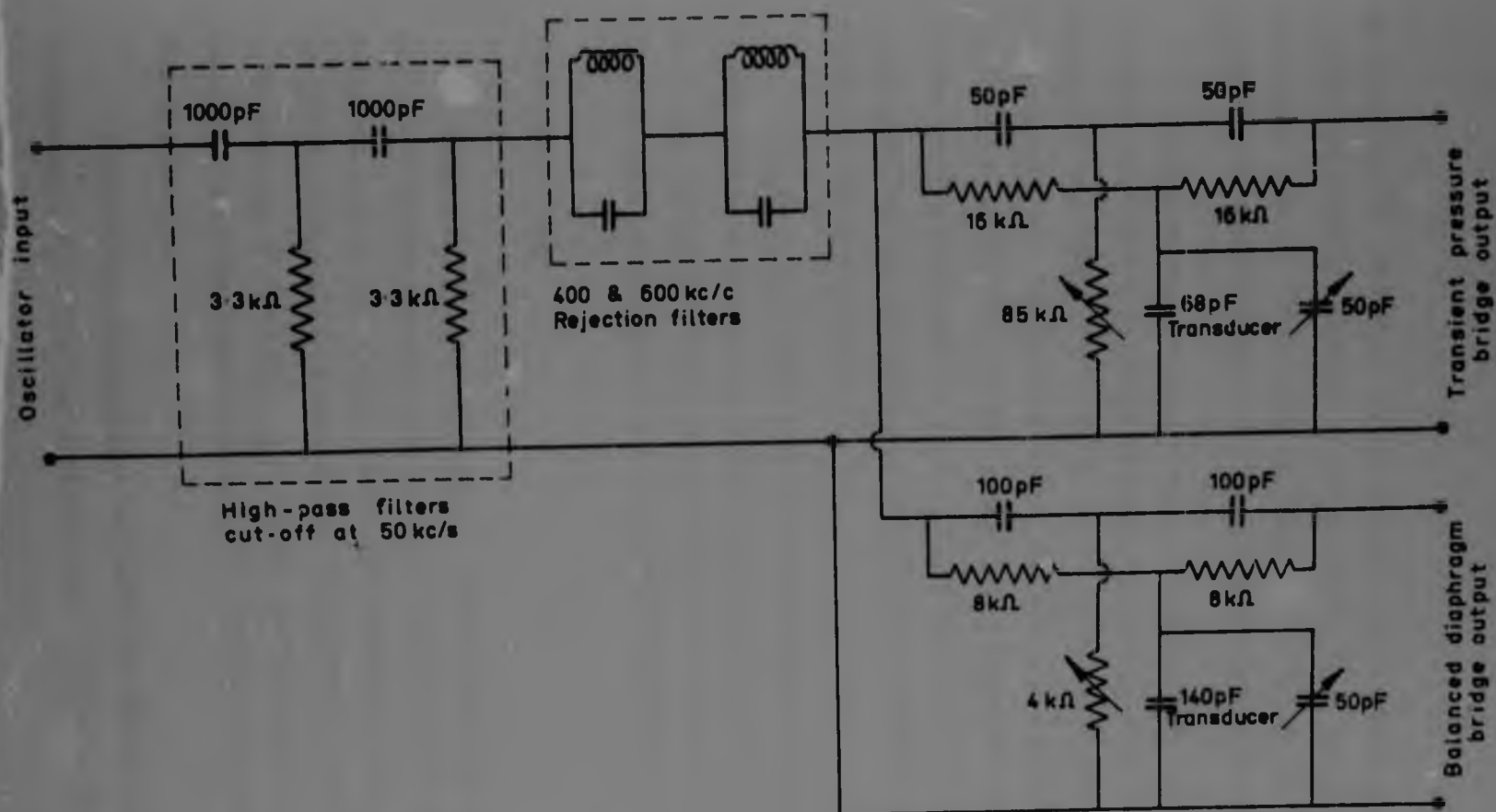


FIG. 6.9 TRANSIENT PRESSURE AND BALANCED DIAPHRAGM
MEASUREMENT CIRCUIT

by supplying the oscillator through a Variac and compensating for mains voltage and frequency changes by manual adjustments. In addition, all tests were done between the periods 12 midnight to 4 am, so as to reduce the possibility of sudden changes in mains conditions during a test.

Particular care had to be taken to reduce hum pick-up by the bridge circuitry from ancillary mains-operated equipment. This was achieved by physically separating the transfer bridge as much as possible from the oscilloscopes and 200 Kc/s oscillator, as well as by thorough shielding of the various units. The whole system was incorporated into a moveable trolley which could thus be used for other research projects as well. The heavy shielding had the additional advantage of preventing radiation interference by the spark ignition circuit.

A further precaution taken to prevent hum pick-up was the avoidance of loop earths in the vicinity of the transducer equipment. To this end, the bomb was separated from its supporting rails by insulating strips so that the only earth connection to it was through the transducer pick-up lead.

6.6.4 Recording

Explosions in spherical constant volume vessels with central ignition are characterised by a low initial rate of pressure rise increasing to a maximum just as the flame reaches the containing walls. To obtain an adequate representation of the pressure changes which occur it was considered desirable to feed the output voltage from the transfer bridge to two separate oscilloscope traces connected in parallel, but operating at different sensitivities.

Initially two oscilloscopes were used for this purpose. The entire phenomenon (Fig 6.10) was displayed on a Tektronix 503 oscilloscope,

whilst the initial stages (Fig 6.11) were observed on a Tektronix 545A, set at ten times the vertical sensitivity and one-quarter the sweep time of the former. Triggering of the 545A was achieved from the spark circuit. The 503 was triggered by the 545A through a delayed trigger facility, which for the tests reported here was set for zero delay. Thus both traces started at the instant of ignition. In these initial tests the oscilloscope traces were photographed using two 35 mm single lens reflex cameras, loaded with Ilford FP3 film.

Analysis of these results however (Section 5.4) indicated that an increase in accuracy was desirable. In particular during the latter stages of the process the rate of pressure rise was very high, resulting in a steep pressure-time trace (Fig 6.10). In consequence it was decided to use a double beam oscilloscope (Tektronix 502) with the two traces set at different vertical sensitivities so as to record a low and high range record. With the oscilloscope time base out of circuit the traces were photographed with a second Southern Instruments drum camera, yielding results such as those shown in Fig 6.12. In addition to stretching out the time scale, this scheme had the advantage that synchronization with the flame-trace records was continually assured, since the instant at which the spark occurred was recorded simultaneously on both films, and the two sets of timing marks were provided by the same oscillator. Further, by restricting the oscilloscope traces to motion in a vertical plane, astigmatism and out-of-focus effects of the electron beam of the CRO tube (as well as possible similar effects resulting from the optical systems in the camera) are considerably reduced.

Calibration of the transient pressure measuring system is described in Section 7.1.2.

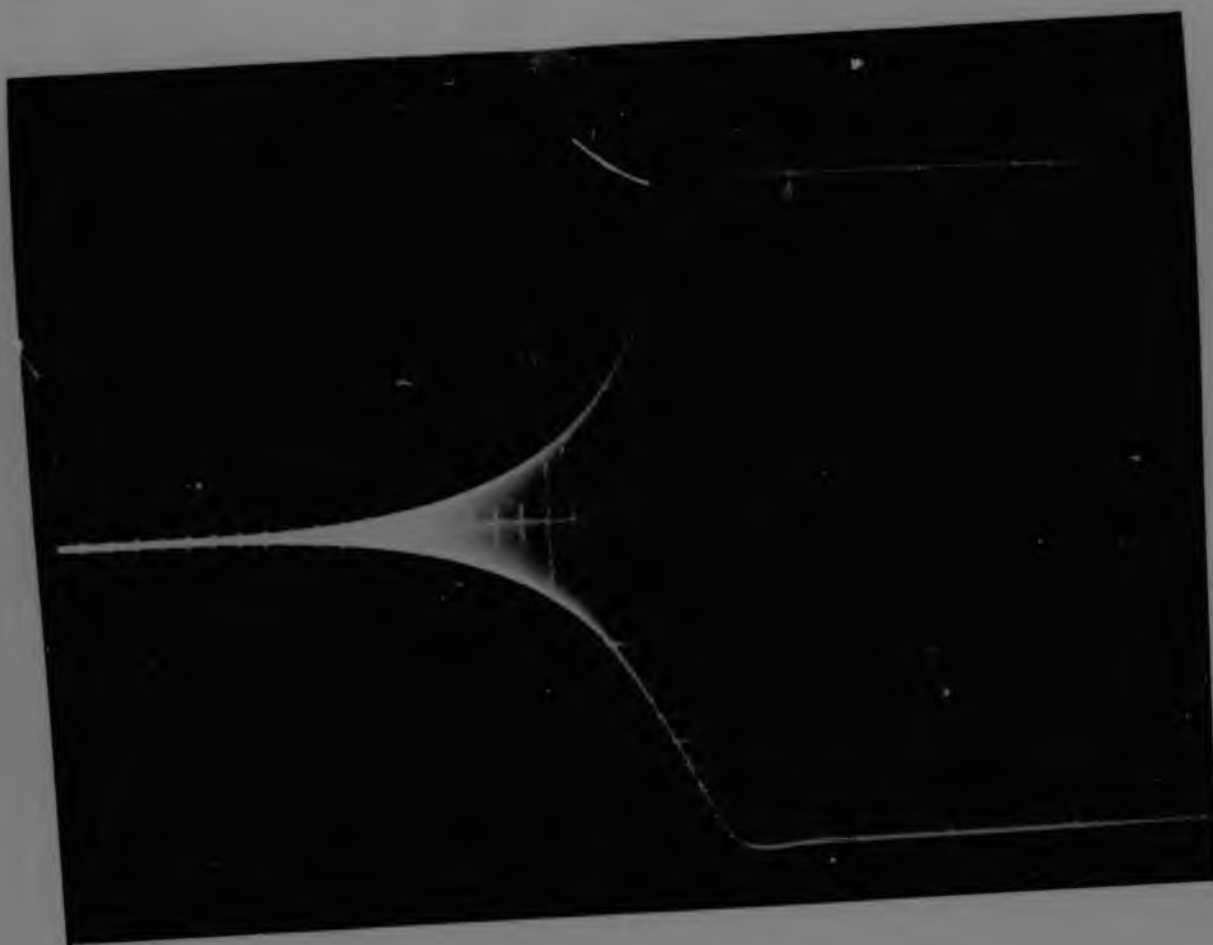


Fig 6.10 High-range pressure record.



Fig 6.10 High-range pressure record.

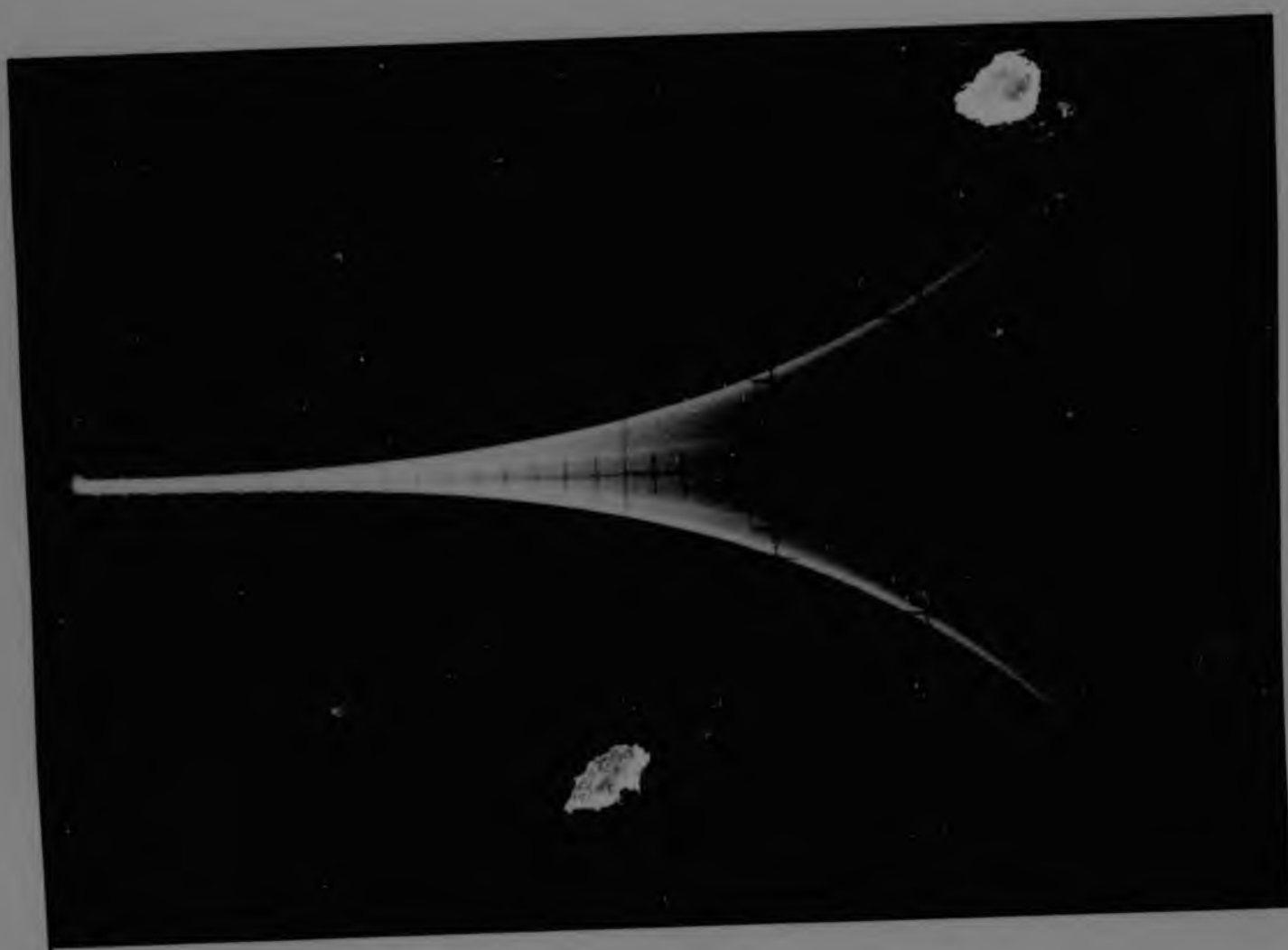


Fig 6.11 Low-range pressure record.

6-30



Fig 5.11 Low-range pressure record.

Neon tube
giving
instant
of spark

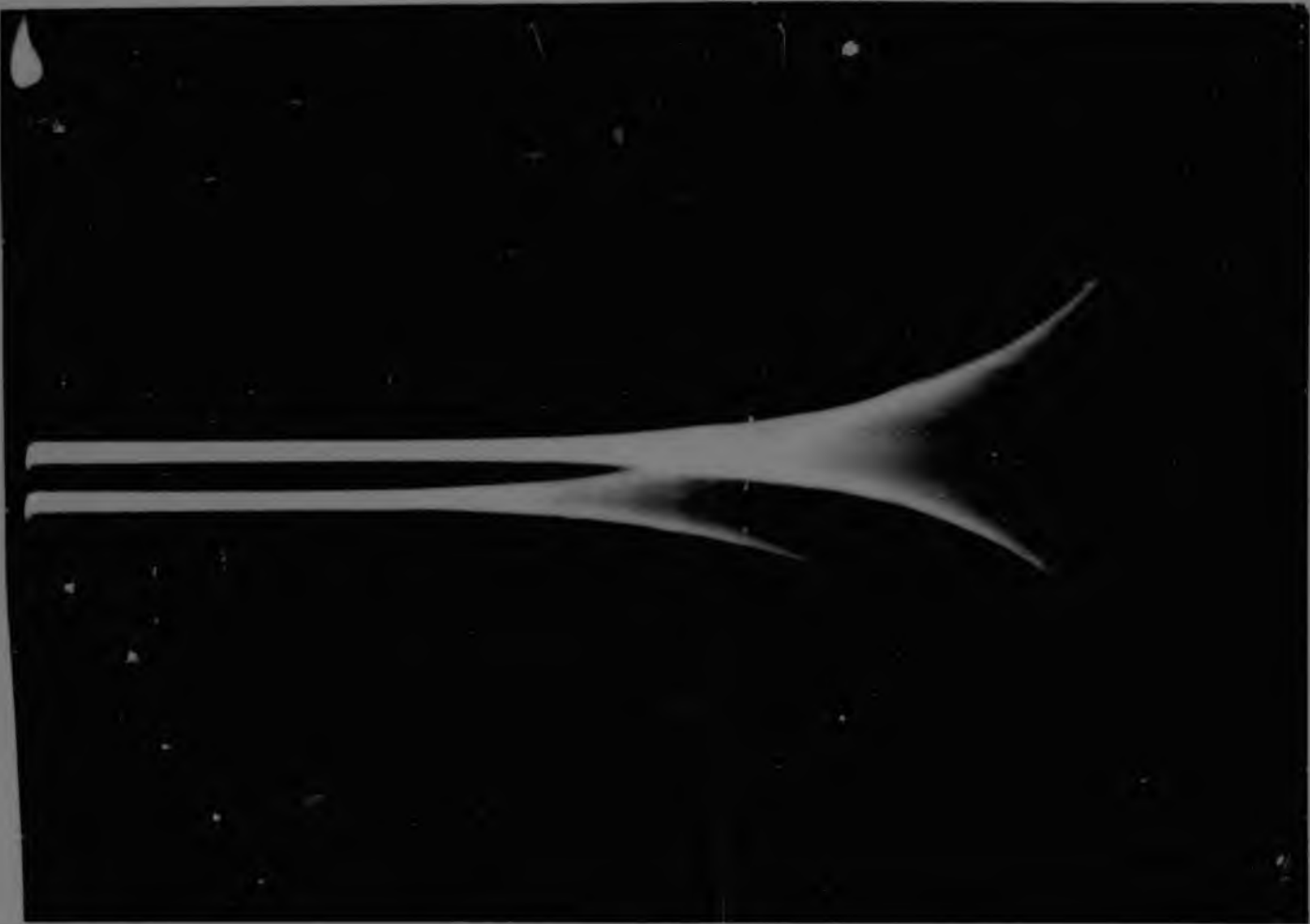


Fig 6.12 Combined high- and low-range pressure records (low-range set at only twice the sensitivity of high-range record).

Neon tube
giving
instant
of spark



Fig 5.12 Combined high- and low-range pressure records (low-range set at only twice the sensitivity of high-range record).

6.7 TRANSIENT TEMPERATURE MEASUREMENTS

6.7.1 Requirements

In developing the theory of the constant volume method (Chapter 4) the assumption of adiabatic compression has been introduced only as a last resort. Thus, provided any two of the properties of state - pressure, temperature or density - can be measured, the assumption of zero heat loss need not be invoked.

Of these three properties the most desirable measurement would appear to be that of density - either of the unburnt or burnt gas: this since a checkpoint is provided by the fact that the mean density of the system as a whole remains constant. However, although various means of measuring this property have been examined, certain experimental difficulties have still to be resolved.

In the circumstances, and particularly since a satisfactory means of measuring transient pressure is available, effort is being directed to the direct determination of transient temperature.

6.7.2 Proposed System

The system at present under investigation has been discussed in Section 6.4.3. Unfortunately since results are still not forthcoming it is pointless to go into any detail at this stage.

6.8 CONTROL CIRCUIT

6.8.1 Requirements

The need for an automatic control and synchronization system is

dictated by the necessity that certain events occur in a predetermined sequence. Thus the mixture in the bomb must be ignited only when the drums of the two cameras are in their correct positions, that is, when their loading slots - marking the start of the films - have just passed their respective lenses. The two drum camera shutters must be arranged to open just before ignition and close after only one revolution of their respective drums. For the spark to jump its gap a connection must be established, at the correct instant, between the storage condenser in the ignition unit and the spark electrodes. (This involves a switching system capable of handling up to 8 KV). At the same time the ignition circuit oscillator (Fig 6.4) must be switched off to ensure that the condenser cannot recharge before the end of the combustion process.

The instant of ignition must be clearly indicated on each film. Timing marks must also be provided.

If the particle track method is to be used, dust particles must be released just prior to igniting the mixture. In this case the timing marks may be provided by the intermittent illumination used - although independent marks would be a useful cross-check.

6.8.2 Circuitry and Operation

The operation of the control circuit is best described by considering the sequence of events after the drum cameras have been brought up to speed. Reference should be made to Fig 6.13.

- (1) The manually-operated sliding shutters of the two cameras are opened, causing switches S3 and S4 to close. This ensures that the mixture cannot be fired if either of these shutters is not fully open.

- (2) The spring-loaded mechanical trip on the film-trace camera is depressed until a cam on the shaft of the drum is engaged. The drum rotates until its loading slot, marking the start of the film, is just past the front of the lens. At this instant its cam-operated timing contacts (S2) close.
- (3) Situated below the drum of the pressure-trace camera are three switches - S5, S6 and S7. These are actuated by an insulated strip-cam attached to the lower face of the drum. This cam subtends an angle of about 180° , whilst the angle between S5 and S7 is about 120° . The start of the cam is arranged to close S5 just after the film loading slot has passed the camera lens.
- (4) Provided switches S2 and S5 on each camera are closed - thus ensuring that their loading slots have passed their respective lenses - a current flows through the coils of relays A/1, B/1, C/1 and D/1, thus causing contacts A1, B1, C1 and D1 to close. Relays A/1 and B/1 are situated inside the flame- and pressure-trace cameras respectively.
- (5) Actuation of relays A/1 and B/1 cause strip shutters attached to their respective armatures to uncover narrow slits in front of the camera drums. This allows light from the time-base and spark-timing lamps, spark terminals, oscilloscope traces, etc., to fall onto the films.
- (6) Both the relays C/1 and D/1 form part of the high voltage supply unit. The high voltage on condenser C (Fig 6.4) is switched onto the spark electrodes in the combustion vessel by closure of C1 (Relay C/1 was specially constructed to handle high voltages.) At the same time contacts D1 open. This removes the screen potential on the oscillator so that no further energy is supplied to the condenser after ignition of the mixture.
- (7) The ignition spark shows up directly on the flame-trace record (Fig 6.6) In order to synchronize the pressure-trace records with the above, the spark is used to fire a neon lamp which is viewed by the pressure-trace

camera (Fig 6.12).

- (8) After somewhat less than half a revolution of the oscilloscope camera drum - and well before its loading slot comes opposite the lens - the interlock switch (S6) opens, thus de-energising all relays and closing both camera shutters.
- (9) Since S2 only rotates once after the mechanical trip on the flame-trace camera is depressed, the above sequence of events will not be repeated unless the trip is again depressed.

The control circuit described is of the hit-or-miss type, since for it to operate the angular position of the camera drums must be approximately the same (within a certain overlap period). Although not ideal - in that the trip-switch on the flame trace camera may have to be depressed a few times before the mixture eventually is caused to fire - it is considered satisfactory. The alternative would be a rather complicated control system designed to exactly synchronize both the angular velocity and position of the drums on the two cameras.

6.9 CLOSURE

The bulk of the apparatus described in this chapter has been successfully used for a considerable number of tests. Arrangements have been made so that wherever possible contentious measurements can be cross-checked by independent means. Thus although it is certainly capable of improvement (some modifications and additions are currently being made) it has in the main yielded reproducible, and it is hoped accurate, results.

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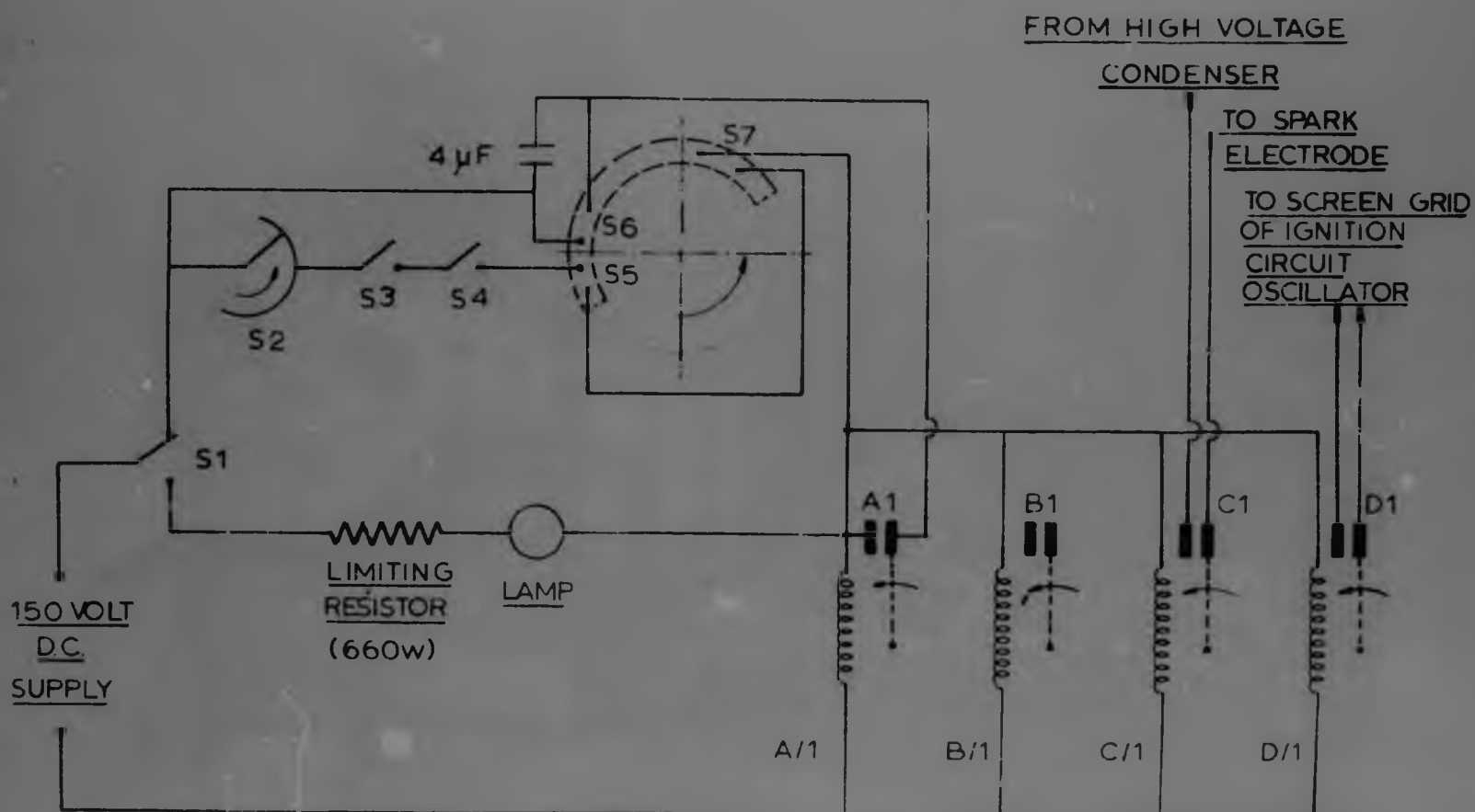


FIGURE 6 13 - CONTROL CIRCUIT

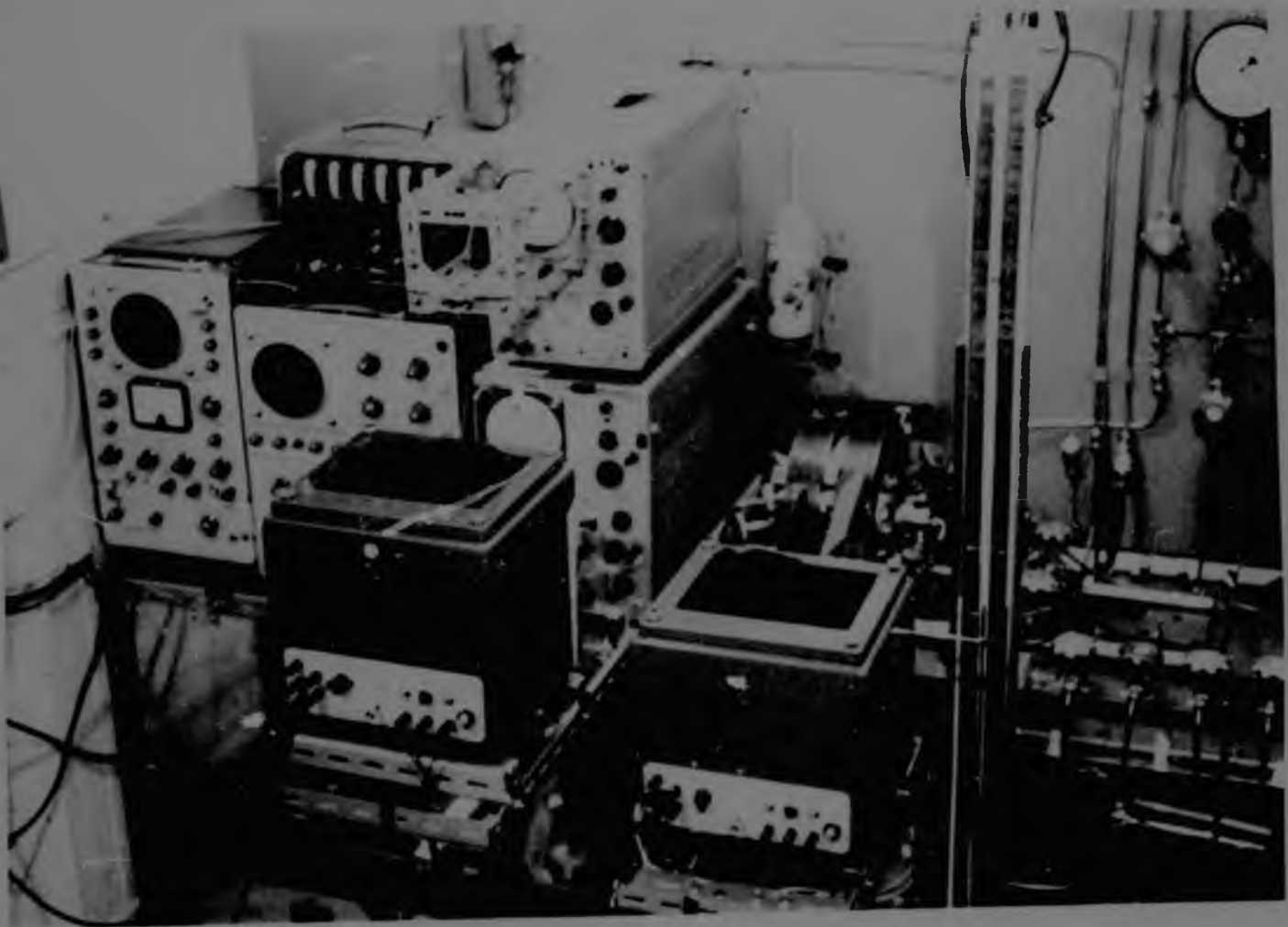


Fig 6.14(a) General view of apparatus

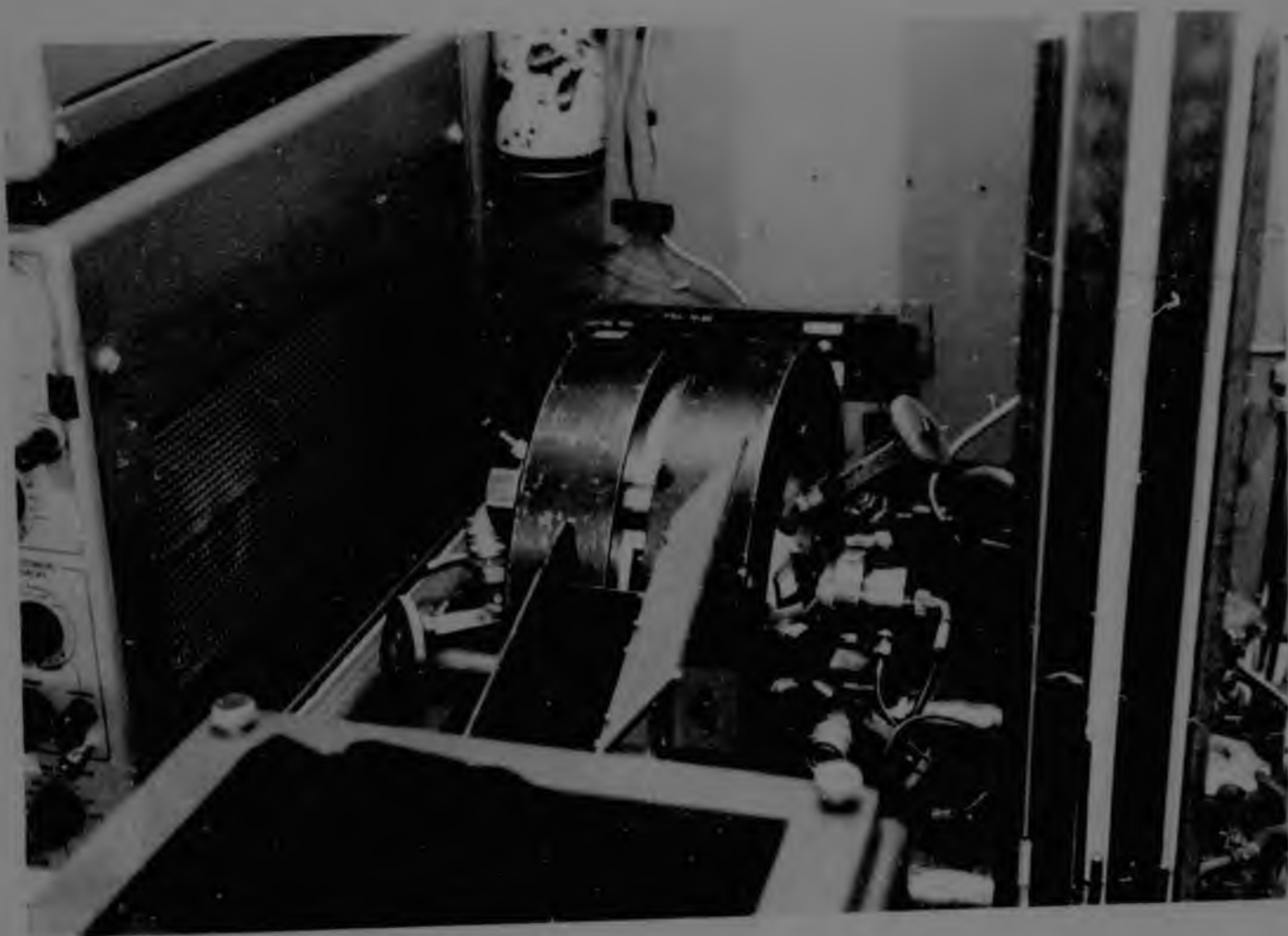


Fig 6.14(b) The spherical vessel

CHAPTER 7

EXPERIMENTAL PROCEDURE AND DATA PROCESSING

The apparatus described in the previous chapter permits a wide range of different types of test to be carried out. However, if the results of such tests are to have significance, considerable care must be exercised in calibrating the various measuring devices, performing the tests, transcribing the observations and calculating the final results. These aspects will be considered in this chapter.

7.1 CALIBRATIONS

7.1.1 Flame Front Radius

The photographic flame traces (see Fig 6.6) recorded on the drum camera were projected onto a large sheet of graph paper for the purpose of measurement. The relationship between the width of the final projected image and the radius of the corresponding sphere of flame within the bomb was established by photographing a range of accurately machined discs of different diameters. These were mounted centrally in the bomb to represent portions of a spherical flame front. The disc images were projected using the same optical system as that subsequently used for analysing the flame traces. A flame-radius calibration curve was thus established by measuring the width of the disc images on the screen and comparing these with the known disc diameters. In this way the magnification of the system as well as its non-linearities were taken into account. These include a tangency effect due to the proximity of the spherical subject to the camera, refraction due to the 'Perspex' window and magnification due to the physical

arrangement of bomb, camera and projection system.

In order to correct for the 'image width effect' discussed in Section 5.4, the maximum penumbra width of the flame trace at each time interval was recorded. This, together with the image of the slit, measured from the disc calibration photographs, then permitted the corrected value of flame-radius image to be calculated from eqn 5.12. These corrected values were then converted, via the calibration curve (Fig 7.1), into flame-front radii.

7.1.2 Transient Pressure

The pressure traces (Figs 6.10, 6.11 and 6.12) were analysed in a similar way to the above, by projecting them onto a large sheet of graph paper. In this case a correlation was required between the projected image width and the instantaneous pressure in the bomb. This was established by filling the bomb with compressed air to various pressures and photographing the corresponding images on the screens of the oscilloscopes. Over the high range, pressures were measured on calibrated precision Bourdon gauges (0 - 160 and 0 - 500 psi), whilst over the lower ranges pressures were measured by means of a water and/or mercury manometer.

Pressure-record calibration curves were established by measuring the width of the images on the screen and comparing these with the known pressures. Image widths were first corrected by subtracting the width of the image corresponding to zero gauge pressure.

Immediately before carrying out the above calibrations, the parallel - T bridge was balanced with atmospheric pressure in the bomb. The internal pressure was returned to atmospheric and the balance checked after each calibration point. The oscillator frequency was set and maintained at $200\,000 \pm 1$ c/s by adjustment of the Variac.

The above procedure permitted a master calibration curve to be obtained (Fig 7.2). However, as a check, at least two pressure calibration points were undertaken prior to each test.

7.1.3. Time Bases

The rate of flashing of the neon glow-lamps used as time bases for both the flame and pressure trace cameras was checked and set immediately before each test against a crystal controlled electronic timer. To avoid errors due to drift of the oscillator during warming up, the timing lamps were left on throughout each series of tests.

7.1.4. Miscellaneous

Since there are no results as yet available on the radius-probe, particle track and transient temperature measurements, the proposed methods of calibrating these devices need not concern us here.

The chromel-alumel thermocouples for measuring initial temperature were calibrated against a standard mercury-in-glass thermometer over a range of temperatures from 0 - 100° C.

7.2 TEST PROCEDURE

The bridge circuit containing the transient pressure transducer was balanced with the oscillator frequency controlled at 200000 ± 1 c/s. Pressure calibration check points were obtained by photographing traces corresponding to set pressures within the bomb. This was done at two points, the zero balance of the bridge being checked each time. These points were subsequently compared with the master calibration curve to ensure that conditions had not changed.

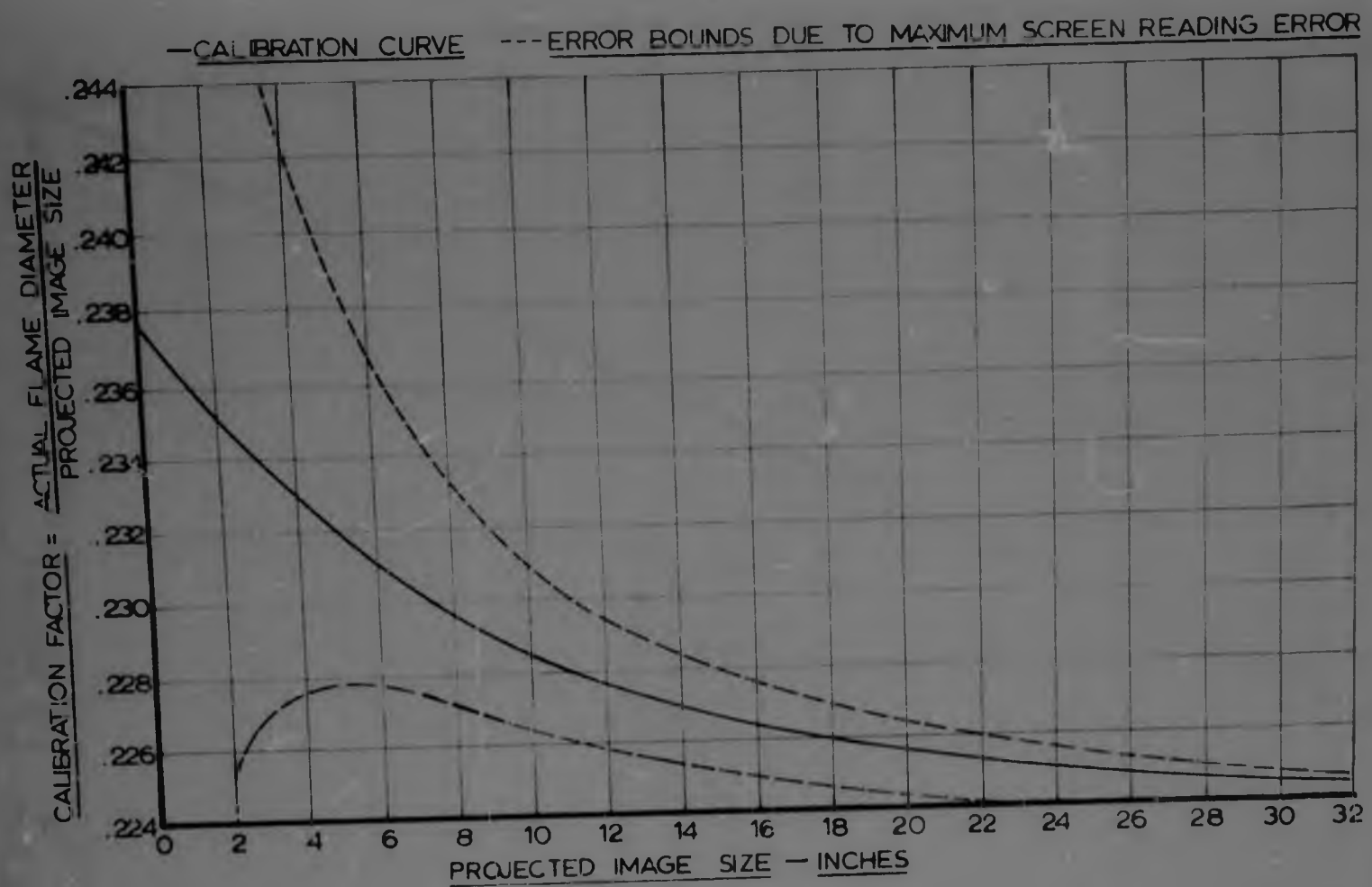


FIGURE 7.1 — FLAME TRACE OPTICAL CALIBRATION CURVE

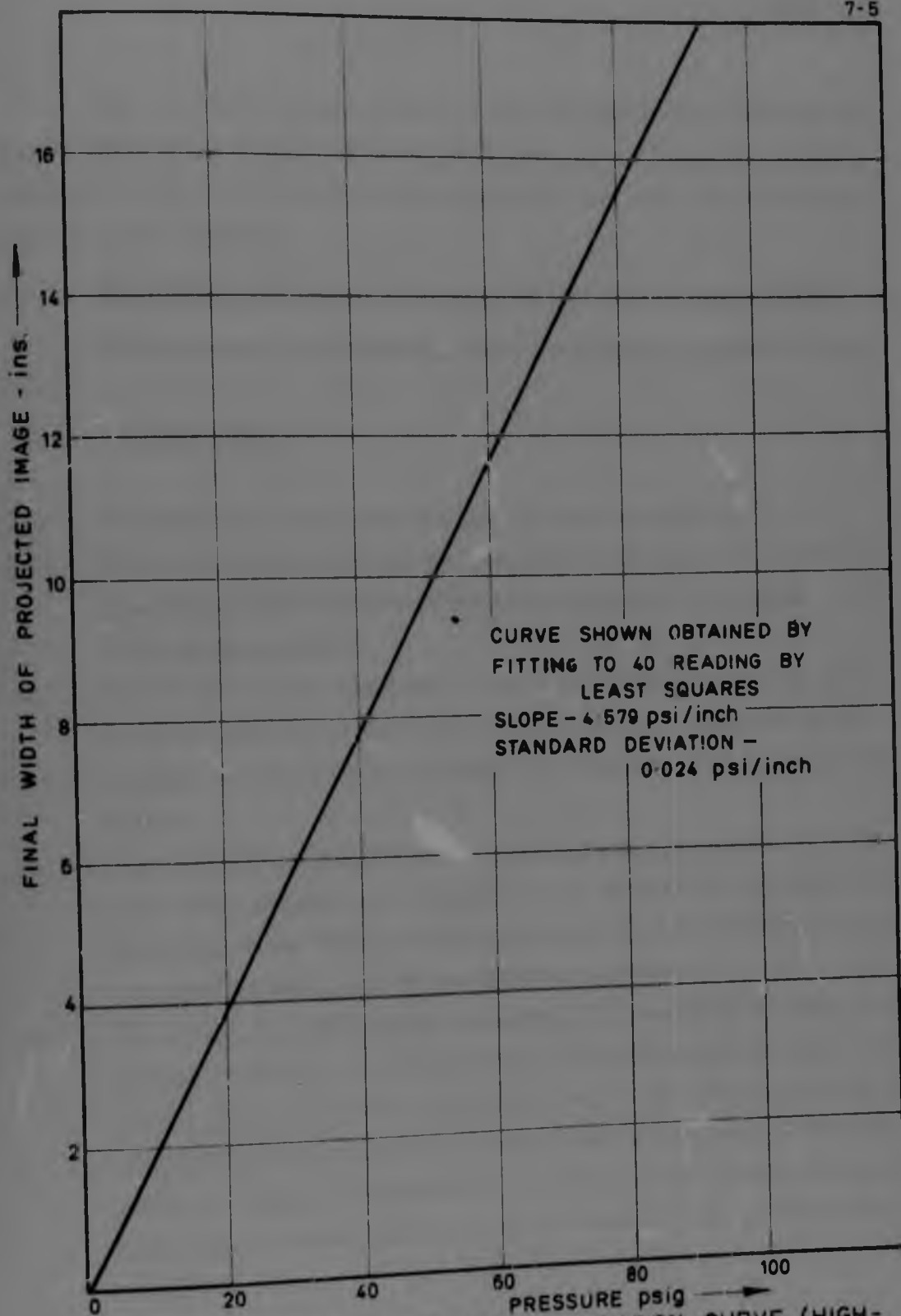


FIG. 7-2 TYPICAL PRESSURE CALIBRATION CURVE (HIGH-RANGE PRESSURE RECORD)

The remainder of the procedure can be considered to fall into two parts: filling of the vessel with combustible mixture, and firing this mixture. Since for all the tests reported in this thesis air was used, only this procedure will be described.

The initial temperature of the mixture used was always ambient.

The comments in parenthesis refer to the high initial-pressure tests.

7.2.1. Filling the Bomb

- (1) The bomb was purged with dry air for several minutes.
- (2) With atmospheric pressure on both sides of the balanced diaphragm transducer, its bridge was balanced for minimum trace width on the oscilloscope screen.
- (3) One of the U-tube manometers (water or mercury depending on the pressure) was set at the desired partial pressure of the air by evacuating or pressurising its one leg. This action unbalanced the bridge.
- (4) Throughout the filling and mixing processes gas temperatures in the bomb were continuously recorded on a strip chart recorder. At each stage of the filling process pressure measurements were made only after thermal equilibrium had been achieved.
- (5) The bomb was then slowly exhausted (or pressurised) until the pressure within it, as indicated on the oscilloscope screen, was slightly below (or above) the desired value. Dry air was bled into (or out of) the bomb until as close a balance point as possible was obtained. Finally, the balancing pressure on the manometer was adjusted to bring the bridge to exact balance. This pressure was recorded.

- (6) The manometer was then set at the desired initial pressure of the mixture. This again unbalanced the bridge.
- (7) Fuel was slowly admitted until the bridge returned to balance. Once again the final balance point was obtained by adjusting the manometer when the system had reached a steady temperature.
- (8) The balanced diaphragm transducer was then unplugged from its bridge, since it had been found to affect the transient pressure bridge if left connected.

7.2.2. Firing the mixture

- (1) The spark voltage control was adjusted and the setting noted.
- (2) The frequency of the neon glow-lamp oscillator was measured.
- (3) The sensitivity of the oscilloscope beams was set at the desired value.
- (4) All the cameras were loaded.
- (5) With the room darkened the drum cameras were brought up to speed and their manual shutters opened.
- (6) The trip switch on the flame-trace camera was depressed thus firing the mixture.
- (7) The mixing time, being the elapsed time between the start of fuel supply to the bomb and the instant of firing the mixture, was noted.
- (8) The bomb was then purged thoroughly with dry air in preparation for the next test.

7.3 TRANSCRIPTION OF OBSERVATIONS

The flame- and pressure-trace negatives were mounted in glass slides and projected onto a 3x4-ft screen, consisting of a large sheet of graph paper attached onto a board.

The total distance between several timing marks was measured and an average length used to establish the time scale. Time intervals were measured with respect to the instance of occurrence of the spark. No variation in the speed of the films over the period of interest was detectable.

The width of the projected images was measured at, typically, more than fifty equally spaced time intervals after ignition. In the case of the flame traces the exact number was dictated by the extent of a clearly defined boundary to the images. For the pressure traces values were recorded until well after the maximum pressure had been reached.

Measurements of image width were recorded to the nearest 0.05-in, since the boundaries were not sufficiently well defined to permit more precise readings to be taken. However every effort was made to use a consistent judgement of the boundaries of the image in the penumbra region. In all cases the projected images were positioned symmetrically about a horizontal reference line drawn on the screen. At each time interval the position of the image boundaries both above and below this reference line were noted. In practice, measurements were taken along the entire upper boundary first, and then along the lower boundary, in an attempt to avoid subconscious bias arising from previous readings. As a check on reproducibility, traces were measured by different observers and the results compared.

7.4 DATA PROCESSING

7.4.1 Introduction

The determination of burning velocities by any of the equations discussed in Chapters 3 and 4 requires the determination of one or both of the time derivatives of flame radius and pressure.

Various methods can be used for obtaining these derivatives. Possibly the quickest is to plot the measured values of r_b and P on a sheet of graph paper, draw the best possible curve through the points, and then measure the slope at intervals by drawing tangents. Unfortunately such a graphical procedure does not give sufficiently reliable results.

First derivatives can be estimated numerically by taking first differences of the basic data. For this purpose it is convenient to have the data tabulated at equal intervals. Using this method, however, it was found that the first differences were rather erratic if they were based directly on the observations. This was a result of unavoidable, though small, random errors in transcribing the observations - accentuated by the lack of sharpness of the edges of the projected images. Attempts to eliminate these errors by plotting the observations and then taking readings from a smooth curve drawn through the points, did not prove entirely satisfactory. To obtain sufficient accuracy from such a graph it was necessary that it be drawn to a large scale; this increased the difficulty of fitting a smooth curve by eye.

The difficulties associated with the determination of derivatives by graphical means were eventually overcome by adopting a numerical-analytical approach. This was based on a least squares method of smoothing the basic data by fitting a third degree polynomial to groups of observations. The particular technique adopted is known as the 'eleven point formula' (Gu 61). Using these smoothed values first derivatives were then obtained, using various forms of finite difference equations over different ranges of the observations, as described in the following section.

7.4.2 Scheme Adopted (See Fig 7.3)

The data processing scheme to be described below was designed for the somewhat restricted facilities available on the IBM 1620 computer at this University.

Image size data for both radius and pressure were punched on cards, using an IBM 870 off-line punch, and then transferred to paper tape in a form suitable for processing by the IBM 1620 computer. Before processing however certain ancillary data is required.

- (1) Determination of a mean value of γ_u (Appendix E); also values of mean burnt gas temperature and molecular weight, at corresponding values of pressure (preferably equally spaced). (See Appendices E and K). Hence $\mu (=M_b/T_b)$ may be determined over a range of pressures. A straight-line log relationship of the form

$$\mu = A - B \log P$$

is fitted to this data using log-linear graph paper and incorporating a maximum pressure ratio of 10. The coefficients A and B in this equation are noted.

- (2) Determination of a mean value of γ_b (Appendix R) and hence the corresponding value of $k = \gamma_u / \gamma_b$.
- (3) Using a regression programme a straight line of the form

$$P_{\text{actual}} = m P_{\text{image}} + c,$$

is fitted to the pressure calibration data for each test, and the constants m and c noted.

- (4) The radius calibration data (Section 7.1.1) is prepared on cards and tape and fed into a polynomial curve fitting programme, capable of fitting an equations of the form,

$$y = A_1 + A_2x + A_3x^2 + A_4x^3 \dots + A_{n-1}x^n$$

to the data. Here n may be increased in steps from 1 to a maximum of 8. A cubic of the above form was found adequate for the radius calibration curve. The coefficients A_1 to A_4 are noted.

With the above data available the procedure is then as follows:

- A) The radius image data is fed into the general smoothing programme, (capable of handling a maximum of 105 equally spaced observations). A cubic is then fitted to eleven consecutive points of the data and a smoothed value of the midpoint of these eleven obtained. The programme advances by one point to obtain a smoothed value for the next consecutive midpoint, and so on for all the points except the first and last five. For each of the latter special factors have to be applied by the programme (automatically) to obtain smoothed values. The derivatives, at corresponding points, dr_b/dt , are obtained in the following way:

(1) For the first five points of the data a forward difference formula is applied, using the first, third, fifth, seventh and ninth points. The reason for taking every second point was to increase the accuracy of the derivatives, since the original points are closely spaced.

(2) For the following three points a first difference method is used, where the derivative at the point i is given by

$$(r_{i+2} - r_{i-2})/4\Delta t$$

r being the value of radius and Δt the time interval between points.

(3) Derivatives for the last 4 points were obtained in a similar way except that a backward difference formula was employed for the last point.

(4) For the remaining points a central difference formula was employed where the derivative at the point i is given by,

$$dy/dt = (y_{i-2} - 8y_{i-1} + 8y_{i+1} - y_{i+2}) / 12h$$

where the interval $h = 2\Delta t$, the reason for the odd spacing being as before.

These derivatives are then smoothed in the same way as the original data. The smoothed values of both radius and its derivative are punched on paper tape. An optional printout on the typewriter is provided.

The procedure for handling the pressure data is similar but with the following differences:

- (1) A facility for searching the data to obtain the maximum value and to print it out is available.
 - (2) The smoothing procedure can be initiated at any point at the operators discretion so as not to smooth the preceding points. This has been incorporated as it was found that for data where the pressure is initially constant over a good many readings, the eleven point cubic smoothing tends to lower the values of these points and introduces a curve where it is evident that none exists.
 - (3) A facility is provided, optionally, to enter the maximum pressure manually for purposes of smoothing and calculating values obtained from the low-pressure record.
- B) The smoothed radii and derivatives data tape is fed into the radius-pressure, correction-calibration programme together with the data shown on the accompanying flow chart (Fig 7.3). This programme corrects the data for the film speed and image width effect discussed in Section 5.4. The corrected values are then calibrated according to the polynomial fitted to the calibration data. A tape of corrected-calibrated values is then punched.

The pressure data and derivatives tape is immediately entered and the corresponding operation is first to calibrate according to the regression straight line calibration data and then to correct for the finite velocity of pressure waves in the combustion vessel as discussed in Section 5.4.

A tape of corrected-calibrated pressure values is then punched.

An optional printout is provided for both pressure and radius operations.

- C) Both output tapes from stage A above, are re-fed into the general smoothing programme singly and smoothed - both original data and derivatives. An optional printout is available (see flow chart - Fig 7.3)
- D) The two output tapes from C are then fed into the final S_t programme (eqn 5.15), the pressure first and radius second, and the final values calculated, printed and punched. The tape punched here is for use in further optional programmes for the comparison of burning velocity equations and the like.

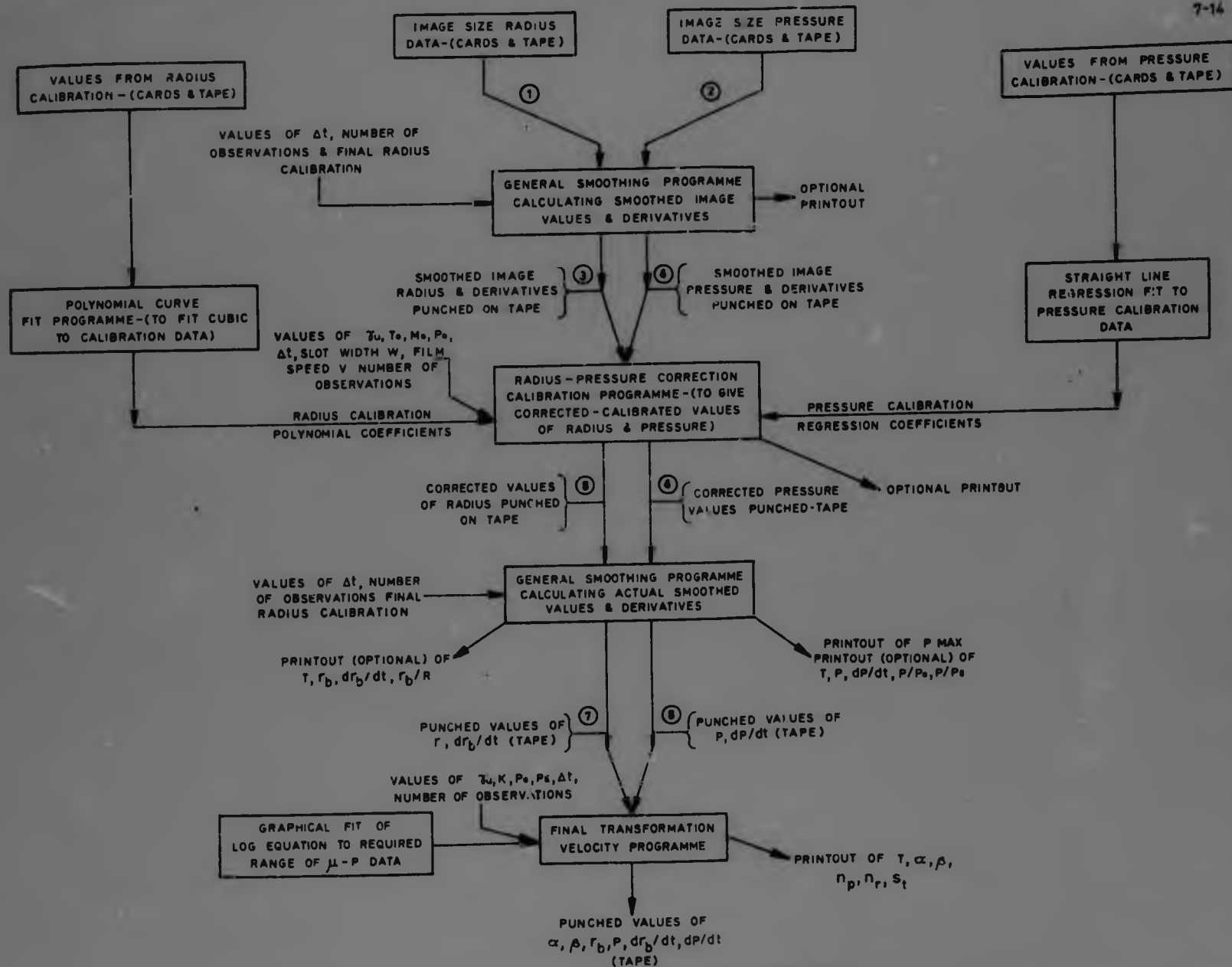


FIG 7-3 DATA PROCESSING FLOW DIAGRAM

CHAPTER 8

EXPERIMENTAL RESULTS

8.1 PURPOSE AND SCOPE OF TESTS

The main purpose of the tests reported in this thesis has been to provide basic data for a critical evaluation of the constant volume method.

To date this technique has generally been used to measure burning velocities only during the earlier stages of the process when the pressure rise is small. By obtaining information covering the whole range of combustion it is thus possible to compare the results of various equations and to decide over which range each is applicable.

4 This is possible since the method possesses the considerable advantage of permitting corroborative data to be obtained at all stages of the process.

The scope of the present series of tests has of necessity had to be limited. Thus although two types of fuel have been used to date (propane/butane and acetylene) only some of the acetylene/air tests will be reported.

In the first series of tests (A to F) the initial conditions of the mixture were always ambient. The purpose of these was to investigate the effects of mixture strength on burning velocity.

The second series (G1 to G4) were all on stoichiometric acetylene/air mixtures, with ambient initial temperatures but variable initial pressures. It is hoped to show that in this way the separate effects of pressure and temperature can be inferred from a limited number of tests.

8.2 ACCURACY OF OBSERVATIONS AND RESULTS

8.2.1 Composition of Fuel

The acetylene used in these tests was obtained from a commercial cylinder of dissolved acetylene and had a guaranteed purity of 97.5 per cent - the remaining 2.5 per cent being mainly air. The cold trap in the gas supply line removed any acetone carried over from the cylinder.

8.2.2 Composition of Air

All air used was dried before entering the bomb by passing it slowly through a U-tube containing freshly activated silica gel. This air was passed through the bomb for several minutes before each test to ensure the complete displacement of any moisture.

8.2.3 Mixture Composition

The initial mixture composition was obtained by measuring the partial pressures of the component gases. With the null method used it was possible to measure pressures to better than ± 0.01 -in (± 0.25 mm) of water. If the slight differences in equilibrium temperatures attained at various stages during the introduction of each constituent into the bomb are ignored, it is estimated that the maximum error in the volume of the fuel in the mixture was ± 0.1 per cent.

8.2.4 Mixture Homogeneity

After admission of the fuel and air into the bomb, the resultant mixture was allowed to stand for, on an average, 6 to 7 minutes before

ignition.

The importance of a standing period is twofold: to ensure that the fuel and air mix thoroughly, and to allow the turbulence arising from the filling operation to subside.

There is at present insufficient evidence to indicate whether the time allowed was sufficient to permit complete mixing. This matter will have to be resolved at some future date by intentionally varying the standing period and observing any effect on the final results. Eschenbach (Es 57) has claimed that if the bomb is not rotated for several minutes after it has been filled, a standing time which may amount to several hours - depending on the initial pressure - is necessary to ensure homogeneity. Since the mass diffusion rate of binary gas mixtures is inversely proportional to the pressure, but increases with increasing temperature, care will have to be exercised in establishing optimum mixing times for high initial pressure or low initial temperature tests.

8.2.5 Accuracy of Time-bases

Prior to the use of a dual-beam oscilloscope for the pressure-traces, there was the possibility of a significant time-base and synchronization error as between the high- and low-range pressure oscilloscopes.

However, since with the present set-up the timing marks on both the flame- and pressure-traces are obtained from the same oscillator, and the instant of firing of the mixture is recorded on both films, phasing errors should have been eliminated.

Due to the high accuracy of the electronic counter used for calibrating the time-base oscillator, the only error in establishing time co-ordinates on the flame and pressure records lies in the accuracy of measurement of the final projected image. It is estimated that this error was ± 0.2

per cent for any instant after ignition.

8.2.6 r_b and dr_b/dt

The projected image of each flame trace had a maximum width of about 32-in, the initial size at the point of ignition being about 1-in. All image widths were read to the nearest 0.05-in. The random error in flame radius should, therefore, not exceed ± 2.5 per cent at the beginning of flame propagation, reducing to ± 0.1 per cent towards the end. Such random errors were considerably reduced by the analytical smoothing technique applied to the observations. A further error, in this case systematic, may be present due to the difficulty in deciding on the exact limit of the penumbra region. A systematic error of 0.1-in could have been made on all image widths. This represents 0.01-in on all values of flame radius. Spatial velocities over all but the initial stages of combustion are likely to be only slightly affected by systematic errors. Ignoring the improvement that smoothing will have on random errors of individual radii, the maximum error on values of spatial velocity over the initial stages is ± 5 per cent. The error in spatial velocity is somewhat less over the later stages of combustion, except near the wall of the vessel when measurements of r_b become difficult, mainly due to internal reflections in the window material.

8.2.7 P and dP/dt

An indication of the overall errors in P and dP/dt , (obtained with the original scheme where two oscilloscopes were used) can be got by comparing the figures from one of the high- and low-range pressure records for Test C, given in Table 8.1 below.

Table 8.1
Comparison of P and dP/dt from low- and high-range pressure records

T - ms	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
P Low	12.09	12.10	12.12	12.19	12.35	12.62	13.06	13.68	14.59	15.72	17.05
High	12.09	12.09	12.09	12.09	12.13	12.32	12.65	13.11	13.75	14.62	15.81
dP/dt Low	0.0	27.3	78.3	209.6	413.5	692.8	1070.	1530.	2022.	2483.	2843.
High	0.0	0.0	0.0	29.7	221.4	494.2	780.6	1090.	1489.	2027.	2738.

The maximum discrepancy between the values of P is about 8 per cent. However as has been suggested this was probably due to a phasing error between the two records.

The overall pressure calibration factor was 4.579 psi/inch width of the final projected image, with a standard deviation of 0.024 psi/in. This represents an error of ± 0.5 per cent. The projected pressure records were read to the nearest 0.05-in, corresponding to an error of ± 0.1 psi. Over the early stages, during which the pressure rise is small, the accuracy is thus limited by the reading error and the sharpness of the image. Over the later stages the absolute accuracy of the pressure measurements is dictated by the accuracy of the calibration factor with a possible increase in reading error due to the steepness of the curve.

In an attempt to improve the sensitivity - and hence accuracy - of the pressure measurements, a new transducer with a larger diaphragm diameter was built and used for the 'G' series of tests. (See Section 6.6.3). Paradoxically, as it seemed at the time, the resultant sensitivity was approximately halved. However, subsequent theoretical analysis by Posel (Po 63a & b) has confirmed these experimental findings. Consequently the pressure measurements of the 'G' tests are not as reliable as those of the earlier variable mixture tests (A to F). Nevertheless the reproducibility of the final S_t results (see Fig 8.5 curves C and G1) is surprisingly good,

particularly when it is noted that much of the other ancillary equipment was changed in the interim period of about one year.

Since no quantitative measurements with the new system have as yet been made, its accuracy cannot be estimated, but it is hoped to effect a considerable improvement over the above figures.

8.2.8 Ignition Energy

The energy delivered to the spark electrodes can affect the early values of flame radius, and hence spatial velocity, in two ways.

Firstly, some of this energy is dissipated as heat in the electrodes, whilst the remainder heats up the gas between, and in the neighbourhood of, the electrode tips. Since the process is essentially a constant pressure one during this stage, this energy release causes this gas to expand. If the flame only starts propagating after this expansion takes place, then the initial radius will be significantly greater than either the radius of the electrodes or half the gap width, whichever of these is larger. The initial radius and hence the spatial velocity should thus be considerably influenced by ignition energy. This has been confirmed qualitatively in an earlier series of tests. To avoid any side effects due to spark energy all the tests described in this thesis were performed at the same setting of the ignition supply voltage (5 kV). Thus since the condenser used in the spark circuit had a capacitance of 0.001 μ F the maximum spark energy was always 18 millijoules.

The second effect of ignition energy is that if a suitable value is not chosen, the initial flame propagation may not be spherical (MV 53). This is one possible explanation of the apparently unreliable values of burning velocities obtained during the early stages of all the tests reported herein. (Another is the low accuracy attainable during this period).

8.2.9 Buoyancy

In order to ensure that any buoyancy effects did not go unobserved the bomb was used with its slit windows always in a vertical plane. No significant buoyancy (indicated by assymetry of the flame-trace about a horizontal centre-line) was observed in the tests reported here.

8.2.10 Heat Transfer

Heat may be transferred during the combustion process by one or more or more of the following ways:

- (1) Radiation from the burnt gas to the wall of the vessel.
- (2) Radiation from the burning gas to the unburnt gas.
- (3) Conduction and radiation from the unburnt gas to the wall of the vessel or vice versa.
- (4) Conduction from the burnt gas along the spark electrodes.

Provided independent measurements of temperature and pressure or density can be made, the quantity of heat lost would be of no great importance, since general equations exist (Chapter 4) from which the burning velocity can still be determined. However since the developement of the instrumentation has yet to be completed it is necessary to assume adiabatic compression. Some estimate of the amount of heat transferred is therefore necessary.

Calculations show that even under the worst realistically possible conditions ($r_b \approx h$) the quantity of heat lost via (1) and (4) is negligible.

The claim that (3) is probably negligible is supported by extrapolating to lower temperatures the heat rate determined from the pressure drop which occurs after the flame has reached the wall of the vessel. However, this may not be a valid procedure if - as is suspected - energy redistribution

or release occurs for some appreciable time after the flame has come into contact with the wall. (In all the tests reported here maximum pressure was always attained some time after the unburnt gas had apparently all been consumed).

Comparison of calculated and observed radii and pressures (Chapter 5) indicates that (3) can probably not be ignored - particularly during the later stages of the process.

Thus it appears that, with the information at present available, the question of heat loss must be left open.

8.2.11 Reproducibility of Tests

In the interests of accuracy and reproducibility, at least three tests were conducted at each of the air/fuel ratios investigated. In the variable initial pressure tests unfortunately only two successful tests were obtained at each pressure.

An abbreviated table of the observations obtained with a near-stoichiometric acetylene/air mixture is given in Appendix V. This is indicative of the degree of consistency which can be achieved.

Further support for the reproducibility possible with this type of apparatus is afforded by Tests C and G1 plotted on Fig 8.5. These were done with different instrumentation and fuel supply, and with an intervening period of over one year. Test C is probably more reliable since the pressure transducer used was more sensitive; also there is some suspicion that for the 'G' tests the smoothing programme introduced perturbations due to the use of too small a time interval between sequential observations.

8.2.13 Estimated Accuracy of Burning Velocity

It is only possible at this stage to arrive at a rough estimate of the accuracy of the burning velocity results.

Thus by considering the range of uncertainty in the various parameters involved in the equation for burning velocity (5.15) it is estimated that over the middle region of the process ($1.1 < P/P_0 < 4.5$), the error in the values of S_t is probably of the order of ± 6 per cent.

8.3 TEST RESULTS

8.3.1 Different Air/fuel Ratios and Ambient Initial Conditions

The burning velocities of six acetylene/air mixtures containing from 3.3 to 12.6 per cent acetylene by volume have been investigated. The pertinent data relevant to each of these mixtures is given in Table 8.2 below.

Abridged results for each mixture are given in Appendix T. These represent the means of at least three tests under as nearly identical conditions as possible. Figures 8.1 to 8.3 show the results of these tests in graphical form.

8.3.2 Stoichiometric Acetylene/air Mixtures at Different Initial Pressures but Ambient Initial Temperature

A series of four successful tests (G1 to G4) were performed on a stoichiometric mixture with variable initial pressures. Because of the sensitivity of the pressure transducer used for these tests (see Section 8.2.7) as well as suspected perturbations introduced by the numerical

Table 8.2
Data for Tests A to F (1961)

TEST	A	B	C	D	E	F
M_o	28.59	28.67	28.74	28.79	28.83	28.87
% C_2H_2 by volume	12.59	9.87	7.72	5.99	4.75	3.31
γ_u	1.3541	1.3624	1.3692	1.3748	1.3790	1.3839
γ_b	1.0079	1.0133	1.0103	1.0065	1.0000	1.0000
$k (= \gamma_u / \gamma_b)$	1.3435	1.3445	1.3552	1.3659	1.3790	1.3839
P_o psia	12.08	12.07	12.09	12.08	12.10	12.10
T_o °R	534.0	533.8	531.5	534.5	535.2	539.0
P_{max} psia	105.5	102.1	100.7	92.99	80.73	64.99
A & B for $A \times 10^{-6}$	5892	6144	6482	6675	7830	9718
$\mu - P$ eqn(5.4) $B \times 10^{-6}$	83.0	148	91.0	-15.85	0	0
No. of obs	radius	35	43	58	54	32
	press.	57	41	49	67	57
Time interval between obs - ms	0.25	0.25	0.25	0.25	0.50	2.50
Time to P_{max} -ms	13.5	9.5	11.25	15.75	29.0	105

smoothing procedure, they are not considered as reliable as the tests A to F. Nevertheless they serve the purpose of this study by providing data for investigating the pressure and temperature dependence of burning velocity.

The pertinent data for these tests is given in Table 8.3 below. (The remaining data is as for Test C in Table 8.2).

Abridged results for each of the above mixtures are given in Appendix U. Because of various experimental difficulties (such as forgetting to load cameras and the like) only two tests are available at each initial pressure. Graphical presentation of these results is on Figs 8.5 to 8.9.

Table 8.3
Data for Tests G1 to G4 (1962)

TEST		G1	G2	G3	G4
% C ₂ H ₂ by volume					
P _o psia		12.11	14.73	19.64	23.45
T _o °R		535	540	540	540
P _{max} psia		111.2	131.9	181.0	212.7
No. of obs.	radius	76	79	76	73
	press	85	84	84	82
Time interval between obs - ms		All	0.125 ms		
Time to P _{max} - ms		10.375	10.375	10.375	10.125

8.4 DEPENDENCE OF BURNING VELOCITY ON MIXTURE STRENGTH PRESSURE AND TEMPERATURE

8.4.1 Literature Values

One of the earliest determinations of the burning velocity of acetylene/air is that reported by Smith (Sm 37). Using the luminous cone of a burner he measured the burning velocities, at atmospheric pressure, of mixtures containing from 7 to 13 per cent acetylene by volume.

The burning velocities of acetylene/air mixtures at atmospheric pressure have also been determined by Linnett et al (LP 51) for mixtures containing 7 to 13 per cent of acetylene, using the soap bubble method and photographing the luminous front; by Pickering and Linnett (PL 51) who reported the burning velocity of a mixture containing 10 per cent acetylene using the bubble method with schlieren photography; by Morgan and Kane (MK 53) for a stoichiometric mixture using a burner technique.

The work of Pickering and Linnett was extended by Wheatley and Linnett (WL 52) who investigated the effect of pressure over the range from 19.5 to 62.9 cm Hg. These authors concluded that the burning velocity was not influenced by pressure over this range.

Other authors who have reported no pressure dependence are: Gaydon and Wolfard (GW 50) using a burner method between 10 and 760 mm Hg; Linnett (Li 50) using the soap bubble method from 30 to 760 mm Hg; and more recently, Gilbert (Gi 57) using a burner method with the wire shadow technique at sub-atmospheric pressures, and Graiff (Gr 59) using a spherical combustion bomb at pressures from 1/2 to 2 atmospheres.

A negative pressure dependence of the form $S_b \propto P^{-1/4}$ was found by Ubbelohde and Koelliker (UK 16) using a burner method between 1/2 and 2 atmospheres. A negative dependence has also been reported by Johnston (Jo 47) using a burner at elevated temperatures and by Egerton and Sen (ES 53) using the flat flame method at 20 and 50 cm Hg.

The burning velocity of lean acetylene/air flames have been measured by the flat flame method by Egerton and Thabet (ET 52) and by Egerton and Sen (ES 53). Bartholome (Ba 53) has used the burner method to determine the burning velocities of a wide range of acetylene/oxygen/nitrogen mixtures including acetylene/air. A recent summary of the results on the pressure dependence of the burning velocities of acetylene/air mixtures has been given by Gaydon and Wolfard (GW 60).

Most authors have neglected to specify the temperatures at which their determinations were made. This is unfortunate, since the indications are that the temperature dependence may predominate.

Two curves have been extracted from Fig 8.2 as a basis for comparison with the literature values of burning velocity. These are the burning

-velocity mixture-strength curves at 12.1 psia, 535°R and 14.7 psia, and 565°R. The former is at room temperature and sub-atmospheric (sea level) pressure; the latter is at a pressure of one atmosphere but at an elevated temperature. These are shown in Fig 8.4, together with values obtained by other methods. In general the agreement with the more reliable results in the literature appears to be good, both as regards absolute values and variation with mixture strength.

8.4.2 Effect of Air/fuel Ratio

The dependence of burning velocity on mixture strength is shown in Figs 8.1 to 8.3.

Fig 8.1 shows the variation of S_t with pressure for each of the mixtures tested. Evidently both the absolute values of burning velocity and the slope of the $S_t - P$ curves increase with increase in mixture strength, reaching a maximum on the rich side (Test B - 9.87% C_2H_2).

Fig 8.2 illustrates directly the effect of mixture strength. The temperatures corresponding to each member of this family of curves are average values, since γ_u is not the same for each mixture.

Clearly it is not possible from such a series of tests to establish the separate effects of pressure and temperature.

It is of interest to note that extrapolation of the family of curves on Fig 8.2 down to zero burning velocity should yield the limits of inflammability. Although with the information available extrapolation on the rich side cannot be justified, it certainly seems permissible on the lean side. Thus the lower limit appears to be at about 2.6 per cent of acetylene and to be independent of both pressure and temperature.

A further point of interest in this connection is that extrapolation of the curve of α_e versus % C_2H_2 (Fig 5.4 a) yields the correct value of unity at this lower limit. If the discussion regarding chemical equilibrium in Chapter 5 is valid, this suggests that equilibrium of the burnt gas would exist at this lower limit.

It is perhaps unfortunate that it was not possible to obtain results at richer mixtures than that of Test A (12.59% C_2H_2). Considerably richer mixtures were in fact successfully fired in the bomb. However, probably as a result of carbon deposition on the slit windows, the flame traces for these tests were so under-exposed as to make transcription of the results virtually impossible.

Two of these very rich mixtures, after burning in the bomb, caused explosions in the manifold system when the valve was opened some minutes after the test, for the purpose of purging the system.

8.4.3 Pressure Dependency

By performing tests at various initial pressures (Tests G1 to G4) or temperatures the separate effects of these two variables on burning velocity may be studied (Section 2.5).

Thus by plotting curves of S_t versus P for each test (see Fig 8.6) and using the corresponding $T - P$ relations for the unburnt gas (assumed adiabatic in this case - Fig 8.9) it is possible to superimpose a family of isotherms onto such a system of curves. Each such isotherm thus shows the variation of burning velocity with pressure at any particular temperature. Fig 8.6 shows the results obtained with a series of stoichiometric acetylene/air mixtures.

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