A STUDY OF THE PREMIXED LAMINAR HYDROGEN-BROMINE FLAME.

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by

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ABSTRACT.

The purpose of this work is to investigate non-interfering methods for simultaneously measuring the distribution of one species and of temperature, through the flame front of a simple system; thereafter to analyse the results and to examine how such an investigation can be used to elucidate flame processes.

The suitability, for study, of the laminar hydrogen-bromine flame is discussed. Methods of measuring the distribution of species are reviewed and one of them, absorption spectrophotometry, is selected for use, together with the inclined slit shadowgraph technique, for the investigation of the flame. For such an optical study a free flat flame is required and apparatus for producing such a flame in hydrogen-bromine-nitrogen mixtures is developed. The appearance and general behaviour of these flames is described and burning velocities for a series of ternary mixtures are determined.

A photographic technique is developed for measuring the light absorption distribution due to the bromine, perpendicular to the flame front. Some preliminary experiments are also carried out with an

alternative electronic method. The optical density distributions, together with the light ray deflection profile determined by the inclined slit technique, are used to calculate, in the first place, the bromine concentration profile and the temperature profile for one flame. A method of calculating the distribution of all significant species except H• from such profiles is illustrated, using the results for this flame. The derivation of kinetic data is discussed.

The errors in the analysis are examined and it is shown that the lack of available transport data is severely limiting. Possible ways of overcoming this difficulty are discussed and suggestions for further experimental developments are put forward.

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CHAPTER 1.

INTRODUCTION.

Chemical and transport processes occurring in premixed laminar flames are of fundamental importance in the field of combustion, but as yet quantitative data on these processes are severely limited. The intrinsic difficulties are twofold. The changes occur at high temperatures over small distances and in very short times so that the classical diffusional, thermal and chemical behaviour of gas molecules, investigated under less extreme conditions, may be considerably modified in flames. Secondly transport and chemical processes in flames are interdependent and must be considered together. Thus the chemical reactions occurring early in the flame may, for example, be considerably modified by the diffusion of species normally only present when the reaction is near completion.

To evaluate such flame processes, several approaches are possible. Firstly measurements can be made on systems in which extreme conditions exist but which are simpler than flames. For example, chemical kinetics can be investigated to temperatures well over 1000°K. in flow systems [1], whilst the effect of efficient mixing of all species present, up to a given fraction of reaction, may

be investigated with a well stirred reactor [2]. Flash photolysis and shock-tube experiments can also give useful results in this connection.

Secondly, theoretical calculations can give transport [3] or thermodynamic data. Such calculations are especially useful in extrapolating from experimental results. The theoretical approach may be applied in other ways, for example, some guide to the relative importance of diffusional and thermal initiation of reaction, early in the flame, might be obtained by comparing measured burning velocities with values calculated assuming only one mechanism is important [4].

Finally, flame processes can be investigated in situ. The variation of burning velocity with composition can give some information, and the variation with pressure of burning velocity or quenching diameter can give the 'order of reaction' if suitable assumptions are made [7]. However, it is only by measuring the micro-structure of flames that an unambiguous knowledge of flame processes can be obtained. For slow premixed flames a knowledge of the temperature and composition profiles through the flame would be adequate since the aerodynamic structure may be assumed and radiation effects are unimportant. The measurement of

temperature [8,9] is probably the more straightforward and a surprising amount of information can be obtained from these profiles [10,29]. Recently, attempts have been made to measure composition profiles by sampling [11,12,13], but such techniques, though now highly developed, are still open to objection on the grounds of interference with the flame processes [14,15]. Absorption spectroscopy has been used to show the presence of active intermediates [16,17,18] but these results ~~are~~ were only semi-quantitative.

From this brief review it would appear that a rational approach would be made if the flame processes of one flame, however simple, could be determined with certainty by techniques which did not interfere with the flame. A quantitative knowledge of these processes would provide a major contribution to flame kinetics. In addition, it would give an immediate check on the use of outside data in flame calculations and could be used to check the reliability of sampling techniques. Possibly most important of all, the value of the experimental technique would have been assessed and it could then be considered for application to more complex flames.

In this project the premixed hydrogen-bromine

flame, a flame which has been the subject of much theoretical study [5,6,19,20,21,22,42], is used to test the potentialities of non-interfering techniques which are selected in the following chapter.

CHAPTER 2.

CHOICE OF FLAME AND EXPERIMENTAL METHODS.

The choice of flame and the selection of experimental methods for use in its investigation must to some extent be considered together. However it has been stated already in the previous chapter that the hydrogen-bromine flame was to be investigated and the reasons for its selection will now be considered.

(1) Selection of Flame.

The basic requirements are that :

(a) The chemical kinetics determined by vessel and flow studies should be simple and well established. Halogen-hydrogen flames and the decomposition flame of ozone would appear suitable from this point of view.

(b) The flame should be free and approximate to the one-dimensional model; with some mixtures this condition is unstable and cellular or vibratory flames are formed [45].

(c) There should be little change in the total number of molecules during reaction. Methods of temperature determination based on density and refractive index measurements would then be simplified. The addition of an

inert diluent would also be an advantage from this point of view. Halogen-hydrogen flames would seem ideal, but the large difference in diffusion coefficient between the major species present would cause a maximum in $(\mu - 1)T$ and ρT (where μ = refractive index, ρ = density and T = absolute temperature) in the flame front. This effect is further discussed in Chapter 10.

(d) Transport properties should be known or calculable. This is a considerable restriction, and there is much to be said for using a large excess of one component - as in lean hydrocarbon-air flames. Useful values of diffusion coefficients and thermal conductivities can be calculated for mixtures of non-polar gases [3] but thermal conductivities, in particular, cannot readily be evaluated for any but the simplest polar/non-polar gas mixtures [22].

(e) Preferably, the chemical reaction should involve two reactant species and be propagated by radical chains. This would be an advantage, since most flame reactions are of this type.

(f) The flame should be suitable for investigation by one of the methods discussed below.

The ozone decomposition flame has been studied experimentally [23] and theoretically [24,25,26]. If the

temperature profile of the flame could be measured by methods not involving density or refractive index then the fraction of overall reaction could be obtained if the profile of either of the latter quantities were also known, providing the concentration of species other than O_2 and O_3 could be shown to be negligible.

The study of hydrogen-halogen flames has been reviewed by Anderson [27]. Hydrogen and iodine are thought to react by a simple bimolecular mechanism up to 800°C. but there have been no reports of hydrogen-iodine flames. In contrast, hydrogen-fluorine mixtures are normally spontaneously inflammable and, for a stoichiometric mixture at atmospheric pressure, the burning velocity is estimated at 10,000 cm./sec. However, both H_2 - Cl_2 and H_2 -Br_2 flames would appear quite suitable, especially as both Br_2 and Cl_2 could be estimated by absorption spectrophotometry in the visible region. The H_2 - Cl_2 flame has the advantage that a large excess of diluent could be added, simplifying transport calculations and temperature measurement, but the composition range, which gives the burning velocities demanded by the Egerton-Powling burner, may be too small for flame stabilisation. Also, the photosensitive nature of the reaction would provide practical difficulties and the

flame emission may significantly affect propagation. For H_2 - Br_2 mixtures the maximum burning velocity is only about 28 cm./sec. and, for mixtures with a large excess of hydrogen, the effect of hydrogen diffusion on the local burning velocity tends to remove deviations from flatness.

On balance the H_2 - Br_2 system appears the most suitable and this is particularly pleasing in view of the great theoretical interest in the flame.

(2) Selection of Experimental Methods.

It has been specified that non-interfering techniques should be used. Such techniques fall into three groups:

(a) those in which the measurement can be shown to have negligible effect on the flame - many optical techniques fall into this class.

(b) those in which the effect on the flame can be extrapolated to zero.

(c) those in which the flame, although subsequently affected by the measurement, can be considered 'frozen' while the measurement is being made - thus gases immediately ahead of a shock wave are almost unaffected but the velocity of the shock wave and the emission at the shock front are functions of the original temperature and composition of the gas.

(3) Temperature Measurement.

Of the methods of temperature measurement which have been used so far [8,9,29,30], those based on the measurement of refractive index gradient appear to be the most suitable even though refractive index is also a function of composition and the flame shape must be accurately known. In the quantitative shadowgraph method of Burgoyne and Weinberg [31] a horizontal parallel beam of light is passed perpendicularly through a slit at 45° to the horizontal. It then passes through an Egerton-Powling flame, parallel to the flame, and onto a screen some distance away. From the shape of the distorted slit image shown on the screen, the refractive index gradient and hence the temperature can be calculated, providing composition effects are small. The technique has given accurate results [10] and appears simple, reliable and adequate for the present investigation.

(4) Composition Measurement.

Since there has been relatively little work done on the measurement of composition profiles by other than sampling techniques, possible methods of study were reviewed in more detail. The major requirements are :

(a) spatial resolution of the order of 10^{-2} cm.

(b) that temperature dependence should not be substantially greater than composition dependence - thus measurements should be based on colligative rather than constitutive molecular properties.

(c) high specificity to each species.

Many gas properties such as density, refractive index and the velocity of sound are non-specific but if several of such properties could be measured with sufficient accuracy, both temperature and composition profiles could be determined. Application to the simple case of the ozone decomposition flame has already been mentioned, but the use of such non-specific techniques is limited.

Other points to be considered are simplicity, accuracy, ease of application and interpretation, and cost. Comments on the use of some superficially applicable gas properties in the determination of composition profiles are given below. (See also the review paper by Fristrom [97]).

Absorption of Electromagnetic Radiation.

X-rays ; absorption is mainly a function of density.

U.V. radiation: useful, especially in the 1900-2300 A. region [32].

Visible Radiation: convenient but limited in scope in the case of gases.

I.R.Radiation: versatile, but difficult to find intense sources and resolution is consequently poor. Interpretation is often difficult.

Microwave Radiation: low spatial resolution.

Emission, Scattering and Diffraction of Electromagnetic Radiation.

U.V.,Visible and I.R.Emission: limited to the high temperature regions of the flame, but the main difficulty is quantitative interpretation which can only be carried out when thermal equilibrium exists. However the easily excitable radicals and atoms can be investigated and vibrational and rotational temperatures also can be determined.

Fluorescence: I_2 and some organic vapours fluoresce strongly, but the intensity is very dependent on the concentration of species of high quenching efficiency.

Raman Spectra: much too weak.

Shock Wave Spectra: interpretation difficult.

Spark Spectra: must cause some interference during emission, breakdown of molecular species is great and little could be learnt from the spectra.

Activation by α-particles: the fluorescence produced by an electron-beam has been used to measure densities in low pressure wind tunnels [33], however, this fluorescence is probably sensitive to the concentration of quenching species.

X-ray Diffraction: this can be applied to gases but exposures of several hours are required.

Absorption and Diffraction of Sub-atomic Particles.

Absorption of sub-atomic species is usually a function of density. The use of low-velocity electron diffraction is confined to very low pressures; neutron diffraction is complex and costly.

Other Optical Properties.

Refractive Index: this is largely a constitutive property and predominantly a function of temperature. It is non-specific.

Refractive Dispersion: may be useful, especially if a wavelength in the anomalous dispersion region of one species is used.

Optical Rotation: this can only be used for reactants and its use would be severely restricted by the supply of optically active materials.

The Kerr Effect: non-specific, the electrostatic field would interfere with flame processes.

The Faraday Effect (Magnetic optical rotation) : non specific, the effect is very weak with gases and the magnetic field would interfere with flame processes.

Sonic Properties.

The velocity of sound depends on all species present and it is difficult to measure directly with high resolution; however, the velocity of a low intensity shock wave could be readily found by schlieren techniques. In addition ultrasonic absorption spectra at frequencies of 10^7 - 10^{10} c/s may be useful for simple mixtures.

From this it appears that absorption spectrophotometry is the most widely applicable method, though refractive dispersion, emission spectra and perhaps optical rotation may be of use in particular cases. The use of refractive-dispersion for composition analysis has been suggested by Olsen [34] and is worthy of a quantitative investigation.

Consider a flat flame burning a mixture 25% Br_2, 35% H_2 and 40% N_2. For the pure components at S.T.P. the relevant refractive indices (μ) are given below :

	$(\mu - 1)\ 10^6$ 5461 A.	$(\mu - 1)\ 10^6$ 6708 A.	Difference
H_2	139.7	138.5	1.2
Br_2	1184.9	1152.5	32.4
HBr	614.9	607.5	7.4
N_2	299.8	297.4	2.4

For the above flame the dispersion at S.T.P. would be 9.4×10^6 for the reactants and 4.7×10^6 for the products - about 2% and 1% respectively of the refractive index. At intermediate stages of reaction the dispersion would be somewhat larger, but the measurement of such small differences in dispersion would probably be very difficult in flames.

Cuthbertson and Cuthbertson [35] determined the refractive indices of both Br_2 and HBr and their values have been used so that the effect of systematic errors in μ would be minimised.

(5) Absorption Spectrophotometry.

According to Gaydon [32] absorption spectra can be regarded as falling into three types:-

(a) those with bands showing open discrete rotational structure,

(b) those with bands, the structure of which is unresolvable, at least at the head of the band,

(c) continua.

In order to observe absorption at all, in the first case, very high resolution is required, unless a background source emitting the same band is used. In either case estimation of the species in question would require an accurate knowledge of the spread of individual lines.

Measurement of absorption would be simpler in the types (b) and (c) but Beer's law cannot be assumed with the former and can only sometimes be applied when using the latter.

For wavelengths of up to about one micron, photographic plates or photomultipliers can be used with very intense sources such as high pressure xenon and mercury arcs, but for the near infra-red region such intense sources are not available[72], and thermopiles have often to be used. In the U.V. region between 1900 A. and 4000 A. oxygen, aldehydes, ketones and many aromatic compounds show strong absorption and active species such as OH can be detected, if not accurately measured. On the other hand, in the near infra-red, H_2O, CO_2, HBr and many organic functional groups can be estimated. In either case there is much to be said for using a chopped signal and tuned source to remove interference due to flame emission.

The application of absorption spectrophotometry

to flames brings with it other problems, in particular those of spatial resolution and the effect of flame shape. The slow flat flames of the Egerton-Powling type [56,57] are particularly suitable for this kind of investigation, having flame thicknesses of several millimetres at atmospheric pressure, but any deviations from flatness, especially at the edges, must be accurately known. Still thicker flame fronts may be obtained by working at reduced pressures, but the increased mean free path can result in fundamental changes in reaction kinetics (e.g. in order).

With thin flame fronts the shape must be very accurately known and it may prove simpler to use an internal source. This may be done by using an intensely lit particle track, a shock front or by using the light emitted by the flame itself. In the latter two cases it would be necessary to record the spectra at two angles to the flame front.

(6) The Hydrogen-Bromine Flame.

It will be shown later that, if the transport data are known, then, for a H_2 - Br_2 flame with nitrogen as diluent, the profiles of temperature (T) and of Br_2, H_2, HBr, Br and N_2 concentrations can be derived from a knowledge of

the temperature and Br_2 profiles alone. The concentration of the only other significant species, H·, is thought to be very small ($< 0.01\%$) at normal pressures. Thus, it would seem adequate for the present purposes to determine the bromine concentration using absorption spectrophotometry in or near the visible region and the temperature using the inclined slit shadowgraph technique. In addition there seems every reason to believe that an Egerton-Powling flame, if it can be stabilised, should be particularly suitable for analysis.

A survey of thermodynamic properties, transport properties and reaction kinetics for the H_2 - Br_2 system has been carried out recently [36]. The values of the thermodynamic functions are available and of satisfactory accuracy [37,38,39] but diffusion and especially thermal conductivity data are unreliable. The low temperature (below 600°K.) reaction kinetics is well established [41]. The mechanism postulated is :-

$$Br_2 \rightleftharpoons 2\,Br \quad \ldots\ldots\ldots\ldots\ldots \quad 1$$

$$Br + H_2 \rightarrow HBr + H \quad \ldots\ldots\ldots\ldots \quad 3f$$

$$H + Br_2 \rightarrow HBr + Br \quad \ldots\ldots\ldots\ldots \quad 4f$$

$$H + HBr \rightarrow H_2 + Br \quad \ldots\ldots\ldots\ldots \quad 3r$$

It is thought that a 'steady state' concentration of hydrogen atoms is set up which is constant under isothermal conditions until the reaction is over 90% complete. If the bromine atom concentration is also maintained at a constant value, it can be shown that this must be the equilibrium value due to the dissociation of Br_2. The expression for the overall reaction rate derived from this scheme agrees with that which has been determined experimentally so that the value of k_3^f and the ratio k_4^f / k_3^r can be determined (where k_j is the rate constant of the j^{th} reaction). Using high temperature flow techniques, Levy [40] has determined k_3^f up to 1400°K. and has shown that k_4^f / k_3^r is almost temperature independent.

There has been much discussion recently regarding the extent of deviations from the chemical steady state in flames. Gilbert and Altman [21] have shown that for H_2 - Br_2 flames [Br] is on average within 20% of the steady state value to above 1600°K., but Campbell [6] has pointed out that small deviations from the steady state have a large effect on the flame processes as a whole. The chemical steady state assumption is valid only when the rate of production of chain carriers is much greater than the overall reaction rate. This point is of fundamental importance to flame kinetics in general and is further discussed in Chapters 9 and 10.

CHAPTER 3.

PROBLEMS ASSOCIATED WITH THE HANDLING OF HYDROGEN, BROMINE AND HYDROGEN BROMIDE.

In the previous chapter it was shown that the hydrogen-bromine flame was particularly suited to the type of investigation envisaged. However, the poisonous and corrosive nature of bromine and hydrogen bromide and the explosion hazard present when dealing with large volumes of hydrogen pose many practical difficulties and indicate the need for suitable safety precautions.

(1) The Toxic Nature of Br_2 and HBr Gases.

Bromine and hydrogen bromide in the gaseous state are irritants when inhaled and affect the upper respiratory tract amd, to a lesser extent, the lung tissues. It has been recommended [43,44] that concentrations above 1 p.p.m. of bromine and 5 p.p.m. of hydrogen bromide should be considered dangerous for normal working. Such concentrations correspond approximately to those which cause slight irritation of the eyes and throat, and which can just be detected by smell.

In order to keep a check on the concentration of atmospheric bromine, air from the neighbourhood of the

apparatus was passed continuously through a solution of potassium iodide and starch. Unfortunately this technique proved unreliable when the concentration of bromine was very low, and it appeared that odour was the most reliable guide. Since persons working continuously in the laboratory would probably not be the best judges of this, it was considered safest for someone outside the laboratory to pay periodic visits.

To reduce the effects of minor bromine leakages the whole of the flow system was enclosed in a fume chamber and the normal ventilation of the laboratory was further supplemented. It has been recommended [44] that a very slight ammonia atmosphere be established when dealing with bromine, but this was found to be unpleasant for normal working.

The above precautions against bromine poisoning were considered adequate for the case of hydrogen bromide also.

(2) The Corrosive Nature of Br_2 and HBr.

The problems arising out of the corrosive nature of bromine and to a lesser extent hydrogen bromide are the health hazard, damage to external apparatus when leakage

occurs, fire hazard due to the strong oxidising power of bromine and the restricted number of materials of construction resistant to bromine and hydrogen bromide. The latter problem will be considered in section (5).

Bromine liquid or vapour rapidly attacks the skin and is especially dangerous to the eyes, so that for first aid treatment running water and a container of dilute sodium thiosulphate were made readily accessible. However, protective clothing including a visor was worn when loading bromine into the apparatus and at other times when there was a significant danger of bromine burns.

Damage to external apparatus was not normally serious but items, such as surface-aluminized mirrors, which would be rapidly affected, were exposed to the laboratory atmosphere as little as possible. As an additional precaution, steel components were greased or painted wherever possible. The major corrosion and fire hazard lay in possible fracture of the bromine boiler, which contained up to 3 Kg. of bromine. To relieve this danger a polythene bucket containing sodium carbonate solution was placed round the bottom of the boiler. Great care was also taken when handling the bottles of bromine supplied by the manufacturers. Because of the high density of liquid bromine these bottles

can be
~~were~~ easily fractured and were therefore kept in their original containers or placed in a special cupboard outside the building.

Outside the laboratory an alarm bell was placed so that warning could be given of any major release of bromine. A respirator and a supply of calcium hydroxide for neutralising any liquid bromine spillage were conveniently placed.

(3) The Explosion Hazard.

The normal explosion hazard present when handling large volumes of hydrogen is increased by possible corrosion damage to components of the flow system, and by the possibility of a minor hydrogen-bromine explosion releasing hydrogen into the atmosphere.

Escape of reactants from the flow system was quickly noticed because of the smell of bromine, but to indicate leakage even sooner a white panel was placed behind any part of the flow system where leakage seemed possible. The possibility of a hydrogen-air explosion was further minimized by flushing out the apparatus with nitrogen before and after each run. In addition, a thick 'Perspex' screen was placed between the operator and the burner

except when a flame was being photographed.

(4) General Precautions.

The following general precautions were taken:

(a) Experimental work involving hydrogen and bromine was carried out only when help was at hand in case of emergencies.

(b) Persons working in neighbouring rooms were informed of the hazards present and the procedure in case of accident. This information was also displayed on notices inside and outside the laboratory.

(5) Materials of Construction.

The number of materials which can be used in the construction of the flow system and burner is severely limited.

Ferrous metals, copper and aluminium are rapidly attacked by bromine, especially in the presence of water vapour, brass is less rapidly attacked whilst nickel, cupro-nickel and lead are resistant to corrosion in the absence of water vapour. Bromine is rapidly absorbed by rubber to form a hard coating and most synthetic plastics dissolve, and are attacked by, bromine. Normal stopcock grease is

unsuitable but petroleum jelly can be used on glass stopcocks for limited periods.

Glass, silica, asbestos and many ceramics are resistant to bromine. Cast iron, copper and aluminium can be given vitreous enamel coatings, but such coatings pose many constructional problems. Polytetrafluoroethylene (P.T.F.E.) dissolves some bromine but is not attacked below 240°C. It can be applied as a dispersion coating to metals but if it is overheated the products are corrosive and dangerous. Fluorinated stopcock grease ('Fluorube') is now available whilst an alternative lubricant is a mixture of phosphoric acid and graphite.

In general it appeared that the flow system should be constructed as far as possible from glass, with cupro-nickel and platinum being used for any metal components necessary, though other metals could be used if suitable ceramic, oxide or fluoride coatings could be applied.

It is pleasing to note that throughout the whole of the practical work to be described, no serious mishap occurred and only on very few occasions was it thought advisable to evacuate the laboratory.

CHAPTER 4.

APPARATUS FOR PRODUCING A FLAT HYDROGEN-BROMINE FLAME.

The components required were :- a flat flame burner with a suitable ignition system, apparatus for the control, metering and mixing of reactants, and equipment for the disposal of products or unchanged reactants. Initially, it was decided to work at atmospheric pressure with nitrogen as a diluent to give added safety and greater flexibility.

(1) The Burner (see Figure 1).

In the Egerton-Powling burner [56,57] the premixed reactants are passed up a packed cylindrical tube in the top of which is placed a flame trap matrix. This arrangement gives a uniform laminar flow across the full width of the burner tube. Under suitable conditions a flame can be burnt as a flat disc above the tube out of contact with any solid body. Because the edges of the flame are slightly upturned, a burner tube of about 6 cm. diameter was chosen to give a flat enough flame for convenient optical analysis. Such a flame must be burnt in a cylindrical housing, otherwise distortion occurs, and yet the housing should be

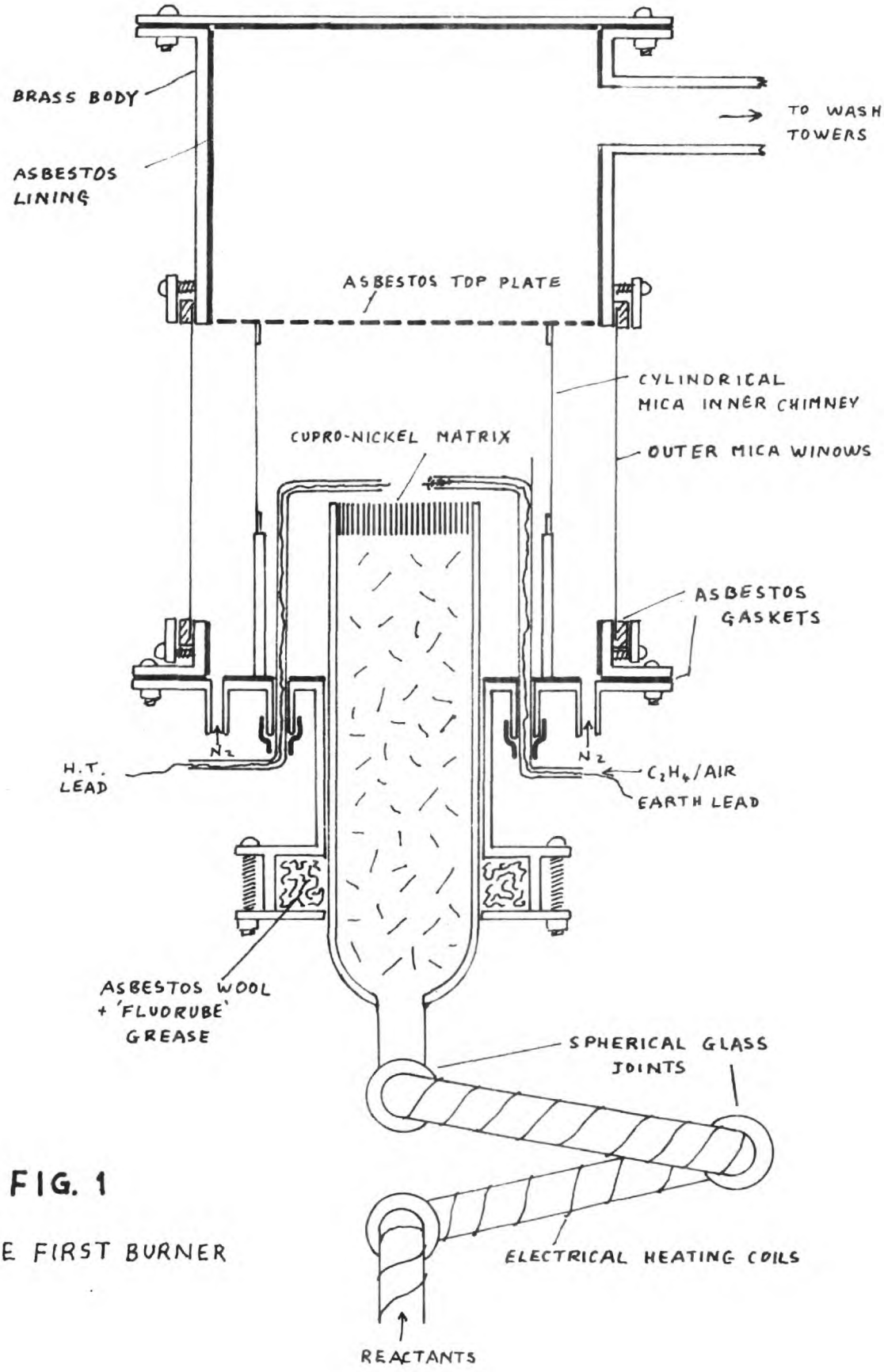


FIG. 1

THE FIRST BURNER

gas tight and have optically good windows. These design problems were resolved by surrounding the burner tube with an inner cylindrical chimney with selected mica walls. The outer burning housing was then constructed with square cross section and having flat mica or glass windows fitted with asbestos gaskets. Provision was made for the space between the inner chimney and the housing to be flushed clear of bromine using nitrogen. For convenience in construction, the housing was made of brass lined with asbestos, and asbestos was also used to make the perforated top-plate which must be placed above the inner chimney if a flat flame is to be obtained.

The matrix construction was similar to that described by earlier workers [29]. Two 1" strips of thin cupro-nickel tape, one plain and one corrugated across its width, were wound together forming a bundle of capillary tubes about 1.0 mm. diameter and 1" deep. The distance between the matrix and the top-plate could be varied by moving the glass burner tube up or down, a gas-tight seal being maintained by an asbestos-Fluorube grease gland packing. Three spherical glass joints were used to make a flexible linkage to the glass flow system (see Figure 1).

Three igniters could be used for initial tests :

(a) a spark gap produced by a hand driven magneto,

(b) a hot platinum wire,

(c) a spark ignited, premixed, ethylene-air pilot flame.

All these could be retracted after ignition so that they would not interfere with the flame.

(2) Control and Metering of Hydrogen and Nitrogen.

The nitrogen (oxygen-free) and hydrogen were obtained from British Oxygen Gases Ltd. Flows were controlled by means of needle valves and metered by glass capillary flowmeters with interchangeable capillaries.

Calibration at three line pressures was carried out using bubble meters. The gas flow from the meter was saturated with water vapour by passing it through an aspirator packed with wet contact rings, the aspirator being immersed in a water bath at 40°C. The warm saturated gas was then passed through a water-cooled condenser into the bubble meter. By adjusting the water flow through the condenser ~~and~~ the temperature on leaving the bubble meter could be kept within 1°C. of room temperature.

Two capillaries were calibrated for each meter so that a greater range could be covered with adequate

accuracy. Reproducibility was within 1% over the normal working ranges and the absolute accuracy was probably of the same order. Since the characteristics approximated to those of orifice, rather than Poiseuille flow, the volume flow was assumed independent of temperature for a given pressure drop. However, the laboratory temperature was normally constant to within ± 1°C. so that temperature effects could usually be neglected.

The ethylene and air for the pilot flame were metered with glass wool plug capillary flowmeters, these being readily adaptable for use with the flow range found most suitable by experiment. Approximate calibrations only were required for these meters.

(3) Control and Metering of Bromine.

The bromine flow can be controlled :

(a) by its rate of production (electrolysis),

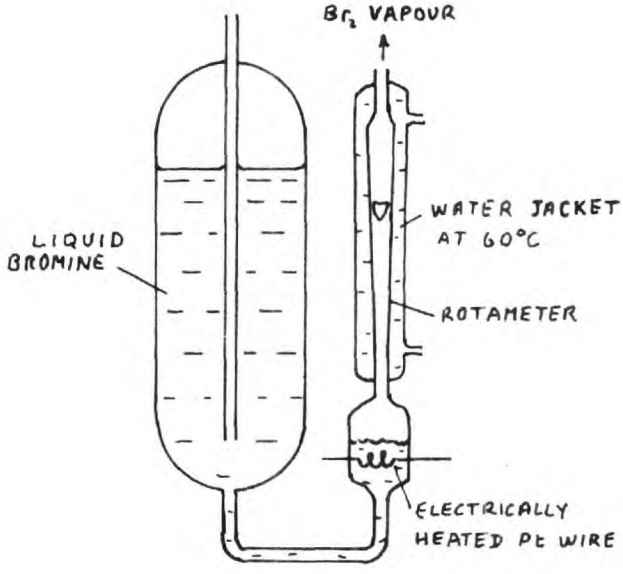
(b) by the heat supply to a boiler or evaporator,

(c) by controlling the liquid flow,

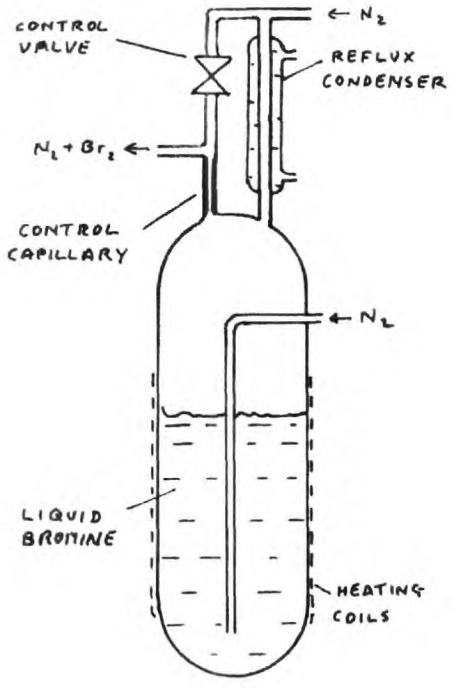
(d) by controlling the gas flow,

(e) by partially condensing the vapour.

Electrolysis would be suitable on a small scale but was considered inconvenient on the scale to be used.


Br_2 VAPOUR
LIQUID BROMINE
WATER JACKET AT 60°C
ROTAMETER
ELECTRICALLY HEATED Pt WIRE

(a)


$\leftarrow N_2$
CONTROL VALVE
REFLUX CONDENSER
$N_2 + Br_2 \leftarrow$
CONTROL CAPILLARY
$\leftarrow N_2$
LIQUID BROMINE
HEATING COILS

(b)

FIG 2

Controlling the heat supply to a boiler or evaporator is simple but response to adjustment would be slow, unless a system such as that shown in Figure 2a were used. Here a platinum wire heater is used to heat only a small fraction of the bromine. An alternative system which was considered was one in which the bromine could be continuously recycled over a heated surface, using a reflux technique. The low kinematic viscosity of liquid bromine creates difficulties in controlling the liquid flow and, though micrometer syringe techniques would give quantitative control, the corrosion difficulties would be considerable.

The gas flow may be controlled with a suitable corrosion resistant valve, though a simpler method is to vary the pressure drop across a fixed constriction as shown in Figure 2b. Here, the pressure in the boiler is equal to that above a needle valve in the nitrogen line.

If the gas flow contains excess bromine, the concentration of bromine can be quantitatively controlled by cooling the gases to a known temperature. The partial pressure of bromine is then equal to its saturated vapour pressure at that temperature. However, heat transfer calculations showed that, for the flow rates to be used, the cooling coils would have to be large and, in addition, it would be difficult to achieve rapid control.

Another approach considered was the use of a reflex condenser of variable temperature so that, although thermal equilibrium between the gas and the condenser was not attained, the bromine flow could be controlled. Unfortunately, preliminary experiments with this device showed that the minor surges in bromine flow, originating in the boiler, tended to be magnified.

However, for simplicity, an electrically heated boiler was provisionally selected. The voltage across the heater (250 ohms) could be controlled by a variable auto-transformer and to reduce 'bumping' a nitrogen bubbler was included in the design. It was considered probable that final adjustments to the flame could be carried out using the hydrogen and nitrogen controls alone, and that the thermal inertia of the boiler control would be unimportant.

Since this form of control was not quantitative a separate bromine meter had to be devised. A Rotameter type of instrument, suitably thermostated as in Figure 2a, would be simple to use. Unfortunately, the presence of a variable amount of nitrogen from the bubbler would make calibration complex. For this reason, and because of the inconvenience of sampling, the bromine concentration in the mixed reactants was measured photometrically in a continuous

flow cell. The light source was a tungsten filament lamp with a narrow-cut green filter and the light intensity was measured with a vacuum cell photometer. However the cell was of poor optical quality, being of glass-blown construction, and so was suitable for use in preliminary experiments only. Calibration was carried out by drawing gas samples of known volume through a U-tube packed with damp soda-lime and calcium chloride. The mass of bromine in each sample was determined by weighing the U-tube before and after sampling.

The bromine used throughout this work was of the redistilled grade (Hopkin and Williams Ltd.).

(4) Mixing.

To prevent back flow in, for example, the nitrogen and bromine lines when the hydrogen flow was suddenly increased, a constriction was placed in the individual lines just above the point of mixing. Large inhomogeneities in the flow were smoothed out by passing the gases through a nozzle tangentially into one end of a cylindrical buffer vessel. On leaving the other end the gases were passed through a tower packed with contact rings. Still further small scale mixing was achieved, together with flow randomisation, by packing the burner tube with contact rings.

(5) Disposal of Waste Gases.

Removal of bromine and hydrogen bromide from the waste gases was carried out by passing them through two scrubbing towers. Down the first tower, which was of Vigreux construction, was passed a 10% aqueous solution of sodium carbonate, whilst a water spray was used in the second tower. The effluent from the scrubbers was diluted with a large excess of water to render it harmless.

One unforeseen difficulty was the blocking of the tube carrying the sodium carbonate solution by a calcium carbonate deposit. This was overcome by adding a small amount of sodium hexametaphosphate to the water used to dissolve the sodium carbonate.

The gases from the second tower carried with them a cloud of acid droplets which had to be trapped out by passing through a bed of glass beads. The remaining hydrogen and nitrogen were passed through a flame trap and the excess hydrogen burnt off as a diffusion flame underneath a separate fume extract. A pilot flame was used to ignite the waste gases automatically when they became inflammable.

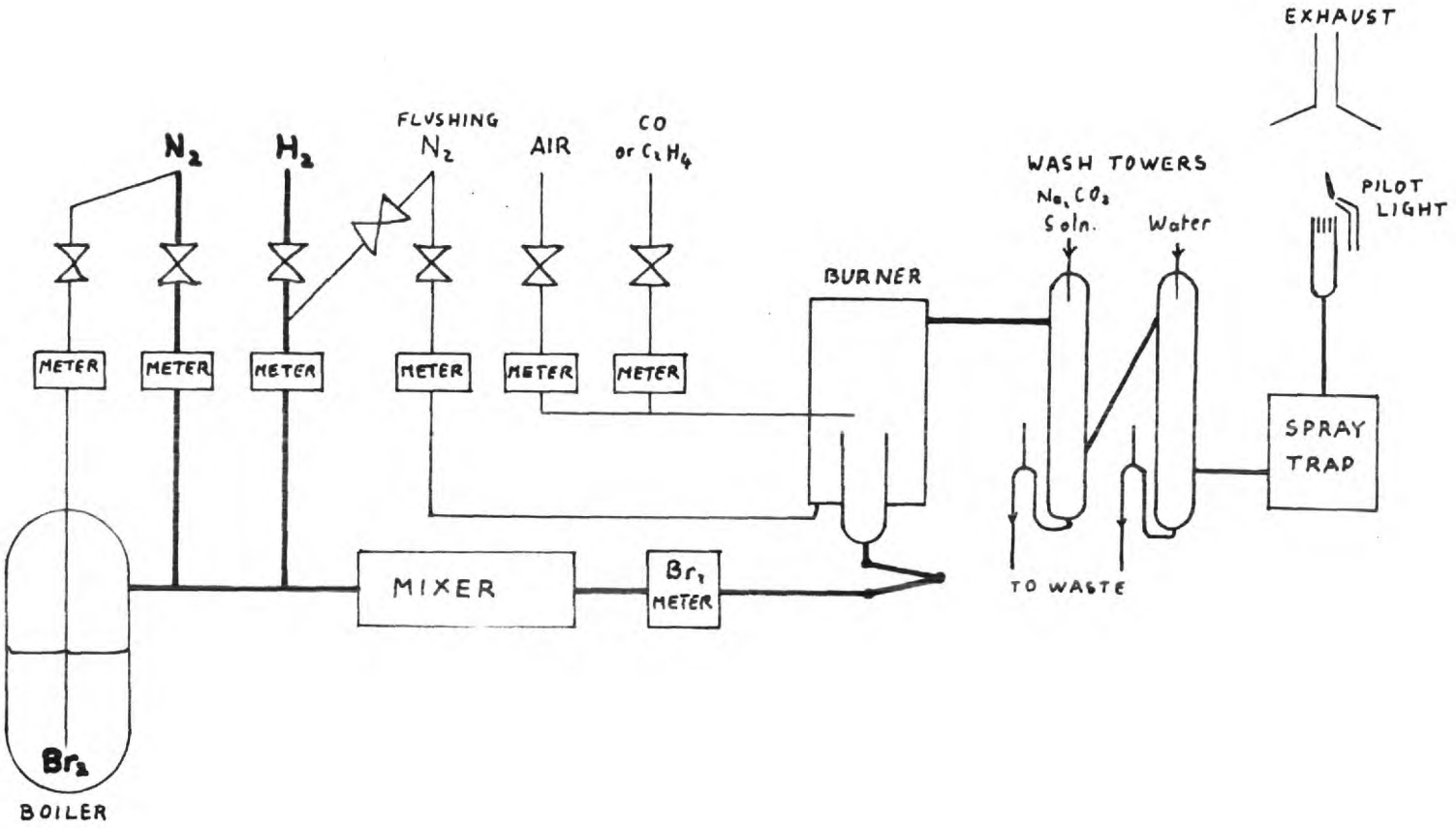


FIG.3 FLOW DIAGRAM

(6) Heating and General Construction.

To prevent condensation of bromine, the flow system from the evaporator to the burner required heating. Initially an attempt was made to place the major part of the system in a thermostated water bath, but it was soon found that electrical heating was more convenient. The nichrome windings used were in two parts, those near the burner tube being switched off when it was necessary to adjust the height of the tube.

The general construction being of glass, it was found very convenient to build the flow system in units connected by glass spherical joints. Repairs and modifications were consequently easily carried out, though the Fluorube grease used on the joints did have to be replaced occasionally to keep a gas tight seal.

Figure 3 is a flow diagram of the apparatus used.

CHAPTER 5.

PRELIMINARY EXPERIMENTS ON STABLIZING FLAT HYDROGEN-BROMINE FLAMES.

(1) Ignition.

First tests of the ignition system and of the burner as a whole were carried out using lean ethylene-air mixtures. Of the three igniters, it was found that the pilot flame was most suitable though lean mixtures could usually be ignited by sparking, if the matrix was hot. The hot wire igniter would not ignite very lean flames at all, although with richer flames catalytic reaction sometimes made it glow white hot and break. Flat flames were readily obtained on the burner and were apparently unaffected by any exhaust flow disturbances induced by the scrubbers.

Ignition tests on the hydrogen-bromine-nitrogen mixtures were carried out as follows. After the apparatus had been flushed out with nitrogen the pilot flame was lit, the nitrogen flow adjusted to 80 cc./sec. and the bromine concentration maintained at about 30%. The hydrogen flow was gradually increased, the mixture being sparked at regular intervals. Ignition by the pilot flame occurred when the hydrogen flow rate was about equal to that of

nitrogen. Neither spark ignition nor hot wire ignition appeared satisfactory and the latter system required constant adjustment because of the large changes in thermal conductivity, caused by the variation in hydrogen content of the mixture. The pilot flame was not altogether satisfactory Firstly, except for a rather limited flow and composition range, the bromine present appeared to extinguish the flame and secondly, the hydrogen-bromine flame would sometimes ignite and, on expansion, blow the pilot flame back down its flow line, extinguishing it. The hydrogen-bromine flame was then often extinguished itself.

The first of these drawbacks was simply overcome by introducing the hydrogen into the burner before the bromine concentration became large, and the second was removed by placing a constriction in the ethylene-air flow line just before the flame. The pressure drop across the constriction was normally larger than the temporary pressure increase which occurred on ignition.

(2) Flame Behaviour.

Initially, flames in contact with the matrix were investigated. These were yellow or orange in colour and the visible emission became less with increasing hydrogen/bromine ratio until with very hydrogen-rich flames it could

only be seen in total darkness. With high bromine concentrations the flames became cellular and if the nitrogen concentration was then reduced, making the flame hc ter, a strong afterglow occurred. These qualitative observations agree well with those reported in the literature [27].

Chemical attack on the cupro-nickel matrix was rapid when the hottest flames were burnt and resulted in a grey deliquescent deposit forming on the inner chimney walls. Rapid attack also occurred when the pilot flame was allowed to impinge on the matrix during ignition.

After these initial experiments, attempts were made to 'lift' the flame by gradually increasing the nitrogen concentration, the bromine concentration being kept at about 25%. During this process the matrix to top-plate distance was about 4 cm. and the gas flow velocity (corrected to S.T.P.) was 6 - 8 cm./sec.

The flame behaviour seemed quite unlike that observed with lean ethylene-air mixtures. The flame lifted steadily and evenly until about 0.5 cm. above the matrix. Above this point the edges, which were downturned, began to vibrate rapidly and, if the hydrogen concentration was high, the whole flame front vibrated vertically and often

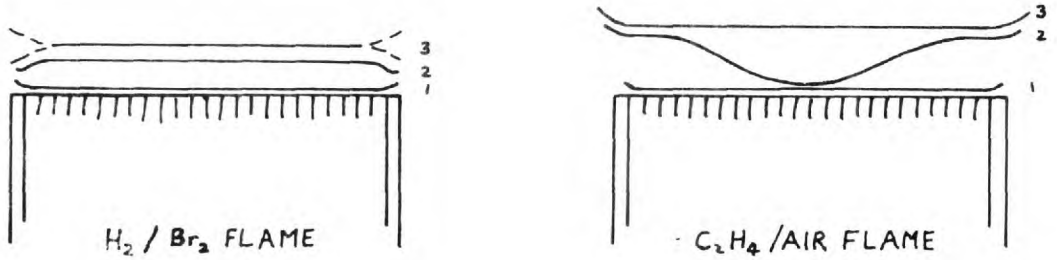
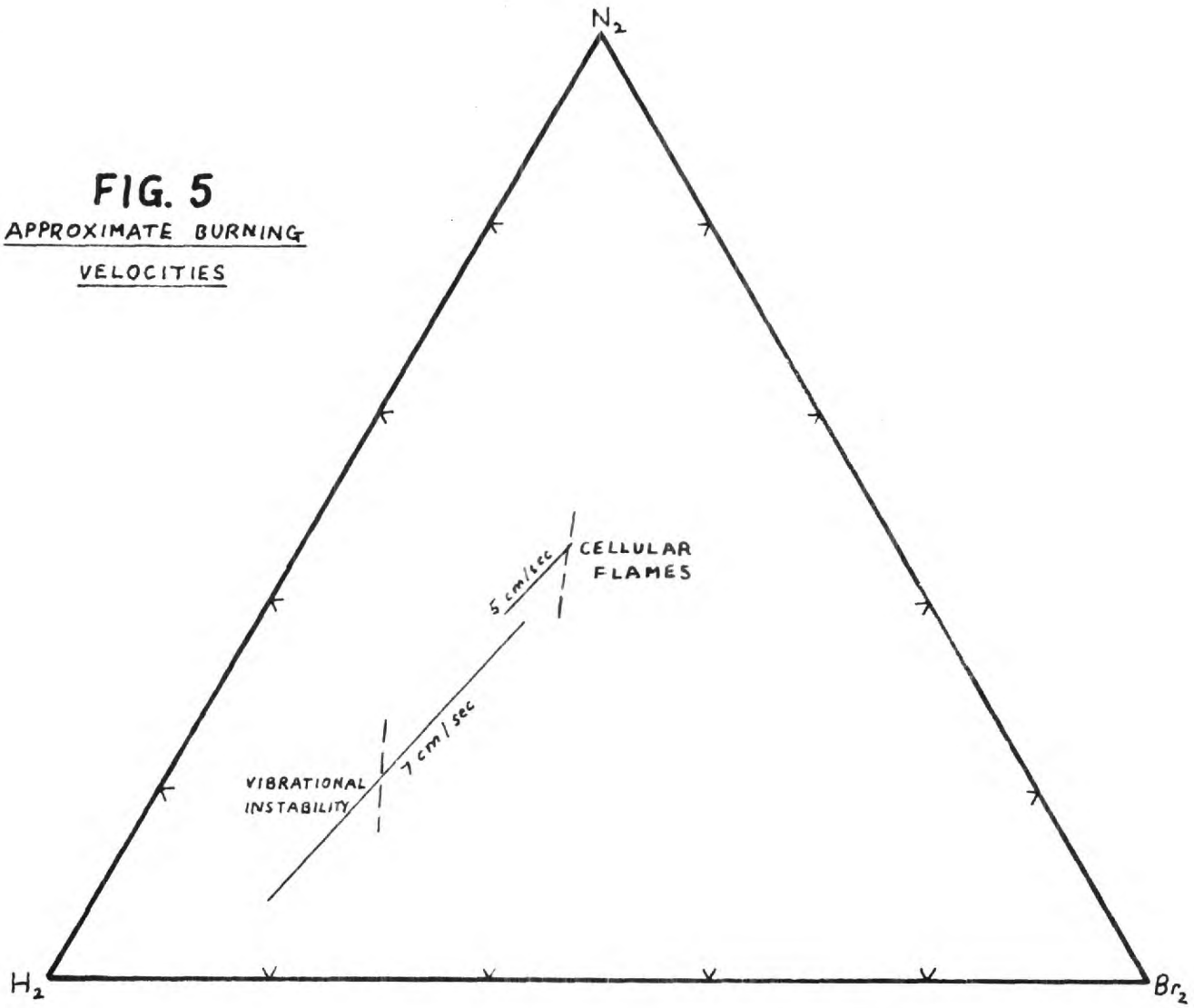


FIG. 4 STAGES OF 'LIFT'

FIG. 5
APPROXIMATE BURNING VELOCITIES



violently, due to resonance. If lifted still further, the flame blew off. The stages of lifting are shown in Figure 4 for the hydrogen-bromine flame and the lean ethylene-air flame on the same burner.

Since the flames could not be stabilized much more than 0.5 cm. above the matrix they were not particularly suitable for optical analysis, but it was possible to determine their approximate range of stability and burning velocities. These are shown in Figure 5. It will be seen that the burning velocities were similar to those of hydrocarbon-air flames which can be stablized on an Egerton-Powling burner. It seemed unlikely that a flat stoichiometric flame could be stabilized on the burner.

The vibrating edge of the flames just before blow-off may be due to diffusion effects. When diffusion occurs between the reactant gases and the hot products at the edge of the burner, the exchange is largely between cold hydrogen molecules from the reactants and hot hydrogen molecules from the products, the diffusion coefficient of the hydrogen being considerably larger than that of the other molecules. As a consequence of this process, which is admittedly over-simplified, the burning velocity would be increased. The edge of the flame would fall reducing the amount of diffusion and possibly being partly quenched, so

that the burning velocity would fall and the flame edge lift back to the original position to start the cycle again. This concept may not be correct but it did appear that the flames investigated depended for their stability on quenching at the edges.

Since it was considered necessary to use a free floating Egerton-Powling flame for the analysis and since lengthy experiments with hydrogen-bromine flames were to be avoided, it was decided to use ethylene-air flames to examine the effects of various modifications to the burner and, if possible, to simulate the hydrogen-bromine flame behaviour described above. If this could be done it might indicate what factors affect the mechanism of edge stabilization in general.

(3) Tests with Ethylene-Air Flames.

For these experiments two of the flow-meters were adapted and approximately calibrated for use with the ethylene and air flows required. In addition, the apparatus was modified so that the gas flow-lines in the burner could be followed by observing particle tracks. Bentonite particles were used and these were placed in the burner tube below the matrix. On tapping the burner tube,

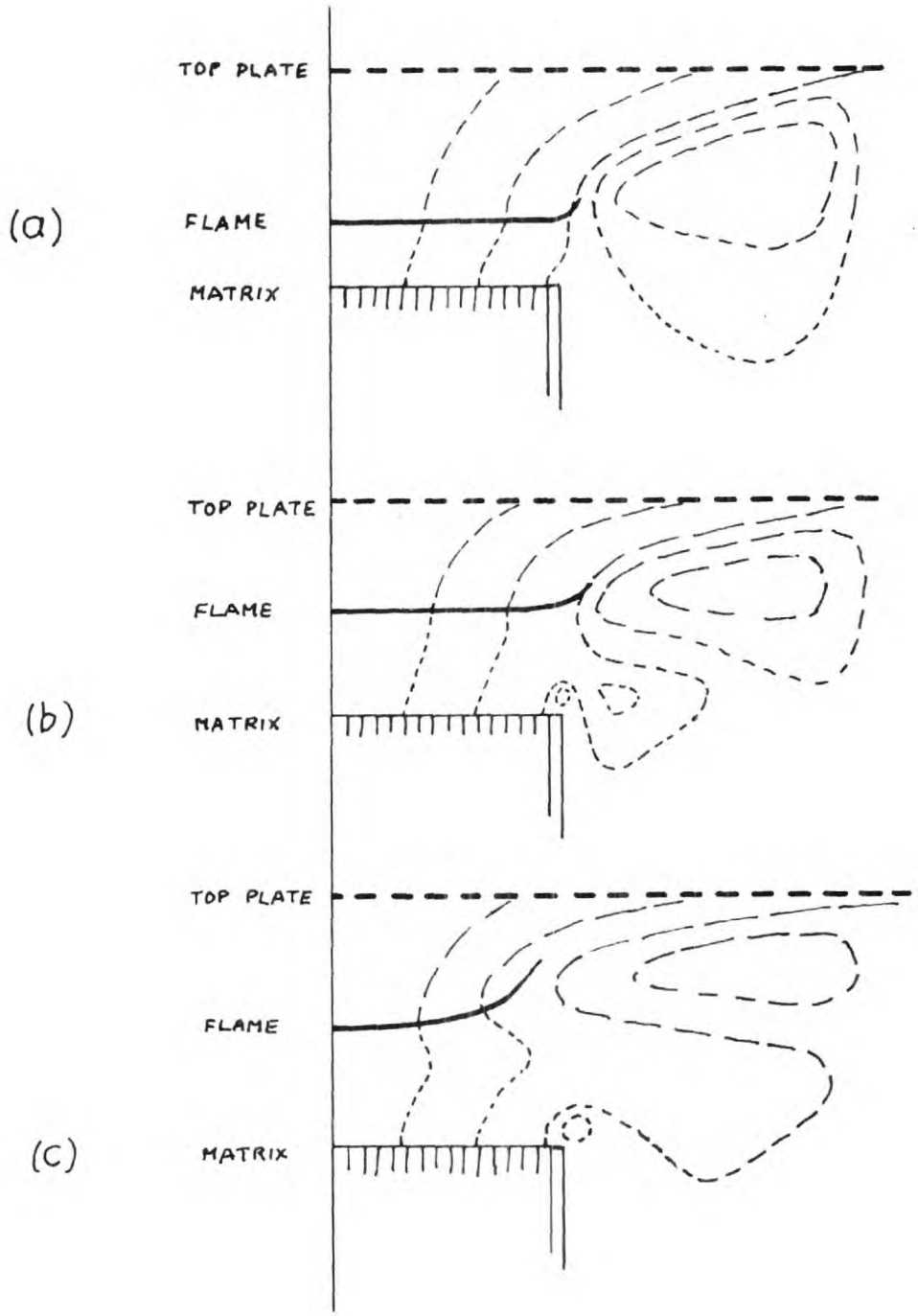


FIG 6 PARTICLE TRACKS - ETHYLENE/AIR FLAMES

particles were released into the gas stream and on leaving the matrix were rendered visible by focussed illumination from a high pressure mercury arc. The various types of flow pattern are shown in Figure 6.

The two basic types of flow pattern appeared to be as shown in Figures 6a and 6b. In the first case, there is one main vortex with the flow-lines close together at the top and far apart at the bottom, where the gas is travelling slowly. As would be expected because of viscous forces, the gas flow in the vortex accelerates (flow-lines converge) as it passes the edge of the flame. The rapid divergence of the product gases above the edge of the flame is essentially due to viscous drag by the gases in the vortex. As the flame was lifted further from the matrix the flow pattern shown in Figure 6a gradually changed into that shown in Figure 6b. Here a second vortex has formed apparently consisting of unburnt gases. As might be expected, flames with this flow pattern tended to have more diffuse edges than those with the first type. A third small vortex was also sometimes formed just above the burner rim.

Sometimes the first flow regime would be maintained right up to blow-off. When this happened -

usually when the matrix was very hot, the flame would hang just under the top plate, being relatively unaffected by the burner position. However, near blow-off an elongated second vortex would normally form as shown in Figure 6c, and high velocity gradients were set up in the main vortex. At blow-off, the flame appeared to peel off from the edges.

The effects of modifications to the burner system are outlined below. Many of these points have been noted elsewhere, but are included because they are relevant to the present attempt to identify factors affecting the stability of Egerton-Powling flames.

(a) GAS FLOW. Increasing the gas flow raised the flame further from the matrix, increased the flame diameter and made the flame dome-shaped. Decreasing the flow rate had just the reverse effect, the flame eventually stabilizing on the matrix.

(b) MIXTURE STRENGTH. Other factors being constant, increasing the mixture strength lowered the flame especially at the edges, whilst lowering the mixture strength decreased the diameter and made the flame rise and become saucer-shaped.

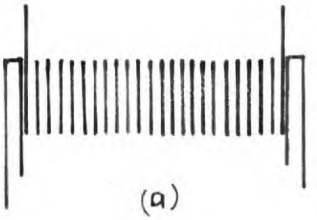
(c) THE BURNER POSITION. Raising the burner normally depressed the centre of the flame. If the burner

tube was lowered several inches, very weak flames blew off and richer flames became unstable and domed - the centre of the flame sometimes blowing out.

(d) MATRIX TEMPERATURE. If the matrix was hotter than normal, flames could be stabilized nearer the top plate - an extreme case has already been mentioned.

(e) THE TOP PLATE. If the asbestos top plate was replaced with one of lower aerodynamic resistance, it appeared that flat flames of rather higher burning velocity could be stabilized. When the holes in the centre were blocked off, there was a tendency for the one-vortex regime to be more stable but if the outer holes were closed, , the two vortex system was more common and it was more difficult to get a good flat flame.

(f) THE MATRIX POSITION. If the matrix was pushed about 2 cm. down the burner tube instead of being flush with the top, there was a tendency for the centre of the flame to drop, unless the flame was well clear of the burner tube. When the matrix projected above the top of the burner tube the flow rates required to produce a flat flame were lowered somewhat, and it was not found possible to stabilize flames on the edge of the burner. However if



(a)

(b)

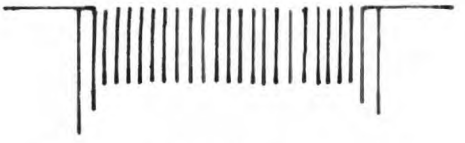


FIG. 7 MODIFICATIONS TO THE BURNER RIM (SEE TEXT)

the matrix was very hot the centre of the flame would sometimes lift before the outside.

(g) THE BURNER RIM. If the rim of the burner tube was effectively thickened by fitting a thin copper annular disc over the burner (see Figure 7b) the tendency for the richer flames to anchor their edges on the burner rim was increased. If a strip of cupro-nickel was wound round the matrix so that it projected about 1 cm. above it, as in Figure 7a, then this effect could not be produced at all. However, the latitude between lifting and blow off was reduced by this device.

(h) THE CHIMNEY DIAMETER. Flames were stabilized using inner chimneys of 8.8 cm. and 10.5 cm. diameter and without an inner chimney at all. With the narrow chimney there was a clearance of less than 1.5 cm. between the burner and the chimney, and it was found to be difficult to stabilize a flat flame more than 8 mm. above the matrix. Using the larger chimney and when no inner chimney was used at all, the behaviour was more satisfactory. An interesting observation in the latter case was that there was little distortion of the flame due to the square enclosure.

(4) Consequences of Findings with Ethylene-Air Flames.

For the edges of a flat flame to be stabilized on the edge of the burner, two conditions must be satisfied simultaneously. Firstly, there must be a region of gas within the inflammability limit just above the burner rim the dimensions of which must be comparable with the flame thickness and, secondly, the gas flow in this region must be substantially slower than that passing through the matrix. These postulates explain qualitatively the observations that stabilization on the burner rim could be prevented by using weak mixtures, fast flows or by having the matrix projecting above the burner tube. When weaker mixtures or faster flows were used with hydrogen-bromine flames stabilized at the edges, the flame immediately blew off. Hence it seemed possible that the use of a projecting matrix might be unsuccessful for the same reason, and it was thought profitable to consider other forms of stabilization for slow flames.

Since the slowest flames on the Egerton-Powling burner are saucer-shaped and the faster flames are domed, it would appear that the restricted range of mixtures which can be burnt on the burner is primarily due to aerodynamic factors. It is perhaps surprising that the Egerton-Powling

flame is flat at all, though over regions comparable with the flame thickness aerodynamic, conductive, and sometimes diffusive mechanisms tend to flatten the flame. The basic requirement for the flame to coincide with a given horizontal plane is that the burning velocity at any point on the plane should be equal to the vertical component of the gas velocity at that point. Thus if the mixture strength is uniform, the vertical velocity component must be the same at any point on the plane. This is the case at the matrix and at the top plate, providing the latter also has a uniform relatively high aerodynamic resistance. In such a case it would appear likely that between the matrix and the top plate, the vertical velocity component would be approximately constant ~~for any~~ at each height above the matrix. The presence of a flat flame would merely add to this vertical velocity component. However, the following factors tend to make the flame domed.

(a) Inertia forces should cause more gas to go through the centre of the top-plates normally used. (In practice however it was found that the distribution of holes in the top plate was relatively unimportant).

(b) The edges of the matrix are hotter than the centre so that the burning velocity should be greater in the outer regions of the flame. Also since viscosity increases

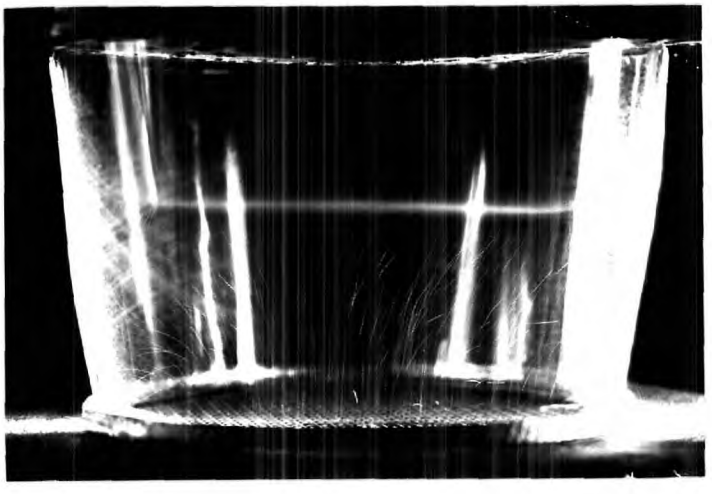


PLATE 1. Divergent chimney burner
(lean ethylene-air flame)

with temperature, the flow rates should be slower at the edges.

(c) Buoyancy effects.

At the edges of the flame, diffusion between reactants and the recirculating products, which have been cooled to some extent by the walls, would normally tend to reduce the burning velocity, resulting in the edges being upturned.

For work on low pressure flames, a conical divergent chimney fitting closely round the matrix, has been used [28,58] simplifying the aerodynamics of the system. A similar system was tried here using a Pyrex cone frustrum 4 cm. long, the cross-sectional area at the top being about 30% greater than that at the matrix (see Plate 1). Flat flames were readily stabilized with this device and the behaviour was, in general, similar to that of Egerton-Powling flames. However the flames were quite stable when the top-plate was raised 5 cm. above the top of the chimney.

The use of wires to stabilize slow flames was also investigated. Such stabilization need not affect the circular symmetry of suspended flames, but it would be simpler to stabilize the flame with wires parallel to the

beam of light used for the optical investigation. It was found that a 16 S.W.G. wire would provide an efficient stabilizing mechanism, even when the flame was 5 - 10 mm. above the wire, the effect of the wire then being marked by a dip in the flame. This type of stabilization would be most useful in long rectangular burners for which the end effects would be small and the absorption path long.

(5) Stabilization of a Free H_2 - Br_2 Flat Flame.

Following the approach suggested by these experiments with ethylene-air flames, attempts were made to produce a hydrogen-bromine Egerton-Powling flame on a burner in which a projecting matrix was used. On raising the flow rate to lift the flame from the matrix, it was in fact found that the edges of the flame lifted first, though less markedly than with hydrocarbon-air flames. However, the flame blew off as soon as the centre of the flame left the matrix.

Next the divergent chimney burner was tried. This was quite successful although the outer centimetre of flame was usually somewhat upturned as in Plate 5a, p. A further drawback to this burner was the difficulty in obtaining a divergent chimney of adequate optical quality.



PLATE 2. An H_2-Br_2 Egerton-Powling flame photographed by transmitted light.

Thirdly, an attempt was made to stabilize the flame on two silica rods 3 mm. diameter which could be swung into position 1 or 2 cm. above the projecting matrix. On ignition the flame flashed back onto the matrix. The flow rate was slowly increased and when the flame blew off it stabilized on the rods. After some minutes it was found that on slowly removing the silica rods the flame would remain as a free floating Egerton-Powling flame. This mechanism of initial stabilization was found quite reliable.

(6) Conclusions.

Although the burner would stabilize an Egerton-Powling hydrogen-bromine flame it was not suitable for use with the optical techniques envisaged. In particular the burner housing, which was made from brass, lined with asbestos, was attacked by the bromine and hydrogen bromide. The products of corrosion were highly deliquescent, and the asbestos became damp whenever the lid of the burner housing was removed for maintenance purposes. As a result of this, as soon as the flame was lit much water vapour was produced which tended to condense on the windows. When the burner assembly as a whole became hot, this condensation evaporated

leaving a dark deposit.

The bromine control too, was considered unsatisfactory since it was found, in practice, that rapid control of the bromine flow was desirable. In addition, before any precise measurements could be made, a more accurate means of determining the bromine concentration would have to be used.

Thus, although the preliminary experiments with hydrogen-bromine flames indicated the limitations of the apparatus, it had been shown that an H_2 - Br_2 Egerton-Powling flame could be stabilized and that further development of the apparatus should enable a flame to be produced, on which an optical analysis could be carried out.

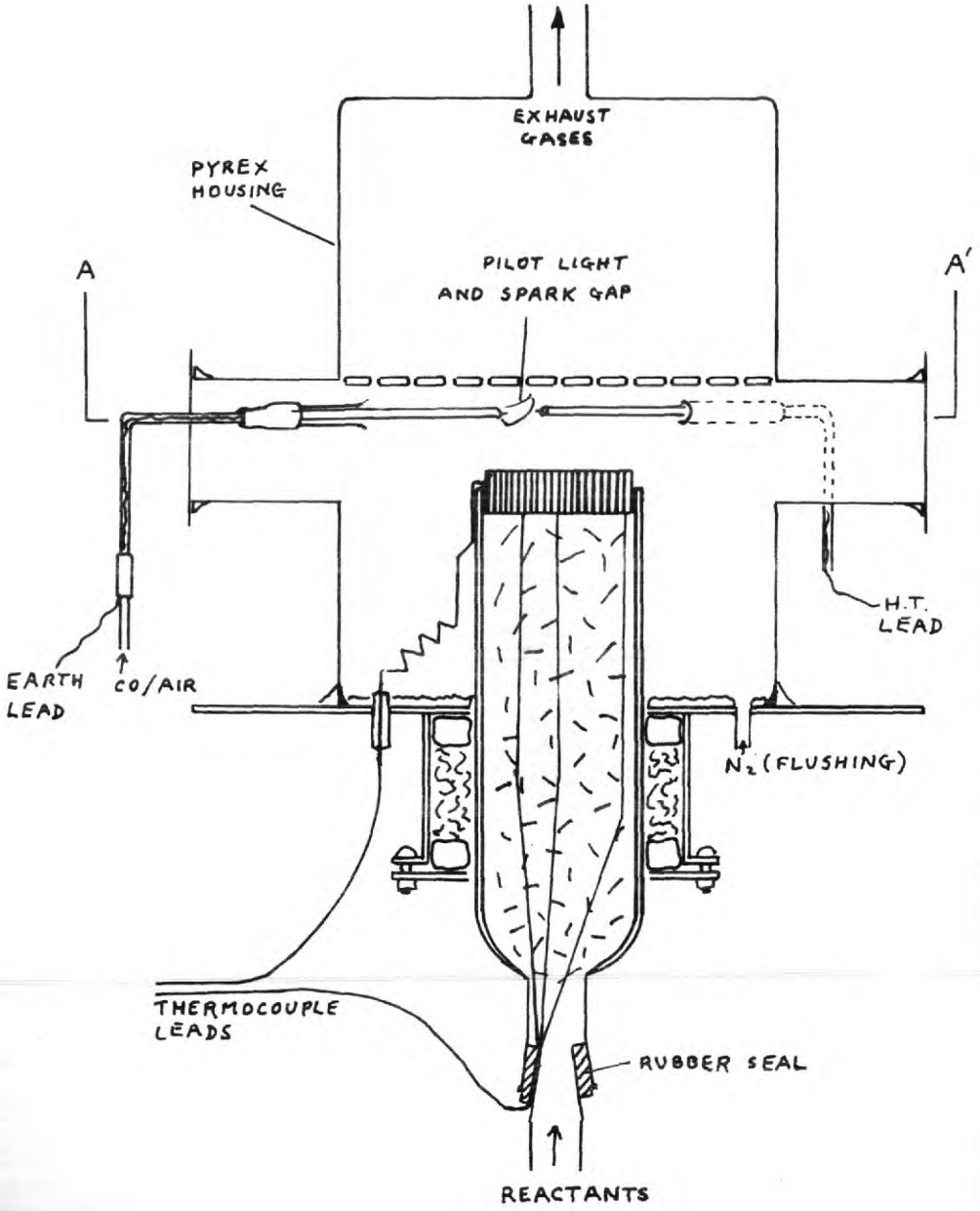
CHAPTER 6.

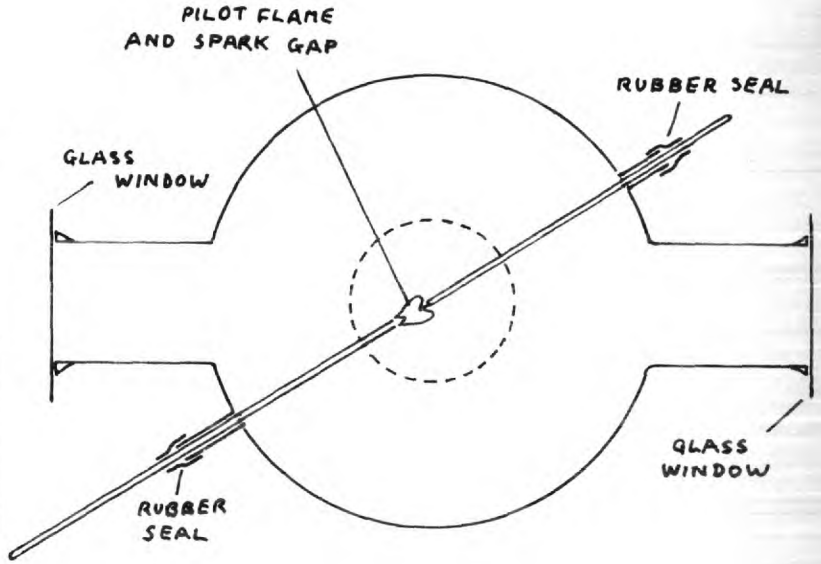
FURTHER DEVELOPMENT AND BURNING VELOCITY MEASUREMENTS.

(1) The New Burner.

The main requirement for the new burner was improved corrosion resistance. However the system, in which an inner chimney was placed inside the main housing, also proved unsatisfactory. Condensation and deposition could occur on six surfaces through which the optical beams had to pass. A further point was that the light transmission of the selected mica sheets, used for the windows, was only about 50% for one of the wavelengths (3660A.) selected for use in the optical analysis.

Two cylindrical burner housings were built, one of Pyrex in which glass windows were clamped onto 4 cm. diameter side-arms, and one of Monel metal in which cylindrical mica windows were used. In the latter design, the top plate as well as the burner tube could be moved vertically but, as the housing was not in fact used, it will not be further described. A detailed diagram of the burner assembly which was used is shown in Figure 8. (See also Plate 3).





CROSS SECTION OF BURNER AT A'-A'

FIG. 8.

The glass housing was clamped onto a brass base-plate, coated with asbestos cement, Bostik sealing strip being used to prevent any minor leakages. The burner tube was similar to that used previously and the gland packing consisted of asbestos wool and petroleum jelly sandwiched between two rings of P.T.F.E.-coated asbestos. As before, the top plate was of asbestos and had 1/8" holes drilled at 1/2" intervals. It was kept in position by three narrow Pyrex legs.

The diameter of the burner-housing was 16 cm. and it was hoped that this would be large enough for the side arms to have little effect on the flame shape. This was later found to be usually the case in practice.

IGNITION. For ignition purposes two tubes, one of silica and one of Pyrex, could be ~~packed~~ pushed together just above the burner. The silica rod carried a high tension lead from the hand megneto. The Pyrex tube carried an earth lead and also a mixture of carbon monoxide and air to be lit as a pilot flame. A carbon monoxide-air mixture was preferred to an ethylene-air mixture because no water vapour would be given off in the absence of hydrogen and corrosion would therefore be lessened. A gas-tight seal between the tubes and the burner housing was achieved with

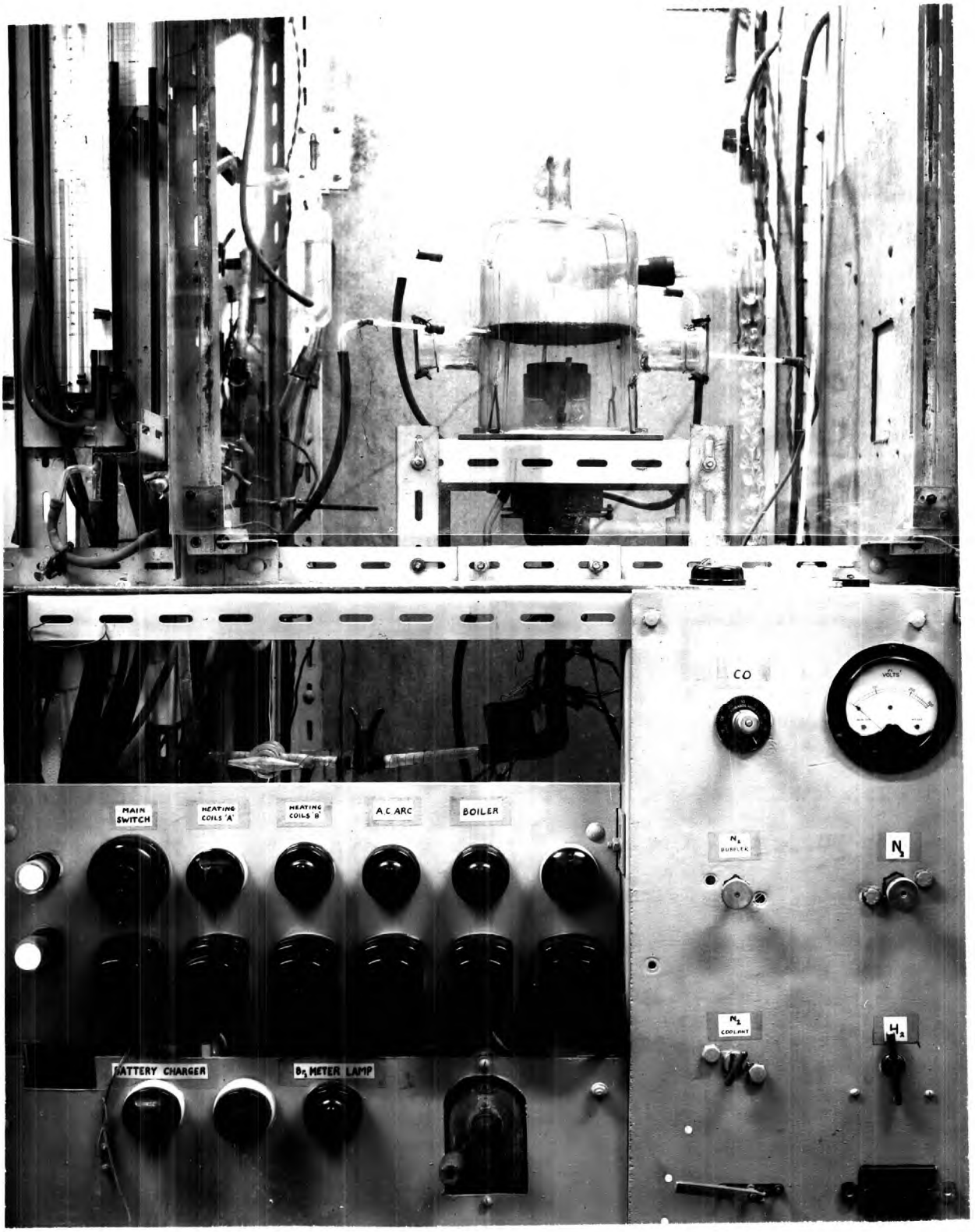


PLATE 3. General view of burner assembly and main control panel.

a short length of rubber tubing, as shown in Figure 8. The rubber was attacked and hardened, but as it had already moulded itself to the shape of the tubes, a good seal was maintained for long periods. If desired, the space above or below the top plate could be flushed with nitrogen.

THERMOCOUPLES. To measure the matrix temperature, thermocouples were used. Since it had been shown that the gas temperature on leaving the matrix is very close to that of the matrix [71], it was thought desirable to use the matrix material itself in the thermocouple. It was found, using the small burner (see p. 72), that a spot-welded platinum to cupro-nickel junction was resistant to the cold reactants and the hot flame products. Several of these junctions on the surface of the matrix were therefore used, the platinum leads being insulated by narrow glass tubes and taken out through the bottom of the burner tube. The cupro-nickel lead was taken outside the tube as shown in Figure 8. If it was taken down inside the burner tube, corrosion rapidly occurred just at the point where the lead entered the rubber seal. For simplicity, a galvanometer, rather than a potentiometer, was used to measure the voltage. The total resistance of the galvanometer and a series resistance was about 700 ohms and the resistance of the platinum and

cupro-nickel leads was about 8 ohms. Since less than half the leads were in the burner tube, the maximum effect of temperature on resistance was thought to be less than 1 ohm. This would correspond to a voltage error of about 0.15%.

CALIBRATION OF THERMOCOUPLES. Calibration was carried out against a mercury in glass thermometer which had been checked at 0°C. and 100°C. The hot junction thermocouple was bound onto the bulb of the thermometer with cotton-covered copper wire and heated in a paraffin bath up to 190°C. Readings were taken with the temperature increasing and decreasing at about 2°C./minute. The cold junction temperature was also measured with a mercury in glass thermometer, as was the case in all the later experimental work.

Initially four thermocouples were equally spaced radially in the matrix. In later work, only three thermocouples were used, two near the centre and one at the edge. For the flame analysis, the effective initial temperature (T_u) of the gases was assumed to be the mean temperature across a diameter.

PARTICLE INJECTOR. Using the method of introducing particles described earlier, it was inconvenient to replace the particles in the burner tube. In addition, it was

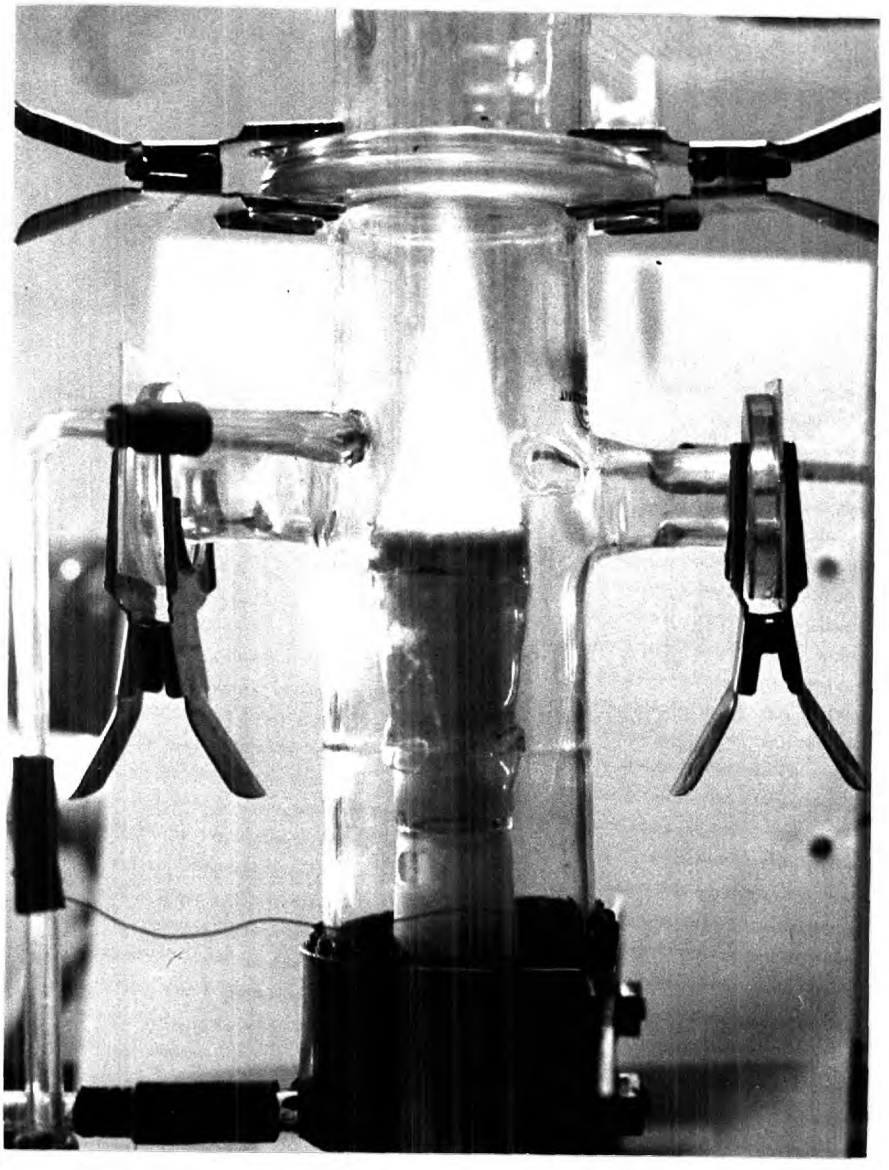


PLATE 4. Small Pyrex burner.

desirable to have the particle injector control with the other controls. In the design adopted, the reactants were passed over a bed of carefully dried bentonite, which was agitated, using an electromagnetically operated stirrer, to introduce particles into the gas flow. The stirrer was an iron rod sealed into a glass tube, the latter being covered with soft asbestos to prevent fracture of the glass and consequent corrosion of the iron rod.

THE SMALL PYREX BURNER. In addition to the main burner, it was found convenient to have a small Pyrex burner on which various tests and measurements could be made. This is shown in Plate 4. The flame was burnt on a 3 cm. square bed of quartz chips. Initial tests with the new igniter were carried out on this burner and it was also used to make sure that a Pyrex construction would stand the temperatures involved.

(2) Modified Bromine Control.

To replace the simple boiler control, the system shown in Figure 2b, p.38 was used. The main reason why this was tried before the quantitative system shown in Figure 2a was that very little modification of the boiler was required. Detail of the construction is shown in

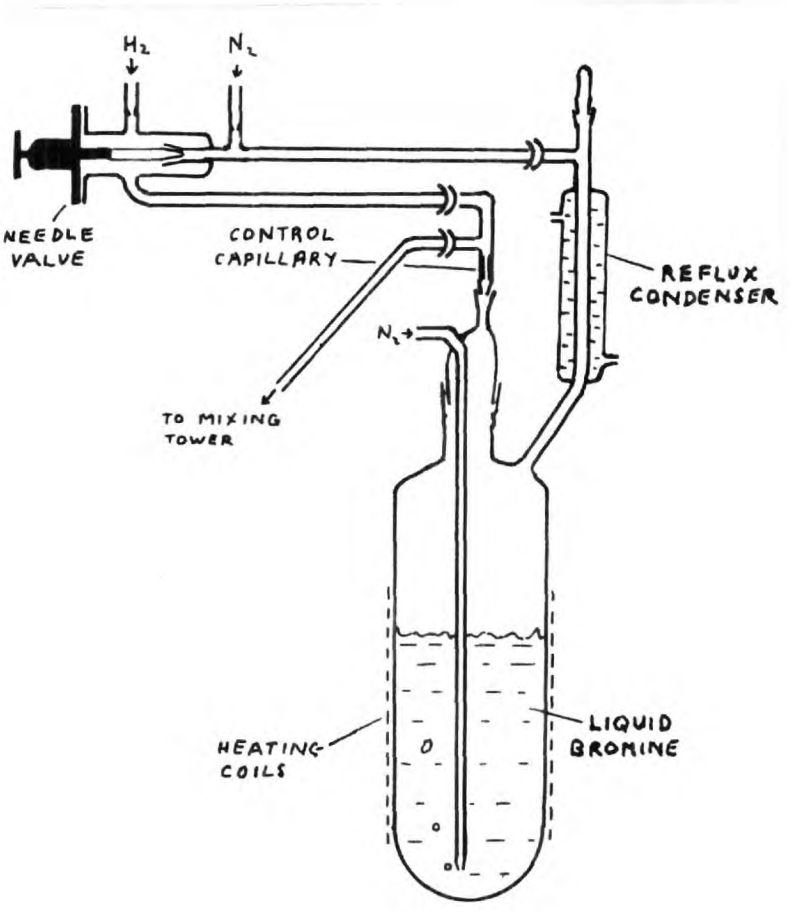

H_2
N_2
NEEDLE VALVE
CONTROL CAPILLARY
REFLUX CONDENSER
N_2
TO MIXING TOWER
HEATING COILS
LIQUID BROMINE

FIG. 9

Figure 9. The pressure drop across the capillary must be equal to that across the control valve, so that the flow through the capillary tube is determined by the main nitrogen flow and the setting of the valve.

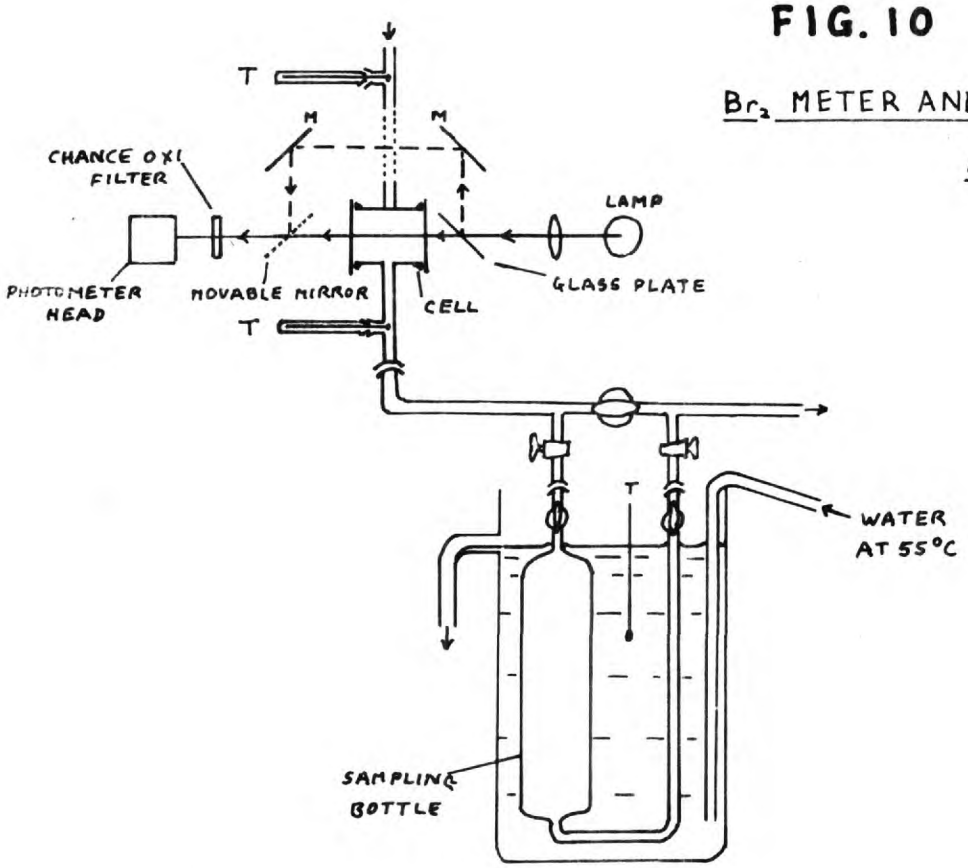
Since a low concentration of bromine was always present in the valve, the construction was largely of glass and control was achieved by screwing a P.T.F.E. needle into a B.7 glass socket from which the gas issued. The rate of production of bromine vapour in the boiler was kept substantially higher than the actual flow required, though if it was very much higher the reflux condenser became choked. In practice this system worked very well.

(3) The New Bromine Meter.

The photo-electric bromine meter, used in the preliminary experiments, showed the method of metering to be largely satisfactory. However it was found that a deposit slowly collected on the windows of the cell and in the new cell, the plane glass windows could be removed for cleaning. In use, they were held onto the body of the cell by springs, Fluorube grease being used to ensure a gas-tight seal. The light source was changed to a car headlamp bulb, run off a 12 volt lead accumulator. The

FIG. 10

Br_2 METER AND SAMPLING APPARATUS



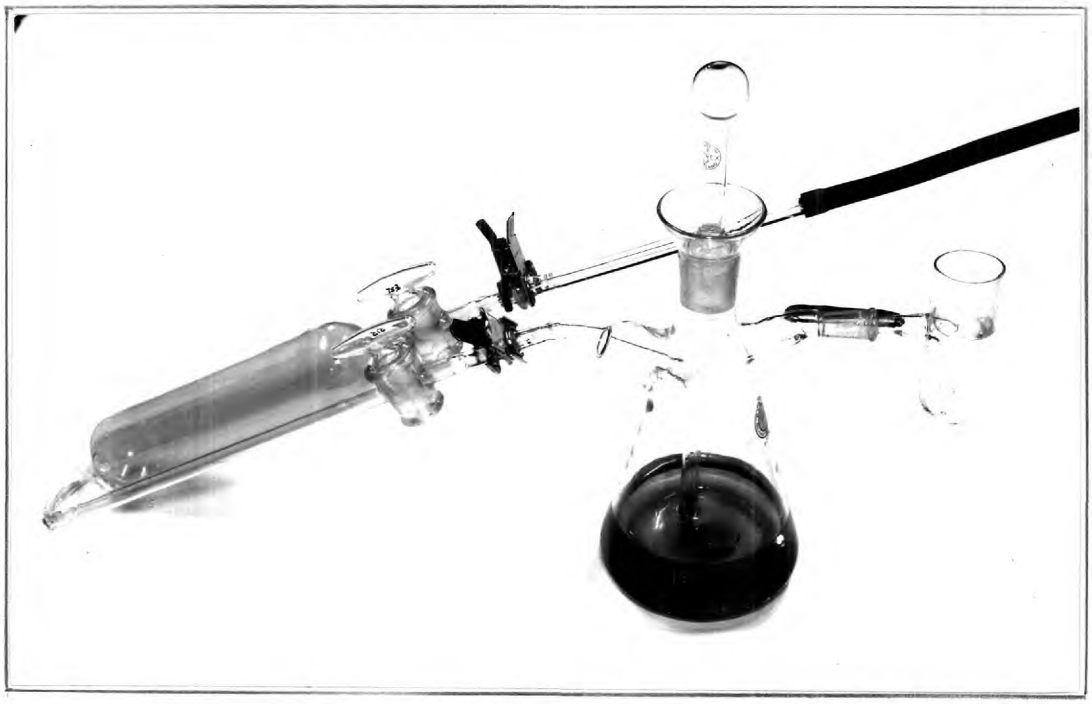


PLATE 5.

latter was found to give a steadier voltage than a transformer linked to the A.C. mains. As a further modification, a Wood's glass filter, rather than a green filter, was used, since the extinction coefficient of Br_2 in the green region is dependent on other gases present [46].

Before each reading, the intersity of the beam incident on the cell could be checked by reflecting part of the initial beam onto the photometer head, the beam emerging from the cell being blocked (see Figure 10).

The slow deposition on the cell windows was found to be reduced on cleaning out the mixing towers and replacing the Fluorube grease, where possible, by ortho-phosphoric acid. However the origin of the deposit remained uncertain and blank readings were taken before and after each run, so that corrections for it could be made.

METER CALIBRATION. Calibration was carried out by sampling, using the apparatus shown in Figure 10. The sample was then flushed out of the bottle through a slightly acid solution of potassium iodide, as shown in Plate 5. The iodine produced was titrated against sodium thiosulphate solution which had in turn been standardised against potassium iodate and found to be 0.1 $\pm$ 0.002 N. To ensure

that all the bromine was absorbed, the gas which had been bubbled through the potassium iodide solution was passed through a second such solution (see Plate 5). The iodine produced in the second solution was always less than 1% of that produced in the first.

POSSIBLE SOURCES OF ERROR AND EXPERIMENTAL PRECAUTIONS. The volume of the sampling bottles was about 240 ccs. and the flow rate through them was approximately 100 ccs./sec.. Since a constant bromine concentration was maintained for at least 30 secs., it was considered that the composition of the sample at the end of this period was substantially equal to that in the meter. Errors due to solution of bromine in the small amount of stopcock grease, used in the sampling bottles, were shown to be negligible by weighing the bottles before and after the grease had been exposed to bromine vapour.

To ensure that the temperature of the sample was equal to that of the water bath, after the meter reading was taken, one of the taps of the bottle was left open for two minutes, allowing the gases to reach the temperature of the bath at constant pressure. In a separate experiment, it was found that when a closed sampling bottle filled with

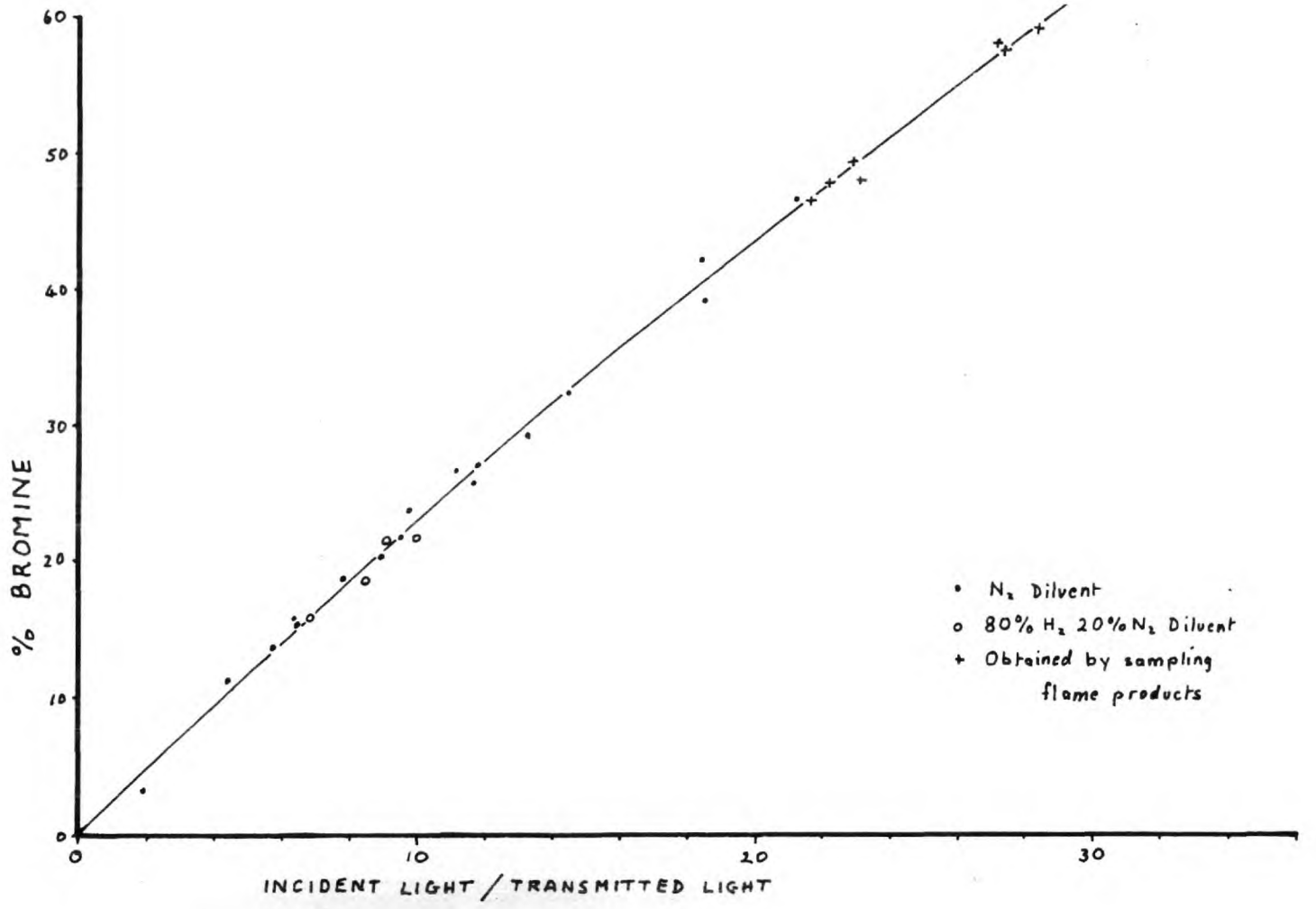


FIG. 11 BROMINE METER CALIBRATION

cold air was placed in the water bath, 99% of the increase in pressure occurred in 45 secs. However the temperature of the bath was normally within 5°C. of the gas temperature. The volume of gas in the parts of the bottle not submerged in the water bath was less than 0.1% of the total volume.

The effect of the temperature of the gas on the meter reading was also investigated. It was found that for a constant fraction of bromine, the light transmission varied less than 0.12% per °C. for mixtures containing between 5% and 40% bromine. Thus it appeared that the effect of thermal expansion of the gas was largely counterbalanced by the increase in effective extinction coefficient.

The calibrations just described were carried out using nitrogen as diluent. Some workers [47] consider that diluents affect the extinction coefficient to the extent of about 10% (depending on the diluent). Several calibrations were consequently carried out in which the diluent was 80% H_2, 20% N_2. The results are shown in Figure 11 and indicate that any diluent composition effect was small.

CALIBRATION FOR HIGH Br_2 CONCENTRATIONS. In calibrations carried out for high bromine concentrations, bromine rich flames were burnt on the small Pyrex burner. The amount of bromine and hydrogen bromide, in the samples of the products, was found by passing them into potassium iodide solution and titrating firstly with sodium thiosulphate and then with borax solution. Providing the combustion was complete and the nitrogen and hydrogen flows were known, the concentration of bromine in the reactants could be determined.

(4) Performance of the New Burner.

The experimental procedure was similar to that described earlier. However, the carbon monoxide-air pilot flame appeared even more sensitive to the presence of bromine than the ethylene-air flame, only 2 or 3% Br_2 being sufficient to extinguish it in the absence of hydrogen. If the hydrogen was passed through the apparatus before turning on the bromine, then the pilot flame was never extinguished.

The behaviour of the flame on lifting from the matrix was rather different to that observed on the first burner and it was found possible to stabilize an Egerton-

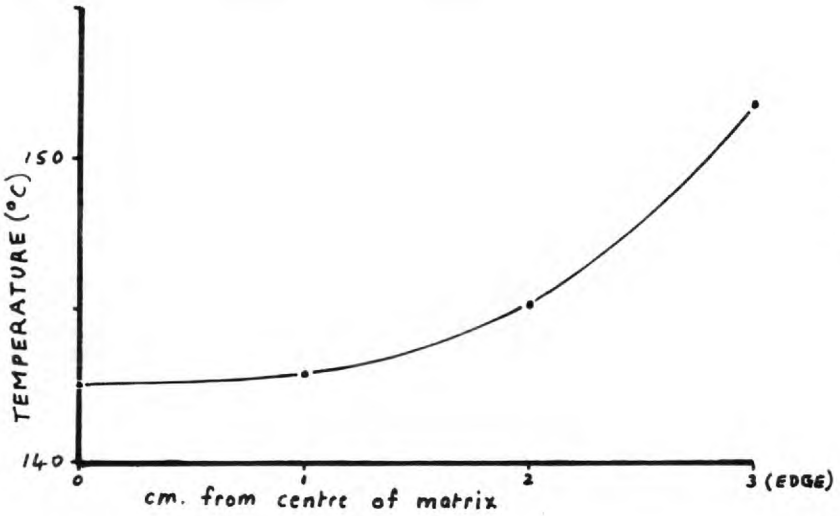
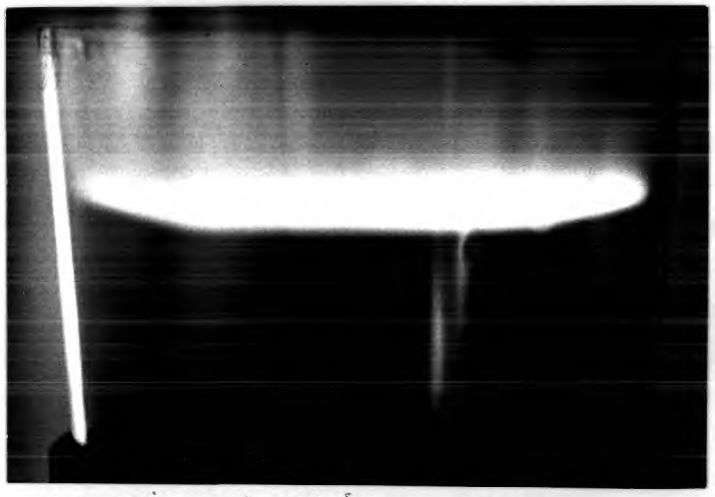
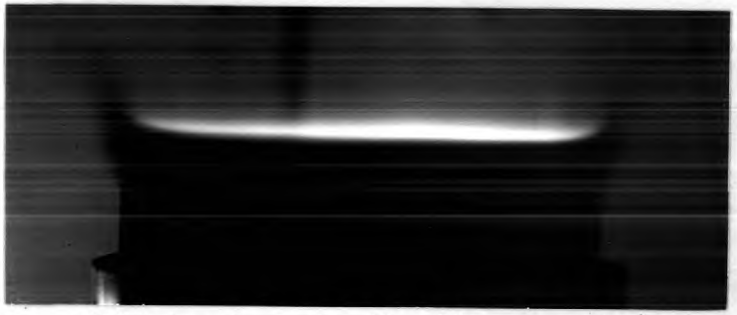


FIG. 12

RADIAL VARIATION OF MATRIX TEMPERATURE



(a) Divergent Chimney Burner
Neur - Stoichiometric flame



(b) Egerton - Powling Flame - Emission



(c) Egerton - Powling Flame - Absorption

PLATE 6.

Powling flame without stabilizing the flame first on the silica rod. As before, it was found that the very hydrogen rich flames tended to vibrational instability and bromine rich flames were cellular. However, it was found possible to obtain nearly flat stoichiometric flames. Photographs of flat flames are shown in Plate 6 and of cellular flames in Plate 7.

In general it was found possible to stabilize flames which were flat to within 0.2 mm. over most of their width, providing a new matrix was used. Unfortunately slow corrosion occurred and, after two or three runs, flames of adequate flatness for optical work could not be obtained without replacing the matrix.

A typical temperature distribution across the matrix is shown in Figure 12. It will be noted that, in common with the lean ethylene-air flames [71], the temperature is a maximum at the edge.

(5) Particle Tracks.

The particle tracks at the edges of the flame were observed at right angles to direction of illumination. However the flow patterns observed differed somewhat from those obtained in the experiments with ethylene-air flames

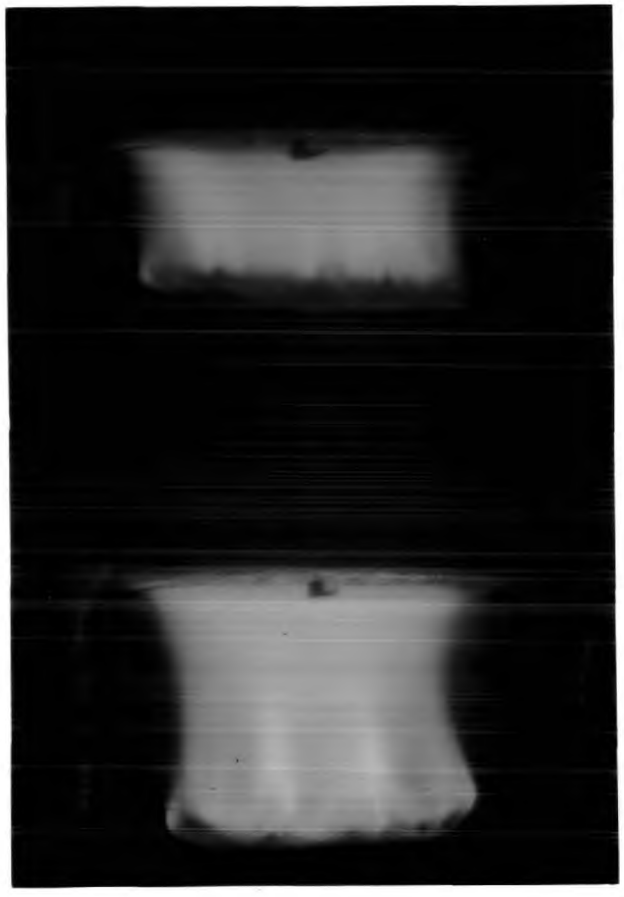
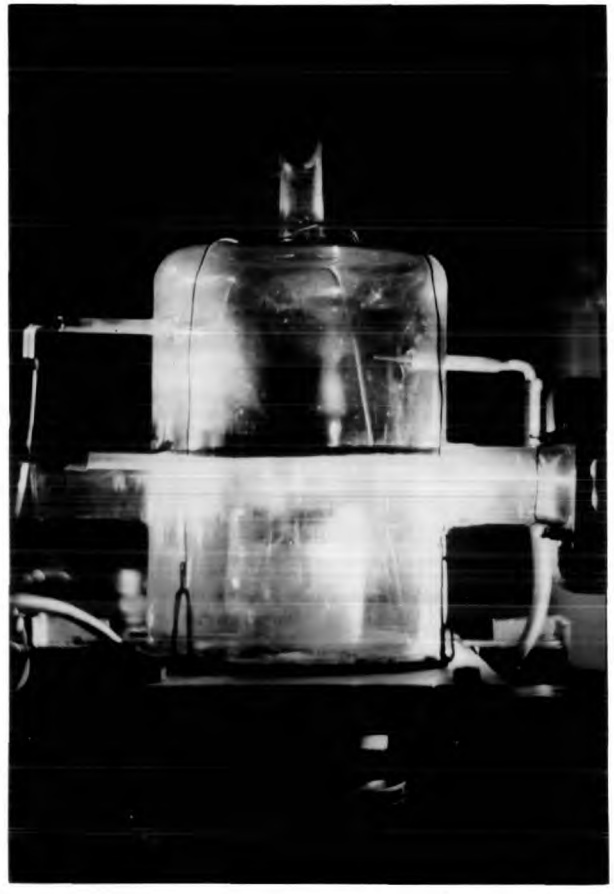


PLATE 7. Cellular Br_2-rich flames by emitted light (divergent chimney burner).

PLATE 8.



The burner assembly during particle track measurements on a very H_2-rich flame, which can be just seen above the burner tube.

(see Figure 13). In particular, the second vortex, described earlier, was much less in evidence and the small third vortex was much larger for the hydrogen-bromine flames. Perhaps associated with this different behaviour was the observation that flat flames with a high bromine content could be stabilized almost in contact with the top-plate.

HEATING EFFECT OF ILLUMINATION. Difficulties arose when attempting to use particle tracks for burning velocity measurements. Firstly, because of the absorption by Br_2, the intensity of light scattered from particles in the centre of the flame was very weak, and only the larger particles were recorded. Secondly, the experimentally determined rate of heat absorption by a blackened aluminium can, placed in the beam from the mercury arc, was found to be 0.25 cals./sec. Since bromine absorbs a considerable fraction of the mercury light transmitted by glass, the heating effect of the beam on the bromine in the flame must be considered.

The major effect of this heating would be in the first cm. of the reactants through which the beam travels, where about 90% of the blue light and half the green and U.V. light would be absorbed. If this first cm. of flame absorbed 0.25 cals./sec. then the rate of temperature rise

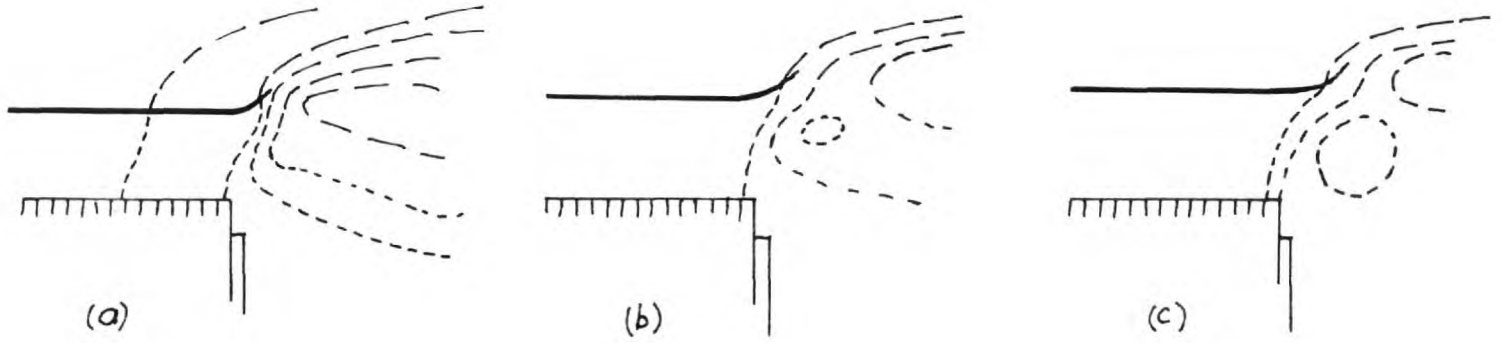


FIG. 13 PARTICLE TRACKS IN H_2/Br_2 FLAMES

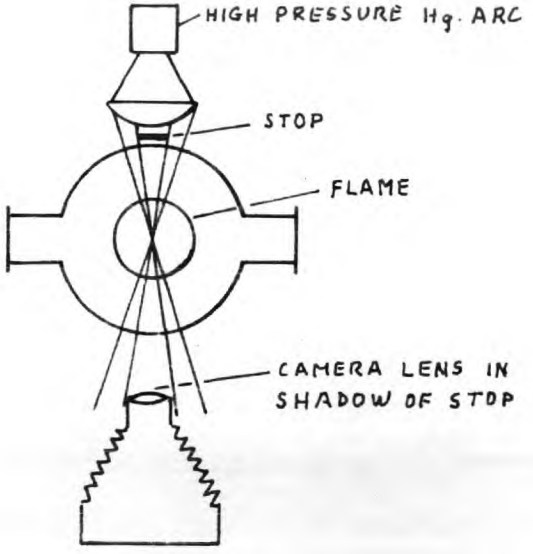


FIG. 14

ARRANGEMENT FOR USING FORWARD SCATTERED LIGHT FOR PHOTOGRAPHING PARTICLE TRACKS

would be of the order of 1000°C./sec. Thus it was clearly advisable to use an orange filter, or preferably a filter of bromine itself, when using particle tracks for accurate burning velocity determinations.

MODIFIED ILLUMINATION. These difficulties prompted the use of a modified optical system. This is shown diagrammatically in Figure 14 and was designed to make full use of the large amount of forward scattering by particles of the size used (5 - 20 microns). It was found that sufficient light was received from the particles for them to be recorded, but the high extraneous light intensity made the method unsatisfactory. A Pointolite, photographic flashbulbs, and a xenon flash-tube were used as alternative sources with little success. Although more satisfactory illumination could have been obtained (e.g. a pulsed xenon arc), it was considered sufficiently accurate to use the projected area method [10] for determining burning velocity in the present investigation. For mixtures containing a low percentage of bromine, it was found that values of burning velocity derived from particle tracks were in good agreement with those obtained by the area method.

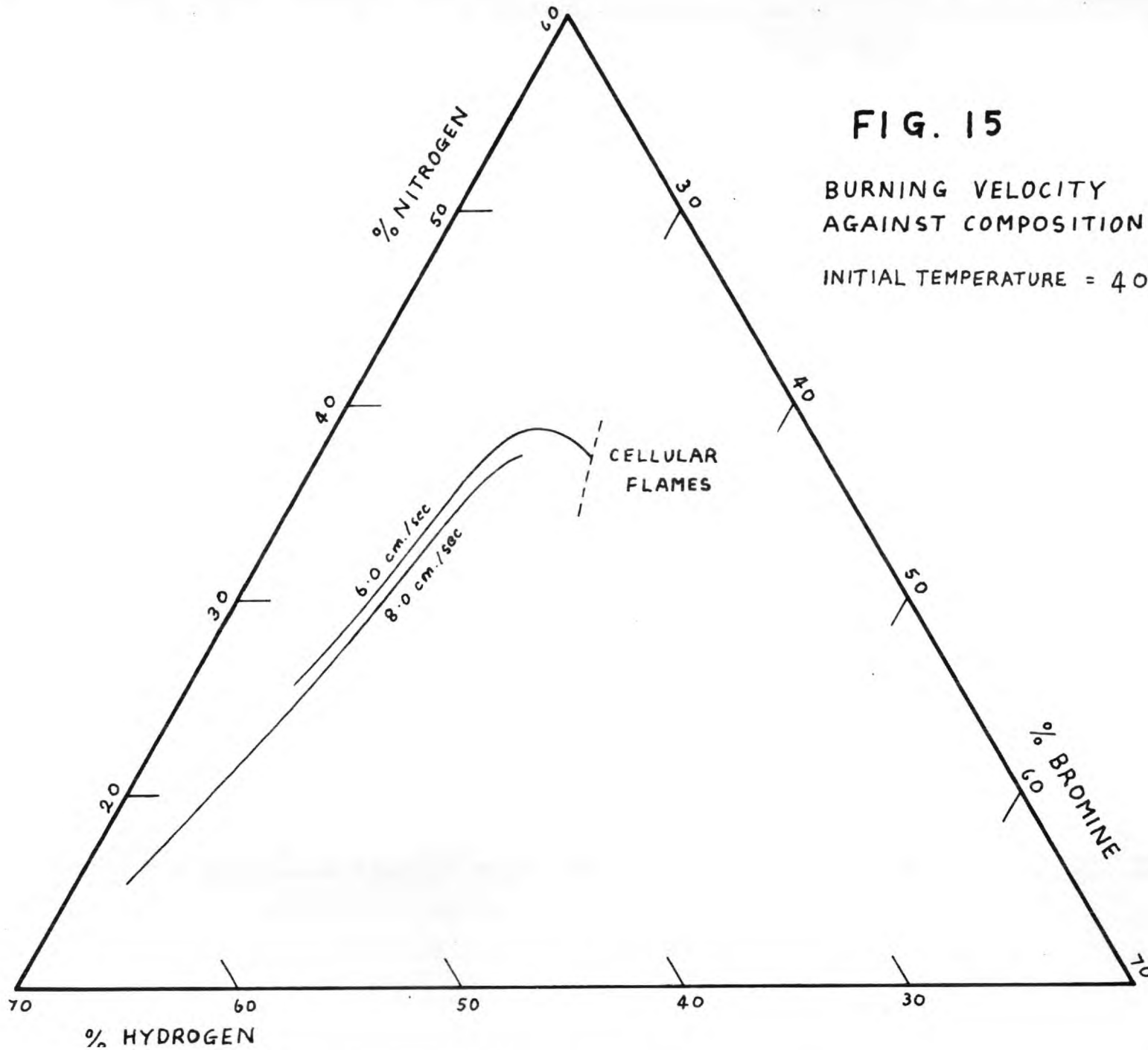


FIG. 15

BURNING VELOCITY AGAINST COMPOSITION

INITIAL TEMPERATURE = 400°K

(6) Burning Velocities.

A graph of the S.T.P. burning velocity (S_o), as a function of composition, is shown in Figure 15 (If S_u is the gas velocity at the cold boundary then $S_o = S_u \times \frac{T_o}{T_u} \times \frac{P_u}{P_o}$ where T = absolute temperature, P = pressure, and the subscript $()_o$ refers to S.T.P. and $()_u$ to the cold boundary conditions).

The values of S_o plotted have been corrected to a T_u value of 400°K. To do this, it was assumed that the change in burning velocity, due to a modified pre-heat temperature, was equal to that produced by the minimum change in composition required to give the new final flame temperature. The corrections required were, however, small.

Table 1 gives the more reliable values of S_o for various compositions. In these data the bromine concentrations were determined directly by sampling as in the meter calibrations.

TABLE 1.

% H_2	% Br_2	% N_2	P_u	T_u	S_o
37.6	27.3	35.1	753	419	8.1
30.9	31.2	37.9	753	428	6.3
58.2	23.8	18.0	757	400	8.2
47.1	26.8	26.1	749	405	8.7
45.1	26.3	28.6	749	398	6.6
47.7	26.1	26.2	738	412	7.8
43.6	27.2	29.2	752	403	8.2
42.0	27.5	30.5	755	405	8.2

P_u is in mm. mercury, T_u is in °K., and S_o is in cm./sec.

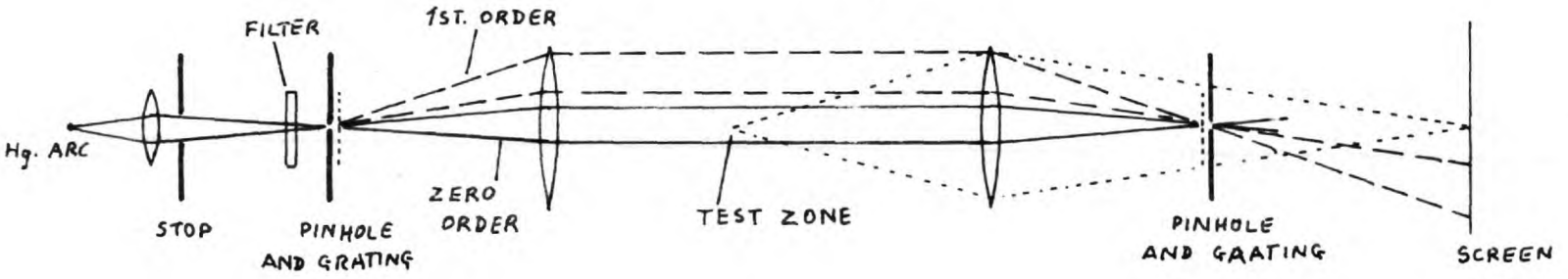
CHAPTER 7.

OPTICAL TECHNIQUES AND APPARATUS.

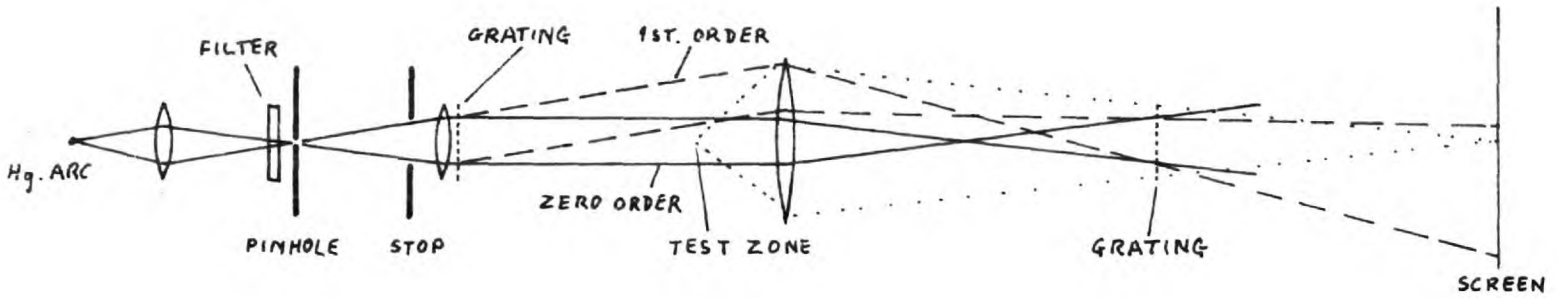
(1) Temperature Measurement.

In Chapter 2 it was stated that the inclined slit shadowgraph technique appeared suitable for the present work. Some preliminary experiments were, however, carried out using two grating interferometers. The reason for this was that in the method adopted for measuring the optical density profile, (see Section (3)), it was desirable to produce images at various standard intensities. One way of doing this is to use the various orders of a coarse diffraction grating. Such a grating might be conveniently used, at the same time, as part of a two grating interferometer suitable for measuring the refractive index in the flame.

If interferometry is to used with flames, then firstly the interferogram must be conjugate with the flame and secondly the interfering beams must have very similar paths, otherwise the fringe deflections are too large. The two interferometers tested are shown diagrammatically in Figures 16a and 16b. The former is that described by



(a)



(b)

FIG. 16 THE INTERFEROMETERS

Kraushaar [48]. A 500 line/inch grating was used to keep the angle between different orders conveniently small.

Both interferometers were easily set up and performed well when tested with a hot metal plate, though they were not tested on a flat flame. To obtain the difference in path lengths with such an instrument, the plan view of the flame would have to be known very accurately and, in common with other interferometric techniques, it would be necessary to measure fringe positions to a fraction of their width to get adequate accuracy. The use of multi-reflection techniques, to increase fringe sharpness, would seem out of the question but they could, in principle, be used to measure the angles of deflection caused by the refractive index gradient.

Since inclined slits placed in the beam before the flame would interfere with the beam used for absorption measurements, a lens was used to focus the flame onto the slits placed after the flame. Another advantage of having the slits conjugate with the flame was that the ratio of the diffraction fringe spacing to the deflection produced by the flame was less than if the slits were placed before the flame.

Because of absorption by bromine (see below) the light used for the inclined slit measurement should be

yellow or preferably red and be approximately monochromatic (about 200 A. band width).

(2) The Bromine Absorption Spectrum.

The extinction coefficient (ϵ) of Br_2 has been measured from about 2000 A. to 5700 A. [49,50,51] at different temperatures [54,55] and, at 5461 A., over a wide range of pressures [52]. The absorption spectrum shows a strong (B) continuum centred at about 4150 A. and a lesser (A) continuum, overlapping the first, centred in the green region. Above about 5100 A. there is a band system superimposed on the continua, and the extinction coefficient is very dependent on pressure, temperature and diluent.

There is disagreement in the literature over the effect of diluents on the continua. Bayliss and Rees [47] find, using densitometric methods, that all diluents tried, including N_2, HBr and He, increased the extinction coefficient by 10 - 20%. However, Evans, using a photo-electric method, found no increase in extinction coefficient on admitting diluents.

Sulzer and Wieland have developed semi-theoretical equations to describe the variation of extinction coefficient with temperature and wavelength. They assumed, for each

continuum, a Gaussian distribution of extinction coefficient with respect to wave number, the area under the curve being constant for all temperatures. The expression derived is:

$$\epsilon = \epsilon_o^m \left(\tan \frac{\theta_o}{2T}\right)^{\frac{1}{2}} \Big/ \exp\left(\tan \frac{\theta_o}{2T}\right)\left(\frac{\nu - \nu_o}{\Delta \nu_o^*}\right)^2$$

where ϵ_o^m = maximum absorption coefficient at 0°K. (190)

ν_o = wave-number of absorption maximum (24,200 cm^{-1})

$\omega_o = \theta/1.439$ = vibration frequency (323)

$\Delta \nu_o^*$ = half-width of absorption curve at 0°K (2000 cm^{-1})

The values in brackets are those given by Sulzer and Wieland for the B continuum.

(3) Measurement of Optical Density.

Either photographic or electronic methods of recording the optical density profile appear suitable. Since optical density (d) = $\log_{10} I_o/I$ (where I_o is the incident light intensity and I is the emergent light intensity), it would be an advantage to use a light receptor whose response was approximately proportional to log I. This is the case with photographic plates, where the density of the silver image may be nearly linear, with respect to log I, for an intensity range of 1000:1. Photomultipliers or vacuum cells show an approximately linear response to

intensity, but this may be overcome by using an amplifier giving an approximately logarithmic response. The use of photo-multipliers has two considerable advantages over photographic methods. Firstly, at low light levels, photo-multipliers would have superior time resolution and, secondly, a chopped light source and an A.C. amplifier could be used to remove any interference, due to flame emission, directly.

Since photographic methods could be expected to be experimentally straightforward and the development of suitable electronic equipment would take some time, it was decided to use a photographic technique whilst the electronic technique was being developed.

THE PHOTOGRAPHIC TECHNIQUE. The estimation of the light intensity, from the optical density of a photographic plate, requires accurately controlled ~~focussing~~ processing. Comparison must then be carried out with standards which have had identical processing and exposure times. With care, the intensity can be measured to an accuracy of 5%.

This procedure was greatly simplified by comparing the optical density, to be measured, directly against standard densities using photographic methods only

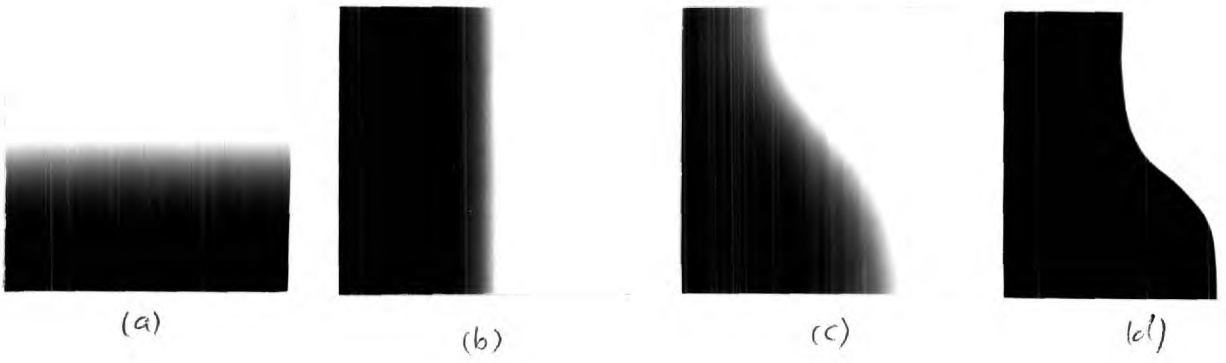


PLATE 9. (see text).

to determine one in terms of theother. The principle of the method is as follows. A uniform collimated beam of light is passed through a flat hydrogen-bromine flame parallel to the flame front. Because of light absorption, the record on a photographic plate just beyond the flame is as shown on Plate 9a. If now a standard density wedge is placed horizontally in front of the photographic plate, then the record on the plate, in the absence of a flame, is as shown in Plate 9b. The record produced in the presence of both the flame and the wedge is of theform shown in Plate 9c. Now if instead of normal development, the plate had been developed to an extremely high contrast, a profile of constant density would be obtained similar to that shown in Plate 9d. Providing the density of the wedge were known at every point, then since the sum of the densities of the flame and the wedge is constant anywhere on this boundary, the density variation through the flame can be calculated.

THE DENSITY WEDGE. A density wedge may have a stepwise gradation in density or a continuous gradation. If a step-wedge rather than a continuous wedge were used, then the density of the wedge at any point could be found

by merely counting the steps. On the other hand, only a discontinuous record of the flame optical density would be obtained.

The first wedges made used a photographically produced silver image. However, it was undesirable to have the wedge actually in contact with the photographic plate, so that the large amount of scattered light produced by the silver image interfered with the photographic record. Also, the step wedges produced photographically, although being of constant density along each step, varied in density across the step due to adjacency effects during processing.

A photographically produced dye image was found to scatter very little light but difficulties were encountered in producing a suitable density range and gradation. A satisfactory wedge was eventually prepared by evaporating aluminium onto glass, the glass plate being placed about 30 cm. above the source and a 5 mm. wide slit being placed 5 cm. below the plate. Thus an 'out of focus' image of the slit was produced on the glass plate by the aluminium. A density range of 2.0 was obtained, making it very suitable for the present work.

A different approach, which was investigated at the same time, was the production of several images of

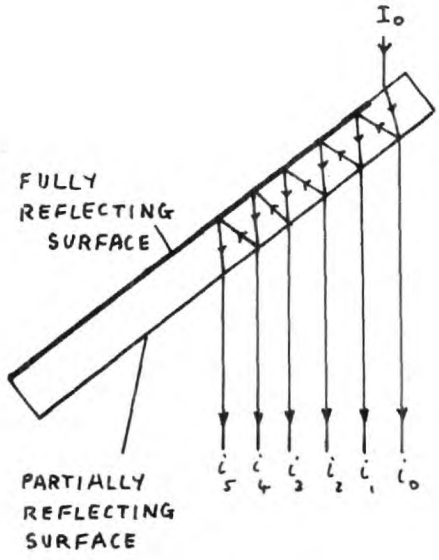

I_o
FULLY
REFLECTING
SURFACE
PARTIALLY
REFLECTING
SURFACE
i_5
i_4
i_3
i_2
i_1
i_0

FIG. 17

different intensity from theoriginal beam passing through the flame. As mentioned earlier, this can be done using the various orders of a diffraction grating but a more efficient use of the light available is to be obtained by using multi-reflection techniques. Thus in the system shown in Figure 17, log I for the emergent beams decreases linearly with the number of reflections. The major advantage of this system is that horizontal variations in intensity across the beam are unimportant. An attempt was made to use the multi-reflection technique, but the partially reflecting aluminium coating used, was found to absorb too much light. Although this difficulty could be overcome by the use of a dielectric multilayer coating, this device was not further developed because the aluminium wedge had already proved satisfactory.

(4) The Light Source.

The wavelength of the light, used in the absorption work, was largely determined by the optical density range found to be most suitable. If blue light were used then the optical density below a typical flame would be about 6.0. This would mean that the intensity of the beam emerging from below the flame would be

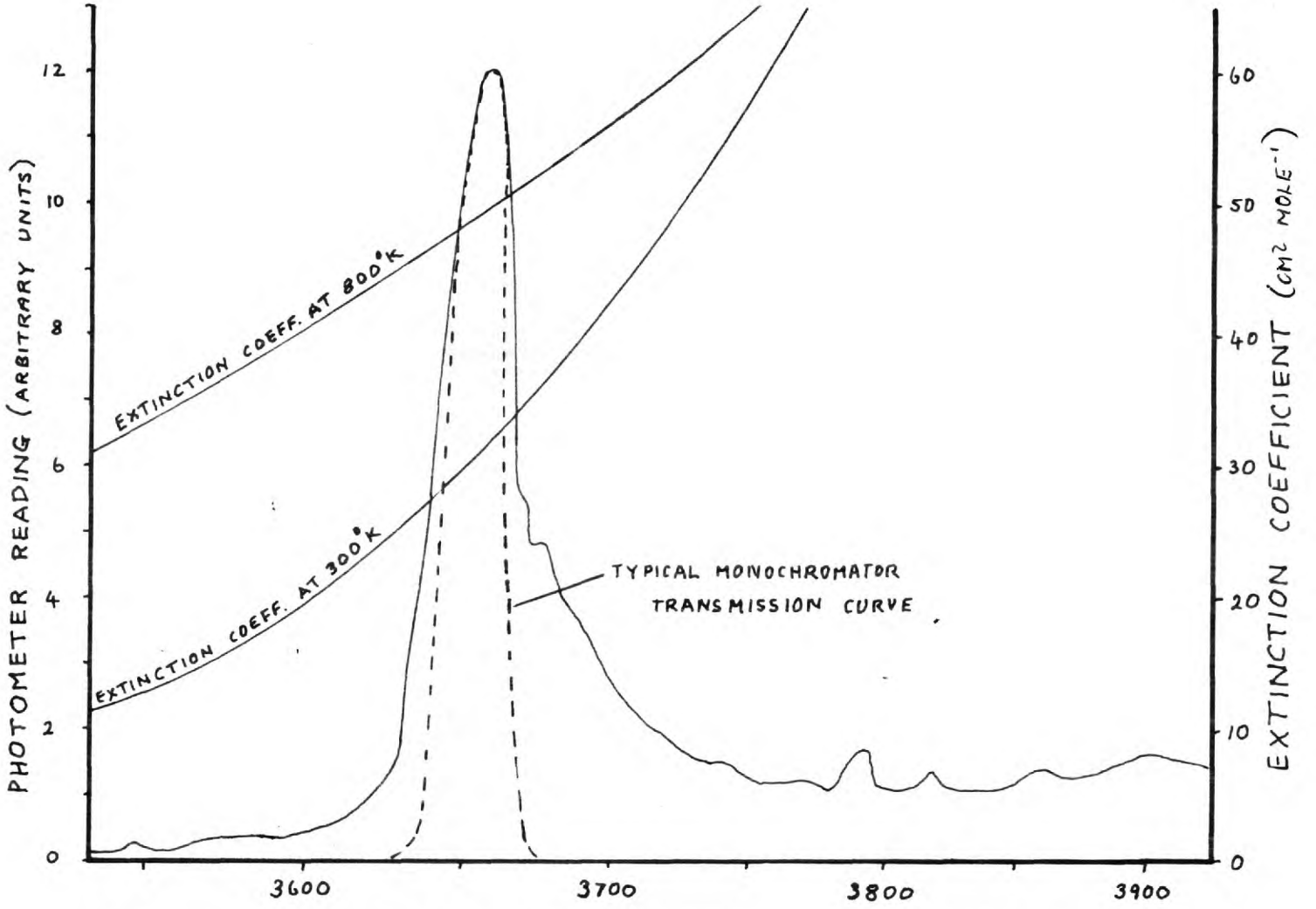


FIG. 18 PHOTOMETER PLOT OF MERCURY ARC SPECTRUM

extremely small. Apart from the difficulty of measuring such low intensities, the light scattered by the burner windows, and by any lenses used, would mask any light penetrating below the flame.

An optical density range between 1 and 2 appeared most convenient. The extinction coefficient which would give such a value would be about 30 cm^2 $mole^{-1}$, corresponding to wavelengths of 3500 A. - 3700 A. The high pressure mercury arc provides an excellent source for this region having three intense lines close together at about 3660 A. Figure 18 shows a photometer plot of the spectrum of one of these lamps - no attempt has been made to calculate the absolute intensity at each wavelength. However it can be seen that considerable line spreading occurs and the background continuum is substantial. Also shown in Figure 18 is the variation of the extinction coefficient with wavelength at 800°K. The half width of a Chance OX1 filter is about 660 A., so that if such a filter were to be used to isolate the emission at 3660 A. then, because of the background emission, light would be present having a wide range of extinction coefficients. Although Beer's law would hold for the intensity of light for any one wavelength, it would not hold for the total intensity.

THE MONOCHROMATOR. Interpretation of optical density measurements would be much simpler if Beers Law held and it was decided to construct a quartz prism monochromator to isolate the 3660 A. emission with a band width of 30 A. or less. The inconveniently low intensity of a highly parallel monochromatic beam of light prompted the use of a horizontal (i.e. parallel to the flame front) exit slit to the monochromator. This resulted in the normal monochromator optics being rotated through 90°. It was also found possible to use the monochromator to produce, at thesame time, a pinhole source of monochromatic red light for use with the inclined slit technique. It was found that glass lenses could be used in the monochromator without undue light absorption.

To test the monochromator, the light issuing from the exit slit (4 mm. x 0.08 mm.) was allowed to fall on the entrance slit of a spectrograph. By taking a series of exposures on the spectrograph, a rough quantitative analysis of the light from the monochromator was obtained. This is shown as a dotted line in Figure 18, and although the slit position was always adjusted before each run to give maximum light intensity the curve shown is probably typical.

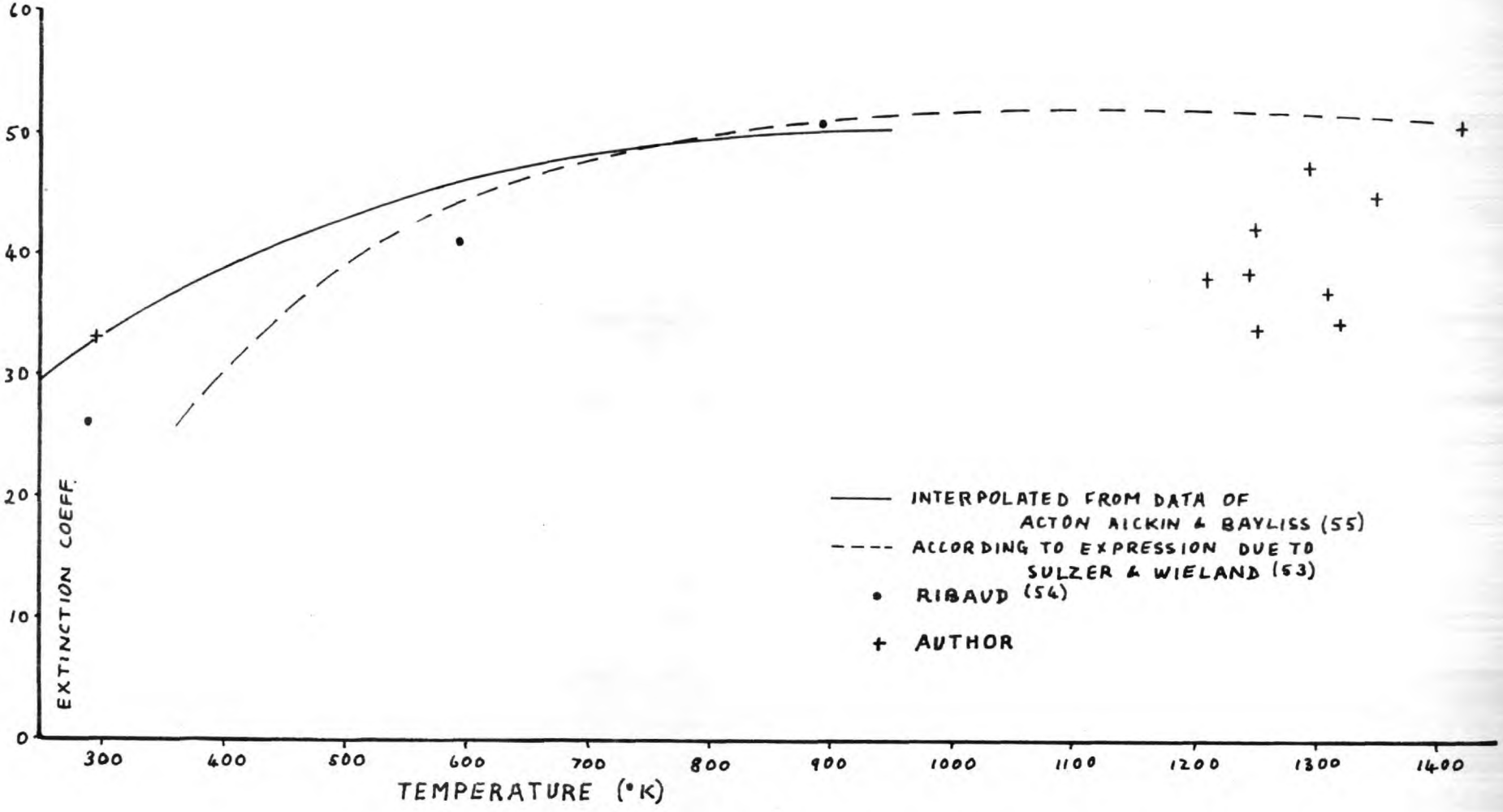


FIG. 19 THE EXTINCTION COEFFICIENT OF Br_2 AT 3660 Å

(5) The Extinction Coefficient at 3660 A.

Figure 19 shows the extinction coefficient of Br_2 for various temperatures. The continuous line has been obtained by interpolating the data of Acton, Aickin and Bayliss [55] and the calculated curve has been obtained from the formula of Sulzer and Wieland given earlier. Agreement is not particularly good and it was thought desirable to try to detect, experimentally, any marked trends in extinction coefficients at temperatures above 1000°K.

This was achieved by measuring the light absorption just above a bromine rich flame. The small Pyrex burner was used for the purpose and a shielding flow of nitrogen was passed round the sides of the burner. Light from the monochromator was passed through the products about 5 mm. above the flame and the intensity was measured with a vacuum cell photometer, fitted with a Chance OX1 filter to reduce the effect of flame emission. However, the photometer was used very close to the limit of its sensitivity and also the calculation of excess bromine involved substracting two large quantities, so that accuracy consequently suffered.

The results obtained are shown in Figure 19, calculated values of final flame temperature being assumed. The method was checked at low temperatures (24°C.) using bromine-nitrogen mixtures and a nitrogen sheath as before. Of theseven measurements carried out for mixtures containing 9 to 25% bromine all gave values for the extinction coefficient of 33.1 $\pm$ 0.8 cm^2 $mole^{-1}$. This value is in close agreement with that interpolated from the data of Acton, Aickin and Bayliss.

After considering the available data, the extinction coefficients based on the results of Acton, Aickin and Bayliss were used in the flame analysis, for temperatures up to 900°K., and for higher temperatures the extinction coefficient was assumed to be constant.

(6) The Optical System.

The optical system is illustrated in Figure 20 - all lenses are of glass. The two probe beams converge on the centre of the burner at a small angle and the flame photograph is taken from a direction at right angles to the probe beams. Separation of the beams is achieved by placing a lens after the flame and reflecting the red beam away using a mirror at the point of focus.

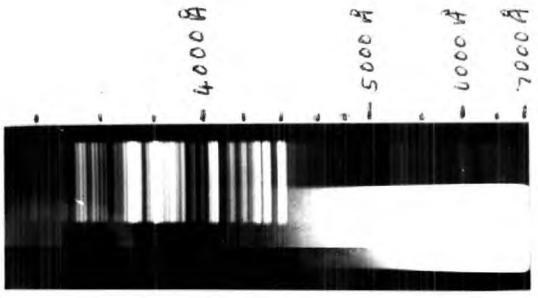
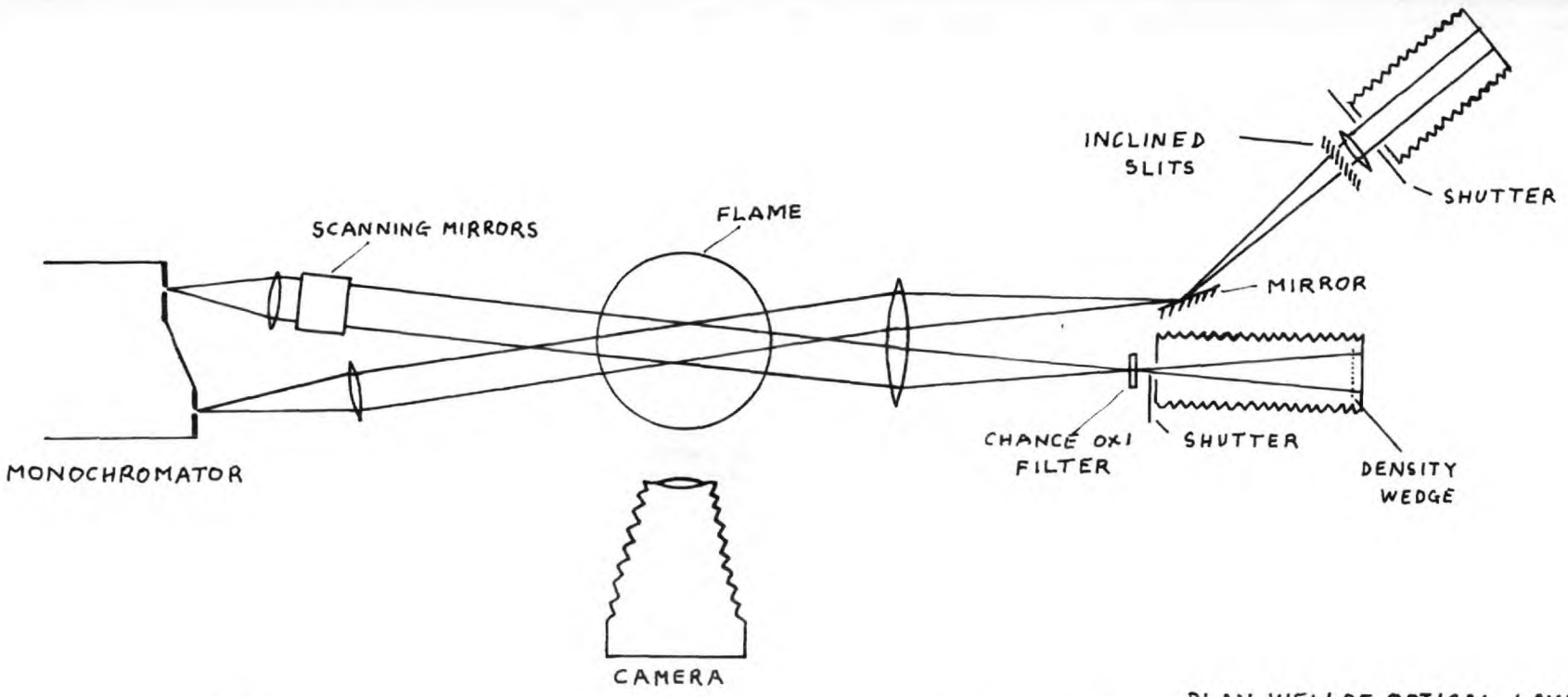


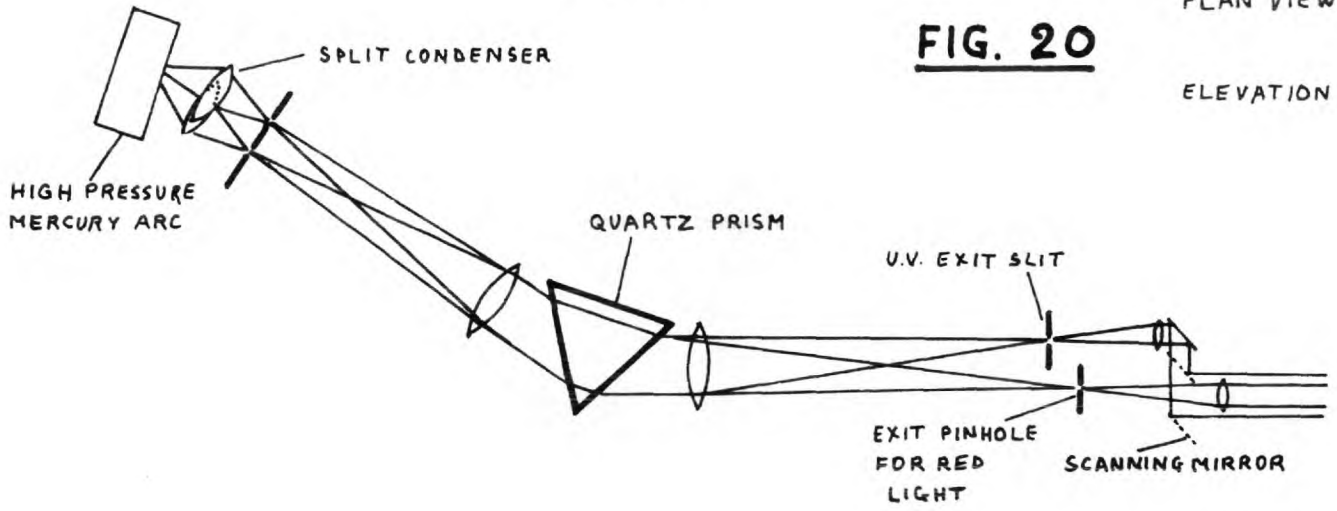
PLATE 10. Emission spectrum of a near stoichiometric H_2-Br_2 flame with an iron spectrum for comparison.



PLAN VIEW OF OPTICAL LAYOUT

FIG. 20

ELEVATION OF MONOCHROMATOR



In order to cut down the amount of emitted light reaching the plate used for absorption measurements, the probe beam was passed through a small aperture at its point of focus, care being taken to ensure that no deflected rays were cut off. The emitted light was further reduced by a Chance OX1 filter, although in any case there was very little emission from the flames in the near ultra-violet region. Plate 10 shows the emission spectrum of a near stoichiometric flame, recorded on an Ilford Astra III plate using an f/8 quartz Raman spectrograph. The slit width used was 140 microns and the expsoure time was 20 minutes.

For the purposes of the absorption record, it was possible to obtain an adequately parallel beam of light using a collimating lens of only 10 cm. focal length. The resultant beam was consequently more intense than if a longer focal length lens had been used, but an insufficient field was covered. However by scanning the light beam vertically through the flame using a moving mirror system, it was found possible to cover an adequate field without a lateral expansion of the probe beam. This system had the added advantage that little variation in intensity occurred vertically through the beam. The cam-driven scanning movement was linear with time, each cycle lasting 1.682 secs.

Since the camera bodies holding the photographic plates were some distance from the burner, electromagnetically operated shutters were built, the controls of which were placed near the burner. One of the camera bodies was adapted so that several absorption profiles could be recorded on the same plate. Also, the aluminium wedge was permanently positioned about 1 cm. in front of the plate.

PHOTOGRAPHIC PLATES. The choice of plates to be used for the absorption work required some care. It was anticipated that the use of a fast plate would be essential to reduce the possibility of flame movement during the exposure. However the large grain and low resolution associated with the fastest plates would require a larger, and consequently less intense, image of the flame to be used, in order to obtain adequate spatial resolution. Also fast plates usually have low contrast in the lower silver density ranges, a fact which would make it difficult to obtain a sharp density boundary.

A further consideration is that many of the fastest emulsions are designed for use with short exposures (< 0.1 secs.) and are much slower for exposures of about a

minute. Further a 'non-colour sensitive' plate would be preferable to the corresponding panchromatic plate since the red and green sensitizing dyes, used in the latter, may absorb some light in the near ultra-violet region. After tests with several plates, the one finally selected was the Ilford Zenith Astronomical Plate.

It was found that almost any fast panchromatic plate was suitable for recording the inclined slit images.

Although the discussion in this Chapter has been concerned primarily with the application of photographic techniques, some of the conclusions reached apply equally to the application of electronic techniques.

CHAPTER 8.

THE DETERMINATION OF TEMPERATURE AND BROMINE CONCENTRATION PROFILES.

(1) Experimental Procedure.

Using the photographic technique for determining the optical density profile, the following data were required for the flame analysis :-

(a) flowmeter readings, including line pressure and meter temperature, for the hydrogen flow and both nitrogen flows;

(b) the bromine meter reading - with the by-pass reading;

(c) the temperature of the cold thermocouple junction and the galvanometer reading for each hot junction;

(d) a photograph showing the shape of the luminous zone;

(e) a photograph of the flame by transmitted light;

(f) a photograph of the inclined slit image;

(g) a photographic record of the density profile with the superimposed flame emission;

(h) a photographic record of the flame emission alone;

(i) bromine meter blank readings before and after each run;

(j) the wedge calibration for the light beam used in (e);

(k) atmospheric pressure;

(l) all optical ~~systems~~ distances involved.

Of these measurements, (d), (e), (f) and (g) were taken as nearly simultaneously as possible, and (a), (b), (c) and (h) were recorded immediately before and after the photographs were taken.

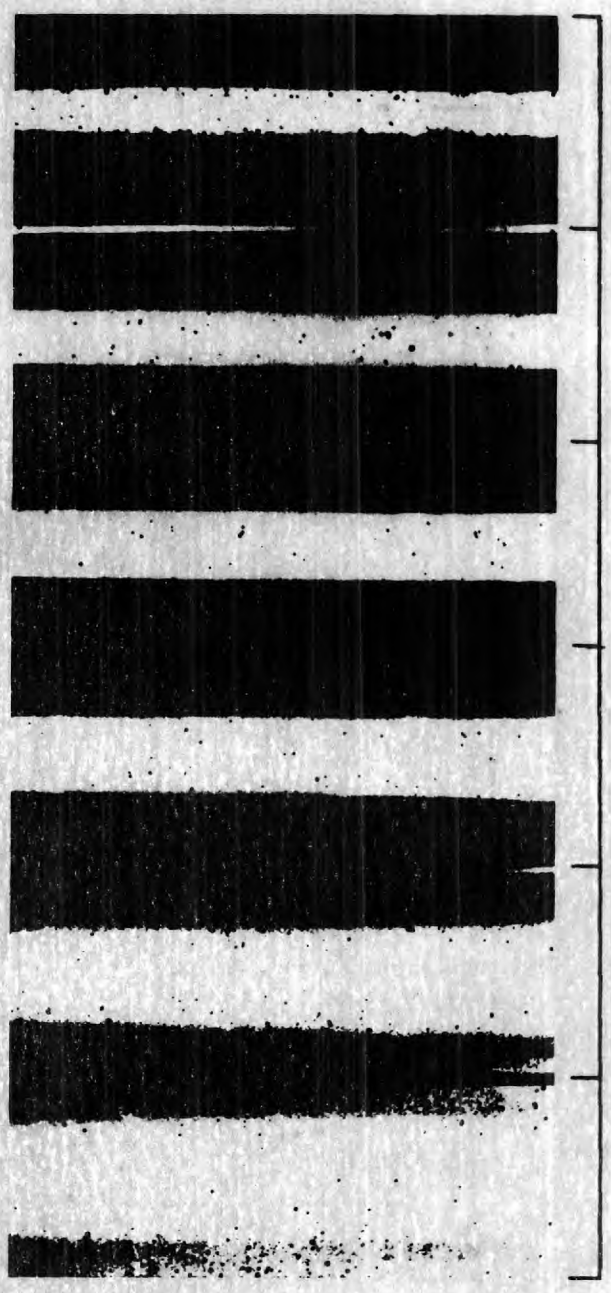
Before attempting to produce a flame at all, the optical system was aligned and focussed, the monochromator adjusted to give the maximum light intensity and all photographic plates placed in position.

For focussing purposes, the arc and condenser used in the particle track experiments were used to illuminate a vertical wire placed in the centre of the matrix. When focussing the wire on the inclined slits, the arc was fitted with a red filter and when focussing on the photographic plate used for the absorption record, a Chance OX1 filter was used. To enable the image of the wire to be seen in the latter case, use was made of the fluorescence of normal photographic printing paper. Further checks were carried out to ensure that the shadow of the wire lay in the centre of the probe beams and that

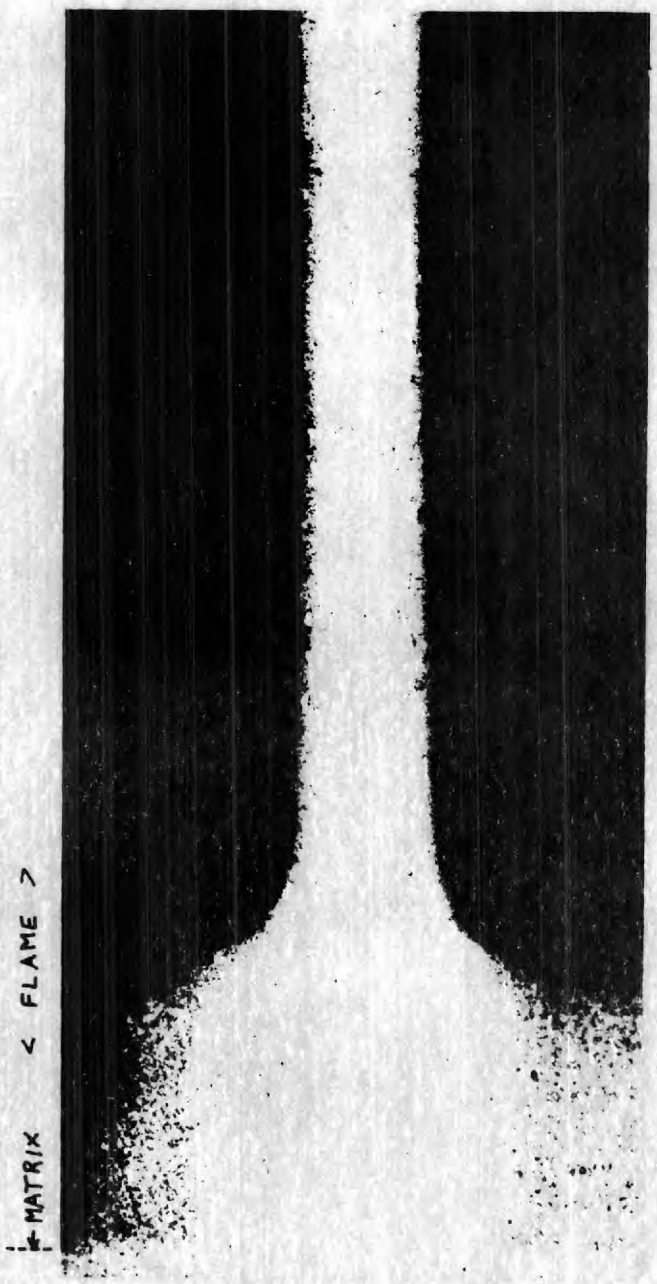
the latter were horizontal and parallel.

Next the flow system was flushed out and the flame stabilized as described previously. As soon as a suitable flame for analysis was obtained, the flowmeter, bromine meter and thermocouple readings were taken, together with the emission blank for the absorption record. A final adjustment was made to the burner tube position, to obtain the flattest flame and the inclined slit image, the density profile and luminous zone were photographed simultaneously. The respective exposures were about 15 secs., 50 secs. and 1 sec., the shorter exposures being taken about halfway through the longest one. Immediately after these exposures had been carried out, a photograph of the flame by transmitted light was taken, an illuminated diffusing screen behind the flame showing up the shape of the column of bromine . Measurements (a), (b), (c) and (h) were then repeated.

Wedge calibration was carried out as soon as the flame had been extinguished and the burner cleared of bromine. The calibration therefore took into account any small variations in intensity across the beam for that particular monochromator slit setting. The procedure was to place a series of filters of known density in the U.V.



(a) WEDGE CALIBRATION PHOTOGRAPH



(b) ABSORPTION PHOTOGRAPH

PLATE II

probe beam, and expose the photographic plate for the same period for each filter.

When processed to give very high contrast, the resultant images were as shown in Plate 11a. The width of the white gaps represents the width of wedge which had an effective density above a given known value. This was because, at the boundary, the effective density of the wedge plus the density of the filter was a constant. Ilford Multigrade filters were used as the standards of known density. These were in turn calibrated against a vacuum cell photometer, whose linear response to light intensity was checked by showing the apparent densities of the filters to be additive.

(2) First Observations - Flame Thickness.

It was found that the most stable flames were not far from stoichiometric and, in this region, the optical density range through the flame was found to be similar to the range of the wedge. This, together with the use of the minimum possible exposures, meant that the accuracy near the cold boundary was low, though the accuracy in the reaction zone was correspondingly high. Plate 11 b shows a typical absorption photograph processed

to give very high contrast. This processing involved successive contact printing onto high contrast plates. No interference from flame emission was observed in any of these photographs.

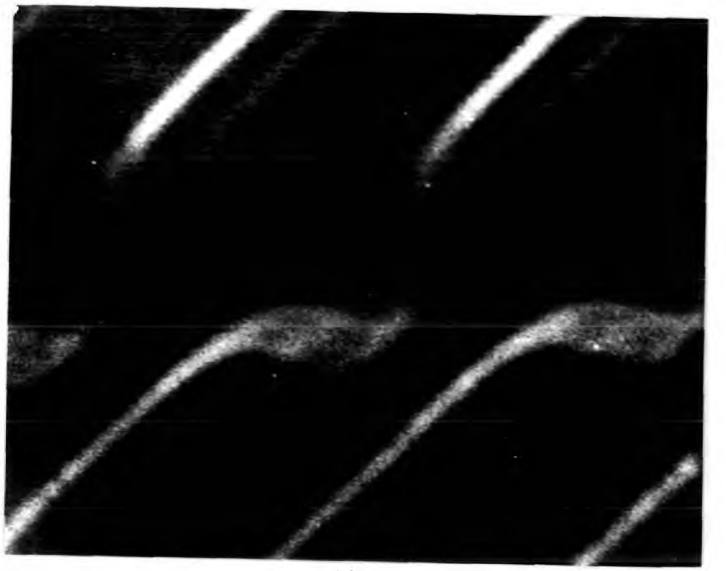
For the inclined slit technique, the slits used initially were 0.6 mm. wide and there was a 1:1 magnification of the flame image on the slits. It was expected that the diffraction effects would be similar to those observed by Levy and Weinberg [29]. However it was found that diffraction interfered with the inclined slit record to a greater extent than in the experiments described by these workers. The reason for this became clear on measuring up the inclined slit and absorption photographs:- the flame thickness was approximately half that observed for lean ethylene-air flames.

The result of the flame front being thinner was twofold. Firstly there was a larger variation in refractive index gradient across the distance corresponding to the slit width, thus creating a more complex diffraction pattern. Secondly there was more interference between light rays coming from different flame zones.

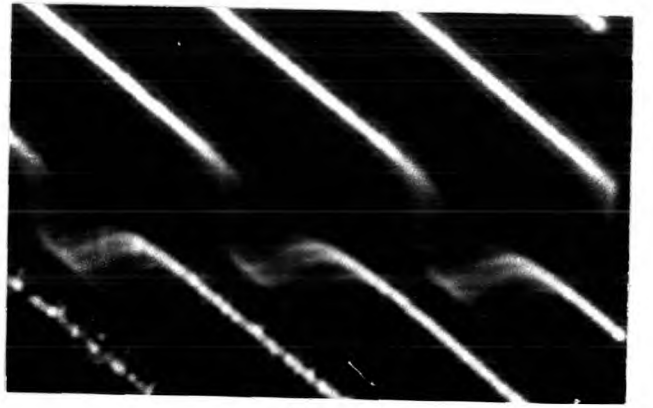
If an enlarged image of the flame were used with a correspondingly enlarged slit width, then the ratio



(a)

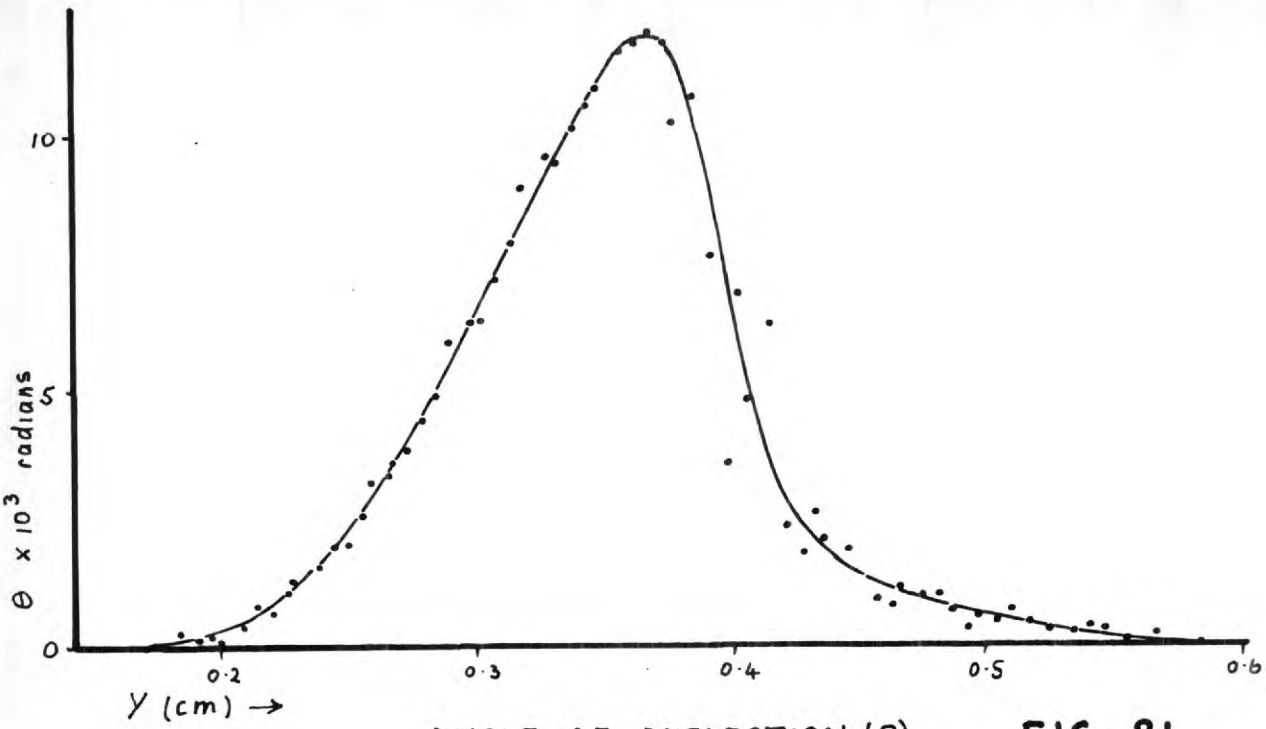


(b)



(b)

PLATE 12. Inclined slit photographs.
(a) 1:1 flame magnification.
(b) 1:1.6 flame magnification.



ANGLE OF DEFLECTION (θ)

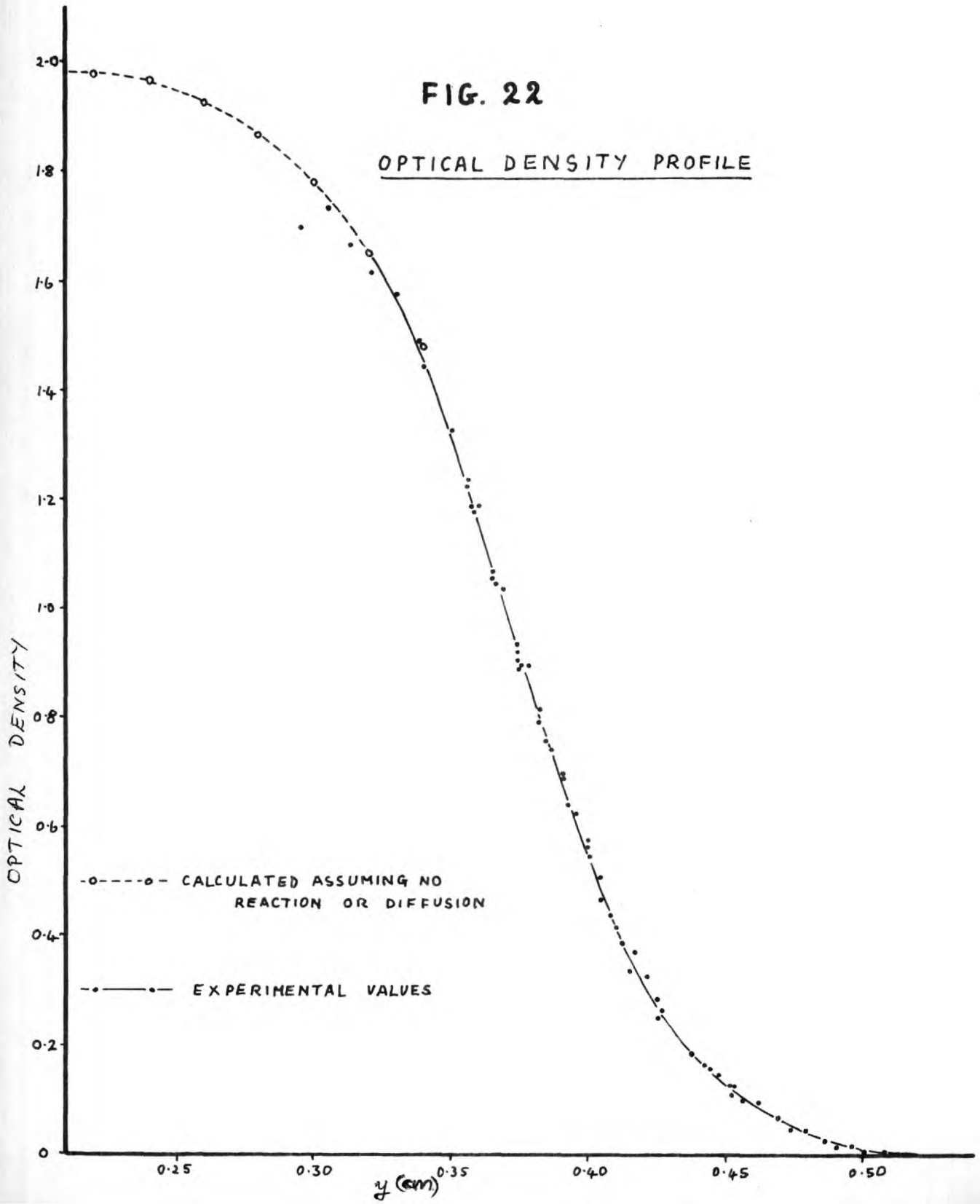
FIG. 21

of angle between diffraction fringes to the angle of deflection would be unchanged. However the outer fringes would become relatively less intense, resulting in a simplification of the diffraction pattern. This modification was carried out and resulted in some improvement (see Plate 12).

During these experiments, it was found necessary to remove the bromine meter and continuous flow cell completely - direct sampling being then used to estimate the bromine concentration. The reason for this was that, on two occasions, bad leakages had occurred round the windows of the cell and the meter was severely corroded. In the first instance, the grease used to seal on the windows was dissolved away and, in the second case, a partial blockage occurred in the burner tube due to bentonite particles and the resulting pressure increase in the cell caused further leakage. However sampling was to be preferred for these experiments, where only one or two sets of results were obtained in each run and where accuracy and reliability were important.

FIG. 22

OPTICAL DENSITY PROFILE



(3) Results Using the Photographic Techniques.

In the following chapters only one flame is considered and used to demonstrate the method of analysis. Consequently, preliminary results are given here for this flame only, though data were obtained for several others.

The modified apparatus enabled usable inclined slit and absorption photographs to be obtained. To measure up the inclined slit photograph, the plate was placed in a projector and enlarged onto a sheet of graph paper. It was thus possible to follow each diffraction fringe through most of the flame thickness. The points plotted by this method are shown in Figure 21, the results for each fringe having been adjusted vertically to give the best fit with the central fringe.

The profile of constant optical density was obtained as described earlier, and several prints were made so that profiles were obtained for different total densities. The resultant flame profile is shown in Figure 22. It will be seen that there is very little scatter of points from different prints over most of the flame thickness. However, in the low temperature region, those points which were obtained were unreliable. The dotted line gives the value calculated from a knowledge of

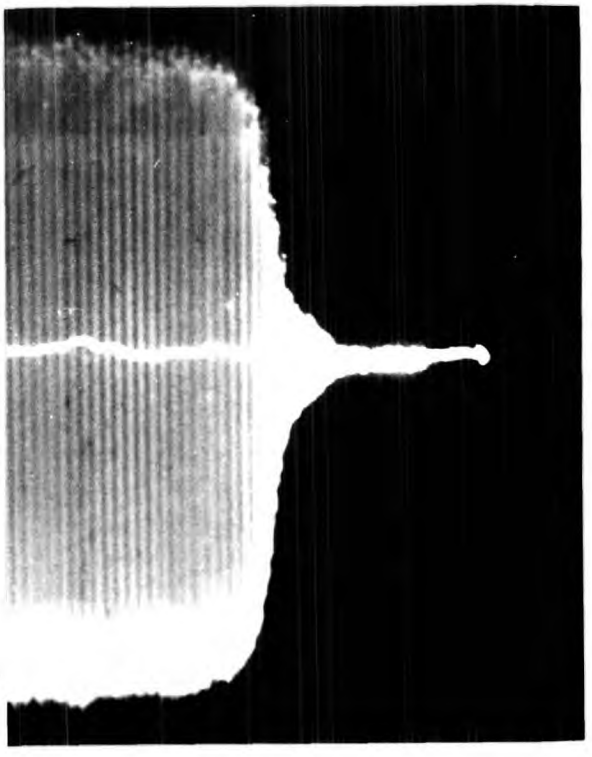


PLATE 13. Typical oscilloscope trace (see text).

the temperature, assuming no reaction or diffusion of Br_2

It was found possible to align the two profiles to better than 0.1 mm. by measuring the vertical distances (y) from the position of the shadow due to the matrix .

(4) Electronic Technique - Preliminary Experiments.

The apparatus used for the photographic determination of the optical density profile was adapted for preliminary experiments with a photomultiplier technique. A D.C. mercury arc was used as light source in the monochromator and the U.V. beam isuuing from the exit slit was chopped at 1,000 c/s. by a rotating toothed wheel. The beam from the scanning device was restricted by a horizontal slit 3 mm. wide, and was focussed on the centre of the flame when the moving mirror was at the mid-point of its travel.

The beam of U.V. light, after passing through the flame, was focussed onto the stationary photomultiplier. The signal from the photomultiplier was amplified and fed onto the Y-plates of an oscilloscope. A typical trace is shown on Plate 13.

The main purpose of these preliminary experiments

was to test the components used and to find out what features it would be desirable to include in apparatus for measuring accurate density profiles. These investigations led to the following observations.

(a) The intensity of the signal was adequate, but the signal/noise ratio was too low for accurate measurement of the light intensity below the flame front. To overcome this restriction, a general reduction in noise level would be necessary; the use of a tuned, narrow band amplifier should help in this connection.

(b) Using the arrangement described, in which the scanning slit was placed before the flame, it was found difficult to obtain adequate spatial resolution. A better system would be to place the scanning slit after, and conjugate with, the ~~slit.~~ flame

(c) It was found that using a static photomultiplier, the deflected beams did not fall on the same part of the receptor as the undeflected beams. The solution would appear to be, to have the photomultiplier behind the scanning slit, and travelling with it.

(d) By using different oscilloscope sensitivity ranges for alternate scans, it was found possible to increase the accuracy of the density determination near

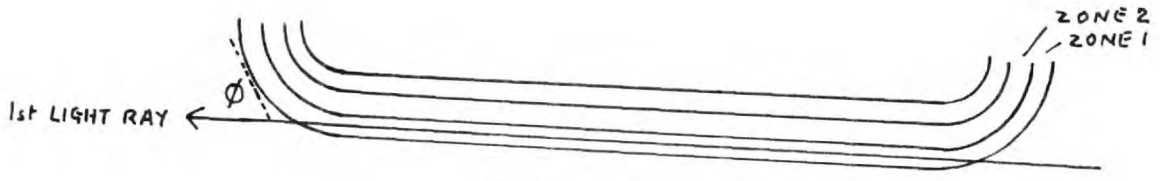


FIG. 23.

the cold boundary. If this could be done automatically, the arrangement would give more accurate results than one which employed an amplifier giving a logarithmic response.

(e) It should prove very convenient, in future work, to,link the oscilloscope time base directly to a potentiometer on the scanning device, so that synchronisation would be automatic.

(5) Calculation of the Temperature Profile.

The ray deflections produced by the flame were calculated from the measured distances between optical components and the shape of the distorted slit image, using simple lens formulae. From these deflections, the refractive index gradient perpendicular to the flame front (grad μ) was calculated by the method described by Levy and Weinberg[29]. For this purpose, the flame was considered to be divided into zones 0.2 mm. thick, the zones being parallel to the lower edge of the luminous zone. Each zone was assumed to have a constant grad μ. If the light ray which showed the first measurable deflection is considered, then this ray will pass through only one zone where there is a significant refractive index gradient, as is shown in a simplified diagram in Figure 23.

If the path length of the ray in the first zone is ℓ_1, then providing the angle of deflection is small:

$$\text{grad } \mu_1 = -\frac{\theta_1}{\ell_1} \qquad (\theta = \text{angle of deflection}$$

A ray passing through the centre of the next zone must also pass through the first zone. Hence before being able to calculate grad μ_2, the deflection due to the first zone must be subtracted from the total deflection to give θ_2. The deflection due to the first zone is readily calculated since, in general, the deflection produced for a ray passing through any zone is given by :

$$\theta = -\ell \text{ grad } \mu \cos \phi$$

(where ϕ is the angle between the zone boundary and the ray). Thus the path length of the second ray in zone 2 and the resultant deflection are known and grad μ_2 can be calculated. By a similar procedure the refractive index gradients through the flame can be successively calculated, and if y is the distance from the matrix then grad $\mu = \frac{d\mu}{dy}$ where the flame is horizontal.

When this procedure was applied to the inclined slit record obtained, it was found that in the high temperature region where $-\frac{d\mu}{dy}$ was rapidly decreasing (see Figure 24), the values obtained for $-\frac{d\mu}{dy}$ oscillated. This

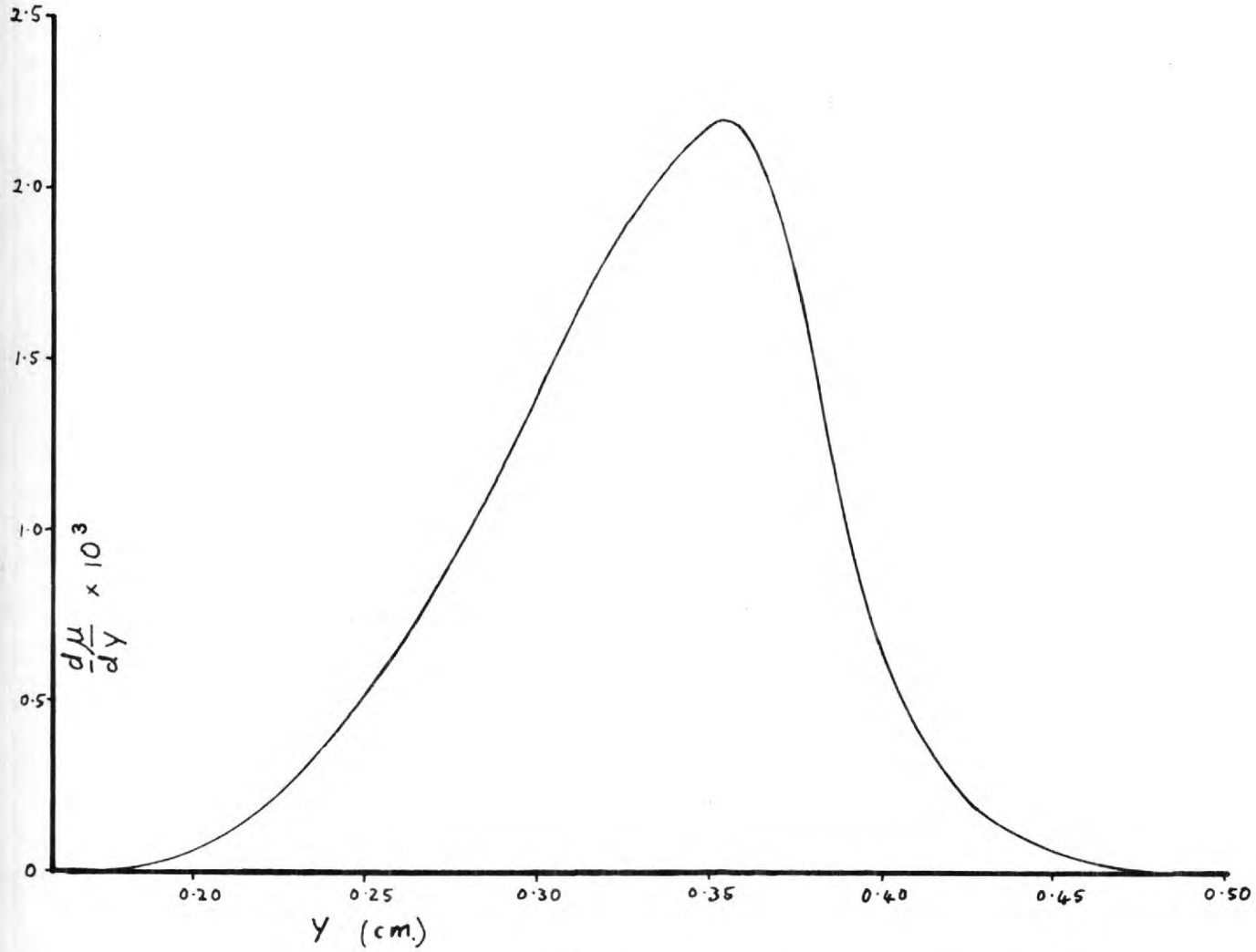


FIG. 24 REFRACTIVE INDEX GRADIENT f(Y)

was due to the fact that, in this region, the deflection due to the outer zones was larger than that due to the zone for which $\frac{d\mu}{dy}$ was being calculated. However it was found that, by a very small adjustment to the maximum value of $-\frac{d\mu}{dy}$, the oscillations could be eliminated.

The resultant refractive index profile for the flame is shown in Figure 24. There are a number of corrections which should be made to this profile [59], the most important of which is the correction due to deviation of the ray within the flame. If $\frac{d^2\mu}{dy^2}$ is a constant then, to within 1% for this flame,

$$\frac{d\mu}{dy} = \frac{du}{dy} \text{ uncorrected } [1 + (l^2/6)(d^2\mu/dy^2)] \qquad (1)$$

The assumption that $d^2\mu/dy^2$ is constant, led to the value of $-\frac{d\mu}{dy}$ near the maximum being nearly 1% low.

From the corrected values for $\frac{d\mu}{dy}$, the refractive index profile, and the first approximation to the temperature profile were calculated. For gases at the temperatures and pressures involved, Gladstone and Dale's equation holds well, so that :

$$\mu - 1 = (\mu_o - 1) \frac{T_o}{T} \frac{P}{P_o} \qquad (2)$$

where μ_o, T_o and P_o refer to refractive index, temperature

and pressure respectively, at S.T.P. Using refractive index values given by Cuthbertson and Cuthbertson [35] and in Kaye and Laby's Tables [60], $(\mu_o - 1)$ was calculated to be 463.5×10^{-6} for the reactants and 441.3×10^{-6} for the products. When the mean of these two values was used to calculate the $\overset{\wedge}{\text{expt.}}$ temperature profile, the final flame temperature was higher than that calculated (see Appendix A). This disagreement could be due partly to experimental error and partly to the effect of composition on refractive index. Since the actual final flame temperature was expected to be close to the calculated value, the $d\mu/dy$ profile was scaled by a factor of 0.909 so that the experimental temperature profile (Figure 25, p.133) reached the calculated final flame temperature.

(6) Calculation of the $[Br_2]$ Profile.

Assuming Beer's Law holds, the intensity (I) of a light ray passing through the flame is given by :

$$\log_{10}\frac{I_o}{I} = \sum_j \epsilon_j \ell_j [Br_2]_j = d \qquad (3)$$

where ϵ_j, ℓ_j and $[Br_2]_j$ are the extinction coefficient, path length and bromine concentration for the j^{th} zone, and d is the optical density. The calculation of $[Br_2]$ from d

was carried out in a similar manner to that described for the temperature calculation. There were, however, three main differences:

(a) $[Br_2]$ at the cold boundary was known but was not zero (cf. $d\mu/dy$).

(b) The zones were terminated at each end of the flame by the boundary between the reactants and the recirculating products (see Figure 23 and Plate 6).

(c) ϵ is a function of temperature and hence varied from zone to zone but optical density does not depend on the angle between the light ray and the zone boundary.

Because d was not known accurately for values of y less than 0.33 cm. and because when y = 0.29 cm. T was only 465°C. the following procedure was used to calculate $[Br_2]$. For values of y less than 0.3 cm., $[Br_2]$ was calculated assuming no reaction or diffusion. The zone for whose mid-point y = 0.31 cm., was given an arbitrary value for $\epsilon[Br_2]$. Values of $\epsilon[Br_2]$ were then calculated successively for higher zones by the numerical method outlined above. It was found that oscillation occurred in the values of $\epsilon[Br_2]$ derived for the next few zones, but it was possible to eliminate it by making small adjustments to the arbitrary value of $[Br_2]_{y = 3.1}$. Table 2 shows the effect of

various values of $\epsilon [Br_2]_{y=3.1}$ on the values in higher zones:

TABLE 2.

y (cm)	Calc. $[Br_2]$	$[Br_2]$ for various values of $\epsilon [Br_2]_{y=3.1}$ (cm^{-1}) 1	2	3	5	7
0.19	0.326					
0.21	0.325					
0.23	0.323					
0.25	0.318					
0.27	0.309					
0.29	0.297					
0.31		0.228	0.270	0.265	0.265	0.265
0.33		0.279	0.214	0.219	0.219	0.219
0.35			0.179	0.169	0.168	0.168
0.37			0.070	0.094	0.1015	0.1041
0.39			0.090	0.066	0.0542	0.0532
0.41				-0.002	0.0152	0.0166
0.43				+0.028	0.0032	0.0001
0.45				-0.054	-0.0169	-0.0124
0.47					-0.0059	-0.0127

It will be noted that $\epsilon [Br_2]$ did not fall to zero at the hot boundary. Consequently, in calculating $[Br_2]$ a small scaling factor was incorporated. Figure 26 (p. 135) shows the fractional disappearance of Br_2 through the flame front.

The bromine concentration and temperature profiles derived here are only first approximations. In the following chapter it will be shown that the composition and hence the refractive index profile can be calculated. Using this profile, the temperatures and consequently the bromine concentrations can be calculated to a second approximation using the methods described above.

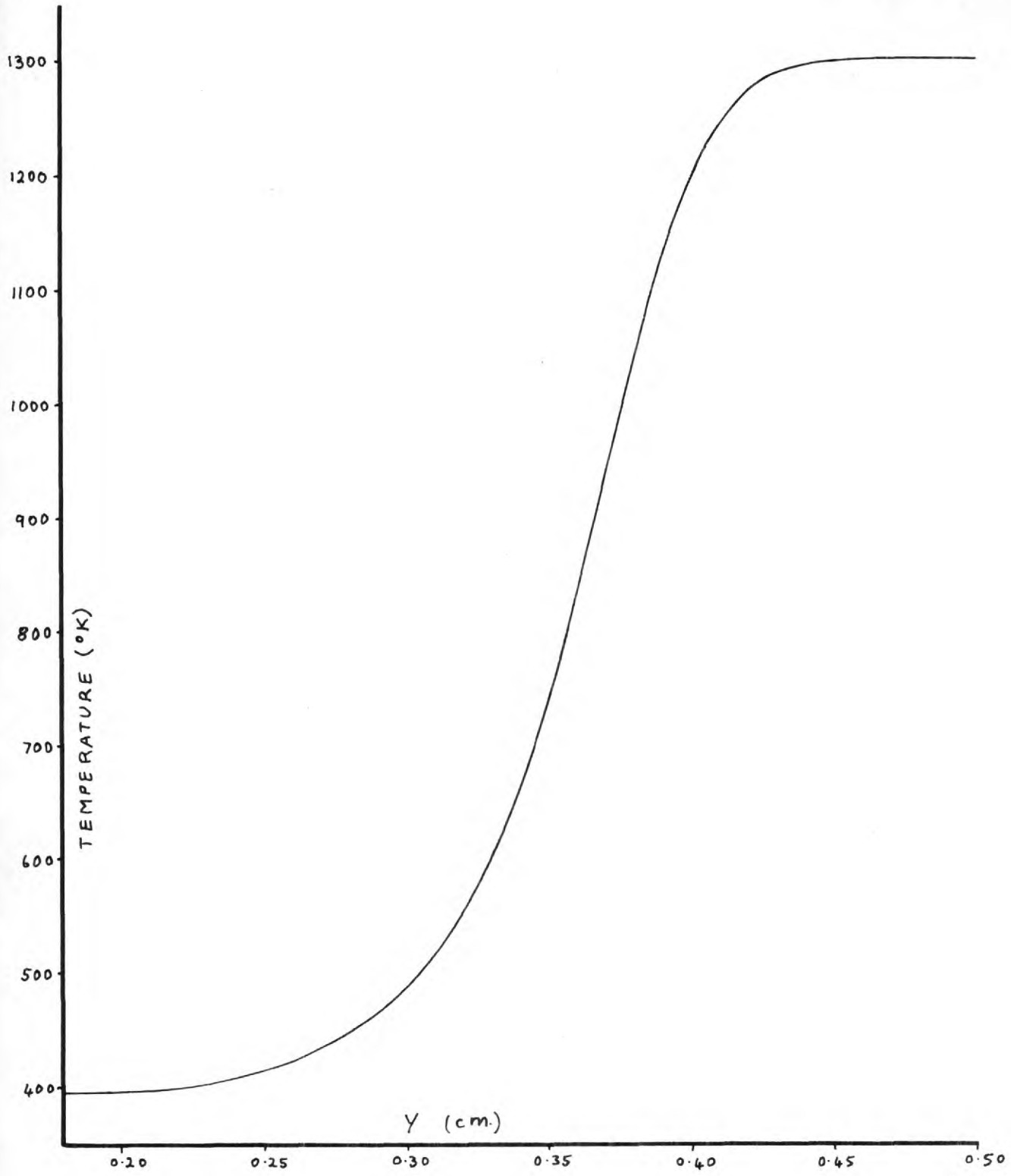


FIG. 25 TEMPERATURE PROFILE

CHAPTER 9.

TREATMENT OF RESULTS.

In this chapter, the treatment of results is demonstrated using the experimental results for one flame and, for this purpose, all experimental errors are ignored. The flame chosen had an initial composition:- 27.5% Br_2, 42.4% H_2 and 30.1% N_2. The initial temperature was 395°K., the final temperature was calculated to be 1302°K. and the measured (S.T.P.) burning velocity was 8.4 cm./sec. Figures 25 and 26 show, respectively, the temperature and bromine concentration profiles, calculated as described in the previous chapter.

(1) The Conservation Equations.

It is convenient to start the flame analysis by evaluating the heat flux and the mass flux for each species and then to calculate the concentrations and reaction rates. In the steady state, the total flux of H, N, and Br atoms, in any form, must be constant, i.e.

$$G_H = 2\,g_{H_2} + g_{HBr} + g_H \qquad (4)$$

$$G_{Br} = 2\,g_{Br_2} + g_{HBr} + g_{Br} \qquad (5)$$

$$G_N = 2\,g_{N_2} \qquad (6)$$

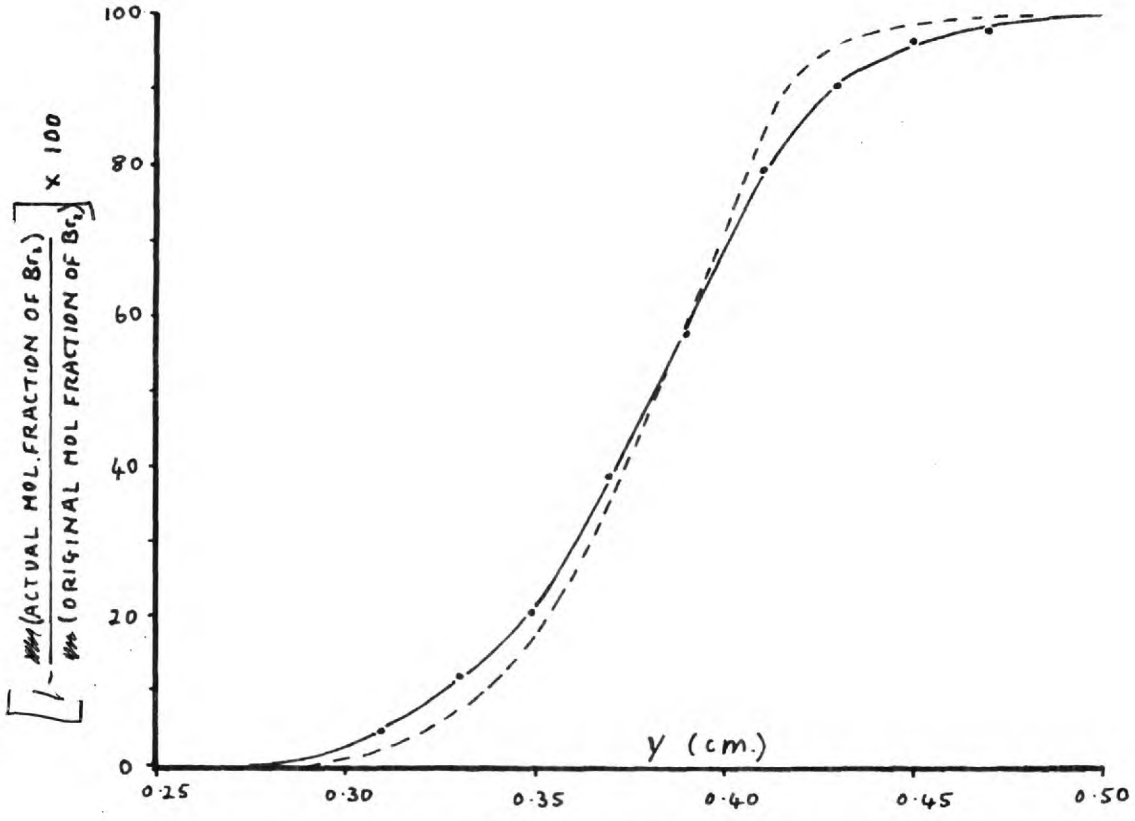


FIG. 2b BROMINE DISAPPEARANCE PROFILE

G_H, G_{Br} and G_N refer to the total flux of atoms, free or combined in molecules and g_j refers to the flux of the j^{th} species present in the flame. Both are expressed in gram-atoms (or gram-molecules) cm^2 sec^{-1}.

Also, the total energy flux (E) must be constant through the flame. Kinetic, radiant and hydrostatic potential energy changes, through the flame front, are not usually important with slow, low temperature flames and to a good approximation

$$\text{Total energy flux} = Q + c \qquad (7)$$

where the heat flux, Q, is assumed to be the sum of the convective and conductive heat fluxes, and c is the chemical energy flux. The standard state for energy flux shall be considered to be that of the reactants at the cold boundary. Hence

$$\text{Total energy flux} = 0 = c_u = Q_u.$$

Assuming ideal gas behaviour

$$Q = \sum_j g_j H_j - \lambda \frac{dT}{dy} \qquad (8)$$

$$c = g_{Br} \triangle H_{Br} + g_H \triangle H_H + g_{HBr} \triangle H_{HBr} \qquad (9)$$

where H_j is the enthalpy of the j^{th} species, the standard state being that of the gas under the conditions at the cold boundary. $\triangle H$ refers to the heat of formation of the species concerned.

In equation (8), the thermal conductivity (λ) can only be obtained if the composition is known. However for a first approximation, the conductivity can be assumed to be a linear function of temperature (see Appendix B). The calculation is further simplified if the specific heat of the mixture is provisionally assumed to vary linearly with temperature from that of the reactants to that of the products. Thus equation (7) becomes :

$$G_H - \lambda \frac{dT}{dy} + g_{Br} \Delta H_{Br} + g_H \Delta H_H + g_{HBr} \Delta H_{HBr} = 0 \qquad (7a)$$

(where H is the enthalpy of the mixture calculated using the above assumption). Since [H] and hence q_H are negligible Equations (4), (5) and (7a) comprise three equations involving g_{H_2}, g_{Br_2} g_{HBr} and g_{Br}.

If g_{Br_2} is now calculated from experimental data, the fluxes of all major species can be obtained to a first approximation.

(2) The Equations of Flux.

The equation for the heat flux has already been given: (equation (8)). Similarly the total flux of any species must be equal to the sum of the convective flux and the diffusive flux. The convective flux is the product of the total molar flux (G) and the mol fraction (n).

At constant temperatures, the diffusion flux for the j^{th} species is given by :-

$$g_j^D = -D_j \, d[j]/dy$$

(D_j = diffusion coefficient of the j^{th} species in the mixture).

A concentration gradient caused by a temperature gradient does not cause diffusion, apart from second order effects (e.g. thermal diffusion). Hence, if the temperature varies, the appropriate diffusion equation would appear to be:-

$$g_j^D = -\frac{D_j}{T} \frac{d[j]T}{dy}$$

Since, for an ideal gas:

$$[j]\,T = P_j/R \qquad (P_j = \text{partial pressure}; \; R = \text{gas constant})$$

the diffusion equation is often written in the form:

$$g_j^D = -\frac{D_j}{RT} \cdot \frac{dP_j}{dy}$$

Since the mol fraction $n_j = P_j/P$

and for 1 mole of an ideal gas $P = RT/V$

$$g_j^D = -\frac{D_j}{V} \cdot \frac{dn_j}{dy} = -D_j [J] \frac{dn_j}{dy} \qquad (10)$$

where $[J]$ is the total molar concentration.

It was convenient to use equation (10) in the form:

$$g_j^D = -D_j [J]_R \cdot \frac{T_R}{T} \cdot \frac{dn_j}{dy} \qquad (11)$$

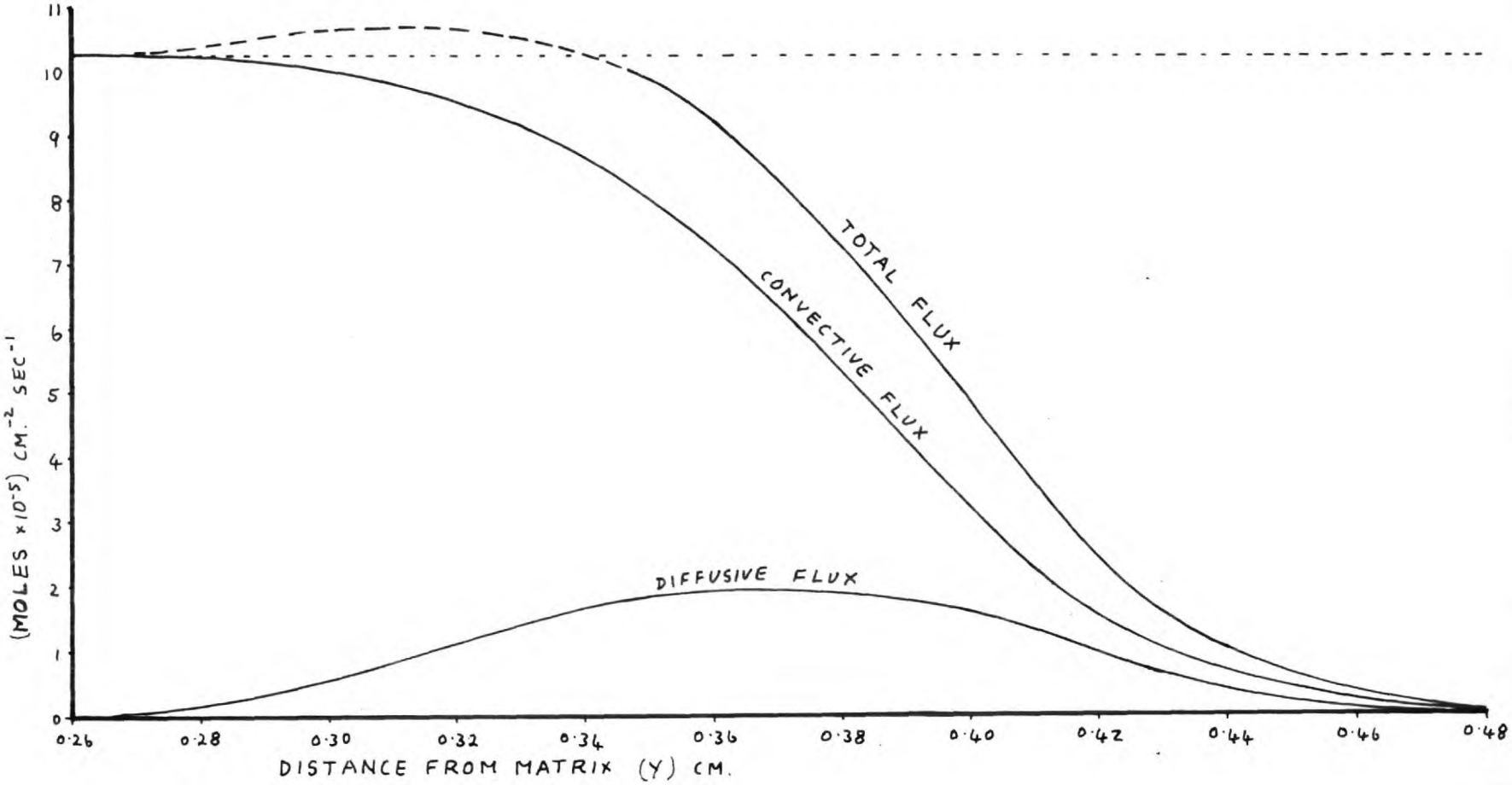


FIG. 27 BROMINE (Br_2) FLUX

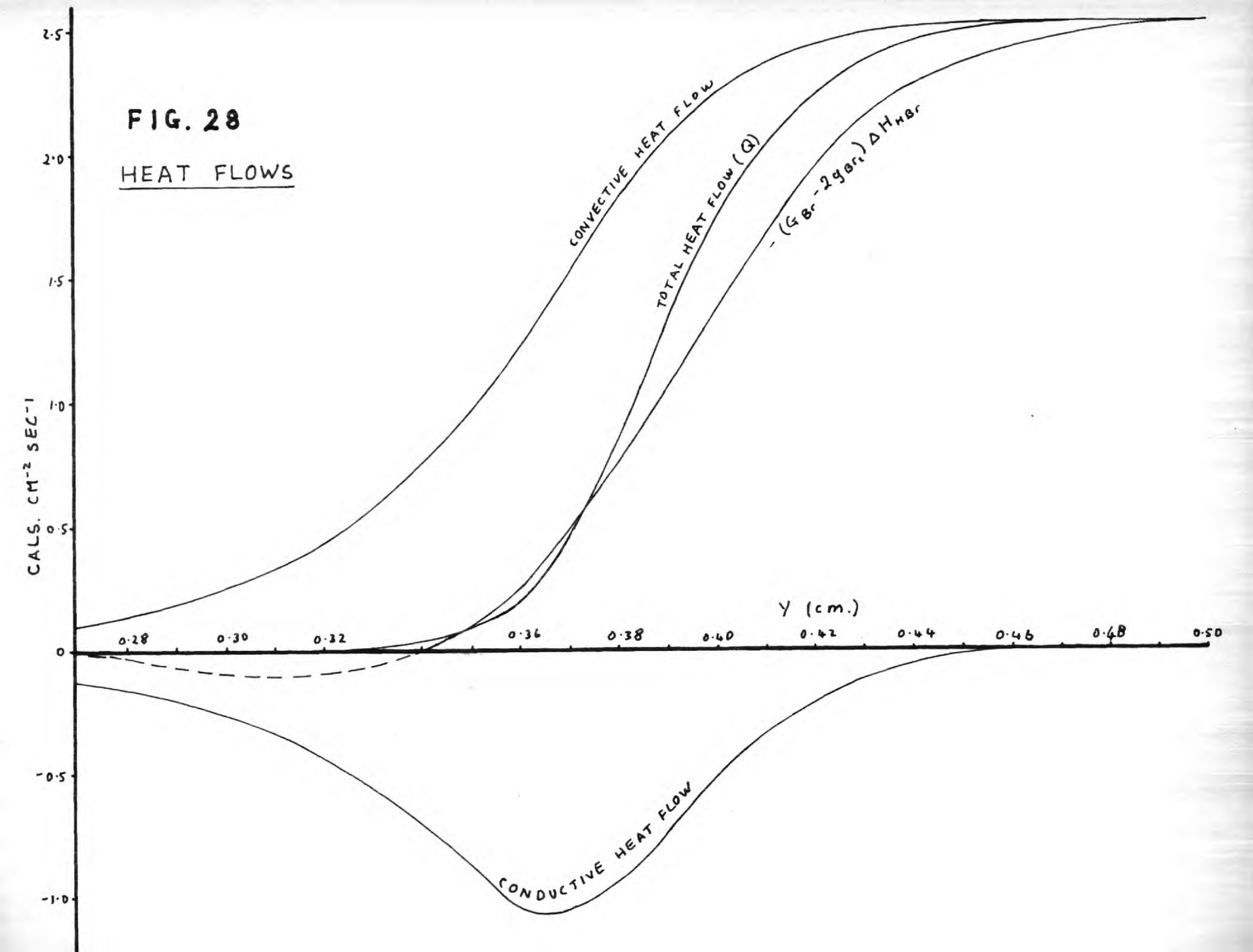
where $[J]_R$ is the total concentration at 0°C., but at the same pressure. T_R is the absolute temperature at 0°C. The full flux equation becomes (using equation (10)):

$$g_j = n_j G - D_j[J] \frac{dn_j}{dy} \qquad (12)$$

The Br_2 flux can now be calculated providing D_{Br_2} is known. However D_{Br_2} can only be found if the local composition is known, so that it is necessary to assume, provisionally, that D_{Br_2} is a linear function of temperature. The calculation of the diffusion coefficient from kinetic theory is discussed in Appendix B.

The convectional, diffusional and total Br_2 fluxes are shown in Figure 27. It will be noted that there is a maximum in g_{Br_2} near the cold boundary. If this were the case in fact, it would mean that a substantial quantity of Br_2 was being produced from products diffusing back from the flame zone. This is unlikely and the effect is probably due largely to errors in $[Br_2]$ or D_{Br_2}.

If g_{Br_2} is known, then from equations (4), (5), (6) and (7), it should be possible to calculate the fluxes for all the major species. Substituting for g_{HBr} in the energy conservation equation, from equation (5), then neglecting terms containing g_{H_2}, and rearranging:


FIG. 28
HEAT FLOWS
CONVECTIVE HEAT FLOW
TOTAL HEAT FLOW (Q)
$-(G_{Br} - 2g_{Br_2})\Delta H_{HBr}$
CONDUCTIVE HEAT FLOW
CALS. CM^{-2} SEC^{-1}
2·5
2·0
1·5
1·0
0·5
0
-0·5
-1·0
Y (cm.)
0·28
0·30
0·32
0·36
0·38
0·40
0·42
0·44
0·46
0·48
0·50

$$g_{Br}\ (\triangle H_{HBr} - \triangle H_{Br}) = Q + (G_{Br} - 2g_{Br_2})\triangle H_{HBr} \quad (13)$$

Figure 28 shows a plot of Q and $-(G_{Br} - 2g_{Br_2})\triangle H_{HBr}$ against y. The value for thermal conductivity (λ) used in the calculation of Q is given in Appendix B. It would appear from Figure 28 that experimental errors and errors due to simplifying assumptions in the calculations are too great for g_{Br} to be obtained at this stage.

If now [Br] is provisionally assumed to be the steady state value, then g_{Br}, g_{H_2} and g_{HBr} can be obtained from the flux equation for Br and from equations (4) and (5). These fluxes are shown in Figure 29.

(3) Calculation of Concentrations.

Since G = S[J], S being the local velocity, then from equation (12) one obtains:-

$$n = \frac{g}{G} + \frac{D}{S_o} \cdot \frac{T_o}{T} \cdot \frac{dn}{dy} \quad (14)$$

Consider the mol fraction of H_2 near the hot boundary, the flame being considered split up into thin zones, each zone having a thickness δ y and constant dn_{H_2}/dy. In the first zone where g_{H_2} deviates measurably from the hot boundary value ($g_u^{H_2}$), dn/dy would be equal to $\frac{n_u - n_{u-1}}{\delta y}$, where n_{u-1} is assumed to be the value of the mol fraction at the lower

FIG. 29 FLUX OF SPECIES OTHER THAN H·

MOLES × 10^{-5} CM.$^{-2}$ SEC^{-1}

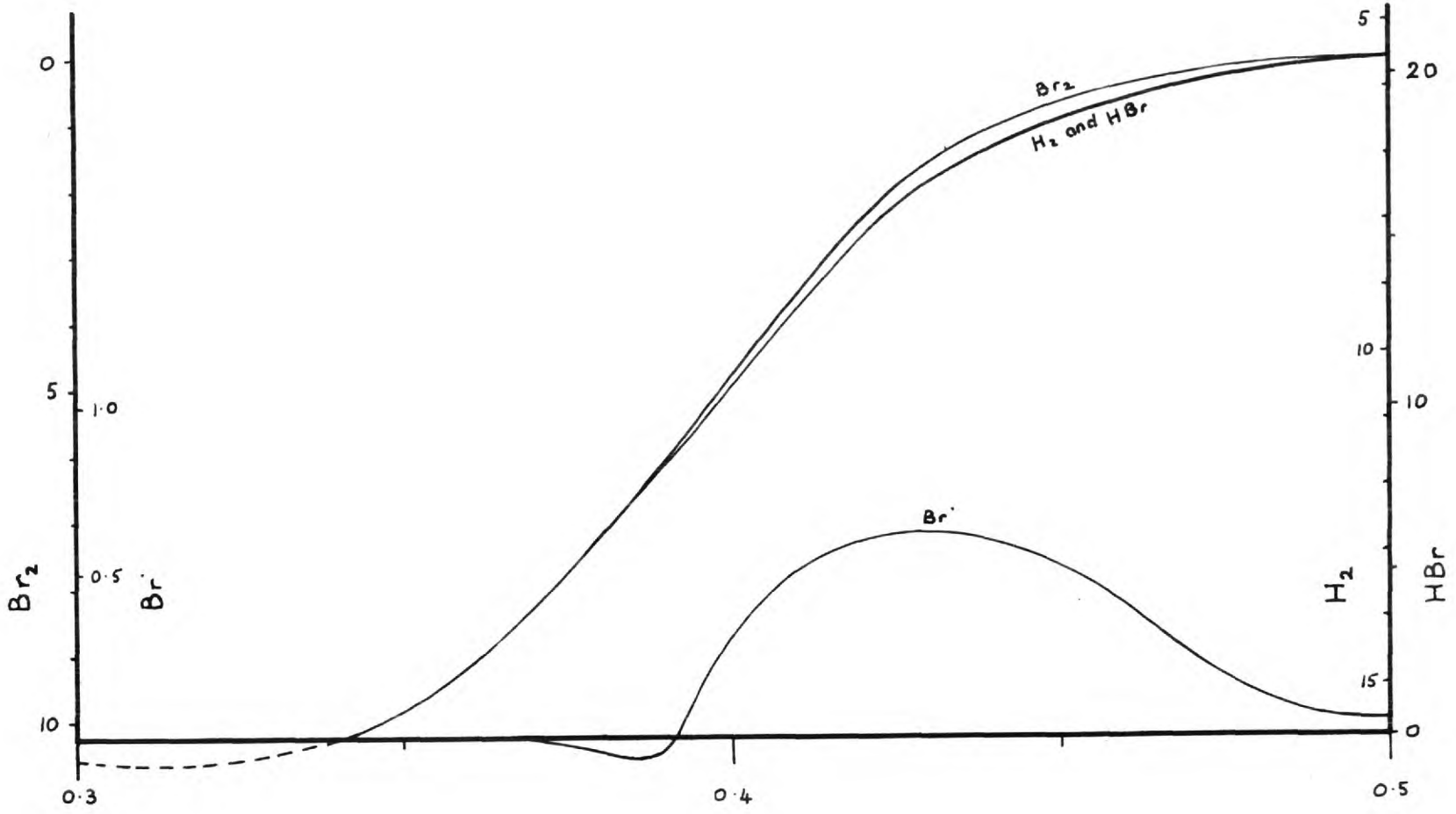


TABLE 3.

FLUXES OF INDIVIDUAL SPECIES $x10^5$ (moles cm^{-2} $sec.^{-1}$)

y(cm.)	g_{Br_2}	g_{H_2}	g_{HBr}	g_{Br}	g_{N_2}	G
0.26	10.25	15.81	0.00	0.00	11.23	37.30
0.28	10.40	15.96	- 0.30	0.00	"	37.30
0.30	10.63	16.19	- 0.76	0.00	"	37.30
0.32	10.66	16.22	- 0.82	0.00	"	37.30
0.34	10.27	15.83	- 0.04	0.00	"	37.30
0.36	9.22	14.78	2.06	0.00	"	37.30
0.38	7.21	12.75	6.13	0.05	"	37.27
0.40	4.90	10.62	10.39	0.31	"	37.45
0.42	2.44	8.30	15.02	0.60	"	37.60
0.44	1.05	6.91	17.80	0.60	"	37.60
0.46	0.46	6.22	19.18	0.40	"	37.50
0.48	0.14	5.76	20.11	0.11	"	37.36
0.50	0.02	5.60	20.42	0.04	"	37.32

boundary of the element. The value of n_{u-1} can then be obtained directly from equation (14), By repeating the operation n_{H_2} can be obtained for successive zones until the cold boundary is reached.

This procedure was carried out for n_{H_2}, n_{HBr} and n_{N_2}, though in the last case the mol fraction was found to be almost constant. Due to errors in diffusion coefficients, the sum of the mol fractions diverged from unity. Accordingly n_{H_2} and n_{HBr} were multiplied by the appropriate scaling factor. The mol fractions of the various species are shown as functions of y in Figure 30. Molar concentrations can be calculated from the mol fraction and the temperature.

Now the composition distribution is known to a first approximation, more accurate values for μ and hence T and $[Br_2]$, can be obtained in the first instance. The calculation of fluxes and concentrations can then be repeated, using more accurate values for enthalpies, conductivities and diffusion coefficients, and if necessary the whole process can be repeated several times to obtain the required accuracy.

FIG. 30 MOL FRACTIONS f(Y)

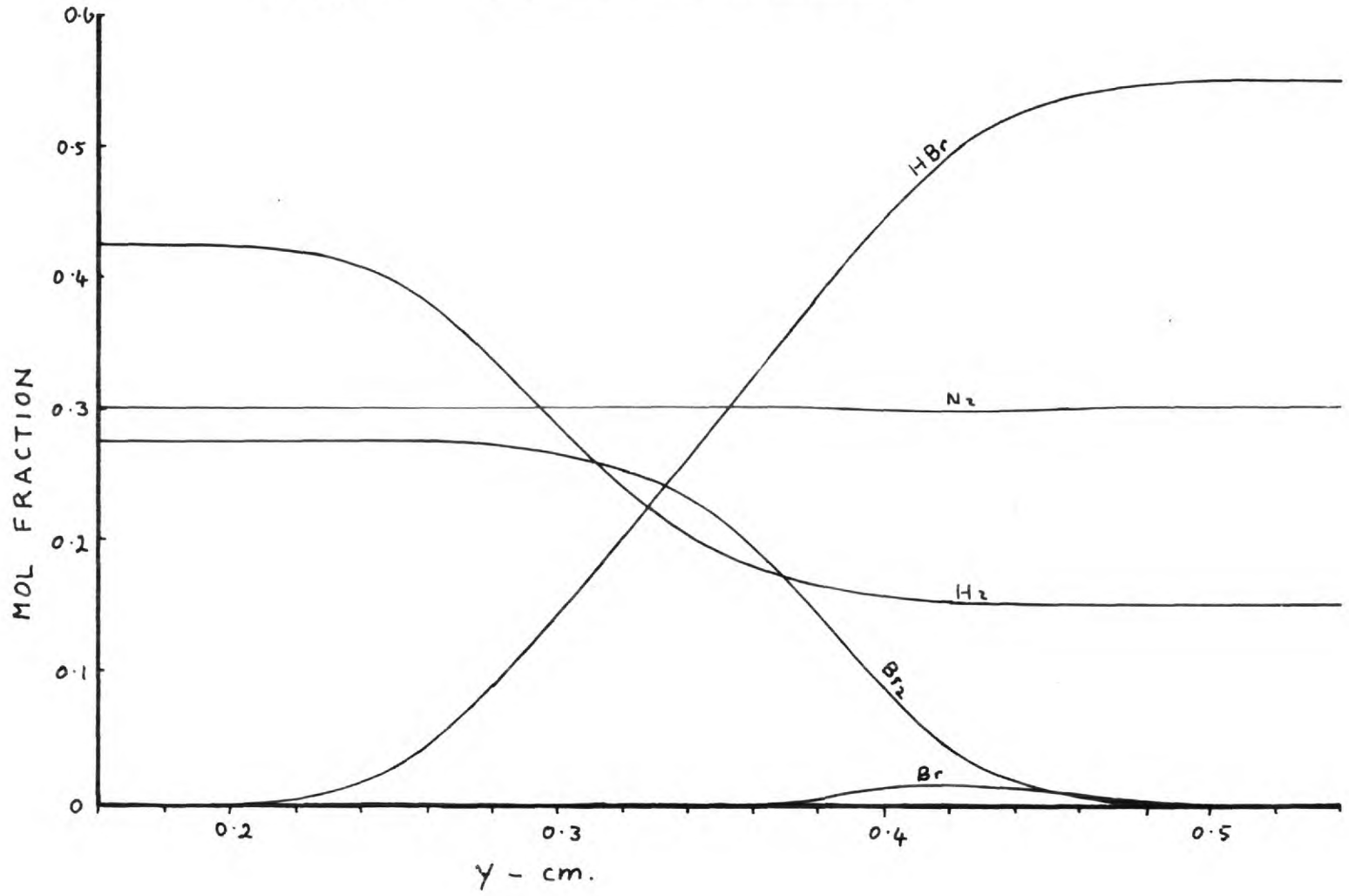


TABLE 4.

MOL FRACTIONS OF EACH SPECIES (x 100)

y	T	n_{Br_2}	n_{H_2}	n_{HBr}	n_{Br}	n_{N_2}
0.18	395	27.5	42.4	0.0		30.1
0.20	396	27.5	42.3	0.1		30.1
0.22	400	27.5	42.0	0.4		30.1
0.24	407	27.5	40.8	1.6		30.1
0.26	422	27.5	38.1	4.3		30.1
0.28	448	27.3	33.8	8.8		30.1
0.30	488	26.4	28.6	14.4		30.1
0.32	554	25.5	24.0	20.4		30.1
0.34	665	23.2	20.3	26.9		30.1
0.36	846	19.5	17.9	32.5	0.0	30.1
0.38	1053	14.3	16.6	38.7	0.4	30.0
0.40	1204	8.8	15.8	44.3	1.2	29.9
0.42	1272	4.0	15.3	49.4	1.4	29.9
0.44	1297	1.7	15.1	52.3	1.0	29.9
0.46	1301	0.7	15.0	53.9	0.4	30.0
0.48	1302	0.2	15.0	54.7	0.1	30.1
0.50	1302	0.0	15.0	54.9	0.1	30.1

(4) Reaction Rates.

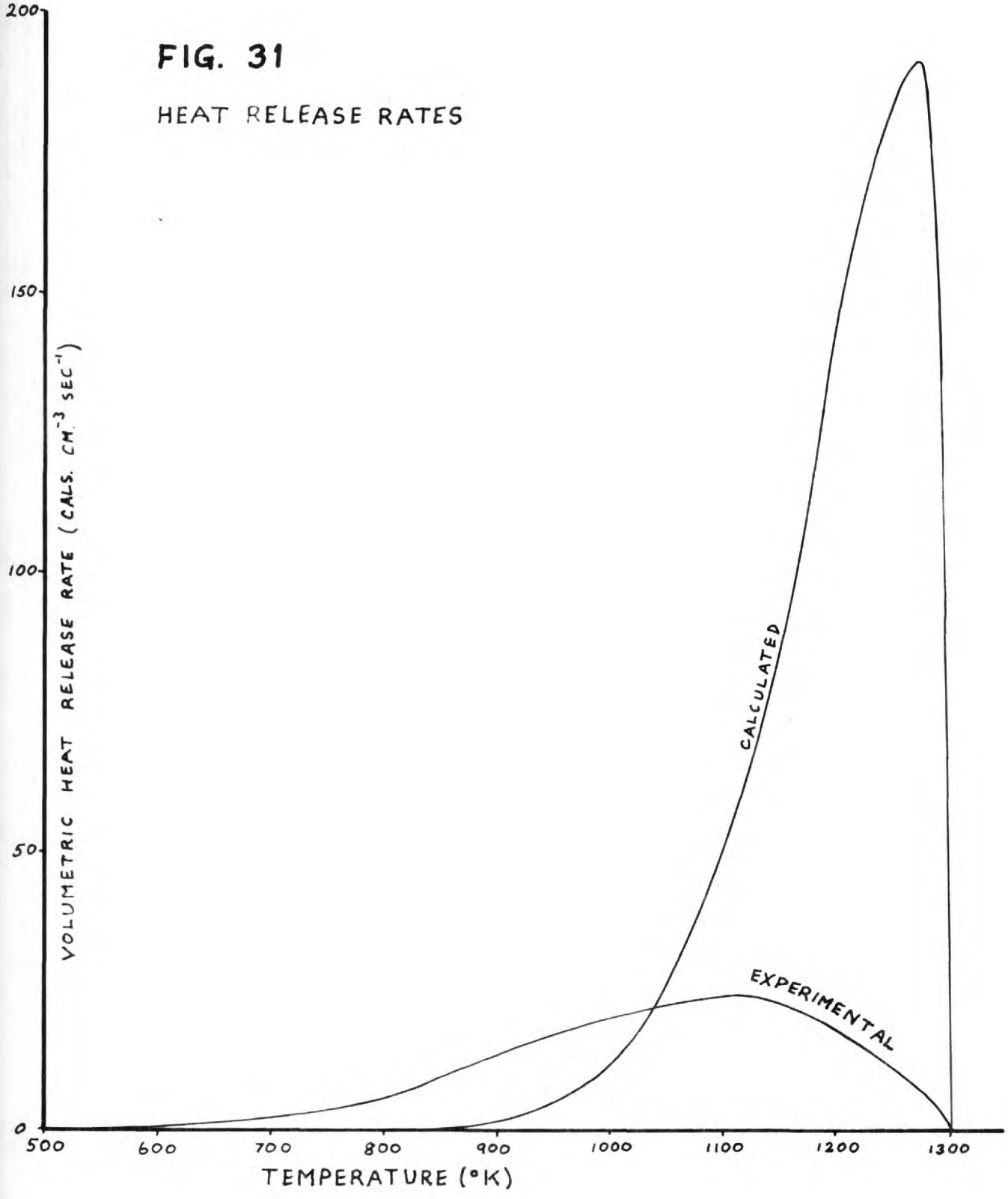
Consider a thin element of flame front of unit area and thickness δy. If the flux of j into that element is g_j and that out of the element is $g_j + \delta g_j$, then the difference δg_j must be equal to the number of moles of j created within that element per sec., per cm^2. Hence the rate of change of flux with distance (dg_j/dy) is equal to the volumetric rate of production of j. Similarly, the volumetric heat release rate is equal to $\frac{dQ}{dy}$.

Thus the rates of reaction of all species except H are known and calculations (e.g.[6]) have shown that $\frac{d[H]}{dt}$ should be close to the steady state value. Only two of these are independent reaction parameters e.g. d[HBr]/dt and d[Br]/dt. However in the classical low temperature studies only one such parameter was measured.

For the purposes of flame kinetics, it is most important to obtain an expression giving the rate of reaction as a function of local species concentrations and temperature, regardless of the detailed reaction mechanism. The concentrations of all species do not necessarily have to be known to calculate such an expression, since the concentration of all species in the chemical steady

FIG. 31

HEAT RELEASE RATES



state is a function of the concentration of the remaining components. It is consequently important to know which intermediates do obey the steady state approximation. Thus at low temperatures, H and Br are in the steady state and it is found (41,36,40) that

$$\frac{d[HBr]}{dt} = \frac{\alpha [H_2] [Br_2]^{\frac{1}{2}}}{\beta + [HBr]/[Br_2]} \qquad (15)$$

where α is a function of T and β is a constant.

In hydrogen-bromine flames, the expression may not be so simple, due to deviations from the steady state approximation for [Br]. However since the latter can be measured, an expression for reaction rate and the rate constants should be calculable from the measured profiles of T, dg_{Br}/dy and dg_{HBr}/dy for flames of different initial composition. The first step would be to find if equation (15) described the reaction rate for any composition and temperature range. Expressions involving [Br] could then be tried.

It is interesting to compare the experimental heat release rate with that calculated from the experimental concentration profiles and the kinetic data derived from high temperature flow studies [40] (see Figure 31). If both heat release curves are accurate, any differences

between the two may be due to

(1) deviation of [Br] from the steady state value,

(2) alternative reaction mechanisms becoming significant,

(3) the kinetic data derived from flow systems being unsuitable for the extreme conditions occurring in flames.

(5) Detailed Reaction Kinetics.

For hydrocarbon-air flames, it appears difficult to obtain a complete expression for the reaction rate, due to the complexity of the reaction, but a simplified rate equation may give useful results (e.g. [29]). In the simpler case of the H_2 - Br_2 flame, it should be possible to obtain a reasonably exact expression for the reaction rate, which can be interpreted in terms of a reaction scheme similar to that postulated for the low temperature reaction (see Chapter 2, p.25).

It is of interest to see how much information can be obtained if a more rigorous approach is used, assuming perfect experimental accuracy. Campbell and Fristrom [36] consider the following reactions may be significant in H_2 - Br_2 flames :-

$$M^* + Br_2 \rightleftharpoons 2Br + M \qquad (1)$$

$$M^* + H_2 \rightleftharpoons 2H + M \qquad (2)$$

$$Br + H_2 \rightleftharpoons HBr + H \qquad (3)$$

$$H + Br_2 \rightleftharpoons HBr + Br \qquad (4)$$

$$M + H + Br \rightleftharpoons HBr + M^* \qquad (5)$$

$$H_2 + Br_2 \rightleftharpoons 2HBr \qquad (6)$$

M refers to any constituent.

If K_j is the equilibrium constant for the j^{th} reaction and k_j^f and k_j^r are the forward and reverse rate constants, then:

$$K_j = k_j^f / k_j^r$$

Also there are three relationships between the equilibrium constants. For example:

$$K_3 K_4 = \frac{[HBr][H]}{[Br][H_2]} \cdot \frac{[HBr][Br]}{[H][Br_2]} = \frac{[HBr]^2}{[H_2][Br_2]} = K_6$$

Similarly $K_1 K_5 = K_4$ and $K_2 K_5 = K_3$.

Using now the experimental data, the expressions for the rate of production of each species can be written. Thus, for the case of Br_2 :

$$\frac{dg_{Br_2}}{dy} = k_1^r [M][Br] - k_1^f [M][Br_2] + k_4^r [Br][HBr] - k_4^f [H][Br_2] + k_6^r [HBr] - k_6^f [H_2][Br_2]$$

In principle, by burning a series of flames of different initial temperatures, pressures and compositions, the concentration of all species can be varied independently for a given temperature. The value of the reaction rate, if both $[Br_2]$ and $[Br]$ were extrapolated to zero, would be given by :

$$\left(\frac{\partial g_{Br_2}}{\partial y}\right)_{\substack{[Br_2]=0 \\ [Br]=0}} = k_6^r \; [HBr]^2$$

thus giving the value of k_6^r. It is not possible, however, to calculate the remaining rate constants in a similar manner because the nature of the third bodies is uncertain. An empirical approach therefore seems necessary.

(6) Measurement of Transport Functions.

The thermal conductivity and the diffusion coefficient of Br_2 can be found for conditions at the cold boundary. Now, heat flux is given by :

$$Q = GH - \lambda \frac{dT}{dy} \qquad (8a)$$

In the pre-reaction zone $Q = 0$ and, as $T \rightarrow T_u$

$$GH \Big/ \frac{dT}{dy} \rightarrow \lambda_u$$

similarly, from equation (12), as $T \rightarrow T_u$

$$(Gn_{Br_2} - g^{u}_{Br_2}) / [J] \frac{dn_{Br_2}}{dy} \longrightarrow D^{u}_{Br_2}$$

These values for the conductivity and diffusion coefficient of Br_2, at the cold boundary, provide very useful reference points for calculating λ and D_{Br_2} elsewhere in the flame. (For comparison with calculated values see Appendix B).

For H_2 - Br_2 flames having low final flame temperatures, [Br] is small and, since $D^{u}_{Br_2}$ is also small, the rate of heat release can be calculated with considerable accuracy from the measured $[Br_2]$ profile. Hence using equation (8a) it would be possible to calculate the thermal conductivity profile. This procedure involves an assumption concerning the chemical kinetics (i.e. [Br] = 0) but it is considered here because it may prove that the chemical kinetics can be evaluated before the conductivity.

(7) Conclusions.

It has been shown that, providing the required thermodynamic and transport data are available, the concentrations and rates of reaction of all significant species except H can be calculated. Since [H] is thought to be close to the steady state value, it should be possible

to obtain a general expression for the rate of reaction, in terms of the local temperature and concentrations of species other than H. In this simple system, the detailed reaction kinetics may be obtained by fitting an empirical reaction scheme to the results, a more rigorous approach appearing unfruitful. A knowledge of the effect of diffusion and convection of Br on the reaction rate, is implicit in such results.

Finally, it has been shown that λ and D_{Br_2} can be evaluated for conditions at the cold boundary and that the former can be calculated for any point in the flame, if D_{Br_2} is known and providing certain assumptions can be made regarding the chemical kinetics.

CHAPTER 10.

EVALUATION OF TECHNIQUES AND RESULTS.

(1) Burning Velocities.

The burning velocity measurements should be accurate to within 5%. It was possible in this work to compare the projected horizontal flame diameter with the diameter of the column of reactants just below the flame, the latter being obtained from photographs of the flame taken by transmitted light. The two values were found to be in agreement to within 2%.

The major errors in the determination of the composition of the reactants, were probably those occurring in the sampling procedure and those due to non-ideal behaviour. These would limit the accuracy of the concentrations to approximately 1% of the total.

(2) The Analysis of the Flame Zone.

For the flame analysed in Chapter 9, the limits to the experimental accuracy were principally due to :

(a) the finite width of the inclined slits, together with the diffraction effects produced by them;

(b) the uncertainty in the recorded flame shape;

(c) possible movement of the flame;

(d) inexact alignment of the deflection profile with the absorption profile.

There are several other experimental points over which there is some uncertainty: - the possibility of pre-reaction, the effect of impurities in the reactants - especially water vapour and products of the attack on the matrix material, and adjacency effects occurring during the processing of the photographic plate used for the absorption measurement. Further experimental work would be required to finally assess the importance of these factors, which are neglected in this preliminary investigation.

The effect of the major sources of experimental error on the temperature and bromine profiles will now be considered.

(3) Slit Width and Diffraction Effects.

Using the thicker lean ethylene-air flat flames, the error due to using an effective slit width of 0.6 mm. would not be a severe limitation. However, with the H_2-Br_2 flame examined, $(d\mu/dy)_{uncorrected}$ falls from its maximum value to 10% of the maximum value in 0.6 mm.

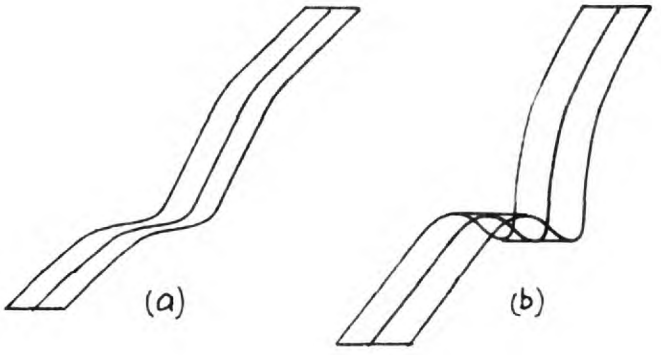
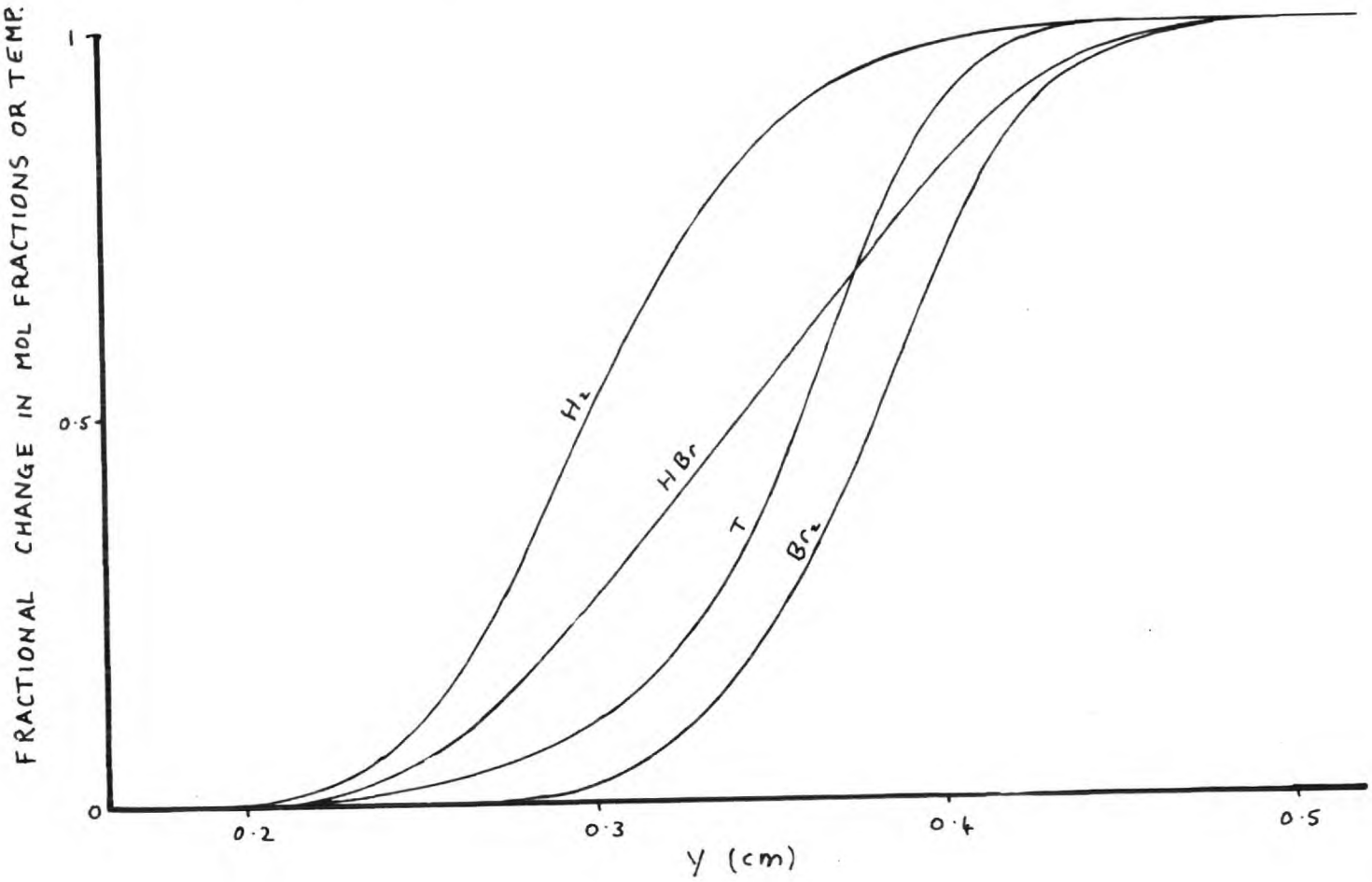


FIG. 32

Hence to obtain sufficient resolution from such a slit, the slit image would have to be measured up to a fraction of its width. Earlier workers [59,29] have either measured the position of the centre of the image when using a relatively wide slit or the middle of the central diffraction fringe if a narrower slit was used. A similar approach to the latter was used in this work, but it is only strictly valid when the refractive index gradient varies linearly across the slit width. Figure 32a shows the images of three thin inclined slits, placed close together, assuming no diffraction. If these images are now considered to be the edges and the centre of a wide inclined slit image, it is clear that it would be correct to use the shape of the edge of the image or the centre measured horizontally across the image. If the rays cross as in Figure 32b, then the horizontal centre profile cannot be measured over part of the curve.

Rigid interpretation is made much more difficult by the presence of diffraction. The position of a fringe depends on the interference of light rays coming from regions of different refractive index gradients. Consequently the fringe shape is difficult to interpret. Photographs showing the complexity of the fringe patterns

FIG. 33


FRACTIONAL CHANGE IN MOL FRACTIONS OR TEMP.
1
0·5
0
0·2
0·3
0·4
0·5
y (cm)
H₂
HBr
T
Br₂

which are often produced are given in a paper by Levy and Weinberg [29].

There is a further, essentially photographic, effect which must be considered. When a fringe is weak the photographic image will appear thinner than when the fringe is brighter, or given a longer exposure. Similarly, where a fringe is curved, the outside of the curve is less bright than the inside, so that the apparent middle of the fringe is displaced to the inside of the real centre. This type of effect also makes quantitative shadowgraphy, using a knife edge, unreliable.

It will be shown later, that the area under the deflection curve is very close to the value calculated from the final flame temperature and errors, due to diffraction effects, can best be judged from the scatter of points in Figure 21 (p.117). This scatter is considerable in the region where the deflection is decreasing with y and the shape of the du/dy curve derived from these results is uncertain. However the temperature profile is relatively insensitive to the form of this curve, providing the values of $d\mu/dy$ are scaled to give the final flame temperature.

This can be usefully demonstrated by considering

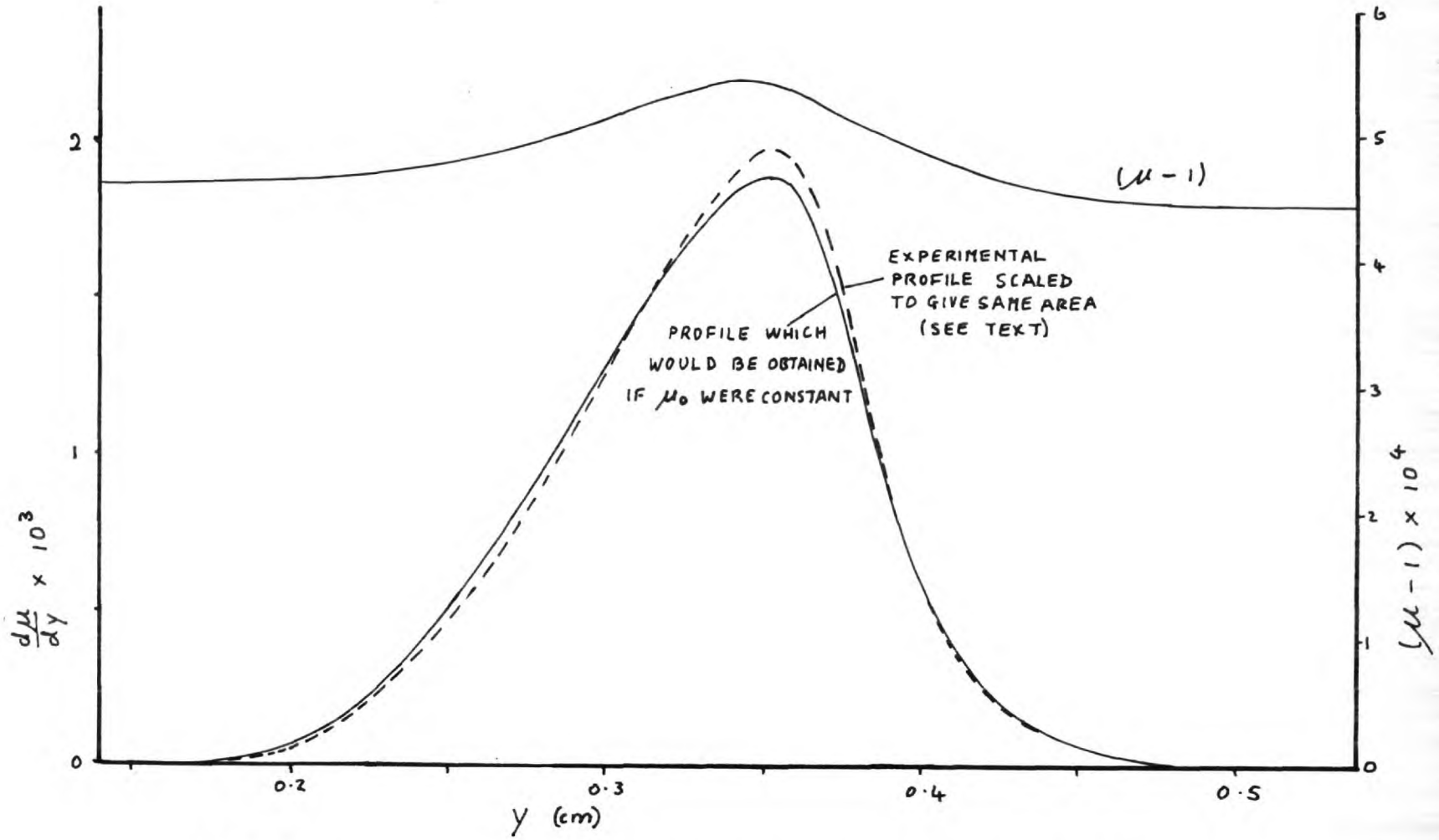


FIG. 34 EFFECT OF COMPOSITION ON μ AN $d\mu/dy$

the effect of composition on refractive index and consequently on the temperature profile. As the reaction zone is approached from the cold boundary, the hydrogen concentration falls off much earlier than the bromine concentration (see Figure 33). Since the hydrogen which has diffused towards the hot boundary must be largely replaced by hydrogen bromide, and because the refractive index of bromine and hydrogen bromide are much larger than that of hydrogen, there is a maximum in μ_o in the flame front. This is shown in Figure 34. Also shown is the $d\mu/dy$ profile which would be obtained if μ_o were constant through the flame and the experimental $d\mu/dy$ profile scaled to give the same enclosed area (which is found to be within 1.7% of that calculated from μ_u and μ_b). These two profiles are seen to be closely similar even though the maximum value of μ_o is over 20% larger than μ_o for the products.

The effect of diffusion on refractive index would be expected to be particularly important with hydrogen-bromine flames, so that it is pleasing to note that, for this flame, the assumption that μ_o is constant through the flame would result in a maximum error of about 12% in dT/dy and

of less than 2% in T. Since the specific heats of H_2, Br_2 and HBr differ much less from each other than the respective refractive indices, the assumption that the specific heat varies linearly with temperature, from that of the reactants to that of the products, can be expected to cause very little error in the convective heat flux.

(4) Flame Shape.

Errors due to inaccuracies in the flame shape are difficult to estimate. The image of the lower edge of the luminous zone was considered to be free from optical distortion due to the refractive index gradient in the flame [71] but the true lower edge may have been masked by parts of the luminous zone which were out of focus. In addition, the plane of the flame may not have been exactly horizontally aligned with the camera. Over the major part of the flame, it is unlikely that the measured position of the luminous zone was more than 0.2 mm. in error, though an error of similar magnitude was possible due to the whole flame front being at a slight angle to the horizontal. The most probable effect of these errors, in the present case, would be to broaden the absorption and deflection profiles, but the very steepness of the latter would indicate that such

effects are not limiting. However the slight negative value for $[Br_2]$, at the hot boundary, obtained in the zone analysis, would indicate that errors, in the recorded flame shape or the bromine boundaries at the edge of the flame, were present. The effect of such errors is largely removed on scaling the bromine profile to give $[Br_2] = 0$ at the hot boundary.

(5) Flame Movement.

The movement of the flame during photographic exposures affects primarily the recorded density profile. From an inspection of photographs taken before and after the absorption record, it would appear that the flame may have moved 0.5 mm., but almost certainly less than 0.8 mm., during the exposure. If however a uniform movement of 0.8 mm. had occurred, the corrected bromine disappearance curve would have been approximately that shown dotted in Figure 26. Thus, even in the extreme case, the assumption in Chapter 9 that zero movement had occurred would, up to 70% reaction, cause an error in the local bromine concentration of less than 5% of the initial concentration.

(6) Alignment of Deflection and Absorption Profiles.

The vertical alignment between the deflection and absorption profiles was probably better than 0.1 mm. However a change in y of 0.1 mm. may correspond to a change in T of 10% or more in some regions, and such an error could also largely account for the maximum in g_{Br_2} (see Figure 27, p.139).

(7) Treatment of Results.

It will be shown in the following section that by far the major errors in this simple treatment of the results are due to the transport data. Several other possible sources of error are discussed here.

Firstly, throughout the calculations, ideal gas behaviour has been assumed. Cooley and co-workers [62] have shown that for Br_2, between 78.4°C. and 132°C., the product PV is 2% lower than that for an ideal gas. However at the temperatures occurring in the reaction zone the deviations from ideal gas behaviour would be expected to be much less than this.

Secondly it can be seen from Figure 18, p.101, that the extinction coefficient varies, with wavelength, by about 4% across the band width produced by the monochromator.

This means that the fraction of light of the shortest wavelengths which is transmitted below the flame is approximately 20% greater than the equivalent fraction for the longest wavelengths. However the mean of these two values is within 0.5% of the fraction of light of the mean wavelength transmitted below the flame. Since all the light was assumed to be of this mean wavelength, errors due to the finite band width will be negligible.

The values for the extinction coefficient, which were used in the calculations, were probably accurate to within 5% up to 900°K., but at 1300°K. they may be 10% or more in error. Any major errors at the lower temperatures seem very unlikely in view of the very good agreement between the author's value for ϵ at 24°K. and that interpolated from the data of Acton, Aickin and Bayliss [55].

Finally, in Figure 31, p. 149the experimental volumetric heat release rate is compared with that calculated from the experimental $[H_2]$, $[Br_2]$ and [HBr] values, using the kinetic data of Levy [40]. Near the hot boundary the 'calculated' heat release rate is very much larger than the experimental value. When the former is integrated with respect to distance, the total heat release is found to be more than three times the experimental value.

This result may be partially explained by the fact that the rate constant k_3^f found by Levy may have been more than 50% in error. In addition, the experimental values for $[Br_2]$ above 1200°K. are almost certainly too large. However, even when allowance is made for these factors, it is clear that the maximum 'calculated' heat release rate must be at least twice the experimental value. In contrast, below 880°K. the experimental heat release rate is more than ten times larger than the calculated value.

It is very unlikely that this is basically due to experimental error or to diffusion effects, but it could be due largely to errors in thermal conductivity. The effect of inaccuracies in transport data will now be discussed.

(8) Transport Data.

The difficulty of measuring the temperature at which appreciable reaction begins has been commented on by several workers (e.g. Linnett [8]). Both Q and dQ/dy, at the beginning of the reaction zone, must be obtained as the difference of two large quantities. Thus since

$$Q = M H - \lambda \frac{dT}{dy}$$

an error of $\delta\lambda$ in λ will produce an error in Q of :

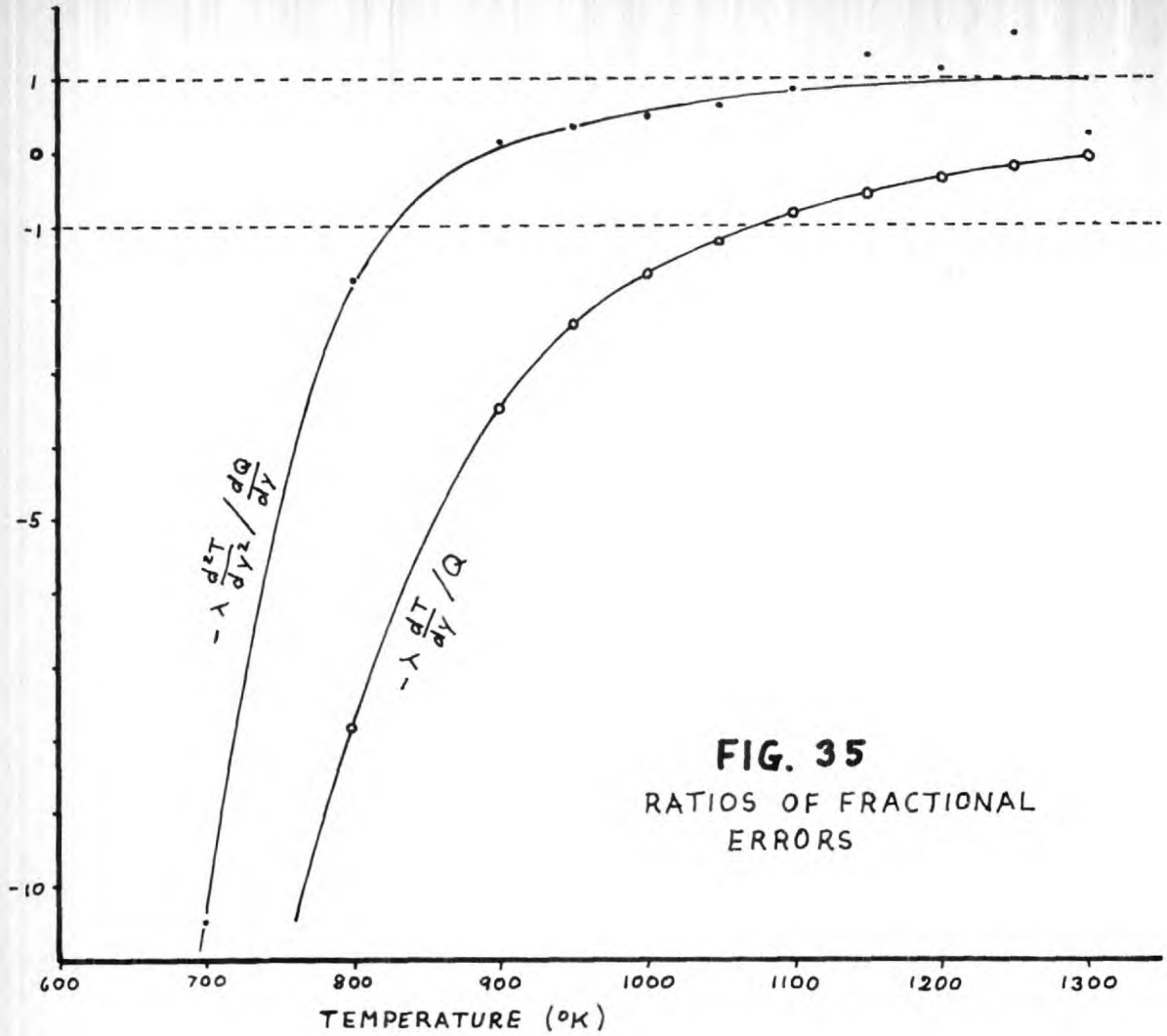


FIG. 35
RATIOS OF FRACTIONAL ERRORS

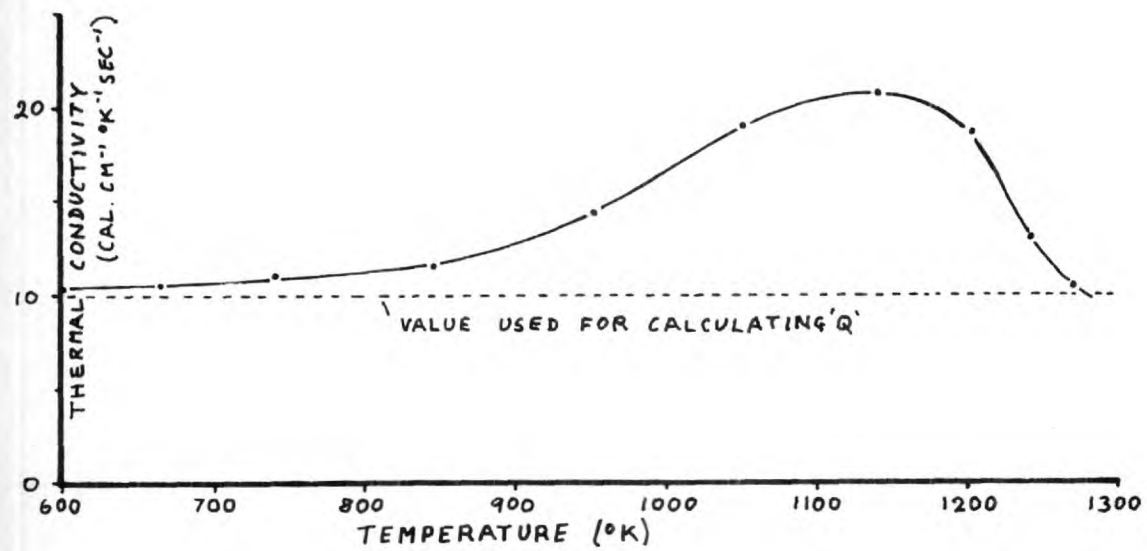


FIG. 36 CALCULATED THERMAL CONDUCTIVITY (See Text)

$$\delta Q = -\delta\lambda \frac{dT}{dy}.$$

$$\frac{\text{Fractional error in } Q}{\text{Fractional error in } \lambda} = \frac{-\delta\lambda \frac{dT}{dy}}{Q} \frac{\lambda}{\delta\lambda} = -\frac{\lambda \frac{dT}{dy}}{Q}$$

similarly in the case of $\frac{dQ}{dy}$, if λ can be assumed approximately constant with temperature :

$$\frac{dQ}{dy} \doteq M \frac{dH}{dy} - \lambda \frac{d^2T}{dy^2}$$

$$\text{and } \frac{\text{Fractional error in } \frac{dQ}{dy}}{\text{Fractional error in } \lambda} \doteq \frac{-\lambda \frac{d^2T}{dy^2}}{\frac{dQ}{dy}}$$

The ratio of fractional errors is plotted in Figure 35 for both Q and $\frac{dQ}{dy}$. Both the fractional error in Q and that in $\frac{dQ}{dy}$ become infinite at the cold boundary (assuming a finite accuracy for λ). It is interesting to note that $\left|\frac{\delta Q}{Q}\right| < \left|\frac{\delta\lambda}{\lambda}\right|$ only for temperatures above 1070°K. whereas $\left|\delta\left(\frac{dQ}{dy}\right) / \frac{dQ}{dy}\right| < \left|\frac{\delta\lambda}{\lambda}\right|$ at 830°K. and above.

To demonstrate the sensitivity of Q to errors in λ, the calculated heat release curve was given in a semi-empirical adjustment so that it gave the experimental total heat release. The thermal conductivity required to make the experimental value of Q (or dQ/dy) equal the calculated value was then calculated and is plotted against T in Figure 36.

Very similar errors occur when calculating the bromine flow, though, since D_{Br_2} is much lower than the thermal diffusivity $\left(\frac{\text{thermal conductivity}}{\text{density x specific heat}}\right)$, the errors are less serious. Inaccuracies in the calculated D_{Br_2}, at the lower temperatures, may be at least partly responsible for the maximum in g_{Br_2} near the cold boundary.

The diffusion coefficient of hydrogen is so large that the shape of the g_{H_2} profile has little effect on the n_{H_2} profile derived from it. However, in the present work, the dependence of hydrogen concentration on the diffusion coefficient is relatively unimportant since the hydrogen was present in excess.

Thus it appears that in spite of the considerable experimental errors, uncertainty in the thermal conductivity data was the most important limitation in the determination of the volumetric heat release rate. In addition the possible inaccuracies in the values used for D_{Br_2} may be responsible for the major errors in g_{Br_2} up to 70% reaction, though beyond this point flame movement and especially errors in the recorded flame shape were more important.

CHAPTER 11.

DISCUSSION AND RECOMMENDATIONS FOR FUTURE WORK.

The substantial practical difficulties associated with the stabilization of a flat hydrogen-bromine flame have been very largely overcome. The behaviour of these flames has been studied and burning velocities have been determined for a series of H_2 - Br_2 - N_2 mixtures. It has been shown that the flame thickness, for the mixtures studied, was about half that for lean ethylene-air flames having the same burning velocity and it was found that half the overall reaction occurred in less than 0.4 mm. The thinness of the flames has magnified some of the difficulties in using the optical techniques and the accuracy of the flame analysis has been consequently limited. However the major stumbling block to an accurate analysis is the uncertainty in the values of the transport data.

The method of analysis of the flame front has been demonstrated and it has been shown that, in principle, the rates of production of all species except H can be obtained from the deflection and absorption profiles and the calculation of initial transport data is also possible. Because of the errors mentioned above, and since the maximum

mol-fraction of Br for the flame investigated was only about 1.5%, the chemical kinetic data obtained was very limited.

However the results of the analysis have proved very useful in assessing the relative importance of the various errors in the experimental and external data used. Thus many improvements of experimental technique have suggested themselves, and the direction for future development has become apparent.

(1) Burner and Flow System.

Although the burner and flow system used were largely satisfactory, several improvements should be made.

(a) The cupro-nickel burner matrix was slowly but steadily attacked during the runs. This attack resulted in the formation of volatile metal bromides which may have interfered with the flame kinetics. Hence it would be desirable to replace this matrix by a porous ceramic disc or perhaps a platinum gauze whose surface had been coated to prevent catalysis.

(b) A burner assembly of mainly glass-blown construction, in which the burner tube was sealed into the Pyrex housing and the top plate was movable, would be simpler than the present apparatus and the possibility of leakages occurring would be further reduced.

(c) A boiler in which the bromine level was automatically kept constant would give a better long-term flow stability than the present boiler. In addition a design such that no nitrogen was required to prevent bumping would enable a suitable Rotameter to be used as a simple and reliable means of measuring the bromine flow. However, for the most accurate composition measurements, sampling of the reactants or the products would be preferable.

(d) The calibration of the capillary flowmeters would probably be made simpler and more accurate if the fluid used in the bubble meter were based on glycerol, so that no vapour pressure correction would be required. 'Soap' bubbles produced from a mixture of glycerol and a non-aqueous detergent have been used, for example, in the determination of burning velocities [65].

(2) Temperature Measurement.

In the previous chapter it was shown that, in general, the inclined slit technique was unlikely to be much restricted in accuracy by composition effects, providing the mean molecular weight remained approximately constant. However the technique, in the form used, was

found to be not entirely suitable for investigating the flat hydrogen-bromine flames burnt. Some improvement would doubtless have been obtained if the optics had been adjusted for each flame, but in practice it would have been very inconvenient to do this.

Since the flame thickness is still some orders of magnitude larger than the wavelength of light, it should be possible to obtain a substantially higher spatial resolution than that achieved with the technique described.

THE CYLINDRICAL LENS SYSTEM. If a vertical slit were placed in the parallel beam of light, before the flame, the diffraction would occur in the direction of constant $\frac{d\mu}{dy}$. Hence if the image were distorted in a horizontal direction, the shape of the outer fringes would remain similar to that of the central fringe and interpretation should be simpler than in the case of an inclined slit. Several methods for producing a horizontal distortion in the slit image, proportional to the vertical ray deflection, are possible. Some preliminary tests were carried out on what was considered the simplest of these systems and the results were encouraging.

A parallel beam of light was passed through the

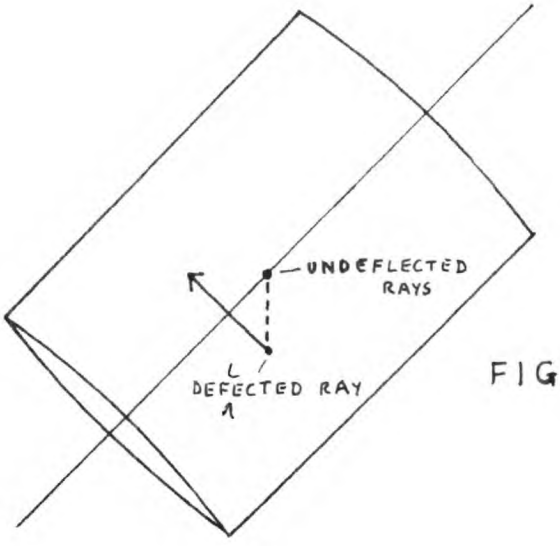


FIG 37

vertical slit and the flame and then focussed onto the centre of a cylindrical lens, perpendicular to the beam, but whose axis was at an angle of about 45° to the h rizontal. Hence any undeflected ray was unaffected by the cylindrical lens, but any deflected ray was refracted in a direction perpendicular to tne axis (see Figure 37). At a certain distance beyond the lens, there was no vertical deflection but the horizontal component of the diagonal deflection, due to the cylindrical lens, caused a horizontal distortion proportional to the original deflection. The position of the cylindrical lens was not critical but, when it was placed away from the focus of the first lens, then distortion of the flame image occurred.

USE OF PINHOLES AND HORIZONTAL SLITS.

A modification of the inclined slit technique which was tested, was the use of a series of pinholes in place of the inclined clits. The pinholes were far enough apart to prevent appreciable interference between the images and small enough for the angle of deflection to be almost ccnstant across the pinhole. With this system a fairly rigid interpretation of the resultant pattern can be carried out, but the discontinuous record and the very low light intensity obtained, made the

method, as it stood, unsuitable for the present work. However, the following modification is worth further investigation. Consider the pinhole, or better a horizontal slit, being scanned vertically, so that the pinhole or slit image falls on a narrow vertical slit in front of the photographic plate. Then, if the plate were moved horizontally during exposure, the trace recorded should give an accurate deflection profile.

WOLTER'S METHOD. Possibly the most promising modification of the inclined slit technique is that due to Wolter [66,67]. Here the slit is replaced by a glass plate, half of which is coated to produce a half-wave retardation. Providing there is a sharp division between the coated and uncoated regions, the two halves of a parallel beam of light passing through the plate would interfere so that, if a screen were placed a short distance from the plate, the division would show up as a fine dark line. The spatial resolution of this device is superior to that of a slit or wire and preliminary experiments with such a plate indicate that it would be very convenient for the investigation of thin flames.

(3) The Measurement of Concentrations of Species.

The photographic technique for measuring the absorption distribution appears sound and accurate. However the exposures which had to be used in the work were of the order of one minute and were usually insufficient to 'freeze' the flame. One way of overcoming this would be to use a mercury arc running at a higher pressure to give a brighter source. Alternatively, two or three times as much light could be obtained if a Woods glass filter or an efficient interference filter were used in place of the monochromator. Beers Law would not then hold for the total light intensities and in order to determine the concentration profile it would be necessary to calculate, or measure experimentally, the optical density for a series of values of the product $[Br_2] \times l$, at each temperature.

Some preliminary experiments have been carried out using a photomultiplier-electronic technique for the measurement of the absorption profiles and several immediate improvements, which could be made to the technique, were given in Chapter 8. The high sensitivity and the ease with which interference due to emission from the flame can be removed, make the technique appear more generally useful than the photographic technique.

FLAME SHAPE. The most important error in $[Br_2]$ near the hot boundary was due to uncertainty in the flame shape. This will always be the case when flames with upturned edges are used because, for large values of y, most of the absorption will occur at the edges. A more accurate bromine concentration profile would be obtained if a flame were used whose edges were down-turned - perhaps anchored above thin silica rods. The reverse would be the case if [HBr] was being measured, but the high temperature zone is the more important, and consequently flames with down-turned edges would be normally the more useful.

When carrying out ray deflection measurements, Dixon-Lewis and Wilson [68] corrected for edge effects by burning flames of different path length and measuring the difference between the respective deflection profiles. Providing flames can be burnt with identical edge shapes this method of correction would be preferable to the calculated correction.

EXTINCTION COEFFICIENT DATA. Although data for bromine is readily available, for most gaseous species which could be estimated by absorption spectrophotometry, either the extinction coefficient is not known or, since Beers Law does not hold, the extinction coefficient has no

meaning. A useful method for measuring the optical density as a function of [j] x l and T at high temperatures, is to measure the light absorption above a flame front, t'e species under investigation being present in the products in known concentration. This method was used for the case of Br_2 (see Chapter 7), but it is applicable to reactants, products or diluents present in the products.

Another convenient method of obtaining absorption data which is worth further consideration is to pass a laminar gas stream, containing the species concerned, through a hot porous disc and examine the temperature and absorption profile ahead of the disc in the same way as for a flat flame. This would have the advantage that some systematic errors in the apparatus and technique would be reduced. A flow system would be preferable to a static system, especially for a gas such as bromine, because there would be less danger of thermal diffusion effects being troublesome.

(4) The Problem of Transport Coefficients.

The determination of thermal conductivities and other transport data, for mixtures of reacting gases, has been discussed by Hirschfelder [64, 61, 63]. It appears

likely that lack of suitable transport data will continue to restrict the conclusions, which can be derived from measured temperature and composition profiles. Consequently if a detailed analysis is to be attempted on a flame front, it would be advantageous to choose a flame for which the thermal conductivity distribution can be found accurately and for which the diffusion of as many major species as possible is made unimportant, with regard to the chemical kinetics.

For example, if a very large excess of one component is used, the thermal conductivity of the mixture will be close to that of the major component and the diffusion coefficients of the minor species will approach their respective self-diffusion coefficients [69].

If any reactant or product is present in large excess, the concentration of that species would not be greatly affected by diffusion. Thus it would facilitate the investigation at a hydrogen-rich H_2 - Br_2 flame, if HBr were used as diluent. In the reaction zone of such a flame, $[H_2]$ and [HBr] would vary little and the chemical kinetics would be simplified. This type of simplification would be even more effective in the case of the H_2 - Cl_2 flame, for which smaller concentrations of the oxidant could be used.

Although it has been shown that much information can be obtained from one composition profile, together with the temperature profile, it would be desirable to measure the composition profiles of as many species as possible, using I.R. and U.V. spectrophotometry. Not only would this mean that the concentration profiles would not have to be calculated, but they would also provide a useful cross check on transport data.

MEASUREMENT OF TRANSPORT DATA. In Chapter 9 (section 6) the measurement of transport data from the composition and temperature profiles in flames was described. However, further useful data could be obtained by carrying out parallel experiments in non-flame systems. If a large excess of an inert diluent were used in the system to be investigated, it should prove convenient to measure the thermal conductivity of a mixture of diluent and one reactant, from the temperature profile set up in the gas flow ahead of a hot porous disc. It should also prove convenient to use the absorption techniques for the determination of diffusion coefficients. One way of doing this would be to measure the rate at which two laminar gas flows inter-diffuse across a planar interface.

(5) Summary.

The principal recommendations for future work on the H_2 - Br_2 system are listed below:

(a) that in view of the thinness of the H_2 - Br_2 - N_2 Egerton-Powling flame at atmospheric pressure, the possibility of using low pressure flames should be investigated;

(b) that Wolter's modification of the inclined slit technique [66,67] should be used;

(c) that the photomultiplier-electronic method for the measurement of optical density profiles should be further developed;

(d) that flat flames with down-turned edges should be considered for use with the optical analysis, and the method of edge correction used by Dixon-Lewis and Wilson [68] should be further investigated;

(e) that analyses of H_2-Br_2 flames, using HBr as diluent, should be considered;

(f) that, in addition to the optical examination of flat flames, parallel experiments, using the same optical techniques, should be carried out to determine extinction coefficients and transport data.

Looking still further to the future, there would be much to be gained by using, in addition to the techniques described here, I.R. absorption spectrophotometry for the determination of [HBr] and also sampling techniques for comparison purposes.

APPENDIX A.

CALCULATION OF FINAL FLAME TEMPERATURES.

The first step is to obtain expressions for the equilibrium concentrations of all species at the final flame temperature.

The total pressure across the flame is constant:

$$P = P_{H_2} + P_{Br_2} + P_{HBR} + P_{Br} + P_{N_2} \qquad (a)$$

Since the total fractions of H, Br and N atoms are equal to the initial mol fractions of H_2, Br_2 and N_2 :

$$P_{H_2} + \tfrac{1}{2} P_{HBr} = n^u_{H_2} (P - \tfrac{1}{2} P_{Br}) \qquad (b)$$

$$P_{Br_2} + \tfrac{1}{2} P_{Br} + \tfrac{1}{2} P_{HBr} = n^u_{Br_2} (P - \tfrac{1}{2} P_{Br}) \qquad (c)$$

$$P_{N_2} = n^u_{N_2} (P - \tfrac{1}{2} P_{Br}) \qquad (d)$$

Subtracting (b) from (c)

$$P_{H_2} - P_{Br_2} - \tfrac{1}{2} P_{Br} = (n^u_{H_2} - n^u_{Br_2}) (P - \tfrac{1}{2} P_{Br}) \qquad (e)$$

Since the gases must be in equilibrium at the final flame temperature

$$P_{HBr} = K^P_{-6} \; P^{\frac{1}{2}}_{Br_2} \; P^{\frac{1}{2}}_{H_2} \qquad (f)$$

$$P_{Br_2} = P^2_{Br} \; / \; K^P_1 \qquad (g)$$

where K^P_{-6} and K^P_1 are the partial pressure dissociation constants for HBr and Br_2 respectively.

Substituting now in equation (a) for P_{HBr} from eqn. (f), then for P_{Br_2} from eqn.(g) and for P_{N_2} from eqn.(d) :

$$P = P_{H_2} + P_{Br}^2/K_1^P + K_{-6}^P P_{Br} P_{H_2}^{\frac{1}{2}} /(K_1^P)^{-\frac{1}{2}} + P_{Br} + n_{N_2}^u (P-\tfrac{1}{2}P_{Br}) \qquad (h)$$

where from equations (e) and (g)

$$P_{H_2} = P_{Br}^2 /K_1^P + \tfrac{1}{2} P_{Br} + (n_{H_2}^u - n_{Br_2}^u) (P - \tfrac{1}{2}P_{Br}) \qquad (i)$$

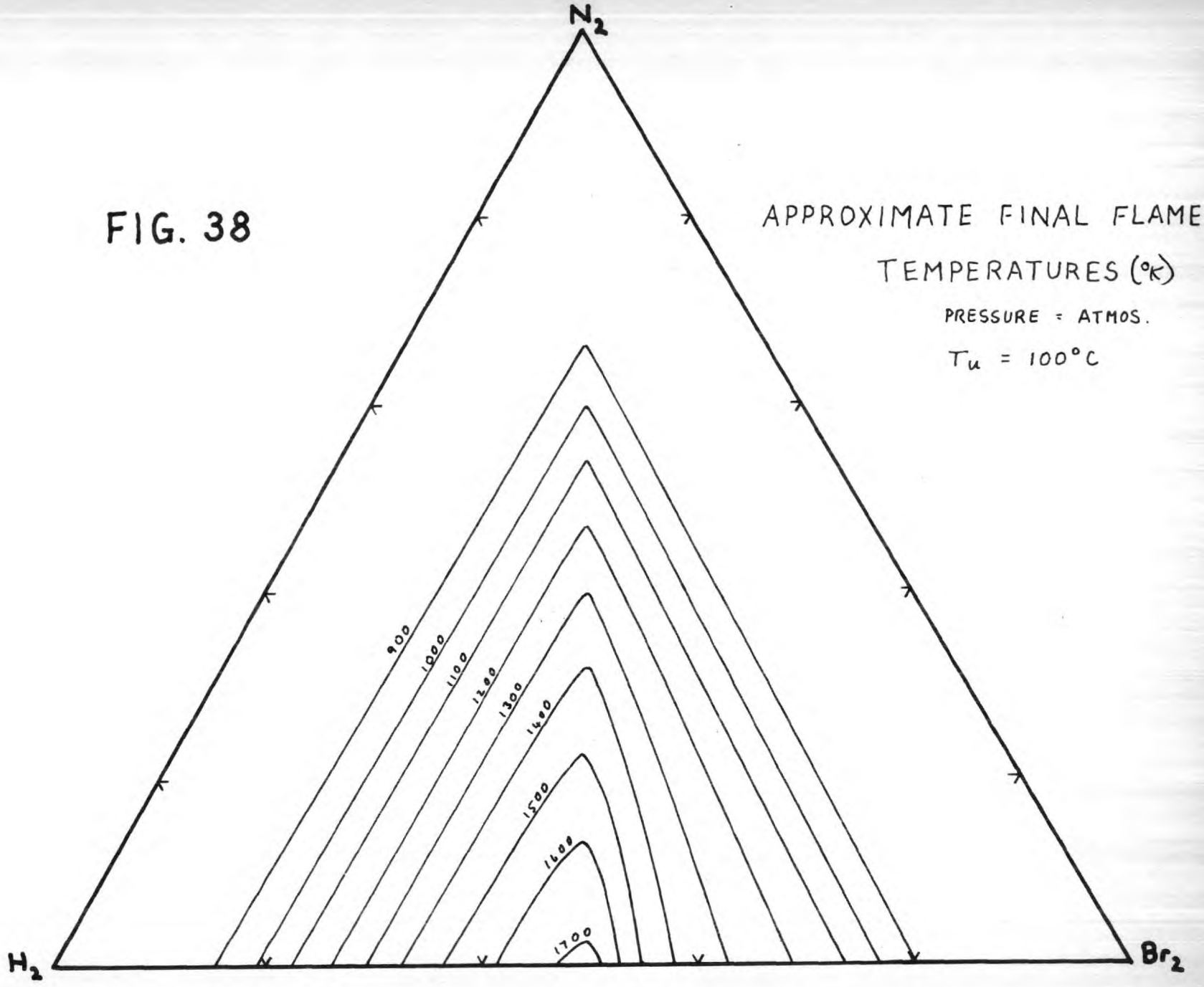
When the flame is hydrogen rich the first two terms in the expression for P_{H_2} can usually beneglected, and for bromine rich flames P_{H_2} can usually be assumed to be zero. If a final flame temperature is now assumed, then on inserting the values for the equilibrium constants [37,38] for that temperature, equation (h) can be solved graphically to give P_{Br}. The values of P_{H_2}, P_{Br_2}, P_{HBr} and P_{N_2} are then obtained from equations (i), (g), (f) and (d).

The products are considered to be formed at T_u and are heated up to T_b by the nett heat of reaction at T_u. This is given by

$$\triangle H = n_{HBr} \triangle H_{HBr}^u + n_{Br} \triangle H_{Br}^u + n_H \triangle H_H^u$$

($\triangle H$ was assumed to be constant with pressure for the flames considered). Thus if T_b is assumed, a first value for $\triangle H$ can be calculated, and with a knowledge of the

FIG. 38


APPROXIMATE FINAL FLAME TEMPERATURES (°K)
PRESSURE = ATMOS.
T_u = 100°C
N_2
H_2
Br_2
900
1000
1100
1200
1300
1400
1500
1600
1700

enthalpy of the mixture [38,39,37,70] the initial temperature (T_u^*) for which

$$\triangle H = H_u - H$$

can be found. Further values for T_b are assumed and the corresponding T_u^* value calculated. By graphical interpolation, the T_b value corresponding to the correct T_u value can be found. Since $\triangle H$ varies little with temperature, this procedure automatically gives the dependence of T_b on T_u for a given composition.

Calculations are simplified if the approximate value of T_b is known. A series of calculations enabled a graph to be constructed giving the approximate final flame temperature as a function of composition. This is shown in Figure 37.

APPENDIX B.

VALUES OF TRANSPORT FUNCTIONS USED IN THE FLAME ANALYSIS.

(1) Thermal Conductivity.

According to Hirschfelder [64], the reciprocal of the thermal conductivity of many gas rixtures varies linearly with composition. However for hydrogen-bromine flame calculations, Campbell and Fristrom [36] recommend that the thermal conductivity should be assumed to be a linear function of molar composition. Thermal conductivitie were calculated for the unchanged reactants at 400°K. and for products at 1300°K., assuming (a) the reciprocal relation and (b) the linear relation between the conductivity of the mixture and that of the components. The results obtained were

	(a)	(b)
Reactants (400°K.)	4.1×10^{-5}	25.6×10^{-5}
Products (1300°K)	16.9×10^{-5}	30.9×10^{-5}

cals cm^{-1} $°K^{-1}$ sec^{-1}

The experimental value for the conductivity at the cold boundary (see Chapter 9, p.154) was 10.0×10^{-5} cals. cm^{-1} $°K^{-1}$ sec^{-1} - intermediate between the two calculated values. However, since these values differ greatly, it was assumed for this analysis that the thermal conductivity remained at its cold boundary value throughout.

(2) Diffusion Coefficients.

The self-diffusion coefficient for each species was calculated using the expression recommended by Hirschfelder, Curtiss and Bird [3] :

$$D = \frac{2.63 \times 10^{-3} \, (T^3/M)^{\frac{1}{2}}}{P \quad \sigma^2 \quad \Omega^{(11)T^*}}$$

where σ = collision diameter in Angstrom units, M = molecular weight, P = pressure in atmospheres, and $\Omega^{(11)T^*}$ is the appropriate collision integral which is tabulated as a function of T*.

T* is the reduced temperature and is equal to $T/\sqrt{r/k}$, where r = depth of potential well and k = Boltzmann's constant. The self-diffusion coefficients calculated for 400°K. and 1300°K. were :

	H_2	N_2	Br_2	HBr	
D(400°K.)	2.37	0.336	0.0535	0.143	$cm^2 \; sec^{-1}$
D(1300°K)	16.7	2.40	0.538	1.25	$cm^2 \; sec^{-1}$

The diffusion coefficient of Br was assumed to be the same as that for Br_2. Binary diffusion coefficients can be calculated in a similar manner. Hirschfelder and co-workers [3,64] give equations for calculating diffusion coefficients in multi-component systems from the separate binary diffusion coefficients. However, binary or self-diffusion coefficients, involving Br_2 or HBr, can only be

calculated very approximately using the expression given above. It was therefore considered adequate to calculate the diffusion coefficient of each species in the mixture using the equation for an ideal binary mixture [69] :

$$D_{jJ} = n_j D_{J-j} + (1 - n_j) D_j$$

where D_{jJ} is the diffusion coefficient of the j^{th} species in a mixture of J species. D_j is the self-diffusion coefficient of the j^{th} species. D_{J-j} is the effective self diffusion coefficient of a mixture of the remaining species and was assumed to be a linear function of molar composition. The diffusion coefficients calculated assuming no reaction at 400°K. and complete reaction at 1300°K. were :

	H_2	Br_2	HBr	N_2	Br	
D (400°K)	1.45	0.46	0.14	0.73	0.054	$cm^2 sec^{-1}$
D (1300°K)	14.4	0.54	4.50	3.05	0.54	$cm^2 sec^{-1}$

However, it was expected that D_{Br_2} would reach a maximum in the flame front (for reactants at 500°K. $D_{Br_2} = 0.67$) and a constant value of $D_{Br_2} = 0.6$ was used for the analysis. Although a maximum in g_{Br_2} was obtained when using this value, it was considered that the accuracy of the $[Br_2]$ profile near the cold boundary did not justify the use of $D^u_{Br_2}$ evaluated as described in Chapter 9.

The diffusion coefficients of H_2, HBr and N_2 were assumed to be linear functions of temperature, for the present analysis.

REFERENCES.

1. e.g. Burgoyne, J.H. and Hirsch, H., Proc.Roy.Soc., A.227, 73, (1954)
2. Longwell, J.P. and Weiss, M.A., Industr.Eng.Chem., 47, 1634, (1955).
3. Hirschfelder, J.O., Curtiss, C.F. and Bird, R.B., Molecular Theory of Gases and Liquids, John Wiley: New York (1954).
4. Simon, D.M., Selected Combustion Problems (Agard) p.59 Butterworths: London (1954).
5. Eyring, H., Giddings, J.C. and Tensmayer, L.G., J.Chem.Phys., 24, 857, (1956).
6. Campbell, E.S., 6th Symposium (International) on Combustion, p.213, Reinhold:New York, (1956).
7. e.g. Potter A.E. and Anagnostou, E., 7th Symposium (International) on Combustion, p.347. Butterworths: London (1959).
8. Linnett, J.W. Selected Combustion Problems (Agard) p.92 Butterworths (London) (1954).
9. Fristrom, R.M., 6th Symposium (International) on Combustion, p.96. Reinhold: N.Y. (1956).
10. Levy, A. and Weinberg, F.J., 7th Symposium (Internat.) on Combustion, p.296. Butterworths: London, (1959).
11. e.g. Fristrom, R.M., Avery, W.H., Grunfelder, C. and Westenberg, A.A., Combustion and Flame, 1, 217, (1957).
12. e.g. Friedman, R. and Nugent, R.G., 7th Symposium (International) on Combustion, p.311, Butterworths: London (1959).

13. Arden, E.A. and Powling, J., 6th Symposium (Internat.) on Combustion, p.177, Reinhold, New York, (1956).

14. Westenberg, A.A., Raezer, S., and Fristrom, R.M., Combustion and Flame, 1, 467, (1958).

15. Halpern, C. and Ruegg, F.W., U.S.Nat.Bur.Stand.J.Res., 60, 29, (1958).

16. Wolfhard, H.G. and Parker, W.G., 5th Symposium (Internat) on Combustion, p.718. Reinhold, New York.

17. Donovan, R. and Agnew, W., J.Chem.Phys., 23, 1592,(1955).

18. Spokes, G.N., 7th Symposium (International) on Combustion, p.229. Butterworths:London, (1959)

19. Cooley, S.D. and Anderson, R.C., Indust.Eng.Chem., 44, 1402, (1952).

20. Hellwig, K. and Anderson, R.C., J.A.C.S., 77, 232,(1955).

21. Gilbert, M. and Altman, D., 6th Symposium (International) on Combustion, p.222, Reinhold, New York (1956).

22. e.g. Brokaw, R.S., J.Chem.Phys., 29, 391, (1958).

23. Streng, A.G. and Grosse, A.V., 6th Symposium (Internat) on Combustion, p.264. Reinhold, N.Y. (1956).

24. Hirschfelder, J.O., Curtiss, C.F. and Campbell, D.E., J.Phys.Chem., 57, 403, (1953).

25. Von Karman, T. and Penner, S.S., Selected Combustion Problems (Agard) p.5. Butterworths; London, (1954).

26. Rosen, J.B., 6th Symposium (International) on Combustion p.236. Reinhold, New York, (1956).

27. Anderson, R.C., Combustion Researches and Reviews, (Agard) p.17. Butterworths:London (1957).

28. Friedman, R. and Burke, E., 5th Symposium (Internat.) on Combustion, p.596. Reinhold.N.Y.

29. Levy, A. and Weinberg, F.J., Combustion and Flame, 3, 229, (1959).

30. Weinberg, F.J., 6th Symposium (International) on Combustion, p.765. Reinhold, N.Y.(1956).

31. Burgoyne, J.H. and Weinberg, F.J., 4th Symposium (Internat.) on Combustion. p.294. Williams and Wilkins, Baltimore (1953).

32. Gaydon, A.G., "Spectroscopy and Combustion Theory", Chapman and Hall, London (1942).

33. Gadamer, E.O., Univ.Toronto Inst of Aerophysics, Ann.Prog.Rep., p.10, (Oct.1959).

34. Olsen, H.L., 3rd Symposium on Combustion, Flame and Explosion Phenomena, p.663. Williams and Wilkins, Baltimore (1949).

35. Cuthbertson, C. and Cuthbertson, M., Phil.Trans.A.213, 1, (1914).

36. Campbell, E.S. and Fristrom, R.M., John Hopkins Univ., App.Phys.Lab. (TG-293), (1957).
also Campbell, E.S. and Fristrom, R.M., Chem.Rev., 58, 173 (1958).

37. U.S.Nat.Bur.Standards Tables of Thermodynamic Properties Series III, (1948).
also Evans, W.H., Munson, T.R. and Wagman, D.D., U.S.Bur.Stand.J.Res., 55, 147, (1955).

38. Gordon, A.R. and Barnes, C., J.Chem.Phys., 1, 692, (1933)

39. Bryant, W.M.D., Indus.Eng.Chem., 25, 820, (1933).

40. Levy, A., Wright Air Development Centre Tech.Rep. 57-486, Astia Document No.142055.

41. Pease, R.N., "Equilibrium Kinetics of Gas Reactions" Princeton Univ., (1942).

42. Campbell, E.S., Hughes, D.R. and Buehler, R.J., Univ.Wisconsin Rep. CF-2109 (19 Oct.1953) NOrd-9938.

43. Patty, F.A., Industrial Hygiene and Toxicology, Interscience: New York, (1958).

44. Chemical Safety Data Sheet SD-49, Manf.Chemists Assoc. Inc. Washington.

45. Gaydon, A.G. and Wolfhard, H.G., "Flames, their Structure, Radiation and Temperature", p.34, Chapman and Hall:London (1960).

46. Evans, D.F., J.Chem.Phys., 23, 1424, (1955).

47. Bayliss, N.S. and Rees, A.L.G., Trans.Farad.Soc., 35, 792, (1939).

48. Kraushaar, R., J.Opt.Soc.America, 40, 480, (1950).

49. Gray, L. and Style, D., Proc.Roy.Soc., A.126, 603,(1929).

50. Aickin, R.G. and Bayliss, N.S., Trans.Farad.Soc., 34, 1371, (1938).

51. Bayliss, N.S. and Sullivan, J.V., J.Chem.Phys., 22, 1615, (1954).

52. Kortum, G. and Luck, W., Naturforsch., 69, 305, (1951)

53. Sulzer, P. and Wieland, K., Helv.Phys.Acta, 25, 653, (1952).

54. Ribaud, G., Ann.Phys., 12, 107, (1919).

55. Acton, H.P., Aickin, R.G. and Bayliss, N.S., J.Chem.Phys., 4, 474, (1936).

56. Powling, J.A., Fuel, London, 28, 25, (1949).

57. Egerton, Sir A. and Thabet, S.K., Proc.Roy.Soc., A.211, 445, (1952).

58. Hall, A.R. and Wolfhard, H.G., 6th Symposium (Internat.) on Combustion, p.190 Reinhold, N.Y., (1956).

59. Burgoyne, J.H. and Weinberg, F.J., Proc.Roy.Soc., A.224, 286, (1954).

60. Kaye, G.W.C. and Laby, T.H., Physical and Chemical Constants, Longmans: London (1941).

61. Hirschfelder, J.O., J.Chem.Phys., 26, 274, (1957).

62. Cooley, S.D., Lasater, J.A. and Anderson, R.C., J.A.C.S., 72, 1845, (1950).

63. Hirschfelder, J.O., J.Chem.Phys., 26, 282, (1957).

64. Hirschfelder, J.O., 6th Symposium (International) on Combustion, p.351, Reinhold, New York (1950).

65. Strehlow, R.A. and Stuart, J.G., 4th Symposium (Intern.) on Combustion, p.329. Williams and Wilkins, Baltimore.

66. Wolter, H., D.P. 819728 K142h, Gr.34,11 (from 12/4/1949).

67. Wolter, H., Handbuch der Physik, pp.555-645. Springer-Verlag: Berlin.

68. Dixon-Lewis, G. and Wilson, M.J.G., Trans.Farad.Soc., 47, 1106, (1951).

69. Carman, P.C. and Stein, L.H., Trans.Farad.Soc., 52, 619, (1956).

70. Tables of Thermal Properties of Gases. N.B.S.Circular 564 (1955).

71. Weinberg, F.J., Proc.Roy.Soc., A.243, 107, (1957).

72. Cole, D.T. and Minkoff, G.J., Combustion and Flame, 1, 241, (1957).