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SECTION

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EXPERIMENTAL TECHNIQUES
FOR THE STUDY OF
FLAME STRUCTURE

by

Robert M. Fristrom

Bumblebee Series

Report No. 300   January 1963

Copy No.

EXPERIMENTAL TECHNIQUES
FOR THE STUDY OF
FLAME STRUCTURE

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

vi

LIST OF TABLES

INTRODUCTION

THE EXPERIMENTAL STUDY OF FLAME MICROSTRUCTURE

During the past decade a number of techniques have been developed which allow the study of the microstructure of flame fronts.

Flame microstructure is the detailed temperature, aero-dynamic, compositional history of the flame. In a one-dimensional flame where the properties vary only along a single coordinate (Fig. 1) the system can be completely described by a family of characteristic profiles which give temperature, gas velocity, stream tube area ratio, and composition as a function of a distance coordinate along the direction of flame propagation. It requires $N + 1$ variables to describe such a flow system together with the mass flow per unit area (i.e., the burning velocity). Composition measurements could be used with the addition of a variable to describe the deviation of the flow from true one-dimensional behavior. This is not usually convenient, however, since concentration must be in absolute units (i.e., mass per unit volume) and most techniques yield mole fraction or other relative units. It is common to present the data for a flame in the form of aerodynamic profiles giving gas velocity and stream tube area ratio, a temperature profile, and a composition profile expressed in mole fraction (Fig. 2). In addition, the ambient pressure and the burning velocity must be specified. Some of the profiles are redundant, but it is convenient to have the extra information directly available and experimentally redundant profiles provide cross checks on the validity of the measurement.

Using these experimental techniques it has been possible to verify the quantitative applicability of one-dimensional models to common laboratory flames by showing point by point conservation of energy and each individual atomic species (Refs. 1, 2) (overall matter

1
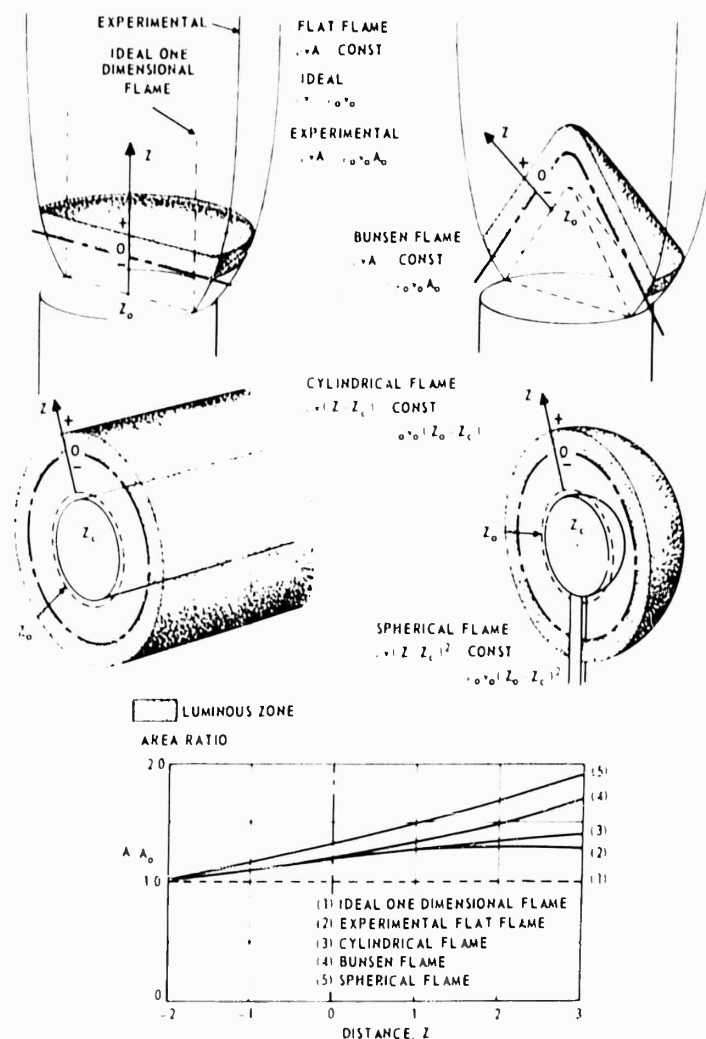
Fig. 1.   COMMON FLAME GEOMETRIES WHICH CAN BE DESCRIBED BY ONE-
DIMENSIONAL MODELS

conservation is of course obtained since it is the sum of the conserva-
tion of all atomic species).   It was found that only in special cases
was it necessary to include the effects of the higher transport process
thermal diffusion: and that inverse thermal diffusion was generally un-
important in flames (Refs. 1 and 2).   Finally, these techniques have
been applied to the study of high temperature reactions in flames de-
termining the rates of heat release, and the net rates of reaction of
the various species (Refs. 1-3).   From these data detailed reaction

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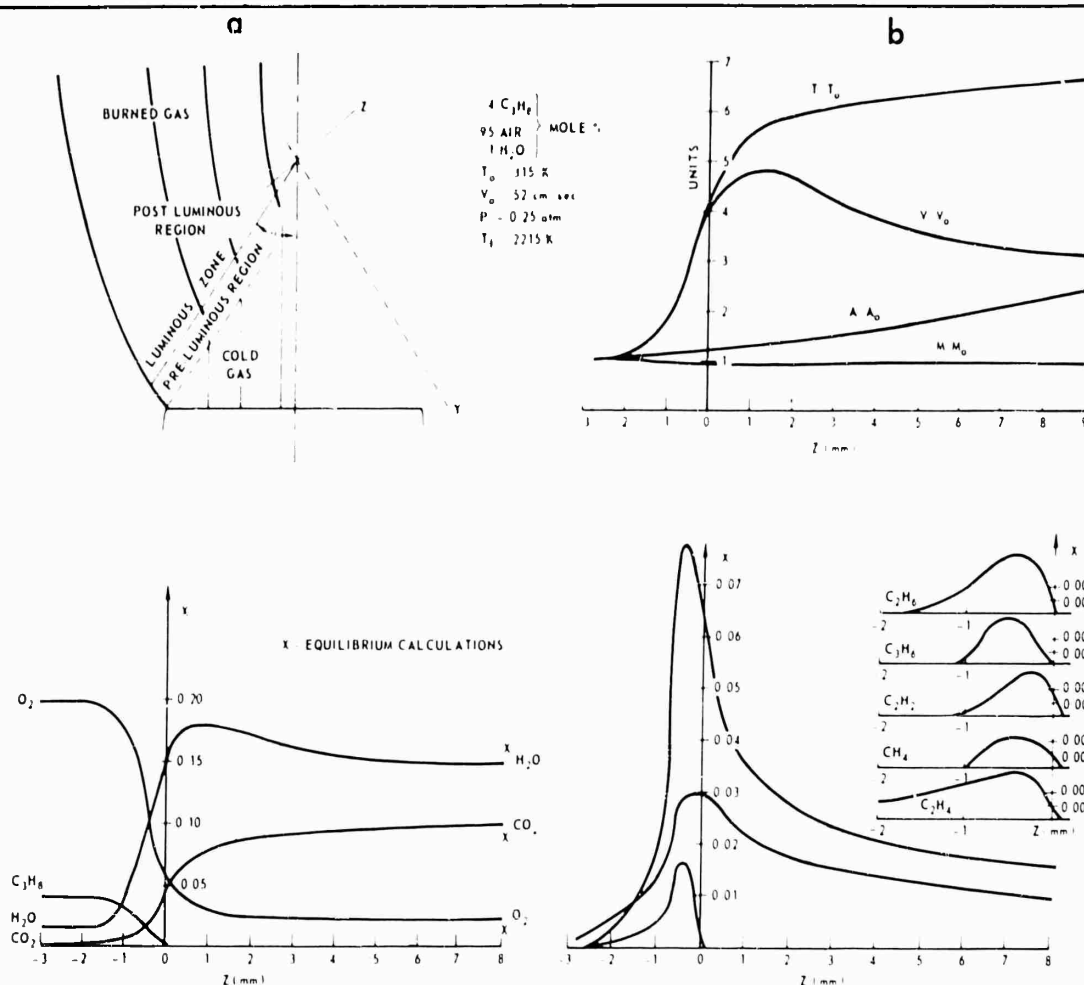
Fig. 2. CHARACTERISTIC PROFILES OF A PREMIXED PROPANE-AIR FLAME
(Ref. 4)

schemes have been worked out for several flames and kinetic constants
derived for a number of reactions (Ref. 3). This technique has the
advantage of providing information on reaction rates at high tempera-
tures which would be difficult to attain by any other method. Since
most of the reactions are of relatively low activation energy and the
temperatures are high, the data usually result in a good determination
of the steric, or frequency factor, combined with a modest determina-
tion of activation energy. By studying several flames with the same
reaction or by combining flame results with low temperature studies,
excellent results can be obtained for activation energy (Fig. 3).

A discussion of various measurements which must be made on
a flame front to provide a complete description is contained in this

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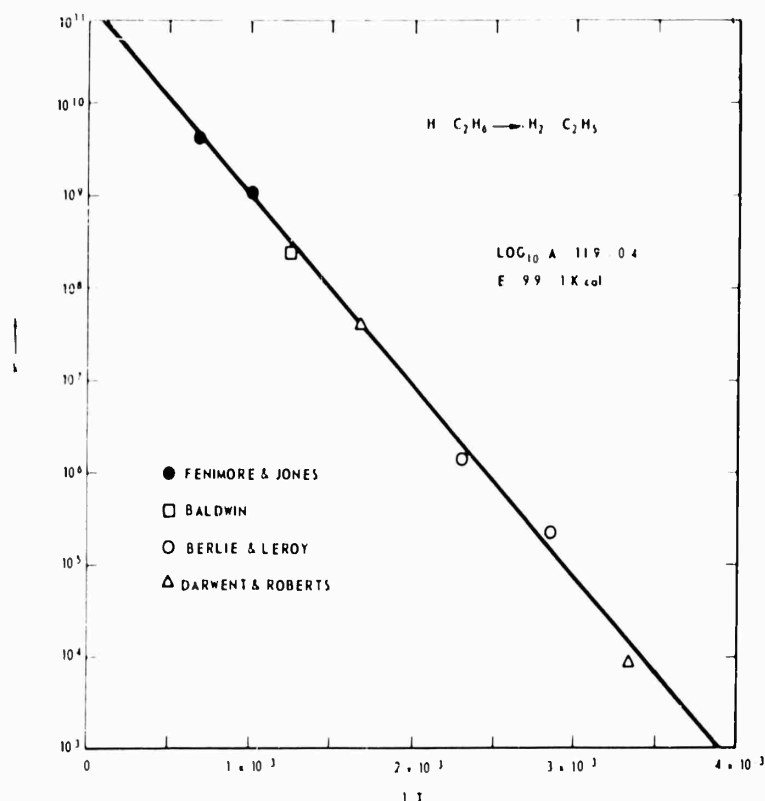
Fig. 3 ACTIVATION ENERGY OF THE REACTION $H + C_2H_6 \rightarrow H_2 + C_2H_5$
Taken from remarks by R. R. Baldwin on Paper #25 at the Ninth Symposium on Combustion (C. Fennimore and G. Jones, "The Decomposition of Ethylene and Ethane in Premixed Hydrocarbon-Oxygen-Hydrogen Flames").

report. Although the discussion will be general it is biased in light of the Laboratory's experience.

Bumblebee Report 300 is divided into six chapters. The first chapter deals with burner systems; the second with aerodynamic measurements; the third with temperature measurements; the fourth with measurement of composition of stable species; the fifth with the measurement of unstable species; and the sixth with the measurement of distance.

This report was produced not only to provide a record of the experience at the Laboratory in this particular field, but also with the expectation that it could be combined later with material on the

4

analysis and interpretation of flame structure data into a monograph.
For this second work the present author is collaborating with Dr. A.
A. Westenberg of the Laboratory.

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I
BURNER SYSTEMS

To study flame structure it is necessary to produce a flame
which is stable in space, possesses suitable geometry, and is of ade-
quate thickness to allow measurements of the desired precision and
resolution.

Special burner systems are required for these studies. The
system includes the burner, a housing, devices for flow measurement and
regulation, pressure monitors, and, if operation is at sub-atmospheric
pressures, a pumping system. Some of these techniques are standard
laboratory practice, but several of them are sufficiently unusual to
warrant discussion.

BURNER SYSTEM DESIGN

The first requirement for quantitative flame structure studies
is spatial stability. This means that the excursions of the flame
front during the period of measurement should not exceed the desired
spatial resolution (see Chapter VI). A usual requirement is ±0.001 cm
over a fifteen-minute period.

It is usually assumed that the mechanism for flame stabiliza-
tion is a heat (or radical) sink. This apparently is a requirement for
a stable solution of flame equations (Ref. 1). In the case of the open-
tube bunsen flames, the sink is the burner lip, and stability can be
correlated with the flame behavior in this boundary layer region (Ref. 2).
This mechanism only directly stabilizes the edge of the flame; the re-
mainder of the flame front is presumably stabilized by lateral heat
transfer. This does not disturb the uniformity of such flame fronts
(Ref. 3) since only an infinitesimal heat sink is required (Ref. 1).[*]

7

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[*]References are on Pages 36-38.

It is difficult to reduce open tube bunsen flame front movements below 10^{-2} cm, while screen-supported flat flames show much higher stability (better than 10^{-4} cm). This is probably due to the damping effect which the screen sink has on the flame front movements.

One flame can be stabilized on the edge of another. The stabilizing flame can be either premixed or a diffusion flame. This phenomenon increases the stability of bunsen flames operated in atmospheres in which edge diffusion increases the local burning velocity. Examples are: Rich flames in an air atmosphere, air flames in an oxygen atmosphere, or fuel-lean flames in a fuel atmosphere. Stable flames can be obtained many diameters above a burner port. In this case the stabilizing sink is presumably diffusional loss at the edge of the flame.

To be suitable for structure studies, the flame geometry must be amenable to quantitative analysis. At the present time this means that the system should be one-dimensional; that is, the properties must be functions of a single distance coordinate (see Chapter VI). This can be accomplished with a number of different flame geometries, bunsen, flat, and sperical (Fig. I-1a).

Burner size is primarily dictated by the requirement of one-dimensional structure. Thus for a flat or bunsen flame the diameter should be at least ten times the flame front thickness. The burner size determines housing size, the ranges of flow to be metered, and the required pumping speeds. The minimum-sized satisfactory burner is usually chosen, since these requirements go up quadratically with burner dimensions.

A rough estimate for flame front thickness can be obtained from Eq. (1). This is empirical and applies specifically to hydrocarbon flames but is reasonable for most systems.

8

$$L = \frac{3}{PV_o} \tag{1}$$

L = flame front thickness (cm)

P = pressure (atm)

V_o = burning velocity (cm/sec)

FLAT FLAME

BUNSEN FLAME

EXPERIMENTAL

IDEAL ONE
DIMENSIONAL
FLAME

LUMINOUS ZONE

CYLINDRICAL FLAME
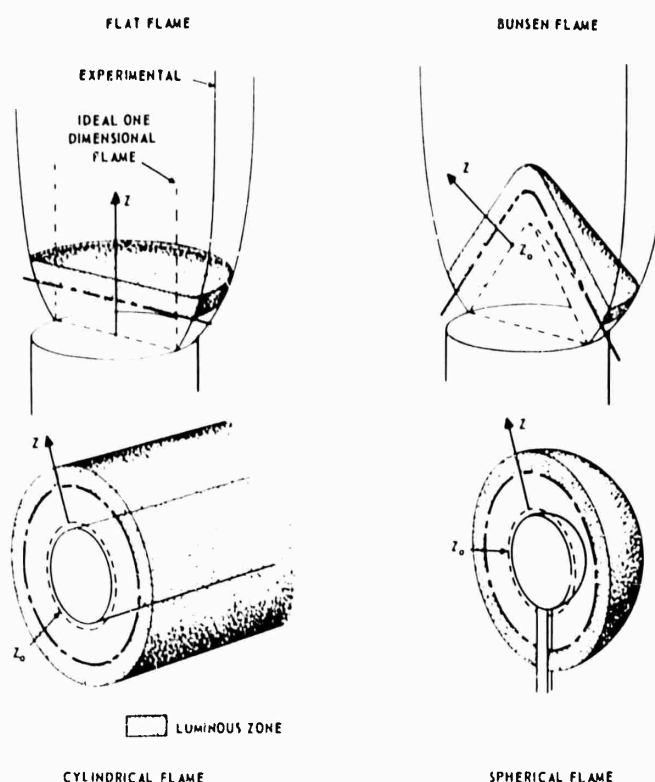
SPHERICAL FLAME

Fig. I-1   FLAME GEOMETRY

a – Geometries of Several Flames Which Can Be Analyzed
Using a One-Dimensional Model

Cylindrical and spherical flames possess one-dimensional
geometry and minimum dimensions are dictated by quenching of the flame.
If the effects of curvature on the flame structure are to be minimized,
the radius of curvature should be large compared with the flame thick-
ness.

The third requirement of adequate thickness depends on the
spatial resolution of the experimental techniques. Since flame front
thickness depends inversely on pressure and burning velocity, (see
Chapter IV, Appendix A), some control is possible. Most studies are
made on flame fronts whose thickness lies between a lower limit of
0.1 cm which is dictated by the precision of the distance measurements,
and an upper limit of 10 cm dictated by practical considerations of
size and available pumping speed.

9

Burners

The basic unit of flame studies is the burner. Almost every research worker has his own design and the literature on special burners is as wide as combustion itself. A number of examples will be discussed.

The burner must provide for stabilization of the flame. There are two types of burners - open tubes and screen supported. In the open tube system, stabilization is in the boundary layer either of the tube or behind a bluff object. The geometry of a tube flame is determined by the approach gas velocity profile, according to the simple burning velocity law (Fig. I-1b). At every point of the flame front

$V_o - V_g \sin \alpha$

☐ COLD GAS
▨ PRE LUMINOUS REGION
☐ LUMINOUS REGION
☐ POST LUMINOUS REGION
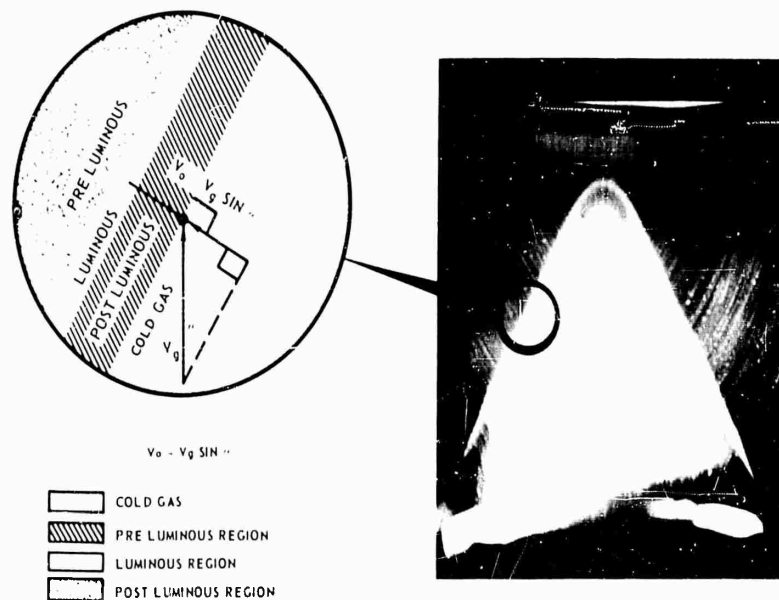
Fig. I-1   b - Burning Velocity Definition for Bunsen Flames
(cont.)

10

there is a balance between the incoming gas flow and the flame propagation rate. In the screen-supported burner the flame is stabilized by interaction with, and a heat loss to, the screen. The flame shape is dictated primarily by the geometry of the supporting screen surface.

Most burners can be used for either diffusion or premixed flames according to whether mixing of the reactants occurs ahead of, or within the flame front.

Burner Housings

Because of the adverse effects of drafts and the desirability of studying flames at pressures other than atmospheric, a burner housing is almost a necessity. The main requirements are that it provide a leak-tight chamber of suitable size with convenient access and visibility.

A very convenient type of housing is provided by a glass pipe cross or tee. They are available in sizes from 1-inch ID to 6-inch ID, together with a large number of standard fittings and flanges. Joints can be made with neoprene or Teflon gaskets or with O-rings. For spherically symmetric systems suitable housing can be fabricated by a glassblower from round-bottomed pyrex flasks which are available up to 100-liter capacity. Other housings are more easily fabricated by conventional machine shop techniques (e.g., Fig. III-2).

Burner housings require windows and access ports. Windows are necessary even in glass pipe housings if photography, optical studies, or cathetometer position measurements are to be made. The windows can be of selected plate glass, provided the flame does not impinge on them directly. Optical quality Pyrex, Vycor, and quartz are available, but are rather expensive. For many flame structure studies, it is necessary to move a probe or other devices. To obtain such movement one can use a shaft seal. Several satisfactory commercial seals are on the market which accommodate from 1 8 to 1 2-inch diameter shafts. In addition, O-ring seals of almost any size can be fabricated in the laboratory. The commercial seals and several of the homemade variety are discussed in Ref. 4.

11

GAS HANDLING

Since flames are gas phase reactions, it is necessary to provide for the handling of gases. Initial pressures, temperatures, and

compositions must be determined, the flows must be metered and for sub-atmospheric systems, pumps must be provided. In addition, special techniques are required for handling corrosive gases, liquids, and solids.

Pressure Regulation and Measurements

Constant pressure (better than one part in a thousand) is necessary for satisfactory flame structure studies. This is best accomplished by using a choking orifice flowmeter input and choking orifice pump-off. This isolates the burner so that burner pressure depends only on the inlet flow and is independent of pumping fluctuations.

If a constant-pressure source of gas is available which is higher than the required metering pressure, then the pressure can be easily reduced by means of a needle valve. Common sources of constant pressure are the laboratory atmosphere or a cylinder of liquefied gas. The atmosphere can be used for regulation of many gases by use of a slack plastic or rubber bag, or a mercury or oil bubbler. A slack bag or balloon is essentially at ambient pressure. A taut balloon is slightly above atmospheric pressure, but because of the properties of rubber this pressure is almost independent of the amount of inflation (up to the bursting point). The only difficulty with balloons is their permeability and fragility. Weather balloons are commercially available with capacities up to hundreds of cubic feet.

The atmosphere is a good - but far from perfect - source of constant pressure. Pressure variations amount to several per cent from day to day and the rate of drift can be as high as several tenths of a per cent an hour. Fluctuations of the order of a few hundredths of a per cent can occur due to wind, air-conditioning systems, and slamming doors.

12   Where atmospheric or phase equilibria regulation is not feasible, excellent commercial pressure regulators are available. There are three principal types of precision regulators: the spring-loaded bypass regulator, the pancake regulator, and the Cartesian diver. The first has a spring-loaded orifice or diaphragm which spills gas to a sink whenever the pressure exceeds a set amount. It can be referenced

against atmospheric pressure or a vacuum. A vacuum is preferable because of barometric fluctuations. Regulations of the order of 0.01 per cent can be obtained with such devices. The pancake regulator utilizes a flexible diaphragm and needle valve which controls the upstream flow and hence does not spill material. Regulation to 0.01 per cent is also possible. These are superior to the spilling bypass regulator inasmuch as they do not waste material, but they can only be used over rather modest pressure ranges, with an upper limit of 30 psi. In the Cartesian diver principle, pressure is referenced against gas trapped in a float. This instrument will regulate flows or pressure to better than 0.01 per cent if it is properly thermostated (so that the reference gas pressure remains constant). It is particularly useful in the low-pressure range, since by filling the instrument with a low-vapor-pressure oil rather than mercury, precision regulation can be obtained at pressures as low as 1 cm of Hg.

These are all mechanical devices and are inherently slow in response, (usually < 10 cps). This is not a serious problem since an orifice and plenum chamber can be used to damp out high frequency fluctuations in the same manner as a capacitor is used to filter electronic circuits.

Of the many devices available for the measurement of pressure, only a few have proven useful in flame studies. These devices can be classified as manometers, diaphragm gauges, gas property gauges, and compression or McLeod devices. Two excellent surveys of pressure measuring devices are available in the literature (Refs. 5 and 6).

The most useful laboratory pressure gauge is the mercury manometer. It can easily be read to a fraction of a millimeter. With precautions, including quelling vibration and regulating temperature, a reproducibility of 0.001 cm has been attained (Ref. 7), but such precision is difficult. The common open-end manometer requires a knowledge of atmospheric pressure, and it is more convenient and accurate to use closed-end manometers.

13

In principle, an order of magnitude improvement in precision can be attained by using a low-density oil in place of mercury, but this is usually only practical close to atmospheric pressure because of problems with solution of gases in the oil, surface tension, and so forth. Another method of improving sensitivity is by tilting the tube; the

practical limit of this is a ten- to twenty-fold increase in sensitivity
at some expense in convenience. The combination of these techniques
allows measurement of pressure differences around atmospheric pressure
to 0.0002 cm of Hg (Ref. 8). The measurement of such small differences
in pressure is limited primarily by the long time-constant of the system,
which may become so long that the pressure reference may change.

Flow Measurements

The flow of gas can be measured by any of a number of different
methods. The most common laboratory method consists of inserting a
known impedance into the flow line and measuring the pressure drop
across it. This impedance can be in the form of an orifice or capillary.
Flow in these cases is well understood (see Eqs. 2 to 4). Accurate
work with these flowmeters requires a knowledge of and regulation of the
pressure. The equipment for regulating and measuring pressure must be
considered as an integral part of the system. The types of flowmeters
that have proven useful in flame studies include critical and non-
critical orifices, capillaries, and rotameters.

The most useful flowmeter for flame structure work is the
critical orifice type (Ref. 9). Its principal advantages are high
accuracy, flow isolation from downstream pressure fluctuation, linear
dependence of flow on upstream pressure, and a low dependence of flow
on temperature. The principal disadvantages of the method are in-
convenience and the requirement of a relatively high-pressure source
of gas.

The principle of the meter is that flow through an orifice
where the pressure drop exceeds the critical value ($P_1 P_2 > 3$) depends
only on the upstream pressure, the nature of the gas, and the area of
the orifice, Eq. (2). Table I-1a gives values of K for various gases.

14

$$ Q = K \cdot \frac{d^2}{4} \left(\frac{P_1}{P_2} \right) \sqrt{\frac{T}{300}} \; . \tag{2} $$

In this equation: Q is the volume rate of flow at the down-
stream pressure (cc/sec); K is a constant (see Table Ia); d is the

TABLE I-1

CONSTANTS FOR CRITICAL ORIFICES

Species i	Mol. Wt.	(c_p/c_v)	$K_v \times 10^{-3}$ **
1. Acetylene	26.04	1.26	2.034
2. Air	28.95	1.40	2.000
3. Argon	39.94	1.67	1.805
4. Carbon Dioxide	44.01	1.30	1.581
5. Carbon Monoxide	28.01	1.40	2.034
6. Ethane	30.07	1.20	1.861
7. Ethylene	28.05	1.26	1.960
8. Helium	4.003	1.67	5.708
9. Hydrogen	2.016	1.40	7.610
10. Methane	16.04	1.31	2.629
11. Nitrogen	28.02	1.40	2.034
12. Oxygen	32.00	1.40	1.902
13. Propane	44.09	1.16	1.518
14. Propylene	42.08	1.18	1.563

** $K_v = \dot{v} \, P^{-1} \, A^{-1}$ cc-atm sec atm cm^2

orifice diameter (cm); $\underline{P_1/P_2}$ is the pressure ratio; and $\underline{T}$ is the temperature (K).

The circuit for such a flowmeter consists of a pressure regulator, a manometer, and an orifice. The flow is as constant as the regulation of temperature and pressure; mass flow through the orifice is a

function of the square root of the temperature and is linear with up-stream pressure. For very small orifices the linearity of flow with pressure and the flow based on the geometrical size of the orifice will show deviations from Eq. (2). This is because of boundary layer effects in the orifice; the layer is of the order of a few mean free paths thick. This does not prevent the use of orifices, but it does make it necessary to calibrate over a wider region than would be otherwise necessary.

Orifices can also be used with less than the critical pressure drop across them, but under these conditions it is necessary to know both the upstream pressure and the pressure drop across the orifice. The circuit for such a flowmeter consists of a pressure regulator followed by two manometers with an orifice between them. The flow through such a system is given by Eq. (3). Again, it is desirable to calibrate the system, although the flows may be calculated from dimensions with moderate accuracy.

$$Q \quad k \; \frac{\ddot{}}{4} \; d^2 \sqrt{\frac{P_1 - P_2}{\rho}} \; P_1 \qquad \begin{array}{l} (k \quad 0.6 \text{ to } 0.7) \\ (P \text{ in dynes}) \end{array} \qquad (3)$$

In this equation ρ is the density ($g \; cm^3$). Flow depends upon the square root of pressure and temperature. The principal advantage of the noncritical orifice is that it can be used over a wider range, particularly in the low-flow regime.

Capillary flowmeters are useful for the very low-flow regime (below a microgram per second). Flow through a capillary follows the Poiseuille law (Ref. 5) and depends on its diameter to the fourth power, its length, the pressure drop, and the viscosity of the gas, Eq. (4). If the capillary is coiled, as is often convenient for long capillaries, then an extra term must be introduced to account for centrifugal acceleration of the gas, and the flow depends on the radius of the coil. This latter correction has been worked out (Ref. 10), and it is possible to make useful predictions of flow. The principal disadvantage of a capillary is the high temperature-dependence (regulation is necessary for precision work) and dependence on downstream flow conditions.

16

The principal advantage is convenience of size measuring very small mass flows.

$$Q = 1.0133 \times 10^3 \, \frac{\cdot \cdot}{16 \cdot} \, \frac{d^4}{L} \left(P_2{}^2 - P_1{}^2 \right) \qquad ; \frac{d^4}{16L} \left(P_2{}^2 - P_1{}^2 \right). \qquad (4)$$

In this equation, $\cdot$ is the viscosity (poises); L is the length of tube (cm); $\dagger$ is a constant (see Table I-2)

Rotameters are commercially available covering a wide range of gas flows. They are convenient instruments, but suffer from two difficulties: They tend to introduce oscillations into a system, and their precision is limited to about two per cent.

It is often necessary to construct flowmeters. The principal requirements are an orifice or capillary, a pressure regulator, and a pressure measuring system. Large orifices can be constructed easily by machining or drilling a hole of suitable size in a metal plate. The orifice can be either sharp edged (length negligible compared with diameter) or contoured; the advantage of contoured orifices is that their effective area is closer to the geometric area. Synthetic sapphire watch jewels are available with contoured holes in diameters between 0.006 cm and 0.1 cm. They are inexpensive and can be mounted in Teflon or soft metals such as brass by a swaging tool. Jewels and special swaging tools are available at jewelers' supply houses. Many jewelers will mount jewels to specifications for a nominal charge. Special glasses can be obtained for sealing sapphire jewels directly to quartz or Pyrex.

Below 0.006 cm diameter, contoured orifices can be constructed from quartz tubing using the techniques for making sampling probes (Chapter IV). Holes small as 10^{-4} cm in diameter can be sized within 50 per cent. Beyond this point capillaries are probably the most practical solution.

17

Capillaries can be conveniently made of two types of material – glass and steel tubing. Glass tubing is available with bores as small as 5×10^{-3} cm. Standard tubing is normally supplied in 4-ft lengths, but lengths up to 100 ft coiled for gas chromatography are available.

TABLE I-2

VISCOSITIES AND FLOW CONSTANTS FOR POISEUILLE FLOW

Gas	η^+ (poises x 10^4)	κ^* (mm of Hg x 10^3)
Air	1.845	2.838
	2.217	2.362
NH_3	0.982	5.332
Br_2	1.700	3.080
CO_2	1.480	3.538
CO	1.753 (21.7°)	2.987
CH_4	1.087	4.817
H_2	0.876 (20.7°)	5.977
HBr	1.819 (98.7°)	2.879
NO	1.876	2.790
N_2	1.781 (27.4°)	2.940
O_2	2.018 (19.1°)	2.595
H_2O	1.255 (100°)	4.172
H_2	1.941	2.698

18

$^+$From Handbook of Chemistry and Physics;
25°C. unless otherwise indicated

$^*\kappa = \dfrac{0.5236}{r}$ (Ref. 5)

Another good material for capillary flowmeters is stainless steel hypo-
dermic tubing which is available with diameters between 0.1 inch and
0.001 inch and in lengths as long as 100 ft.

The most straightforward and satisfactory method of flow
calibration is to use a known volume and time the rate of pressure rise.
A few precautions must be observed: (a) Pressure must be low enough
so that compressibility effects are negligible; (b) temperature must
be known, and (c) the volume must be isolated from the flowmeter by a
critical orifice.

For very low flows an attractive method of calibration is the
soap bubble technique, in which the rate of passage of a soap film
through a calibrated burette is used. This technique is satisfactory
except for low molecular weight gases such as hydrogen or helium,
which diffuse rapidly enough to produce significant errors. Conven-
tional gas flowmeters are satisfactory but rather clumsy.

Pumping Systems

Since most flame structure studies are made at reduced pres-
sure, pumps are an important piece of equipment in the combustion labo-
ratory. For a satisfactory burner system, the pump must be capable of
handling the flow of material through the burner and must provide
choking flow across the exit orifice so that the pressure inside the
burner will be independent of pumping fluctuations. It must be capable
of handling the combustion gases, which may be condensable and corro-
sive.

Pumps are described by two parameters, pressure range and
pumping speed. These data are usually available from the manufacturer
in the form of a graph. The ordinary laboratory pump (both rotary and
piston) is a constant-displacement device and has, therefore roughly
constant pumping speed limited in the low pressure range by leakage
and the vapor pressure of the oil. Piston pumps are normally useful
down to about 1 inch of mercury, while rotary pumps are useful down to
10 microns (single-stage pumps) or 0.1 micron (double-stage pumps).
The most generally useful pumps for flame work are the rotary pumps
having a feature called "air ballast." In these pumps air is injected

19

into the second stage, sweeping out condensable gases. This allows
the pumping of such vapors as water, kerosene, acetone, etc.
For high-speed pumping, steam ejector pumps and the Roots mechanical
booster pump could also be useful. A good discussion of pumps and
pumping problems is given by Dushman (Ref. 5).

For the lower pressure ranges, diffusion pumps, ion pumps
and cryostatic pumps are available, but because of size problems, flame
studies have not been undertaken in this pressure range.

One important point to consider in any pumping system is the
size of the piping. If pipes that are too small are used, only a frac-
tion of the pump capacity may be effectively used. If continuum flow
is involved (that is, the pipe diameter is large compared with the mean
free path) then the impedance offered by the line is proportional to
its length and inversely proportional to the fourth power of the radius,
Eq. (5):

$$S = \frac{1}{1/S_{pump} + 1/S_{line}}$$

$$S_{line} = \frac{8 \pi L}{\pi P d^4} \quad .$$

(5)

In this equation: S is pumping speed (liters/sec). A good
discussion of flow problems in vacuum systems is also given by Dushman
(Ref. 5).

The pumping capacity required for a given flame system is
determined by the flow rate. Since burner dimensions should be larger
than the flame front thickness, it follows that the minimal burner size
is inversely proportional to both pressure, and burning velocity,
Eqs. (6a-d).

20

Flat Flame	$S = \pi d^2 v_0 R$	(a)	
Cylindrical Flame	$S = \pi d v_0 R$	(b)	
Spherical Flame	$S = 4\pi d^2 v_0 R$	(c)	(6)
Bunsen Flame	$S = \frac{\pi d^2}{4 \sin \theta} R$	(d)	

Using Eqs. (1) and (6), the required burner size and pumping
capacity can be established as a function of pressure and burning
velocity (Fig. I-2). The required pumping speed rises quadratically
as pressure is reduced, since flame thickness depends inversely on
pressure and burner size quadratically on flame thickness. This factor
has limited flame studies to moderate pressures.

Fig. I-2   PUMPING SPEED REQUIREMENTS FOR BURNER SYSTEMS

Lines of constant pumping speed and constant pressure (atm)
are plotted against burning velocity and burner diameter   21
which is chosen to be ten times the flame front thickness
estimated from Eq. 1.   S = pumping speed required at sys-
tem pressure (liters sec): $S = 3 \, v_o D^2$ where v_o is the burn-
ing velocity (cm sec): D = burner diameter (cm).   This
assumes the burned gas is cooled back to the initial tem-
perature and no mole number change occurs.   A safety factor
of 3.82 is included to provide for variations from these
conditions and allow for choking exit flow.

Special Equipment

The handling of solids, liquids, and corrosive gases involve special problems. Several useful techniques will be mentioned here.

Regulators and valves are available for most corrosive gases, but they are usually designed for handling rather large amounts and pressure regulation is generally not of high precision. A pressure transducer has been described (Ref. 11),(Fig. I-3), which allows the handling of small amounts of corrosive gases with high precision pressure regulation. It has the additional advantage that no loss of material occurs so that it is suitable for handling small amounts of expensive materials such as isotopic species. It consists of a slack teflon bag in a chamber whose pressure is regulated with an ordinary precision regulator.
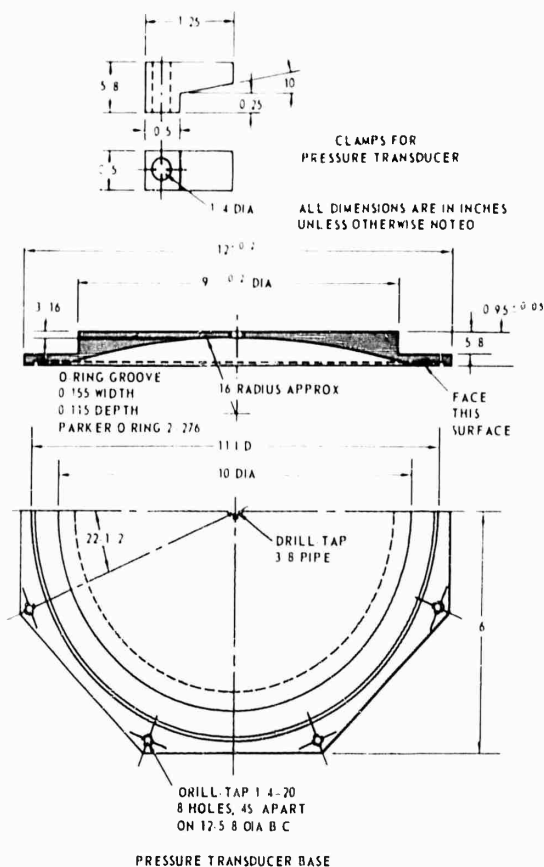
Fig. I-3 PRESSURE TRANSDUCER FOR HANDLING CORROSIVE GASES (Ref. 11)

22

The metering of small amounts of liquids is difficult. Their high density multiplies the problem relative to gases. It is difficult to avoid flow fluctuations when vaporizing a liquid. Capillary and orifice flowmeters can be employed and special techniques have been devised for extremely small flows (Ref. 12). It is usually better to prevolatize a liquid and handle it as a gas where this is practical.

Devices are available for metering powders, but the problems are even more severe than was the case with liquids and prevolatilization is by far the best technique.

PROBLEMS IN BURNER SYSTEMS

Movement of the flame front can be a major problem in burner systems. Flames drift, flicker, and in extreme cases whistle and/or roar. These difficulties can be due to poor flow metering, poor temperature control, drafts in open burners, acoustic or flow instabilities, and even external vibration or noise. These are not new problems, as witness the flickering candles of the pre-Edison period, but because of the multiplicity of possible sources of difficulty the combating of these problems more often resembles witchcraft than science.

The spatial stability of a flame front is affected by any change in flow, pressure, temperature, or composition. For small excursions there is an approximately linear relation between the changes of these variables and movement of the flame front. Thus, if one wishes to restrict flame front movement to one part in a thousand of its thickness, one must regulate these variables (flow, pressure, inlet temperature, and composition) to better than one part in a thousand.

Another major problem is oscillation of the flame front. In closed burner systems, they can be induced by vibration or periodic disturbances or flow, pressure, composition or temperature (particularly fluctuations due to poor mixing of the fuel and oxidizer). Usually, however, oscillation is due to acoustic or pressure disturbances.

23

True acoustic disturbances lie in the audio region for most burner systems, since the characteristic dimensions of the burner and housing usually do not exceed a few tens of centimeters, and the disturbances are propagated at the speed of sound. Such whistles are easy

to detect and can usually be destroyed by strategic placement of sound-absorbing material on the housing walls. An exception to this generalization is the organ pipe oscillation of a long burner tube with a flame at the mouth. The flame can amplify such oscillations, and almost the only practical method of combating this problem is to shorten the effective tube length by inserting screens so that the frequencies become high enough to be easily damped out.

Pressure oscillations, on the other hand, are flow relaxation phenomena which occur when two volumes are connected through a flow impedance. For sustained oscillations, a driving force is required, however the flame can furnish this energy. Oscillations of this type are analogous to electrical relaxation oscillations and are governed by similar laws; unfortunately, the frequency is the function of a driving force which is too complex to allow useful estimates.

The usual method of combating these problems is to raise the minimum frequency of oscillations by reducing chamber and burner volumes with screens and packing and damping the higher frequencies with acoustic absorbers.

These oscillations are a major limitation of open-tube burners, but of lesser importance with screen stabilizer burners. This would be expected, since with screen burners the volumes are almost completely decoupled by screens and packing, and the packed chimney offers an effective acoustic damper.

Flow instabilities of normally stable flames have two common causes: vibration-induced eddies, and the Taylor instability of a hot gas column (Fig. I-4). Vibration-induced instability is not usually a problem in laboratory burner systems, although it might become a problem under some circumstances. This could be combated by using a vibration-free platform.

The inherent instability of a rising hot gas column is a more serious problem with flame systems. This is responsible for the flickering observed with candle flames and in the tips of laboratory bunsen flames. It is best combated by introducing a chimney which captures the hot gas column before the instability can develop (Fig. I-5). This provides a reference hot boundary and adds to the stability of a flame.

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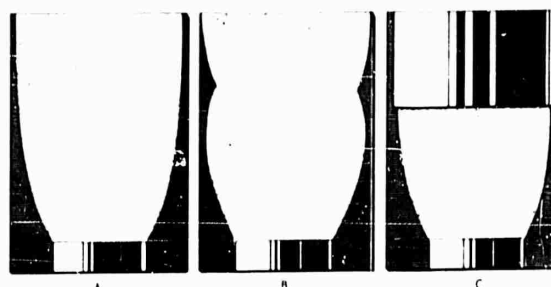
Fig. I-4   INSTABILITIES OF OPEN-TUBED FLAMES AND THE STILLING EFFECT
OF A CHIMNEY

a – Flame Disturbed by Externally Induced Vibration
b – Flame Disturbed by Buoyancy Instabilities
c – Flame Stabilized by Chimney

TYPICAL BURNER SYSTEMS

A large number of burners have been described; we have selected
several representative types from the literature and our own experience.
Other burners of interest for spectroscopic studies have been discussed
by Gaydon (Ref. 23) and the flat flame burner has been reviewed by
Powling (Ref. 14).

Bunsen Burners

The original premixed flame burner is the open tube bunsen
burner. It consists of an open tube with provision for premixing the
fuel and oxidizer. The flame is stabilized on the lip of the burner
in the boundary layer region.

A number of geometries are possible (Fig. I-5). If a long
uniform tube is used the velocity profile takes on the characteristic
parabolic distribution of Poiseulle flow and the flame will have curved
sides. If it is desirable to have a straight-sided flame, a uniform
velocity profile can be easily obtained by using a Mach-Hebra nozzle.
The nozzles can be fabricated by machining, metal spinning or electro-
forming techniques (Ref. 13). The exact form of the curves used in
the nozzle are not critical, but it is important that they be smooth
and that the area contraction be greater than 4:1.

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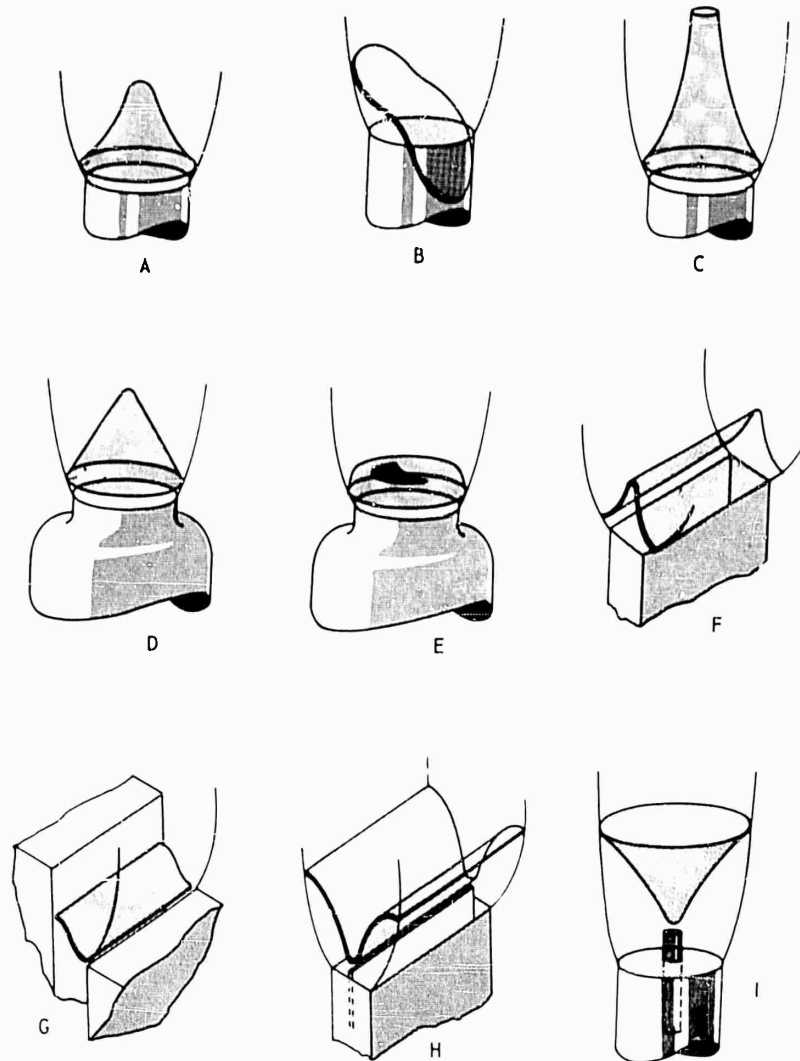
Fig. I-5   FLAME GEOMETRIES OBTAINABLE WITH OPEN TUBE BUNSEN BURNERS

    a - Open Tube, Moderate Flows - Typical Bunsen Flame[*]
    b - Open Tube, Very Low Flows - Asymmetric Flame Partially
        Extending Inside Tube (Ref. 2)
    c - Open Tube Burner with High Flows - Yielding a Conical
        Flame with No Tip (Ref. 28)
    d - Constant Velocity Profile Mach-Hebra Nozzle with
        Moderate Flows - Yielding a Straight-Sided Conical
        Flame (Ref. 13)[*]
    e - Nozzle Burner with Low Flows Yielding a Button-Shaped
        Flame[*] (Ref. 29)
    f - Rectangular Burner Yielding a Tent-Shaped Flame (Ref. 2)
    g - Slot Burner Yielding a Single-Sheet Flame (Ref. 30)
    h - Open Tube with Inverted Flame Stabilized Above a
        Coaxial Rod[*] (Ref. 2)
    i - Open Tube with Butterfly Flame Stabilized Above a
        Crossed Rod

[*]Center line indicates axial symmetry.

26

The burner illustrated in Fig. I-6 was made for microprobe sampling studies of a propane-air flame. It has a half-inch Mach-Hebra nozzle, a packed chimney, and minimum-size chamber consisting of a 2-inch, Pyrex pipe cross. A screw drive in the base of the cross allows the burner to be moved vertically through an O-Ring seal. Critical-orifice flowmeters were used in series with rotameters; pressure regulation was accomplished by using slack bags.
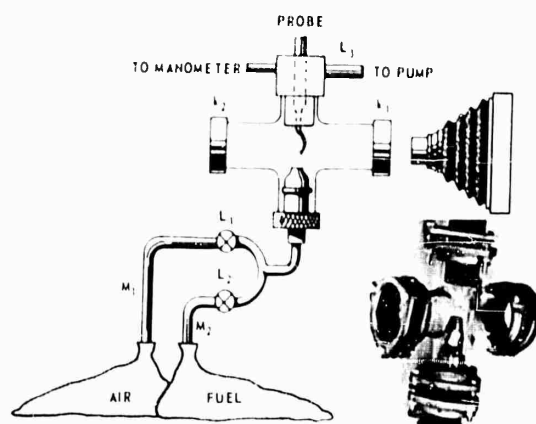
Fig. I-6   SCHEMATIC DRAWING OF GLASS PIPE HOUSING FOR STUDIES OF LOW PRESSURE BUNSEN FLAMES

Legend: A   - Water-cooled chimney
         d   - Burner traversing mechanism
         J   - 2" glass pipe cross housing
         K_1-K_2 - Windows
         L_1, $L_2$$L_3$ - Critical flow orifices
         $M_1$$M_2$ - Rotameters

27

Flat Flame Burner

It is often desirable to have a flat flame whose structure approximates the ideal one-dimensional flame of theory. In theory this could be accomplished with a uniform approach stream velocity exactly balancing the burning velocity. This is not practical because the flame distorts the flow profile and a button-shaped flame results. The system is also unstable to small disturbances. This problem has been solved by the development of two ingenious burner systems. The first is the grid burner in which a stabilizing grid is introduced into the incoming stream (Ref. 14). The second is the baffle in which a uniform obstruction is placed in the hot exit stream (Ref. 15).

With grid burners suggested by Sir Alfred Edgerton, stability is obtained by making the incoming gas slower than the burning velocity so that the flame tends to burn back toward the screen. As it approaches the screen, heat is lost by conduction. This lowers the burning velocity until balance is obtained between the incoming gas flow and the burning velocity of the new, enthalpy deficient flame. This loss need not be large and the system can be considered as one with an enthalpy corresponding to a flame lower inlet temperature. This relation has been studied in some detail (Ref. 16).

In the case of the burners with an obstruction in the burned gas (Ref. 15) the operation may be as follows: The inlet velocity slightly exceeds the burning velocity at the throat of the burner, but beyond the throat the stream tubes expand so that a point of balance is reached where the increased cross section reduces the velocity to the burning velocity. The function of the plate is to suppress the conical configurations and provide a flat reference surface.

The burner illustrated in Fig. I-7 is a flat screen burner suitable for the production of low-pressure flat flames. It has produced stabilized flames over the pressure range from one-third of an atmosphere to one-hundredth of an atmosphere.

In the experience of this Laboratory, the most uniform results are obtained by using either electroformed screens of sintered ceramic plates. Velocity profiles uniform to one per cent are feasible a few mesh diameters downstream of such an array of screens or

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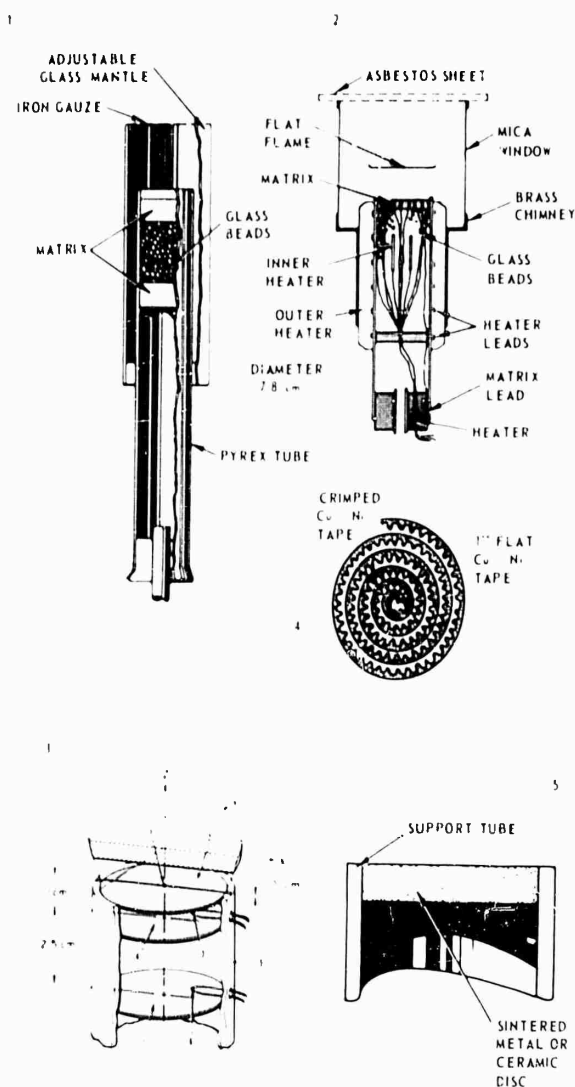
Fig. I-7   FLAT FLAME BURNERS

a - Schematic Diagram of Flat Flame Burner Using a Heat
    Sink Inlet Matrix. The inlet matrix may take a number
    of forms:
       (1) Arrays of small tubes (Ref. 14)
       (2) Sintered metal discs (Ref. 14)
       (3) Electroformed metal screens (Ref. 31)
       (4) Spirals of crimped metal tape (Ref. 17)
       (5) Sintered porcelain and quartz discs (Ref. 27)

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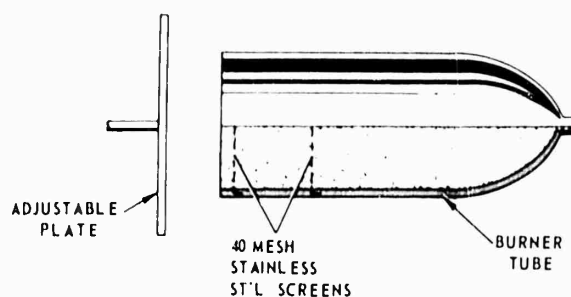
Fig. I-7b - Hot Plate Flat Flame Burner (Ref. 15)
(cont.)

porous plates. However, any uniform screen or porous material could
have been used. For example, successful burners have been produced
using sintered porous metal (Ref. 16), bundles of small tubes (Ref.
14), and a roll of corrugated metal (Refs. 17 and 18). Other possi-
bilities include stacks of thin metal sheets, and arrays of wire or
quartz rods.

Because of the small volume of the flat enclosed burner, the
most satisfactory method of ignition is to use a pilot diffusion flame.
Usually air or oxygen is passed through the burner, and fuel through
the pilot is ignited by a high-voltage spark. Fuel can then be added
slowly to the burner, the flame will quietly seat itself on the burner:
and the pilot diffusion flame can be extinguished.

Spherical Flame Burner

Spherical symmetry is often desirable in a flame since it
fixes the flow geometry and thus reduces the number of independent
measurements necessary to describe a flame front. For premixed flames
it is necessary to have a stabilizing surface analogous to the screen
of the flat flame burner. The particular model illustrated in Fig.
I-8 utilizes a 1-inch diameter sphere of sintered aluminum oxide.
Stable flames of satisfactory symmetry have been produced over the
range from 1/5 to 1/100th of an atmosphere. The range depends on the
chemistry of the system and available pumping speed. Sintered metal
spheres have been tried, but the commercial material was not suffi-
ciently uniform.

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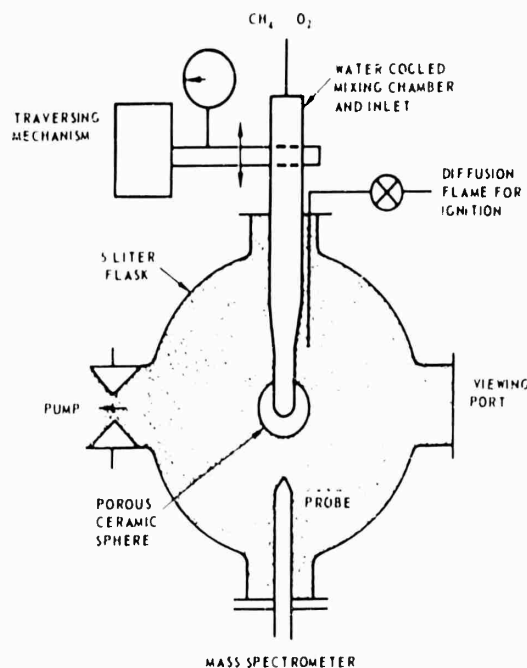
Fig. I-8   SPHERICAL FLAME BURNER (Ref. 32)

The housing for this system is a modified 3-liter Pyrex flask. Symmetry does not depend strongly on the number of pumping ports, or their relation to gravity at low pressure (Ref. 19). Gravitational effects are appreciable above one-tenth of an atmosphere. As with the flat flame, the most satisfactory method of ignition is by use of a pilot flame.

The spherical burner can also be used for diffusion flame studies (Ref. 20), using the ball as the source of fuel (or oxidizer) in an atmosphere of oxidizer. Obviously the atmosphere must be replenished as it reacts and a flow system of some kind is necessary. If a large container is used the distortion of spherical symmetry is slight.

Diffusion flames of reasonable spherical symmetry can be obtained at low pressure, using a "point source," i.e., a small tube. If low pressures are employed where diffusion coefficients are high, the diffusion velocities can be made large compared with mass velocities, and gravitational effects and the symmetry will be good.

31

Linear Burner for Studying Cellular Flames

A long narrow burner provides a convenient system for studying cellular flame phenomena (Ref. 21). It presents the cellular flame in the form of a one-dimensional array. The system in Fig. I-9 was used to make composition profiles at atmospheric pressure. Presumably it could be adapted to reduced pressure studies with a suitable housing.
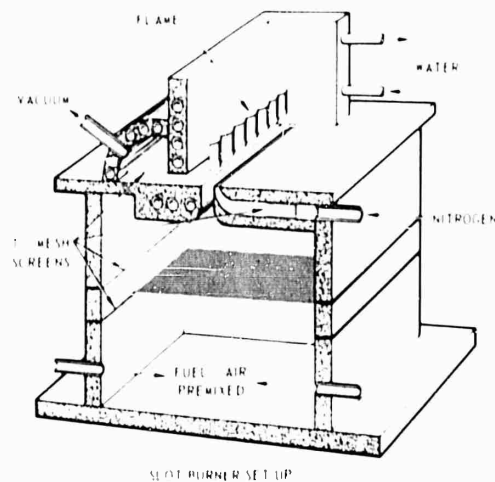
Fig. I-9. SLOT BURNER FOR STUDYING COMBUSTION WAVE INSTABILITIES (Ref. 20)

Flat Diffusion Flame Burner

A diffusion flame can be maintained at the boundary between two streams of uniform velocity profile, separated by a thin septum. The geometry of this system is particularly suited for spectroscopic studies and it has been so applied (Ref. 22). In designing such a system (Fig. I-10) some care is necessary to obtain uniform equal velocity profiles and in minimizing the thickness of the septum since these factors introduce disturbances in the system. Reduced pressure operation could presumably be obtained with such a burner in a suitable housing. Other burners of interest for spectroscopic studies have been discussed by Gaydon (Ref. 23).

32

BURNED GASES

FUEL LEAN FLAME

FUEL RICH FLAME

FUEL OXIDIZER
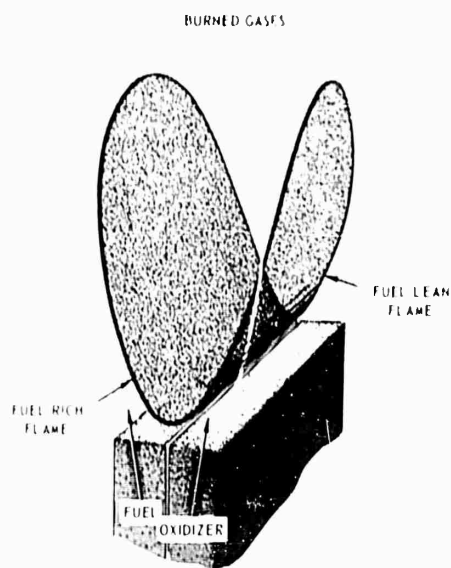
Fig. 1-10. A FLAT DIFFUSION FLAME BURNER FOR SPECTROSCOPIC STUDIES (Ref. 21)

Opposed Jet Diffusion Burner

A convenient apparatus for studying diffusion flames is the opposed jet burner (Ref. 24), (Fig. 1-11). Here the streams of fuel

GAS (O₂ N₂) INLET

COLLARS HAVING THREE LEVELLING SCREWS

COOLING COILS

WATER

OUTER MATRIX

MATRIX FOR RECTIFYING GAS FLOW

THERMCOUPLES (six)

GLASS BALLS

BRASS CYLINDER (6 31 cm dia 72 cm long)

RUBBER BUNG

THERMOCOUPLES LEADS

GAS INLET (C₂H₄ · N₂)

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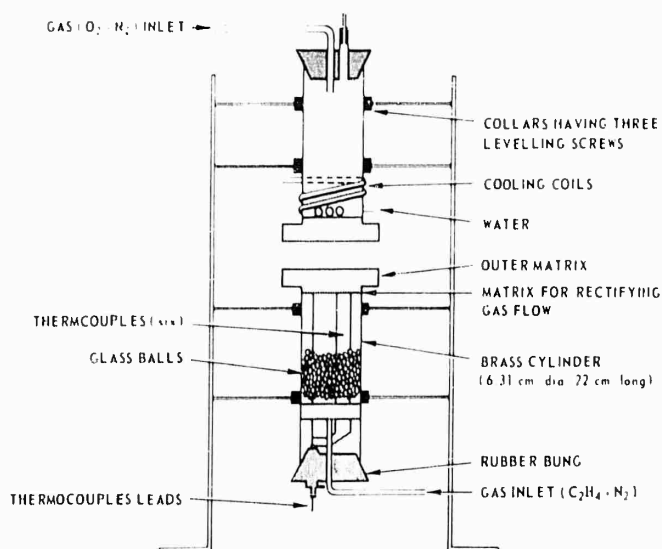
Fig. 1-11. OPPOSED JET DIFFUSION FLAME (Ref. 23)

and oxidizer are introduced '' opposed balanced streams. If uniform velocity streams are employed using burners similar to those employed with the flat screen burner, very excellent flat flames are obtained (Ref. 25). Since the burned gases leave the system radially it is necessary to provide for their removal. At atmospheric pressures, it is desirable to keep the axis of the system vertical to preserve the symmetry. The theory of this type of burner system has been worked out particularly with respect to interpreting the position of the flame fronts and the blow off point (Ref. 26).

Multiple Diffusion Burner

The multiple diffusion burner (Ref. 27) (Fig. I-12) allows the study of flames whose reactants cannot be premixed. It consists of a bundle of tubes which are fed from a source of one reactant and a jacket which is fed by a source of the second reactant. The result is an assembly of small diffusion flames which tend to merge as the characteristic diffusion mixing length becomes comparable with the flame front thickness. In the limit where the tube spacing is small compared with the flame front thickness a premixed flame results.

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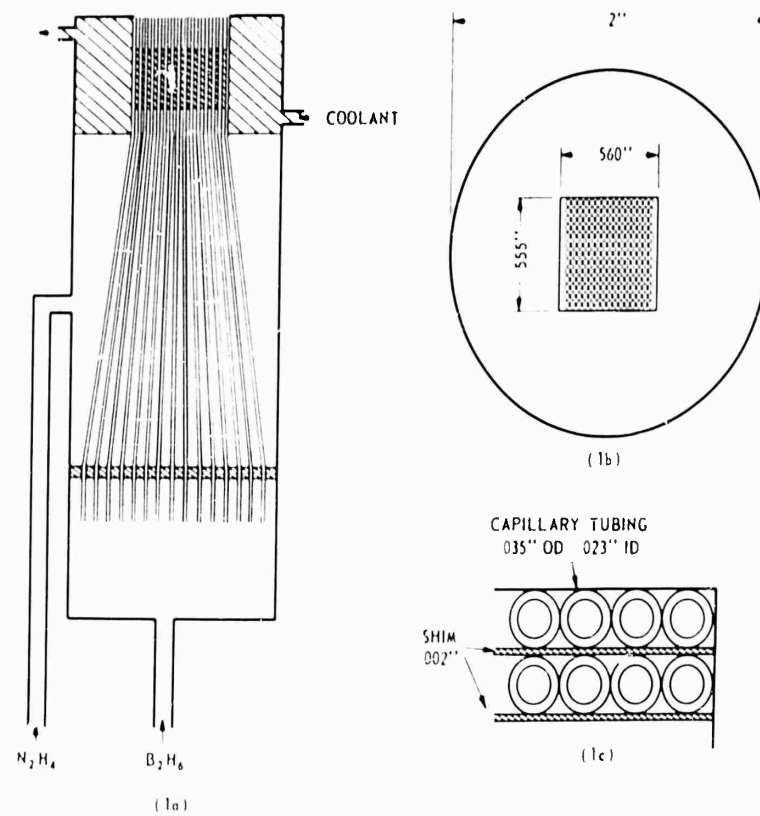
Fig. I-12   A MULTIPLE DIFFUSION BURNER FOR STUDYING SYSTEMS WHICH
CANNOT BE EASILY PREMIXED (Ref. 26)

35

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38

II

LOCAL AERODYNAMICS OF FLAME FRONTS

INTRODUCTION

A flame is a laminar flow system involving heat release,
chemical reaction, thermal conduction, and molecular diffusion. Aero-
dynamically, such a system is characterized by specifying the geometry
of the stream tubes, the local velocity, and the local density. These
variables can be measured experimentally to provide an important
technique for characterizing flame fronts (Fig. II-1).

At constant pressure the three aerodynamic variables, area
ratio, velocity, and density are related through a continuity equation,
Eq. (1), which expresses gross conservation of matter. For flame sys-
tems which have appreciable gradients only in the direction of propa-
gation, the general three-dimensional continuity relation (Ref. 1) can
be simplified to Eq. (1) (Ref. 2).

$$\rho v \mathcal{A} = \rho_o v_o \mathcal{A}_o = \dot{m}_o .\tag{1}$$

Here ρ is the density at any point; v is the total velocity
(or any component of it); $\mathcal{A}$ is the cross section of the stream tube
measured normal to v (Fig. II-2); and $\dot{m}$ is the mass flow g/sec. The
subscript "o" indicates initial gas condition.

A stream tube is defined as any volume in a flow system
which can be enclosed by path lines. Equation (1) applies to any
infinitesimal streamline or finite stream tube (providing lateral grad-
ients are negligible), and mass flow through such a volume is con-
served. If the stream tube cross section does not change through the
flame front, Eq. (1) reduces to the one-dimensional continuity equa-
tion Eq. (2), used in theoretical studies. This is not a good approxi-

39

References are on pages 61 and 62.

mation for laboratory flames since lateral expansion is appreciable (Ref. 3).

$$\hat{c} v = \hat{c}_o v_o = \dot{m}_o \qquad . \qquad\qquad (2)$$
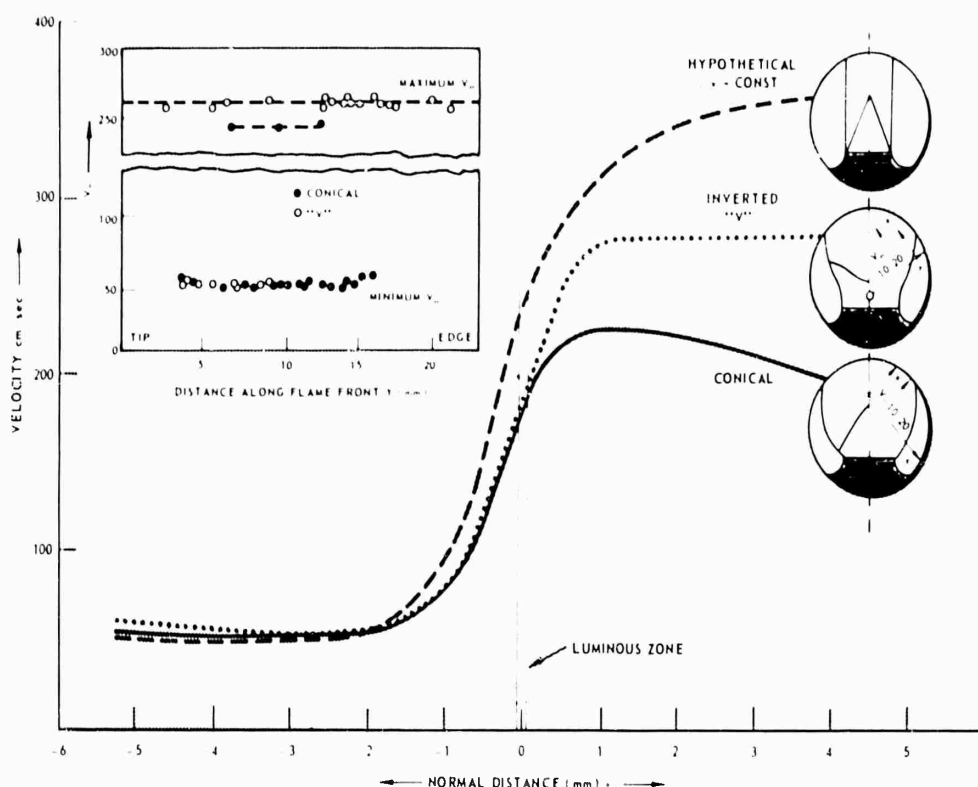
Fig. II-1   VELOCITY PROFILES FOR CONICAL BUNSEN AND INVERTED VEE
FLAMES   (Ref. 3)

(Stoichiometric Propane - at 0.25 atm) Velocity in cm/sec
is plotted as a function of the distance through the flame
front normal to the luminous region. Conical and inverted
vee flames are compared with the ideal flame with no ex-
pansion. The insert shows the invariance of the results
with position along the flame front.

40

Velocity

Velocity is the time derivative of the distance variable.
It is a vector quantity having the dimensions of length per unit time.

In a one-dimensional system velocity reduces to a scalar variable, which is completely described by a single profile, giving it as a function of distance. It is convenient to measure distance and velocity in the direction of flame propagation (normal to the flame front as visualized by the luminous region).

Area Ratio

The area ratio is the relative cross-sectional area of a stream tube measured orthagonally to the velocity measurement. The reference cross section is usually chosen in the cold approach gas. Experimentally it is usually determined by visualizing and measuring the path lines. For an arbitrary geometry the problem of interpretation of path lines would be a complex exercise in solid geometry, complicated by the restrictions of experimental techniques. This problem can be avoided by studying flames with axial symmetry which are completely specified by path lines in a single plane. This involves no loss in generality since flame microstructure is not affected by external geometry, if the curvature of the flame front is large compared with the flame front thickness (Ref. 3).

Five geometries have been used to make area ratio measurements in flame studies: the conical or common bunsen flame, the flat screen-supported flame, the spherical flame, the cylindrical flame, and the ducted flame. They possess one-dimensional flame fronts, have flow patterns which can be visualized in a single plane (Fig. II-2) and can be experimentally realized. The first four of these systems possess one or more axes of symmetry, so the visualization of path lines in any plane passing through an axis will define the flow pattern.

Density

In aerodynamic measurements density is a derived quantity, related to temperature and composition through an equation of state. Most flame systems can be adequately represented by the perfect gas law, Eq. (3). Since T and $\bar{M}$ are variables this provides a link between

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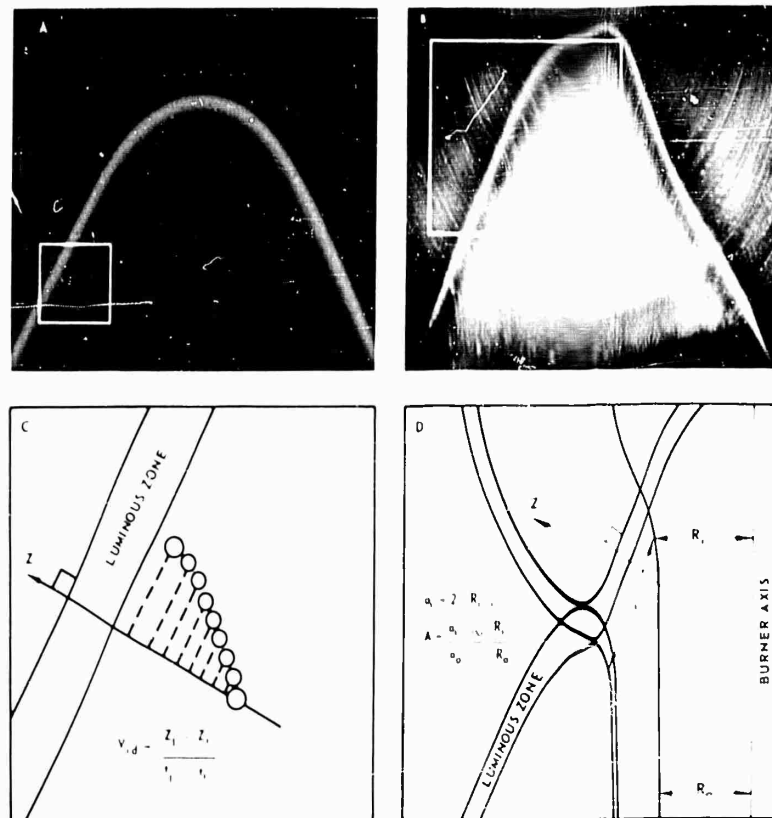
Fig. II-2   MEASUREMENT OF VELOCITY AND AREA RATIO USING PARTICLE
SPOT AND PARTICLE TRACK PICTURES

   a - Particle streak pictures (Magnesium flash bulb 0.03
       sec duration)
   b - Particle spot picture (100 watt-sec flashes spaced a
       nominal 100 microseconds apart)
   c - Measurement of gas velocity normal to luminous region
   d - Determination of area ratio using stream tube geometry
       measurements

the pure aerodynamic description when T and $\bar{M}$ are presumed to be speci-
fied and the thermodynamics and chemistry of the flame.

42

$$\rho = \frac{P\bar{M}}{RT} . \tag{3}$$

   In Eq. (3), P is pressure (atm); $\bar{M}$ is   average molecular
weight (g/mole); T is temperature (°K); and R is   the molar gas constant
82.05 cc atm/mole/°K.

Nevertheless, it is often convenient for engineering problems to separate the aerodynamics from the chemistry. This is usually a valid approximation, since flame microstructure is not strongly coupled with the flame geometry or flow pattern. In such a treatment it is usually assumed that the flame can be represented by a density discontinuity. A number of special two-dimensional flames have been solved numerically using this model. General equations have been set up for the three-dimensional case (Refs. 4, 5, and 6). These models take no account of the flame microstructure, and are of no use in detailed flame studies. The use of density determination to avoid direct aerodynamic measurements is discussed in the last section of this chapter.

Experimental Methods

The two measurable aerodynamic quantities are stream tube area ratio and velocity. Velocity is the principal variable and area ratio can normally be considered as a correction factor on ideal one-dimensional flow which, however, must be considered in quantitative work.

FLOW VISUALIZATION WITH PARTICLES

The most successful method for studying flame aerodynamics has been that of flow visualization with suspended microscopic dust particles. This is a standard technique in aerodynamic studies which has been applied to flames by a number of authors (Refs. 3, and 7-14). The early work utilized streak photographs and made the assumption that lateral expansion of the flame could be neglected. More recent studies (Ref. 3 and 13) have shown that this approximation is unacceptable for quantitative work and provision must be made for the direct measurement of velocity in the flame front itself.

43

Apparatus

To make aerodynamic measurements by use of particle tracers, it is necessary to visualize their path and measure it quantitatively. This is done photographically with a timed, repetitive illumination system. From such a picture, velocity can be obtained by direct measurement (Fig. II-2).

Because of the small size of particles, the shortness of time intervals, and the high spatial resolution required, the experimental techniques are unusual and will be discussed in some detail. The requirements are a burner with a method for injecting a few particles of suitable size, an optical system for viewing the flame, and an illumination system for visualizing the particles. (See Fig. II-3).
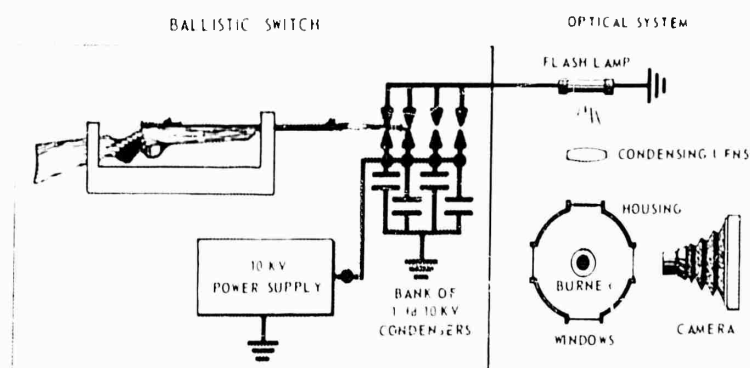
Fig. II-3. OPTICAL ARRANGEMENT AND BALLISTIC SWITCH FOR MAKING MULTIPLE IMAGE PARTICLE PICTURES USING AN ELECTRONIC FLASH LAMP

Particle Illumination 90° from Camera View. See Fig. II-5 for dark field (180° illumination) optical arrangement with Mg flash lamp for streak pictures. The optical and illumination arrangements of these two figures are interchangeable.

44

Particles---To be suitable for tracer studies a particle must be small, non-volatile, non-reactive, and non-catalytic. A number of materials suggest themselves for these studies, some of which are listed in Table II-1. The table is divided into two groups: Particles

which volatize at a relatively low temperature and hence are useful
for marking a particular isothermal surface; and non-volatile

TABLE II-I

PHYSICAL PROPERTIES OF SOME MATERIALS
FOR PARTICLE-TRACK FLAME STUDIES*

Material	Thermal Conductivity, k (cal cm^2 ...)	Melting Point	Boiling Point	Density (gm)	Remark
Volatile					
Al	0.53 .28	660	... 30	...	Reacts ...
SbCl		Subl. ...	...		For ...
TiCl$_4$		30	136	1 ...	Very ... flames
ZnO		1800		1	... flame ...
Non-volatile					
Al$_2$O$_3$	0.04 8 2050	2050	...	4	
Glass (Pyrex, Scotch Lights)	0.002 .20	100		... 4	Very reflective
MgO	0.0002 .20	2800	3600	4	Generally considered best before II-I
Quartz	0.010	1200 softens	2230	2.6 .20	
TiO$_2$		2100	decomposes 1.5 t		
ZrO$_2$		4000	4300	5.4	

*Source: Handbook of Chemistry and Physics; International Critical Tables.

particles, which are suitable for quantitative studies. In the latter
group the most useful material has been magnesium oxide, which is
commercially available as a powder whose unclustered particles range
from one to five microns in diameter. Other particles, such as quartz,
glass, and aluminum have been used, and special requirements of the
system should be considered before choosing the particle material.
Particles for quantitative work must not be volatile at the highest
temperature in the flame, and they should not react with species found
in the flame. Zinc oxide particles for example, are not suitable in
rich hydrocarbon flames because they are reduced to metallic zinc.

45

Particle Injection System---Since dust spoils optical systems, and thermomechanical forces preferentially coat cold windows and lenses it is advisable to minimize the amount of material by injecting in the illumination plane and only during the actual photographic period. In addition it is necessary to avoid flow disturbances which distort the flame. A number of techniques have been used to accomplish this (Ref. 7-14). A satisfactory scheme is illustrated in Fig. II-4. Parti-

46
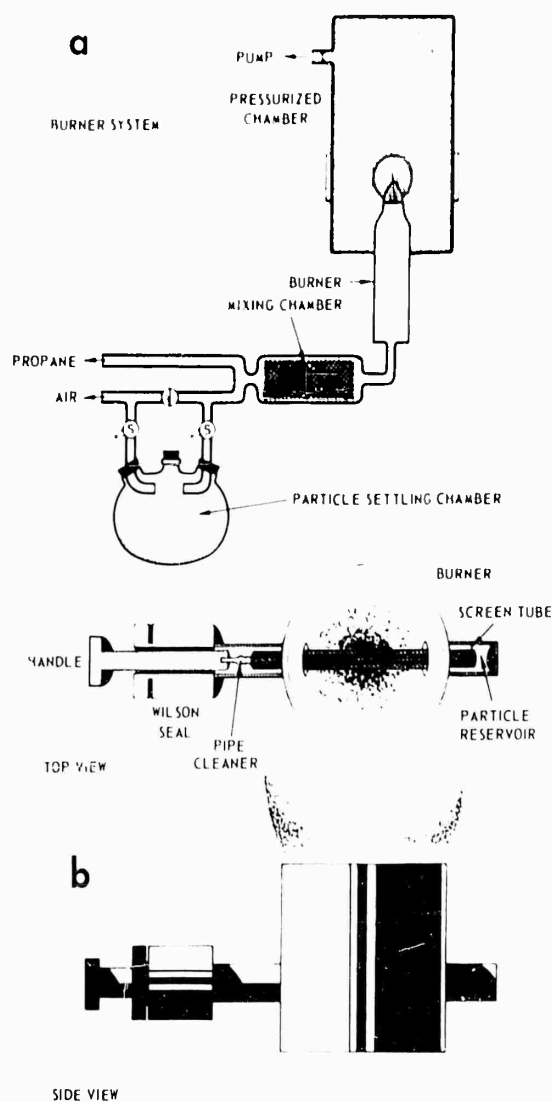
Fig. II-4   METHODS FOR INTRODUCING PARTICLES INTO BURNERS

a - Settling Chamber Method
b - Pipe Cleaner Method

cles are introduced by sifting the dust held on a pipe cleaner through a
fine screen into the gas stream. Even this system requires frequent
cleaning.

Photographic System---Since the study of flames requires
high resolution, care must be taken with the photographic arrangement.
The techniques are essentially those of photomicrography. In a cy-
lindrically symmetric flame it is only necessary to study the
path lines in the diametral plane. Precision high-aperture optics
should be used for light gathering power and to sharply define the
plane of focus, so that images are limited to the diametral plane.

Optical aberrations come from three sources: the lens, the
window, and the flame. A satisfactory lens used properly will intro-
duce less than one per cent distortion into the field, and will show
a resolution exceeding 10^{-3} cm. A check of lens performance can be
made by photographing a standard grid. It should be remembered that
most camera lenses are designed to have a smaller image plane than
object plane, while in flame studies the opposite practice is common;
therefore, the best performance is obtained by reversing the lens.

The flame itself can introduce image distortion (Chapter VI),
since the density gradients in the flame deflect light beams. The
effect depends on the density of the gas and the steepness of the
gradients; it is important for high-pressure, high-velocity flames and
negligible for sub-atmospheric flames with burning velocity below one
meter per second. The selection of the diametral image can also be
made with a narrow beam of light provided by a set of slits. The
optical method of defining the plane wastes less light than the slit
technique, and this can be important since light intensity is often
marginal. A synchronizing shutter is required, since both the flames
and the particles emit light, but no special filters are required to
prevent fogging by particle luminosity, providing the illumination is
adequate and the minimum number of particles is used. A sharp luminous
zone image is desirable since this provides a coordinate axis and
allows correlation of these with other flame structure measurements
(Chapter VI). Both high resolution and high speed film are desirable
for these studies, but adequate resolution is the primary requirement.
It should be compared to the resolution provided by the lens. Figures
II-3 and 5 give a diagram of a photographic system which has proven

47

useful in such studies. A number of useful film types are listed in Table II of Chapter VI.

Illumination System---This is the critical component of the experiment. The tracer particles are so small that they are viewed by scattered rather than reflected light. This calls for high light intensities; brightness rather than total luminous flux is desired. This is accomplished most easily by focusing the image of a very bright light source directly on the area to be photographed. The maximum illumination per unit area is thus obtained. Since an optical image can never be brighter than its source, only the brightest light sources are suitable. These include electronic flash lamps (Ref. 15), exploding wires (Ref. 16), and high intensity shock waves (Ref. 17), and recently a new possibility, Lasers (Ref. 18). Flash bulbs which depend upon the combustion of magnesium, or preferably zirconium, are marginal (unless dark-field illumination is used) (Figs. II-5 and 6).
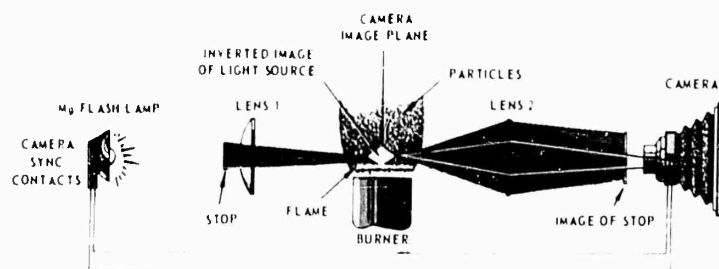
Fig. II-5   DARK FIELD ILLUMINATION SYSTEM FOR MAKING PARTICLE STREAK PHOTOGRAPHS USING A MAGNESIUM FLASH LAMP

(See also Fig. II-2.)

Despite their high luminous flux, the intrinsic brightness is limited by the vaporization temperature of their oxides. Because of power requirements, continuous lamps are ruled out. (To operate a lamp continuously at the same intensity as a high-power flash lamp would require a power source of the order of 100 megawatts.) It has been shown experimentally that the velocity normal to the luminous surface of the flame is independent of position along the flame front (Ref. 3) (Fig. II-1). Therefore, it is not necessary to restrict the study to a single stream tube, and a two-flash illumination system is adequate.
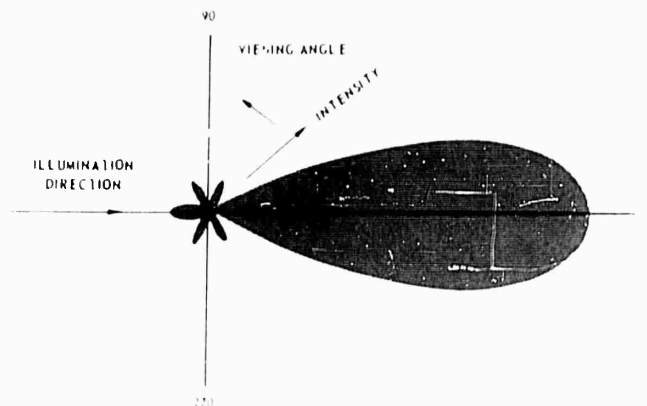
Fig. II-6   LIGHT SCATTERED BY A SMALL PARTICLE
Scattered Light Intensity as a Function of the Angle Between Illumination and Viewing

In cases where this convenient approximation cannot be used — this point should be investigated in each new flame system studied — systems are available which allow the generation of as many as fifty repetitive flashes of high intensity (Refs. 19 and 20).

Because of interference phenomena, the intensity of light scattered from a particle is a function of the angle between the illuminating and viewing axes (and also wave length of illumination and particle size) (Ref. 21). Forward interference is constructive and there is an enormous gain in scattered light intensity resulting from illumination being supplied along the viewing axis (Fig. II-6). This can be accomplished with a "dark field" system of illumination (Fig. II-5). However, much of this gain is offset by the sensitivity of the optical elements to dust and dirt, and it is usually easier to use brighter luminous sources with 90 degree illumination to keep light from the photographic optics.

Table II-2 lists a number of high-intensity illumination sources suitable for this type of work, along with their characteristics and manufacturer. Most of the electronic flash lamps are filled to pressures around half atmospheric with one of the rare gases (Xe, A, or Kr). A number of ingenious schemes have been put forward for the control of such electronic flash lamps. The problem is not simple, since the instantaneous power requirements are high and

49

TABLE II-2

SOURCES OF HIGH-INTENSITY ILLUMINATION

Source	Manufacturer	Type	Geometry	Luminous Area	Duration
Mg-filled flash bulb	Sylvania, G.E.	Med. peak	bulb	10-25 mm dia.	1/30 sec
Zr-filled flash bulb	Sylvania	Med. peak	bulb	10-25 mm dia.	1/30 sec
Low-pressure Hg arc	G.E.	AH6	tube	10 x 30 mm	continuous
High-pressure Hg arc	G.E.	BH6	tube	3 x 30 mm	continuous**
Low-pressure flash lamps	Amglo	48U4X	spiral	5 x 300 mm	5 μsec
Moderate-press. flash lamps	G.E., Sylvania	FT 108 4340	tube spiral	3 x 30 mm 5 x 300 mm	1 μsec
Moderate-press. flash lamps	E.G.G.*	FX1	tube	4 x 150 mm	1 μsec
Libessart spark gap	(Ref. 28)		spot	0.5 mm dia.	1 μsec
Exploding wire	(Ref. 16)		line	0.5 mm dia.	1 μsec
Zr arc	(Ref. 18)		spot	0.5 mm dia	continuous
Lasers					

*Edgerton, Gereshausen and Greer, Cambridge, Massachusetts

**These lamps can be pulsed with up to 10 watt-sec of energy (no more) with a considerable gain in brightness (Ref. 29).

ground wave pulses make shielding the trigger of electronics difficult. A number of mechanical systems have been used including relays (Ref. 19), bullet-triggered spark gaps (Ref. 20), spark-induced shocks and spring-loaded switches.

Time Monitoring---Time calibrations are necessary for quantitative work, because motor-driven choppers have slippage errors, and high-intensity light sources show statistical delays in electrical

breakdown. A convenient apparatus for monitoring light pulses is a photocell pickup and a driven oscilloscope. The oscilloscope should be placed at a considerable distance from the switch, with the photocell connected physically across the oscilloscope terminals. (Because of the intensity of light the sensitivity of such a system is adequate and can be increased by using lenses or a light pipe.) Another satisfactory method involves photographing a pinhole in a rotating disc. Both the oscilloscope and motors should be calibrated. The normal line frequency furnishes a secondary standard which is accurate to a fraction of a per cent. The built-in oscilloscope time standards are only good to five per cent, and the oscilloscope screen gives an image linear with angle of deflection rather than distance.

Errors can occur even with a perfect time standard, because of nonlinearities in oscilloscope presentation, film distortion, or the finite duration of the light pulses. In the case of flash lamps the initial light buildup is rapid, and accurate measurements can be made using the leading edge of the particle image.

Measurements and Interpretation

The data from these studies are a pair of negatives which particle positions can be determined and the time intervals established (Fig. II-2). Distance measurements will be discussed in Chapter VI.

Velocity is determined from repetitive flash pictures, using the primitive definition of velocity as displacement per unit time (Fig. II-2). As previously mentioned, the component of interest is usually that in the direction of flame propagation.

Area ratio is determined from long-period streak pictures utilizing the particular flame geometry involved. It is measured normal to the velocity measurements and hence parallel to the luminous region. Typical results from area and velocity measurements are shown in Fig. II-1.

A one-dimensional continuity equation can usually be applied to flames; therefore, if both velocity and stream-tube area are measured, and the density is known at any single point, then the density profile can be derived using Eq. (1). The procedure can, of course,

51

be reversed and velocity derived from density and area-ratio measurements. Density measurements are discussed in the chapter on temperature (Chapter III).

Range of Applicability

If a precision of three per cent is acceptable, then particle-tracer techniques can be used for quantitative studies of flame front aerodynamics. Where higher precision is required, it is advisable to investigate other methods. The region of applicability of particle tracer techniques is summarized in Fig. II-7.

The introduction of particles disturbs a flame. The degree depends on the type, size, and number of particles; in an extreme case the flame could be extinguished. Particle injection densities should
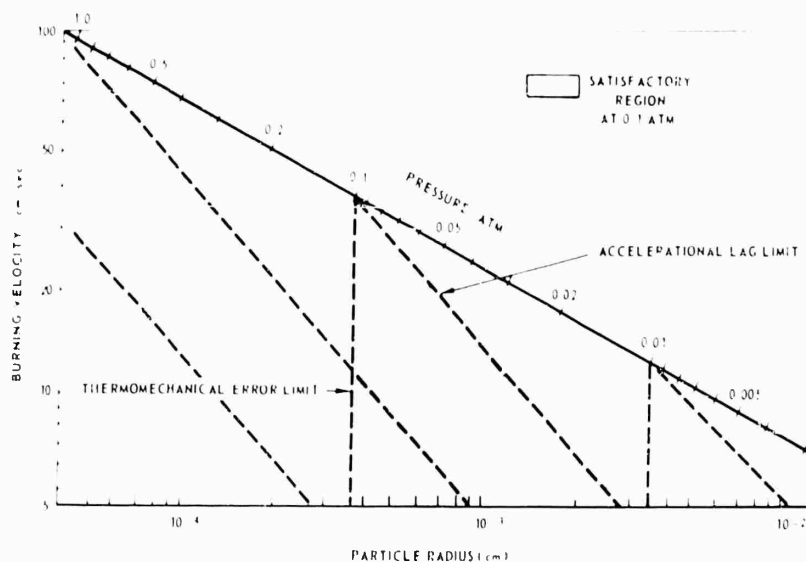
Fig. II-7 REGIONS OF QUANTITATIVE APPLICABILITY OF PARTICLE TRACK STUDIES

52

Burning velocity (cm/sec) is plotted against particle radius (cm). The region for satisfactory particle track studies (error less than 3%) at 0.1 atm is cross-hatched. To outline the region for any other pressure, locate the pressure on the diagonal axis. From this point drop a normal to the particle radius abcissa and run a line parallel to the pressure diagonals.

be chosen so that the results show no dependence on particle density.

The physical effect of the particles is heat abstraction, due to the heat capacity of the particles and radiation losses. In a typical case these mechanisms dissipate only a small fraction of a per cent of the energy liberated in the flame front, and hence physical disturbances should be small.

The chemical effects of particles on a flame are harder to determine. A particle could act as an accelerator, inhibitor, or change the course of the reaction. Because of the short residence time in the flame front, the effect should be confined to a diffusion limited region around the particle.

The flame gases and tracer particles are strongly accelerated upon passing through a flame front. In the case of the particles the accelerational force must be balanced by aerodynamic drag caused by slippage of the particle relative to the carrier gas. This is a source of error since particle movement does not correspond to gas movement. The order of magnitude of this error can be estimated by equating the forces of acceleration with particle drag using Stokes Law, Eq. (4). This is valid for spherical particles which are large compared with the mean free path, and it sets a lower limit for drag. It is suitable for estimating the range of particle sizes suitable for tracer studies. More sophisticated treatments are available which allow detailed numerical calculation of trajectories for particles of various shapes under varying flow conditions (Refs. 23 and 23).

$$F_{acc} \quad F_{drag} \qquad m\bar{a} \quad 6 \pi r v$$

$$v \quad v \qquad m \quad 4 \, 3 \, r^3 \, \rho \qquad \bar{a} \quad \frac{(T_f \, T_0)^2 - 1}{2 \, v_0^2 \, L} \qquad L \quad \frac{2.5}{P v_0} \quad (4)$$

$$r \quad \frac{3.36}{(T_f \, T_0 - 1)^{1/2}} \quad {}^{1/2} \qquad {}^{1/2} \qquad p^{-1/2} \, v_0^{-1} \; .$$

53

In this equation F_{acc} is the accelerational force on the particle (dynes); F_{drag} is the viscous drag force on the particle due to slippage; m is the particle mass (g); $\bar{a}$ is the average accelera-

tion of the particle in the flame front as defined above (cm/sec^2); $\cdot$ is the viscosity of the gas (poises); r is the particle radius (cm); Δv is the slippage velocity (cm/sec); T_f/T_o is the ratio of initial to final temperature in the flame front; ϵ is the fractional error in velocity due to accelerational lag; ρ is the particle density (g/cm^3); v is velocity (cm/sec); L is flame front thickness (cm); and P is the pressure (atm). The subscript zero indicates initial gas conditions; the subscript f indicates final gas conditions; and the superscript bar — indicates an average.

Another source of error which is important in flame front particle track studies is the thermomechanical effect. This is a force which particles experience in a temperature gradient. It results from the unbalance in molecular collisions on the hot and cold side of a particle. It is also called the radiometer effect and can be considered as the macroscopic analog of thermal diffusion. It was discovered by Atkin in 1884 and has been studied by Raleigh, Maxwell, and others. The most recent work has been a theoretical study by Waldman (Ref. 24) and an experimental evaluation made by Schmidt (Ref. 25). The agreement between theory and experiment is good (Fig. II-8).

54
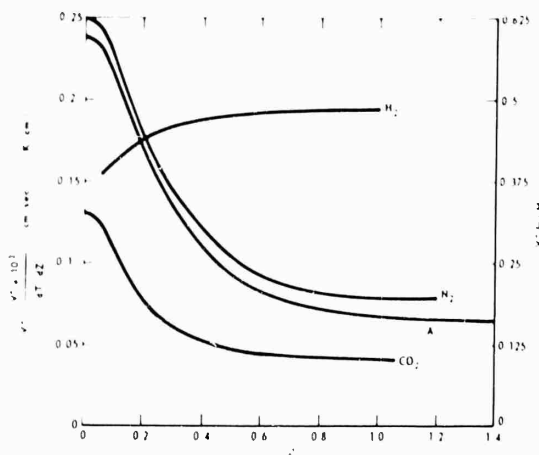
Fig. II-8   THERMOMECHANICAL EFFECT   (Ref. 25)

Reduced Thermomechanical Velocity (cm sec per °K cm) as a Function of Particle Radius (microns) for Several Gases

There are regimes of importance where the particle is small compared with the mean free path and when it is large. In the former case it can be treated as a giant molecule by the techniques of kinetic theory and the velocity is given by Eq. (5).

$$v_{TM} \quad \frac{\cdot}{P(5 + \frac{a}{8})} \frac{dT}{dZ} \quad \overset{\sim}{=} \quad 10^{-4}T^{3.4} \frac{dT}{dZ} \quad . \qquad (5)$$

In this equation $\cdot$ is the thermal conductivity (in dyne sec/cm^2/sec): P is the pressure (in dynes per cm^2); a is the accommodation coefficient for molecular collisions which is a number ranging from 0 to 1 and usually about 0.75. It should be noted that this equation has the same form as the relation for thermal conductivity in a one-dimensional system with a heat source at the origin. The equation provides an adequate description of most flames over a major part of their temperature rise. For such flames the error for particles smaller than the mean free path is constant at 15-20 per cent.

The thermomechanical effect falls off sharply when the particle becomes large compared with the mean free path dropping to a limiting value about one fifth that of the small particles (see Fig. II-8). Thus with large particles, errors no larger than 3-4 per cent would be introduced depending on factors such as drag, accommodation coefficient, etc. Estimates can be made of the effect using Fig. II-8. In practice, particles should be chosen to be large compared with the mean free path.

Small particles show random movement called Brownian motion. This is due to incomplete cancellation of molecular collisions at any given moment. For particles which are large compared with the mean free path this is a negligible source of error.

Many of the particles in the flame are charged, and the flame itself is a dilute plasma. There is very little separation of charge in a flame, however, and unless there are stray fields the electrostatic effects should be negligible. Stray fields from line pickup may explain the occasional "drunken" particle which follows sinusoidal paths in otherwise normal particle pictures.

There are three major limitations of particle tracer studies

55

in flames: Accelerational lag, thermomechanical effect, and the requirement that the particle be very small compared with the flame front thickness. (See Fig. II-7.) These effects restrict the quantitative use of particle tracer studies in flames and 2-4 per cent is the best precision which can be expected without complicated corrections based on particle size and shape.

PITOT TUBE MEASUREMENTS OF VELOCITY

The pitot tube method of measuring velocity is standard in aerodynamics (Ref. 26). The principle is simple. If a tube connected to a pressure-measuring device is directed against a fluid flow, it will register a pressure which is proportional to the square root of the velocity. This is because the gas is brought to rest and at the mouth of the tube the change in momentum of the stagnated gas is reflected as a local pressure increase. In flame fronts these pressures are low, but it has been possible to measure the pressure profiles of a number of flames (Ref. 27) (Fig. II-9). It is difficult to interpret these measurements because the probe must be small compared with the flame front thickness and boundary layer effects become important. The measured pressure depends not only on velocity, but also Reynolds number which is in turn a complex function of temperature and probe diameter. A discussion of these problems can be found in Ref. 26.

The apparatus consists of a small probe of quartz or stainless steel, a micrometer drive for the probe, and a sensitive pressure-measuring device (Fig. II-9). Pressure can be measured with a micrometer-driven tilting oil manometer (Refs. 26 and 27) or a pressure balance (see Chapter V). The principal problem is the tediousness of such measurements, since with the small orifices used and the small pressure differences, even a well-designed system will take many minutes to reach equilibrium.

56
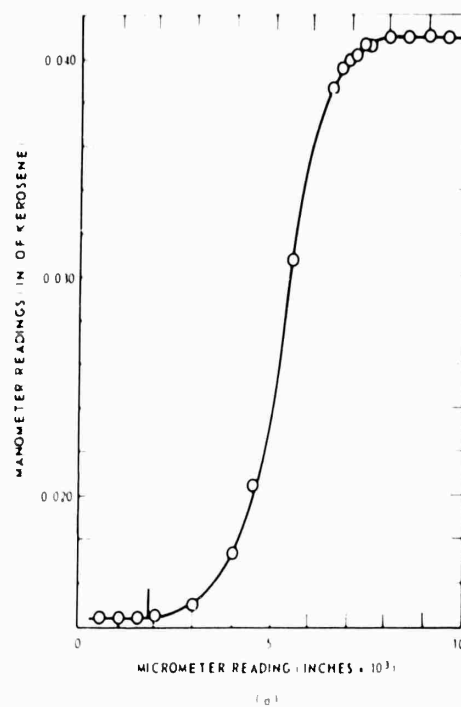
Fig. II-9   PROFILE AND APPARATUS FOR PITOT TUBE MEASUREMENTS

     a - Pressure Profile of a Stoichiometric Propane Air
         Flame at Atmospheric Pressure Micrometer Reading
         (inches) vs Micrometer Reading (inches of kerosene)
     b - Experimental Arrangement for Measuring Pressure Pro-
         files   (Ref. 27)
     c - NACA Standard Micrometer (Ref. 26)

57
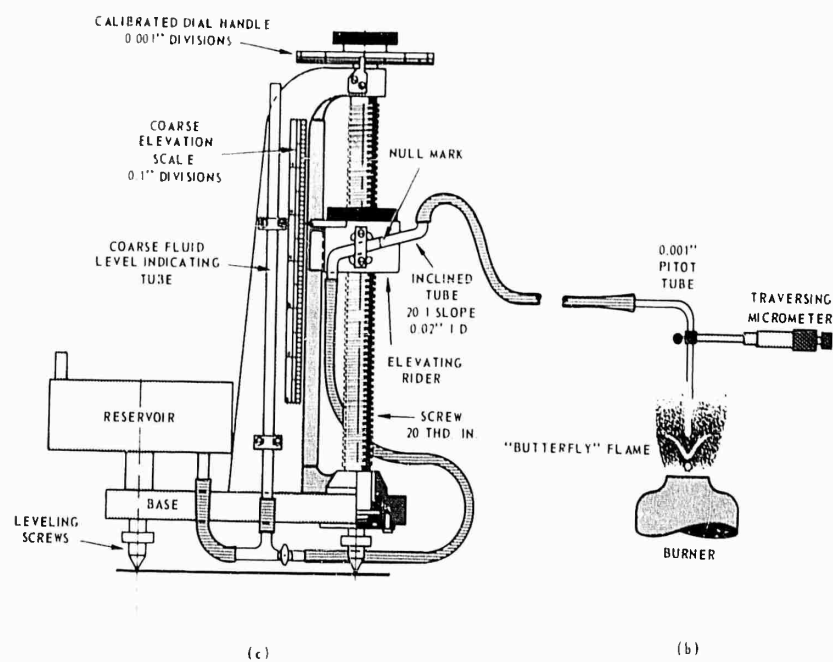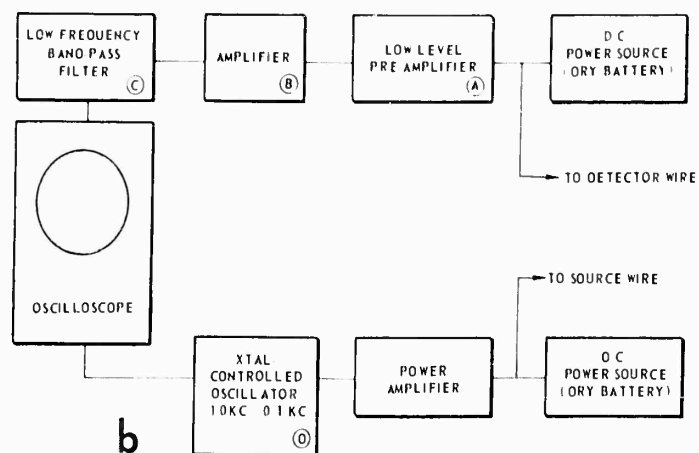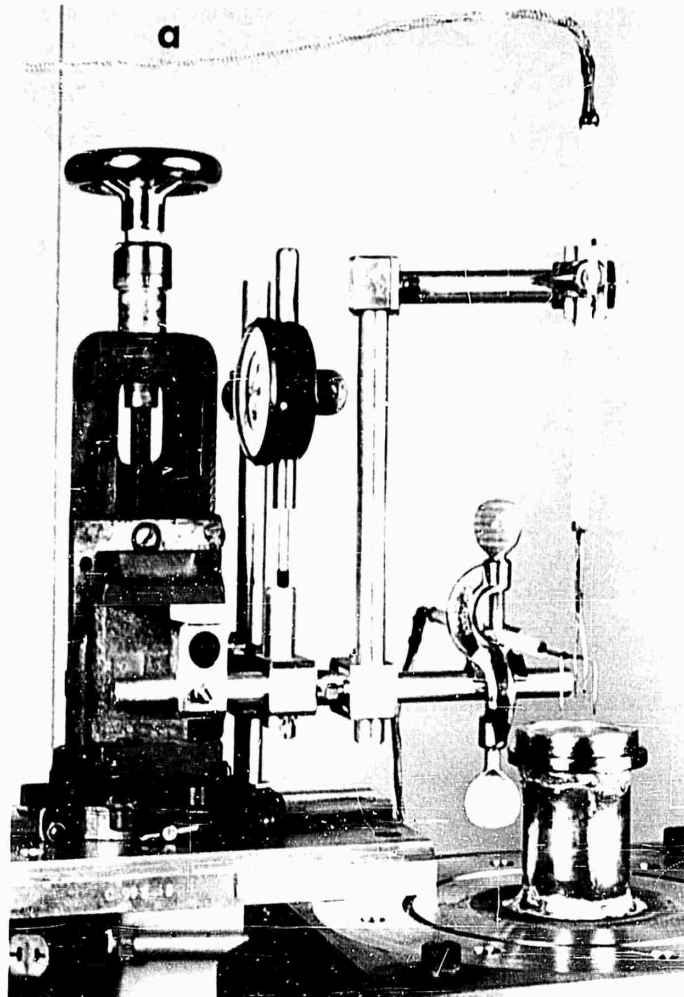
Fig. II-10   PULSED HOT WIRE ANEMOMETER

a - Sensing Wire Schematic
b - Photograph of Electric Components for Anemometer

OTHER METHODS OF MEASURING GAS VELOCITY

There are a number of other methods of measuring velocity,
but most of these are not applicable to flame studies, because of the
high temperatures or high spatial resolution required. The hot wire
methods used to study boundary layer, turbulence, and so forth, are
subject to serious errors in flame systems because of the temperature
gradients. An interesting variant is the pulsed hot wire of Westen-
berg and Walker (Ref. 28) (Fig. II-10) which uses the heated wake of
a pulsed hot wire as a tracer. These pulses are detected by a second
hot wire a known distance downstream. The distance between successive
temperature maxima in the wake of the pulsed wire is inversely pro-
portional to the velocity. The technique would require modification
to yield the resolution required in flame structure studies.

AVOIDANCE OF AERODYNAMIC MEASUREMENTS

Aerodynamic measurements are the most difficult and least
precise of the techniques used for flame structure study. Therefore,
it is desirable to avoid such measurements and minimize the dependence
of final results on aerodynamic parameters. It is common practice to
calculate velocity profiles from area ratio measurements, and density
determinations obtained from thermocouple or pneumatic probe traverses
(Chapter III). In the case of spherically symmetric flames, the sym-
metry fixes the area ratio profile, and it is not necessary to measure
the aerodynamic variables directly. The only problem connected with
the use of symmetry or area ratio measurements is the general one of
superimposing the profiles measured by two different techniques. This
requires a determination of effective position of sampling: the prob-
lem is discussed in Chapter VI.

59

SUMMARY

There are several techniques for making aerodynamic measurements. The most useful technique has been the particle tracer method whose precision can be as good as 2-4 per cent; Because aerodynamic measurements are generally less precise than the companion measurements of temperature and composition, it is common to use only area ratio measurements in quantitative studies, leaving velocity as a derived quantity. Because the area ratio is a geometric quality of the system, even these measurements are not necessary in dealing with spherical flames.

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    Harvard University, Report 5 (May 1953).

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    Phot. Eng. 3, No. 3, 121 (1952).

62

III

THE EXPERIMENTAL DETERMINATION OF LOCAL TEMPERATURES
IN FLAME FRONTS

INTRODUCTION

Flames are normally and correctly associated with high tem-
peratures and steep gradients. A one-dimensional flame is character-
ized by a unique temperature profile which provides the most valuable
single index of flame behavior. Rigorous analysis of flame structure
requires the complete set of characteristic profiles. However, tem-
perature profile can be used to give: Velocities (assuming the stream
tube area ratio is unknown or fixed (Chapter II)); heat release rate
(Ref. 8) (assuming known thermal conductivity); and in simple cases,
reaction rates. It is convenient to present such measurements in the
form of profiles (e.g., Fig. III-2), which give local temperature as
a function of distance through the flame front (Chapter VI). This
profile is usually a function only of the initial state (composition,
temperature, and pressure) of the incoming gas and is only secondarily
affected by external aerodynamic variables such as geometry, incoming
gas velocity, and ducting. From the thermodynamic point of view, tem-
perature is a single valued energy parameter; from the molecular
point of view, temperature is the parameter which characterizes the
distribution of energy among energy levels of the molecules and it is
not obvious that a single parameter will be sufficient. The most
probable distribution of energy is found in most systems because of
the long times and large number of molecules involved. However, this   63
convenient approximation breaks down when energy is transformed rapidly
and it proves necessary to define several different temperatures,
translational, vibrational, rotational, etc. (Ref. 1) (Fig. III-3).
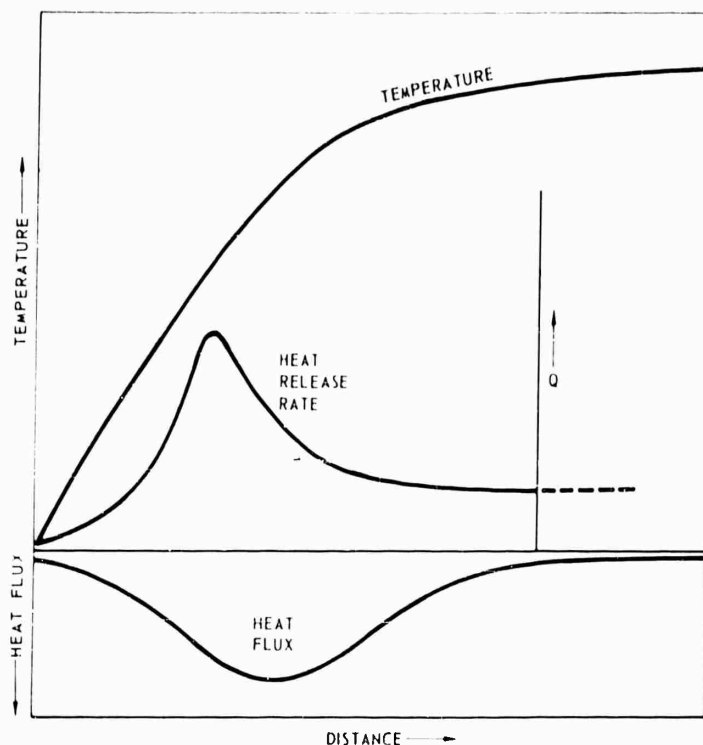
Fig. III- 1   FLAME TEMPERATURE PROFILE

Since temperatures change rapidly in flame fronts, the question of the existence of a unique local temperature must be discussed. It can be shown that the single temperature approximation is adequate provided properties do not change appreciably over distances comparable to the mean path (Ref. 2). In flames, it is generally possible to assign a valid translational temperature profile from which transport coefficients and collision numbers can be calculated. The energy levels in the major species will also be in equilibrium with this temperature, but certain species (e.g., CH, OH*, C_2) whose concentrations are maintained by chemical reaction will not be. Their energy distribution and apparent temperature will be characteristic of the reaction which supports their population (Refs. 1 and 3) (Fig. III-3b). These species represent such a minute fraction (10^{-7}) of the total system that they can be safely ignored in a quantitative description of flames. These species, however, often radiate. Since the emission

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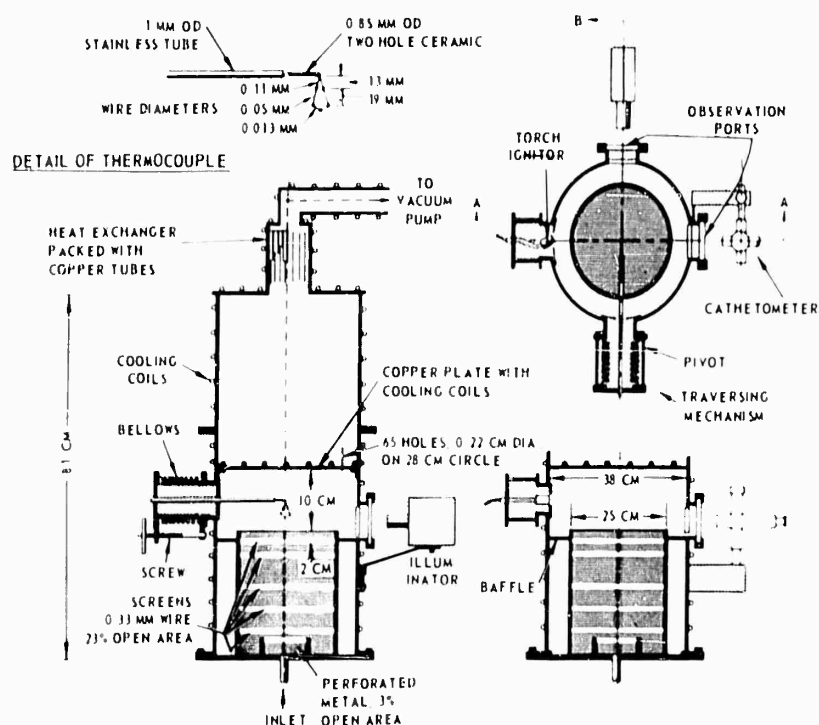
Fig. III- 2   TEMPERATURE PROFILE MEASUREMENTS

a - Flat Flame Apparatus for Determining Temperature
Profiles

is conspicuous, it has been considered a major characteristic of
flames.   The existence of such excited species and their emissions
provide clues to the detailed reaction processes.   The discussion of
these is a specialized problem and should await the unraveling of the
behavior of the major species in the system.   In describing flames it
is assumed that temperature (and the other thermodynamic variables)
can be defined at every point in the flame (Ref. 2).   The temperature
of interest in flames is the translational or perfect gas temperature.
This is also called the stream temperature by aerodynamicists (Ref. 4),
i.e., the temperature which a thermometer riding with the stream would
assume.   The distinction made by aerodynamicists between stream and
stagnation temperature (i.e., the temperature of a stationary ther-
mometer which brings gas to rest adiabatically) is superfluous for
these systems, since the velocities are so low that the stream kinetic
energy is a negligible part of the total enthalpy of the system.

65
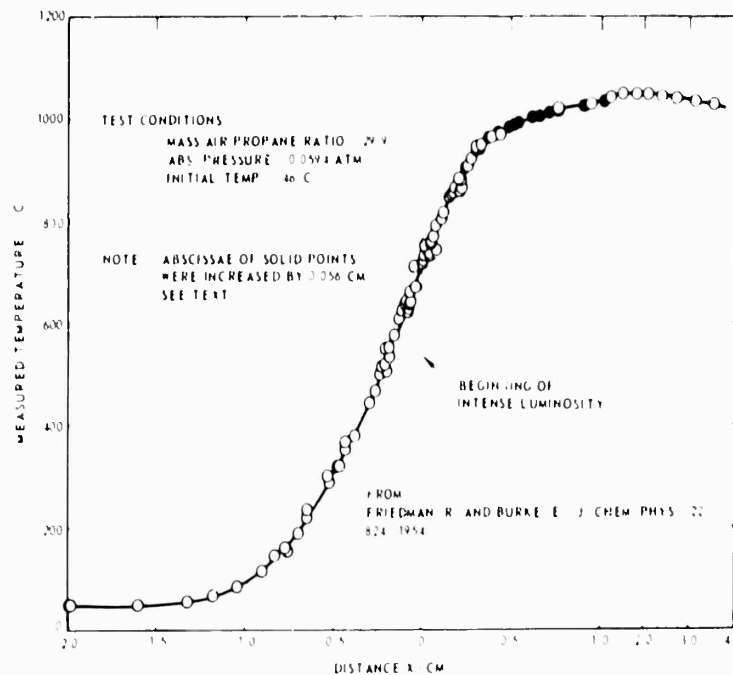
Fig. III-2   TEMPERATURE PROFILE MEASUREMENTS
         (Cont.)

         b - Experimental Temperature Profile Derived from Thermo-
             couple Probing. (Temperature (K) vs. distance (cm)
             propane-air flame 0.0594 atm $X_{C_3H_8}$ 0.0228;

             X_{air} 0.973)(Ref. 8).

METHODS OF DETERMINING TEMPERATURE

         Although there are many methods of temperature measurement
(Tables III-1 - III-3), only a few techniques possess sufficient relia-
bility and spatial resolution for satisfactory local measurements in
flames. These techniques can be classified into three groups:

         1. Direct probe thermometry

         2. Radiation measurement techniques

         3. Flame-gas density measurements.

66

TABLE III-1 SUMMARY OF COMMERCIALLY AVAILABLE TEMPERATURE-MEASURING INSTRUMENTS OR SYSTEMS

KIND OF INSTRUMENT	GLASS STEM LIQUID IN GLASS		BIMETAL	FILLED SYSTEMS			RADIATION PYROMETER	OPTICAL PYROMETER	PYROMETRIC CONES	MELTING PELLETS
	MERCURY	OTHER LIQUIDS		VAPOR PRESSURE	LIQUID FILLED	GAS FILLED				
LOW TEMP. LIMIT	-38 F -39 C	321 F -196 C pentane	100 F -73 C	427 F 2?? K	125 F 5? C	300 F 4?	950 F room temperature	?? F 75? C	1085 F 585 C	113 F 45 C
HIGH TEMP LIMIT	1100 F 593 C		1000 F 538 C	600 F 315 ?	1?? F 6?? C	1?00 F 538 C	65 to 85 very soft rod	65 to 85 very soft rod	3659 F 2015 C	2500 F 13?? C
REMARKS	Low price. Reasonable accuracy. Easily broken. Short scale length		Easily injured. Too slow. Sluggish. Somewhat corroded by overheating	Normal range. 100 deg.F. Too hot. Cross ambient effect. Compensating features	Can be temperature sensitive. Too hot temperature sensitive	Sluggish. Temperature sensitive. Requires large bulb	Can be read to ?. reproducible, accurate, simple	Cannot sample temperature. As accurate as optical		A long corridor of accuracy is affected and temperature and cannot inspection sense

No A.S.I. have equipment required.

KIND OF INSTRUMENT	THERMOCOUPLES					RESISTANCE THERMOMETERS			
	IRON CONSTANTAN	CHROMEL ALUMEL	COPPER CONSTANTAN	PLATINUM PLATINUM RHODIUM	PLATINUM	COPPER	NICKEL	THERMISTORS
LOW TEMP LIMIT	about -325 F -196 C	about 322 F 198 C	424 F 2 K	common -32 F 0 C	3? F 18? C	32 F ? C	32 F ? C	? F 4? C noticeable
HIGH TEMP LIMIT	1400 F 760 C in oxidizing atm; 1800 F 982 C in reducing atm; 2000 F 1093 C spot readings	2100 to 2300 F 1145 to 1260 C; 2400 F 1316 C spot not to be used in reducing atm.	550 F 3?? C; 750 F 39? C spot readings	2500 to 2900 F 1425 to 1538 C; 3215 F 1?4? C spot not to be used in reducing atm	?? to ?? F; ?? to 85? C	?? F 1?? C	?5 F 3?? C best accuracy	-5? F 30? C best accuracy
THERMOELECTRIC POWER MICROVOLTS PER DEGREE C						R 0? C R ? C R ? C			
	64 at 760	38 at 1100 C	41 at 25 C	12 at 1200 C alloy 10% Rh; 11 at 1200 C alloy 13% Rh	0.39	??	?	0.003 once rise
REMARKS	The couple most widely used in industry. Poor reproducibility above 1600 F (871 C)	Chromel is 90 Ni 10 C; chromel P: Al rest; 94 Ni, 3 Mn, 2 Al, 1 Si	Constant an is 57 C, 13 N	Expensive	Most defined temperatures	G is greater accuracy than thermocouples for the same treatment. High sensitivity, open, then suitable for narrow range instruments		High sensitivity. Only four steps	

Can give very rapid response, matched only by the radiation and optical pyrometers.

67

TABLE 111-2 COMPARISON OF CALIBRATED AND ULTIMATE THERMOCOUPLE RANGES

APPROXIMATE MELTING POINT OF LESS RE
FRACTORY LEG OF THERMOCOUPLE

LIMITS OF CALIBRATION CITED BY COR
RESPONDING REFERENCE

RANGE OF CALIBRATION

THORIA (ThO₂) — 5500

MAGNESIA (MgO) — 5000

STABILIZED
ZIRCONIA (ZrO₂) 4500

BERYLLIA (BeO)

ALUMINA (Al₂O₃) 1500

SILICA (SiO₂) 1000

TUNGSTEN
RHENIUM
TANTALUM
MOLYBDENUM
NIOBIUM
IRIDIUM
RHODIUM
PLATINUM

REFERENCE																		REFERENCE
ATMOS USED IN CALIB																		ATMOS USED IN CALIB
MAXIMUM OUTPUT MV																		MAXIMUM OUTPUT MV
EST MAX ERROR F																		EST MAX ERROR F

	SEE TEXT	MATERIAL	Al₂O₃	B₂O₃	MgO	ThO₂	ZrO₂	
..	VAC As H₂ N₂	Thermal shock resistance	2	1	4	5	3	
		Mechanical shock resistance	1	2	4	5	3	REPRINTED FROM "REVIEW OF HIGH TEMPERATURE IMMERSION THERMAL
		Chemical inertness	4	2	5	1	3	SENSING DEVICES FOR IN FLIGHT
...	PROB H₂ N₂	Electrical insulation value	3	1	2	4	5	ENGINE CONTROL " V.D. SANERS THE
		Reciprocal thermal expansion	2	4	5	3	1	REVIEW OF SCIENTIFIC INSTRUMENTS
		Thermal conductivity	3	1	2	4	5	VOL. 29 NO. 11 P 917-928 (NOV 1958
		Vapor pressure	5	3	4	1	2	
		Melting point	5	4	2	1	3	
		Material cost	2	4	1	5	3	

PROBE THERMOMETRY

The most direct method of determining local temperature is
to insert a thermometer probe into the flame. For these measurements,
the thermometer must be small compared with the thickness of the
flame front, and must be rugged enough to stand the high-temperature
corrosive flame environment. Two types of probes have been used in
flame studies, thermocouples, and resistance thermometers. Only the
former has found wide usage. In the following section we will dis-
cuss the two techniques together with the interpretations and general
problems associated with probe thermometry. This discussion will be

68

made with direct reference to thermocouple thermometry, but most of the discussion can be applied to resistance thermometry or other probe type thermometers.

TABLE III-3

COMPARISON OF METHODS TO DETERMINE TEMPERATURE PROFILES IN FLAME FRONTS

Technique	Upper Temp Limit ($^\circ$K)	Spatial Resolution (cm)	Precision ($^\circ$K or % T)	Displacement (cm)	Corrections	Effect in Flames	Cost of Apparatus
Thermocouples	1000	10 dia (10^{-2})	1	5 dia (5×10^{-4})	Radiation	Aerodynamic Wake & Catalysis	Moderate, low
Resistance Thermometer	1000	10^{-1}	1	10^{-2}	Radiation		Moderate
Aerodynamic Measurements	3500	10^{-1}	13	slight	Acceleration, lag & thermo-mechanical effects	Quenching	Moderate
Optical Pyrometry	None	5×10^{-1}	5	None	Non-equilibrium Additives Radiation		Moderate
Spectroscopic Line Intensity	None	5×10^{-1}	5	None		None	High
Pneumatic Probe	2500	10 dia 10^{-2}	25	5 dia 5×10^{-4}	Orifice Coefficients	Wake & Catalysis	Low
X-ray Absorption	None	5×10^{-1}	13	None	Mol Weight	None	High
Interferometer	None	5×10^{-2}	13	None	Mol Weight	None	High
Inclined Slit	None	5×10^{-2}	13	None	Mol Weight	None	Low

Thermocouple Measurements

These measurements make use of the thermoelectrical property of metals. If two dissimilar conductors are connected electrically, and the two junctions are maintained at different temperatures, a potential is developed which is proportional to the difference in temperature. This potential is reproducible and is a function of the materials chosen for wires; it is independent of the method of making the junction (wires may be welded, soldered, or simply twisted together) so long as good electrical contact is maintained, and provided there is no appreciable temperature gradient across the joint. The stringency of this latter requirement depends upon the gradients and the required precision. A large number of thermocouple pairs

69

have been studied (Table III-2), but only a few are suitable for use
at flame temperatures, notably the Pt, Pt-10% Rh and Ir, Ir-40% Rh
couples.

The principal advantages of thermocouple measurements are:
(a) they can be made with the high precision characteristic of elec-
trical measurements (b) extremely small thermocouples (0.001 cm
diameter) can be made, so that high resolution can be obtained and
aerodynamic disturbance of the flame front minimized, and (c) they
can be made of materials which withstand high temperature.

The principal source of error is radiation loss. Correc-
tions can be made so that temperatures reliable to 10 to 20 K, posi-
tioned within 50 microns, can be obtained (Refs. 8 and 9) and the
error can be completely eliminated by using the "null method" in
which the thermocouple is heated electrically to balance the radia-
tion loss (Ref. 10). Temperature derivatives are primarily limited
by the size of the wire used and the disturbances of the vibration
and catalysis. Temperature differences as small as 0.1 C can be
reliably measured, with positional uncertainty of 10^{-3} cm. Such meas-
urements are satisfactory for determination of derivatives, since the
main sources of error tend to cancel out.

The techniques of thermocouple thermometry are described in
the literature (Refs. 4 and 5) and are discussed in many courses on
electrical measurements. The apparatus consists of a suitably mounted
thermocouple (see Fig. III-2) and a device for measuring the EMF de-
veloped. The techniques of fabrication of noble metal couples as
small as 0.001 cm diameter and coating them with silica are described
in Appendix III-A. A reference temperature is required at the second
junction which usually can be furnished by room temperature and a good
mercury thermometer. This allows the use of a single junction. For
measurements to the nearest degree (C) the EMF must be measured with
a potentiometer. Where $10°$ precision is satisfactory, a good milli-
voltmeter can be used, with a correction for voltage drop through the
meter.

70

Resistance Thermometry

Resistance thermometry has been used to determine the maxi-
mum temperature of a low-pressure acetylene-oxygen flame (Ref. 6).

The experimental setup requires a source of constant current and methods of determining the wire resistance. For the wire sizes commonly used, the resistance is rather low and a Kelvin double-bridge is best adapted to the resistance measurement. The problems of catalysis on the wire surface, mentioned in the literature (Ref. 6), could probably be eliminated by silica coating, which would also minimize the problem of volatilization of the wire. As was the case with thermocouple measurements, precision of this method can be a few degrees. The possibility of canceling out the radiation correction through null measurements improves the significance of these measurements, which is better than 10 K. Resolution as high as 0.1 mm can be obtained by careful alignment and tension-mounting of the wire. The apparatus is straightforward but the technique is somewhat less convenient than thermocouple thermometry, and as a consequence is used less.

Problems

A thermometer immersed in a gas stream will record a temperature differing from the true stream temperature due to kinetic energy transfer by stagnation in high velocity streams, conduction and radiation losses, and vibrational effects. These problems can be classified into two groups: The effects of the probe on the flame, and direct errors.

The central problem is what effect the probe has on the flame itself. This error is reduced by reducing the size of the thermometer. The limit to this approach is set either by practical problems of fabrication or the heat transfer difficulty encountered when thermometers smaller than the gas mean free path are used. These disturbances can be classified into aerodynamic, thermal, and chemical, and are discussed in some detail with respect to sampling probes in Chapter IV. The significant differences between the actions of probe thermometers and sampling probes can be summarized as follows.

The principal aerodynamic effect is the velocity deficient wake behind the thermometer which to a first approximation can be visualized as a local propagation of the flame front in this region.

71

As a result a thermocouple will record a higher temperature than would be characteristic of the undisturbed stream. This effect is proportional to the wire diameter, and the necessary corrections are described in the chapter on position measurements (Chapter VI).

The thermal effect of a probe is a function of the temperature difference between the stream and the thermometer. Since reliable thermometry requires that the difference be small, this is not a problem. An order of magnitude calculation treating the thermometer as an energy sink* indicates that this is the case for thermometers of the size usually employed.

The principal chemical disturbance of probes is the promotion of catalytic reactions on the thermometer surface. This results in spuriously high temperatures and hysteresis in the temperature profile (Ref. 8). The effect is serious with metal surfaces, but it can be made negligible by coating with non-catalytic materials, such as silica (see Appendix A) (Refs. 8 and 9).

Even in the absence of flame disturbance, a thermometer will register a temperature which is different from the true stream temperature. This is due to a number of factors (Eq. 1):

T (true, stream) = T (observed, stagnation) - T (kinetic energy)

$$(1)$$

, T (radiation loss) + T (conduction loss).

These corrections can be estimated by making an energy flux balance between energy received by conduction from the gas and lost by radiation and conduction along the supports (see Refs. 4, 5, and 8). In general, the errors will be reduced if the size of the thermocouple

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*This is analogous to the discussion of the disturbance introduced by a sampling probe considered as a matter sink (see Chapter IV) (Ref. 7). Since the temperature and concentration fields are similar when reduced to dimensionless form, the treatment is directly applicable. The sink strength is identified with the radiation loss and the transport flux with thermal conduction. A 0.001" diameter platinum thermocouple represents a sink of 10^{-5} cal sec, which in dimensionless form is smaller than the sink of Ref. 7 which had a negligible effect on the concentration field. Therefore, the disturbance introduced by such a thermocouple on the temperature field should also be negligible.

is decreased (to the limit where it becomes comparable with the mean free path) and the gas density and velocity are increased (up to Mach 0.1).

Errors due to stagnation kinetic energy will be negligible for the flames under discussion, since the velocities generally lie below Mach 0.1. Conduction losses can be made negligible in most flames, since the support wires can be aligned with the surfaces of constant temperatures.

Radiation remains as the important source of error. It is proportional to the fourth power of the temperature and the emissivity of the probe, and is inversely proportional to its diameter (Eq. 2). In many cases these parameters are not sufficiently well known for quantitative application.

$$T \text{ radiation} \quad k(T_{exp} - T_{wall})^4 - k r \sigma (T_{exp} - T_{wall})^4$$

$$k \quad \frac{T_{flame} - T_{exp\ max}}{(T_{exp\ max} - T_{wall})^4} \quad . \tag{2}$$

Where the correction is large (100°C) a more accurate correlation based on heat transfer using the Nusselt-Reynolds Number correlation for cylinders (Eq. 2a) should be used.

$$T_{rad} \quad \frac{1.25 \cdot T^4}{d^3 \cdot 4} \cdot {}^{1 \cdot 4} \quad . \tag{2a}$$

Kaskan (Ref. 9) derives this equation. Based on his measurements on quartz-coated wires, he suggests on emissivity that 0.22.

In this equation is the emissivity of the wire; is the Stephan-Bolzmann constant; is the thermal conductivity of the gas; d is the wire diameter; and is the viscosity of the gas. In these cases the effective constant for a given thermometer can be determined by putting it in a gas stream at a known temperature and measuring the resulting temperature. Since it is not always easy to provide a calibrating gas stream, this constant is often estimated by assuming that

the highest temperature measured corresponds to the adiabatic flame temperature. This is usually the case, but it is desirable to check this point by some independent method of measuring the maximum temperature. It is also assumed that the thermal conductivity of the gas and the gas velocity are uniform over the region of application of Eq. (2). This is reasonable, since the correction is important only in the high temperature region where velocity and conduction variations are not great. Nonetheless, this correction remains as one of the most serious sources of error in thermocouple measurements of flame temperatures. This can be avoided by using a sufficiently small device or by the "null-method" in which the energy losses are balanced by electrical heating. The thermocouple absorbs heat from the flame if its temperature is lower than the flame gases, and gives off heat to the flame if it is hotter than the flame gases. This results in an inflection in the temperature versus heating-current curve at the point at which the flame temperature is reached. The principle can be applied to resistance thermometers and thermocouples (Refs. 6 and 10).

Since temperature measurements must be associated with a position, another serious source of error is movement or vibration. Vibration can also induce turbulent burning with the associated complication of defining position, position-time averaging, etc. Induced vibrations offer the most serious problem, since flame-thermometers usually consist of long sections of thin wire in which forced vibrations are easily set up. Oscillation with amplitudes as great as half a millimeter and frequencies of the order of 50 cps have been observed. Since the vibration is in the direction of flow and of relatively low frequency, it is probably not due to the shedding of von Kármán vortices. It occurs in regions of steep temperature gradient and the driving mechanism may be the thermal expansion and contraction of the wire. This problem is best avoided by using heavier support wires and shorter leads.

74

RADIATION THERMOMETRY

Measurement of the emission or absorption of electromagnetic radiation provides a very versatile method of determining temperature. The techniques range from the simplest optical pyrometer to the most

sophisticated form of spectroscopy and may involve wave lengths from the X-ray to the microwave region. The principal advantages of these techniques are that they do not disturb the system being studied, and they have no high-temperature limit. The principal disadvantage lies in their poor spatial resolution and that they give an average over the entire path length used.

Viewed from the molecular standpoint, the energy of a system is distributed among the various molecules in quantized energy levels. If the molecules are far enough apart so that interactions are negligible, as is the case with gases at moderate pressures, the energy can be divided into translational energy, which can be considered classically, and internal energy which is quantized. The quantization of the internal molecular energies results in light being absorbed and emitted only at particular wave lengths which are functions of the molecular parameters. If the interactions between molecules become strong, as is the case with very dense gases, liquids, and solids, then the emission and absorption lines are broadened and in the limit they coalesce into the black-body distribution. If equilibrium is attained, the energy will be distributed according to the Maxwell-Boltzman distribution function. (At flame temperatures the difference between the classical M-B and quantum statistics is negligible.) The probability that a molecule will have a particular amount of energy (that is, that a particular set of energy levels is filled) is proportional to $e^{-h\nu/kT}$, where T, the characteristic parameter, can be identified with the ordinary thermodynamic concept of temperature (Ref. 11). Radiation in equilibrium with such a system will also show this same distribution, and since temperature is a single number, it should be necessary to make only a single measurement of absorption or emission of radiation to determine the temperature. In practice, because of difficulty in making absolute determinations of emissivities, it is more convenient to make two or more measurements at differing wave lengths and derive temperature from the intensity versus energy plot (see Fig. III-3a). This latter method has the added advantage that deviations of the system from the assumptions of Maxwellian distribution, and independence of absorption-emissivity on wave-length can be detected (see Fig. III-3b). A great many methods have been devised for making such measurements (Ref. 15); several of these will be described.

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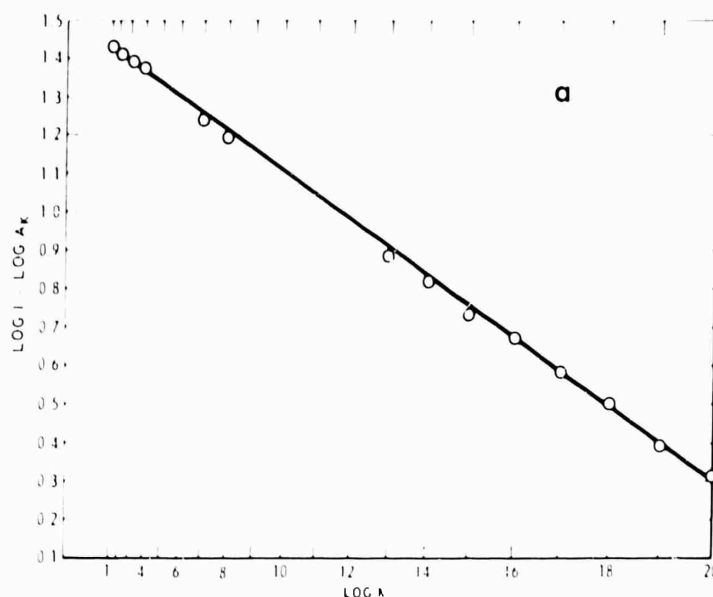
Fig. III- 3   ROTATIONAL POPULATION

a – Plot of Relative Rotational Population (log I – log A_k) as a Function of Rotational Energy Level (k) Showing that a Straight Line Results (from Ref. 3). The slope of this line is proportional to temperature.

Most systems consist of three elements: (a) a flame with suitable geometry so that homogeneous regions can be optically probed; (b) an optical system consisting of a monochromator and a receiver for measuring intensities; and (c) a comparison emitter.

Optical Pyrometry

The simplest radiation method is optical pyrometry; this is essentially a measurement of emissivity. Temperature is measured by comparison of the flame emission with a light source at known temperature. In commercial pyrometers, the filament of an incandescent lamp is superimposed optically on the image of the flame region being studied. Filament temperature is adjusted by changing the applied voltage. When the two images are at the same temperature, they will tend to merge. The equivalence point can be determined visually, or
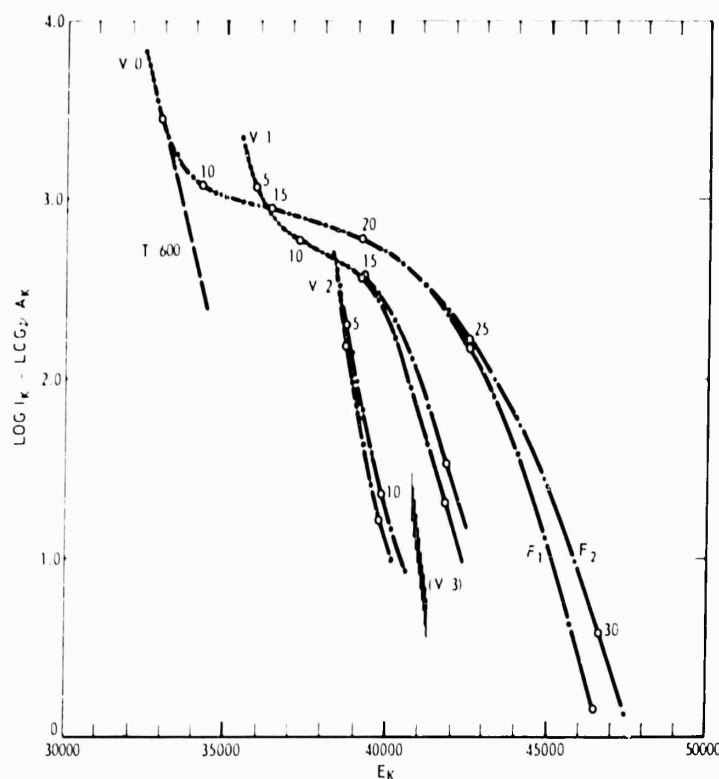
Fig. III-3   b - Distribution of OH Rotational Population in an
(cont.)   Electric Discharge Through Water Vapor at 0.5 mm.
                Plotted as a function of rotational energy in
                calories. Note variations in slopes of these plots
                and the general lack of equilibrium which would
                be indicated by a single slope (Ref. 3).

by the use of a photocell, with a precision of a few degrees. Tung-
sten or carbon filaments are used for general pyrometry; they are
calibrated against a black body whose temperature is measured by some
auxiliary method. The technique of measurement and calibration of
optical pyrometers is covered in the literature (Ref. 12). This tech-
nique can be directly applied to flames containing solids, although a
small correction should be made for the dependence of emission on
particle size (Ref. 13). Flames are not optically dense in the visi-
ble region; therefore, in the absence of solids, they must be colored
with a material which emits in the region being studied (e.g., salts
of lithium, iron, iodine, etc.). These additives are foreign to the

77

flame system, and the question of disturbance arises, but the amounts required are small and the problem is usually not serious. The most important limitation of colored flames is that no appreciable emission occurs below 1700°K for most of these additives. In an experimental setup it is necessary to provide a flat geometry and add the emitter to a uniform section of the flame, otherwise a meaningless average temperature will be measured. This can be accomplished, and the details of one such burner are given in Fig. III-4. Spatial resolution of the order of 1 mm is attained and the afterburning region of flames can be studied using this technique (Ref. 14).

When two spectral regions are compared, it is not necessary to know the emissivity, although it must be assumed constant in the two regions. Measurements are usually made in the infrared region,

78
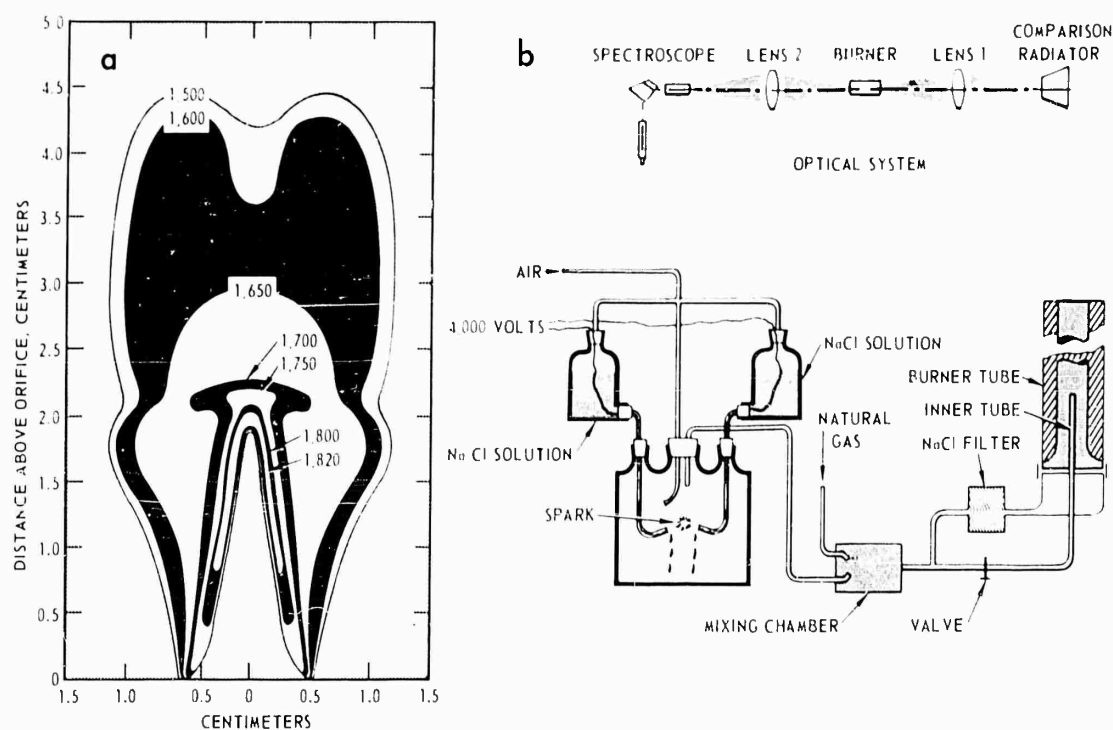
Fig. III- 4   APPARATUS AND TEMPERATURE DISTRIBUTION FOR FLAME PHOTOMETRY

    a - Apparatus for Flame Photometry Using Colored Flames,
        the Sodium Line Reversal Method.
    b - Temperature Distribution in a Flame (0.076 natural
        gas; 0.924 O_2; P = 1 atm) Distances in cm; iso-
        therms in $^{\circ}C$. (Ref. 14).

where flames show a high density of emission. Some care must also be taken to avoid problems of averaging, line broadening, etc., since finite spectral regions rather than spectral lines are being compared. These problems have been surmounted and measurements of good precision can be made (Ref. 15). The limitations, precision, and resolution are similar to those in colored flames ($\pm 5°$C and 1 mm); the advantages of the method are twofold: (a) no extraneous materials need to be introduced; and (b) emissivity need not be known directly.

Another convenient technique is the two-path method which consists of measuring the intensities of radiation for one and two traversals using a mirror. This is essentially a reversal method in which the source is used as its own background. This is particularly useful if the radiation varies with time. To apply this method it is necessary to know the reflectivity of the mirror and to assume that the emissivity is only a slowly varying function of wavelength. Resolution comparable to other optical methods can be obtained, although the double traversal complicates the problem of maintaining the narrow light beam required for high spatial resolution. The main uncertainties are associated with density of emission in the region chosen, the assumption of constant emissivity, and the effects of heterogeneities in the optical path. Errors in unfavorable cases can amount to hundreds of degrees, although careful work can hold them down to a few degrees.

Line Intensity Methods

The most accurate and detailed temperature information is obtained from the study of relative intensities of individual spectral lines. If a system is in thermal equilibrium, a plot of the log of line intensity multiplied by an a priori probability versus the initial energy level will yield a straight line whose slope is the temperature divided by the Boltzman constant (see Fig. III-3). As has been mentioned, this is a very sensitive test for equilibrium, but great care must be exercised to avoid spurious results (Refs. 3 and 16) (Fig. III-3b). These studies give the temperature associated with particular species, indicate if it is a thermal equilibrium and often provide clues to reasons for non-equilibrium behavior. At pres-

79

ent most of the non-equilibrium cases are too complicated for quanti-
tative interpretation, and their consideration should be deferred un-
til the simpler equilibrium situation is understood.

In competent hands, this method is capable of high precision
and great delicacy. However, spatial resolution is poor, and the
method is restricted on the low-temperature side. Rotational fine
structure of vibration-electronic bands provide a particularly favora-
ble case for such an analysis, since they provide a set of lines
spaced closely enough so that the problem of changes of sensitivity
with wavelength are minimized. In the case of diatomic molecules,
the probability factors for the energy levels involved are usually
available. This is not the case generally for polyatomic molecules,
which have extremely complex spectra. However, most of the important
molecular species of flames have been analyzed. The OH radical has
been a particular favorite for such studies, since it has a well-known,
easily available spectrum in the near ultraviolet. Other molecules
(and atoms) which have been successfully used are CH, Li, Fe, I_2, HCl,
etc. An experimental difficulty associated with such studies is that
high-resolution grating spectrometers must be used to resolve the
lines. This is expensive equipment which many combustion laboratories
do not possess. Only lines that are weakly absorbed (and hence weakly
emitted) should be studied, since the intensity relationships are dis-
torted by "self-absorption" (Ref. 16) and equilibrium may not be
established (Ref. 15).

Studies can also be made using absorption (Ref. 10) (Fig.
III-5) rather than emission spectra; similar problems are encountered
and it is difficult to define the optical path. Using iodine as a

80
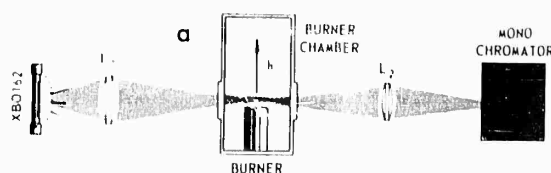
Fig. III- 5   THE DETERMINATION OF TEMPERATURE PROFILES USING
ROTATIONAL ABSORPTION.

a - Apparatus.
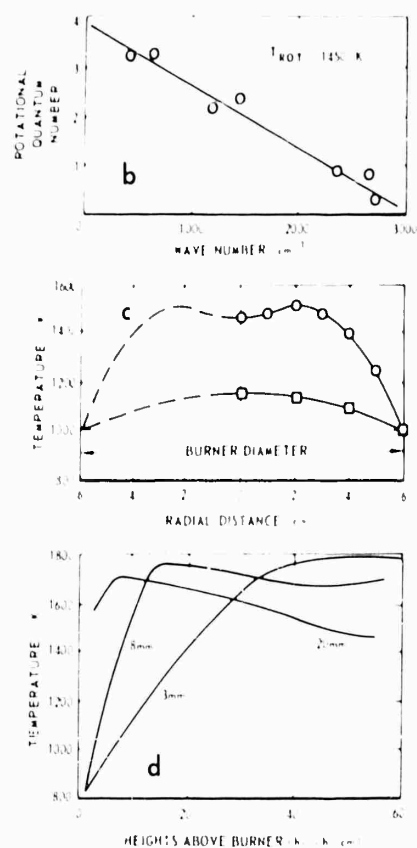
Fig. III-5   b – Example of a Determination of Temperature from OH
Absorption. Ordinate-ratio of maximal absorption
to the transition probability (x 10⁰) abcissa-
wave number (cm⁻¹).

c – Temperature Cross Sections at Several Heights above
a Stoichiometric Methane-Oxygen Flat Flame (P   8
mm; burning velocity 120 cm/sec).   Curve 1 - 1.3 cm
above burner; curve 2 - 2.6 cm above burner.

d – Temperature Profiles of Several Stoichiometric
Methane-Oxygen Flames. (Temperature °K vs. distance
(cm)). Determined through the rotational absorption
of OH. Taken from Ref. 10.

81

tracer, it is possible to make studies at relatively low temperatures (Ref. 17), although care must be exercised since I_2 is an inhibitor which may enter the flame reaction.

Line Shape Methods

If the mechanism of line broadening is known for the case under study, it is possible to determine temperature from the line shape. This is usually done by determining half-width at half-height. Line broadening can stem from many different factors, however, and caution should be exercised in interpreting such data. In the optical region the principal source of line broadening is the doppler effect due to random distribution of molecular velocities relative to the observer. This can be directly related to temperature. On the other hand, in the X-ray region, the principal source of broadening is natural line width, which is independent of temperature. Line shapes can be studied using an interferometer such as an etalon. No flame structure studies have been made by this method, but a very ingenious study has been made of rocket exhaust gases, where spatial resolution problems are not severe (Ref. 18). From the shape of the sodium-D doublet, it was possible to deduce both the temperature and gas velocity which, in this case, was comparable to molecular velocities and made the line asymmetric. In the infrared region, the presently available resolution is marginal for such studies. In plasmas, line broadening is due principally to the Stark effect, but this can also be interpreted in terms of temperature.

THERMOMETRY BY GAS DENSITY MEASUREMENTS

82

In general, gas density can be directly related to temperature through an equation of state such as the perfect gas law (Eq. 3). Therefore, any method of measuring density or its derivatives can be used to derive temperature, provided the average molecular weight can be determined. This is a mild restriction since this information is usually available or can be estimated with sufficient accuracy.

The thermodynamic definition of temperature relates it to the gas density through the concept of a perfect gas. Such a relationship between temperature, gas density, pressure, volume, and molecular weight is called an equation of state. The simplest is the perfect gas law (Eq. 3) which can be related to a statistical mechanical model of point-mass molecules with negligible intermolecular forces. Experimentally, it is valid for real systems in the limit of low density (where molecular volume becomes negligible) and high temperature (where kinetic energy of the molecules becomes large compared with intermolecular forces). Most flame gases meet these conditions and the perfect gas law can be applied to temperature measurements if fractional per cent precision is satisfactory.

$$T = P \bar{M} R \rho . \qquad (3)$$

There are a number of experimental methods for measuring gas density, and several of them meet the temperature and spatial resolution requirements of flame studies.

Aerodynamic Measurements of Density

Measurements of the detailed aerodynamics of flame fronts provide a method of determining the local density, and hence, local temperature of flames. Laminar flames are unidimensional flow systems in which conservation of mass can be conveniently expressed in the form of Eq. (4).

$$\rho v a = const = \rho_0 v_0 a_0 = \dot{m} . \qquad (4)$$

83

Combining Eqs. (3) and (4), the relation of temperature to aerodynamic parameters becomes:

$$T = (P \bar{M} R) (v v_0) (a a_0) = T_0 (v v_0) (a a_0) (\bar{M}_0 \bar{M}) . \qquad (5)$$

The experimental techniques are discussed in detail in Chapter II.

Assuming that the gas is only accelerated normal to the flame front and that the stream tubes do not expand in the reaction region, is equivalent to assuming that ρV = constant - a simplification commonly used in flame theories. Under this restriction velocity can be inferred from slope measurements on streak photographs of particles passing through the flame front (Eq. 6a), and area ratios determined by measuring adjacent streamlines. Temperatures can be derived using Eq. (6b).

$$V = V_0 \tan \alpha \tag{6a}$$

$$T = T_0 \tan \alpha \ (a/a_0) \ (\overline{M}_0/\overline{M}) . \tag{6b}$$

Detailed measurements of velocity have shown it to be a poor assumption (Chapter II) (Refs. 19 and 20).

Direct determinations of local velocity can be made (Chapter II). The average molecular weight factor can be determined from composition profiles (Chapter IV), estimated if the change in mole number is small or measured by some independent method. Representative experimental errors in temperature determination lie around 2 to 4% (Fig. III-6).

Pneumatic Probe Measurements of Density

If the pressure drop across an orifice is sufficiently high (pressure ratio $\cdot$ 2) a sonic boundary forms in the throat and the flow becomes a function of the upstream pressure, temperature, molecular weight, and specific heat, with a minor Reynolds number correction for the effects of boundary layer. If two orifices are connected in series, the ratio of this pressure to the upstream pressure becomes primarily a function of temperature (Ref. 21) (Eq. 7).

$$T_1 = T_2 \ (P_1/P_2)^2 \ K \ (\text{Reynolds Number}) . \tag{7}$$

84
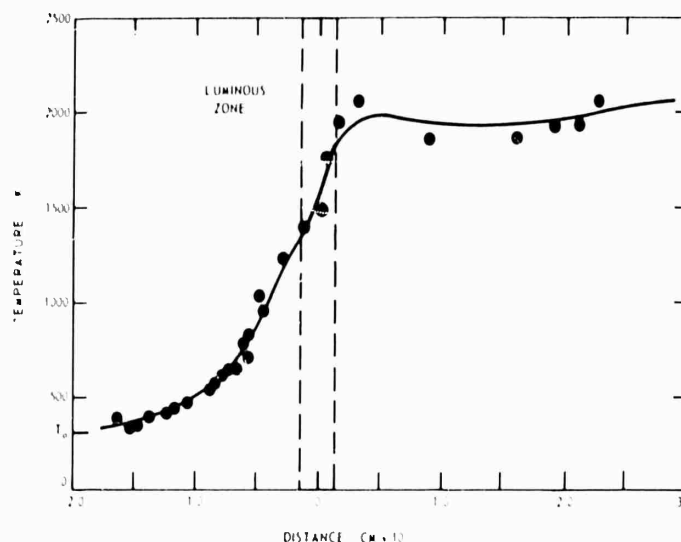
Fig. III-6   TEMPERATURE PROFILE OF A STOICHIOMETRIC PROPANE-
              AIR FLAME   (Ref. 19)

              (P   0.25 atm)

This provides a promising method of temperature measurement
since it provides a connection between composition and temperature
studies. Although calibration is required for quantitative work, it
is not influenced by the external environment as is the radiation
correction of thermocouple studies. Since the correction is a func-
tion of Reynolds number of each orifice considered separately, it is
not necessary to calibrate in a high temperature environment. The
corrections can be evaluated by changing density and molecular weight.
This is important since it is difficult to provide calibration tem-
peratures above 1500 K.

It is necessary that both orifices operate in the continuum
flow regime and the temperature be low enough so that the radical and
atom concentrations are not high, since they recombine before enter-
ing the second orifice, changing the molecular weight and ratio of
specific heats.

In experimental setups (Fig. III-7), it is convenient to
make the first orifice a quartz probe of the type used in composition
sampling studies (Chapter IV); the second orifice choice is not criti-
cal. Usually the ordinary laboratory rotary oil pump is quite ade-
quate, although the pressure ratio should be checked across both ori-
fices to insure choking flow conditions (pressure ratios greater than
2-3).

85
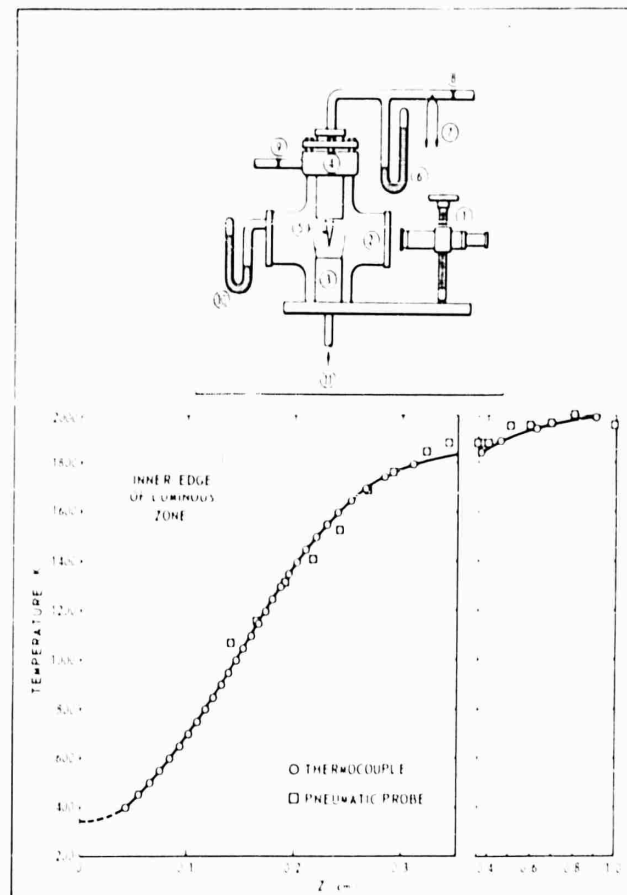
Fig. III- 7   TEMPERATURE PROFILE DETERMINED BY USE OF PNEUMATIC
PROBE

Insert: Diagram of Apparatus.   (Ref. 42)
1 - Precision Cathetometer.
2 - Glass Pipe Cross.
3 - Flat Flame Burner.
4 - Water-Cooled Chimney.
5 - Cathetometer.
6 - Precision Mercury Manometer.
7 - Thermocouple in Gas Stream.
8,9 - Chimney Orifices.
10 - Manometer
11 - Gas Inlet

86

For convenient operation it is necessary to minimize the
volume between the two orifices since the equilibration time is pro-
portional to this volume. Pressures can be measured by any convenient
method that has a precision higher than one per cent. Diaphragm

gauges and mercury manometers are most common. McLeod gauges cannot
be used on the condensible gases found in flames, and most of the
other common gauges are composition sensitive. The mass spectrometer
provides a convenient pressure measuring device if composition studies
are being made – the total pressure being the sum of the partial pres-
sures.

Sound Velocity Measurement

The temperature of a gas can be derived from measurement of
the velocity of sound. Simple mechanical considerations indicate
that there should be a relationship between the velocity of sound and
the density and modulus of elasticity in a fluid (Eq. 8). In the case
of ideal gases the passage of sound through the gas is an adiabatic
process,[*] and the volume modulus of elasticity is given by the product
of the ratio of specific heats times the pressure; the density is
taken to be equal to RT PM as required by the perfect gas law:

$$v = (k \; c)^{1/2}$$
$$v = (\frac{RT}{M})^{1/2} . \tag{8}$$

Since flame gases approach ideality rather closely, it would be ex-
pected that Eq. (8) would be a reasonable approximation. This method
has been used to measure the temperature in electric arcs (Ref. 22).

To apply this technique to the measurement of flame tempera-
ture profiles, it is necessary to know both the average molecular
weight and the average ratio of specific heats. This information can
be obtained either from a composition profile, from the assumption
that $\bar{M}$ is constant throughout the flame front, or from some other
experiment which determines this ratio. This requirement is not strin-

87

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[*] It is also assumed in this simple analysis that the composition of
the mixture is not changed by the sound disturbance, i.e., the com-
position is "frozen." This is true at moderate temperatures < 1000°K
and also for high frequency sounds · 10 mc. For other regions it is
better to assume that the composition follows the sound disturbance
and the "equilibrium value" should be used.

gent and is typical of density methods. The problem of spatial resolution is probably more acute. On the other hand, this does not limit the method so far as determining final flame temperatures, and this may ultimately be a very attractive method. It need not disturb the system during the period of measurement, since a single sonic pulse can be used that transmits no disturbance ahead of itself.

Radiation Absorption Studies

Density can be determined through the absorption of suitable radiation by a tracer species that does not enter into the flame reaction. Any spectral region can be used, but the ultraviolet and X-ray regions are usual because absorption coefficients increase with frequency.

The most suitable transitions are those from the ground state to the first excited state. It is desirable that there be no other states with appreciable population at flame temperatures, since a correction must be made for the change of ground state population with temperature.

Mercury vapor provides a convenient tracer, although the possibility of catalysis must be considered. The 2537 A resonance line in the quartz ultraviolet is the usual choice.

The absorption of oxygen in the Schumann region of the ultraviolet has been used to study density in the low-pressure wind tunnels (Ref. 23), and this might be applied to flame studies. Vacuum spectrometry is required since air absorbs strongly in this region. This technique is experimentally difficult.

The absorption of alpha particles, neutrons, and electrons are proportional to gas density, and some modification of these techniques might be used. Alpha particle absorption has been used to determine a final flame temperature (Ref. 24), and electron beam absorption has been used to map density in low-pressure wind tunnels (Ref. 25), but neither of the methods has been used to study local temperatures in flames.

88

Alpha particles and neutrons are scattered by nuclei, whereas electrons are scattered by the electron cloud around the atoms. The scattering is almost independent of the molecular composition of the system. This is a distinct advantage for making density measurements, since it makes the method insensitive to composition.

Flame temperature profiles have been determined using X-ray absorption (Ref. 26). The method is one of the favorites for studying the structure of detonation waves (Refs. 27 and 28).

X-ray absorption is a function of the total number of electrons and is therefore determined primarily by the number of atoms present and their atomic weight rather than their particular molecular arrangement. Absorption is thus directly proportional to the density (see Eq. 9). The presence of diffusion introduces no error in such measurement, since each atomic species is separately conserved in flow systems such as flames. Most of the flame systems of interest consist of molecules with light nuclei, which have low absorption. In these cases, it is desirable, and usually necessary, to add a highly absorbing tracer gas such as xenon. The absorption of X-rays becomes proportional to the density of this tracer gas: and since the tracer gas is unaffected by the combustion reactions, this density and the absorption of X-rays are proportional to the total density of the gas (Eq. 9):

$$T \quad T_0 \, \frac{I}{I_0} \qquad \text{(see page 16)}$$

Soft X-rays are usually used for convenience and safety: they can be generated either with pulse tubes or obtained from radio-isotopes such as Fe^{55}. The former are of particular convenience for studying transient systems, such as shock or detonation waves. Suitable designs for such flash X-ray tubes are available (Ref. 28) with microsecond duration and high power. Fe^{55}, on the other hand, provides a convenient stable source for steady-state measurements such as flames (Ref. 26). An apparatus schematic is given in Fig. III-8. Several different detectors have been used, such as the direct electron multiplier and the scintillation counter.

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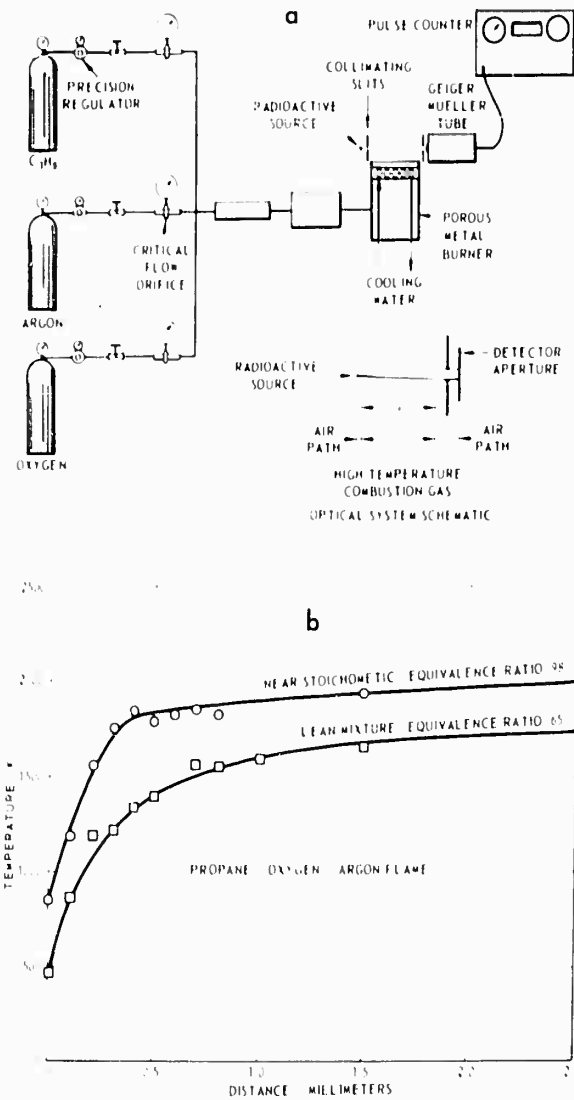
Fig. III-8   TEMPERATURE PROFILE DETERMINED BY USE OF X-RAY
               ABSORPTION

               a - Apparatus when Using X-Ray Absorption from
                   a Radioactive Source
               b - Propane Oxygen-Argon Flames at Atmospheric
                   Pressure

90

Density from Interferometry

Gas density can also be measured using the optical techniques of interferometry (Refs. 29 and 31) (Fig. III-9). The velocity of light is a function of the density of the medium so that beams passing through gases of differing density have different traversal times. If the beams were initially coherent,* they will then be out of phase
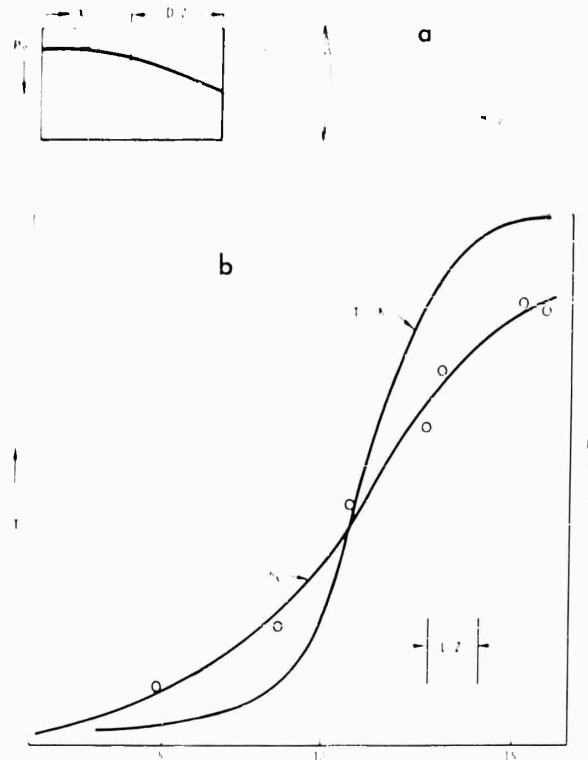
Fig. III-9   INTERFEROMETRIC DETERMINATION OF TEMPERATURE PROFILES

a - Schematic Diagram of Apparatus
b - Temperature Profile of Ethylene Flame (Ref. 29)

91

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*To be coherent, the two beams must have the same source. This is usually accomplished with a half-silvered plate which transmits part of a beam and reflects part of it. Interference does not occur between beams of non-identical sources, except in the radio or microwave region or with lasers, where phase of the source can be controlled. Monochromatic radiation is not required, but greatly simplifies experimental adjustments.

and can interfere. This phase difference, or retardation, is proportional to the difference in density between the path taken by the measuring beam and that taken by the standard. The resulting interference pattern can be interpreted quantitatively in terms of density by simple counting and measuring techniques. The possible application of these techniques to flame studies was pointed out a number of years ago by Olsen (Ref. 30), but only one such study has been made (Ref. 29). The method has the advantage of optical techniques that it does not disturb the system. Excellent precision can be obtained, although the problem of defining the path in the case of two-dimensional flames or of interpreting the complex result with three-dimensional flames is formidable. The composition-sensitivity is a second order effect, since to a first approximation, refractive index is proportional to the atomic volumes. Shock tube studies (Ref. 32) have shown that the simple relation between density and refractive index holds even in the presence of large concentrations of oxygen atoms and electrons. On the other hand, the presence of nitrogen atoms seriously disturbs this relation, and the method becomes composition sensitive. This means that ordinary combustion systems can be studied quantitatively by interferometry up to the temperatures at which appreciable dissociation of nitrogen occurs: namely 5000°K.

Temperatures Derived from Measurement of Gas Density Gradients

Temperatures can also be derived from measurements of spatial derivatives of density. They can be conveniently determined by optical methods: the first derivative by schlieren techniques, and the second derivative by shadowgraph techniques. Strictly speaking, these techniques measure $1 \, T^2 (dT \, dZ)$ (schlieren), and $2 \, T^3 (dT \, dZ)^2 \, (d^2T \, dZ^2)$ (shadowgraph). Most optical studies of flame microstructure have used some variant of the schlieren method, and many studies of flame geometry have been made using these techniques. Shadowgraph techniques have been discussed in detail by Weinberg (Ref. 31).

92

A number of methods have been used for measuring refractive index gradient (Refs. 31 and 33-41), but the most successful technique has been the inclined slit method (Ref. 39). The principal advantages are: (a) the apparatus is simple, and (b) the flame is not

disturbed by the measurements. The principal disadvantage is the ne-
cessity of composition and edge corrections. The apparatus (Fig. III-
10) consists of a well-collimated light beam (±15 sec angle), a de-
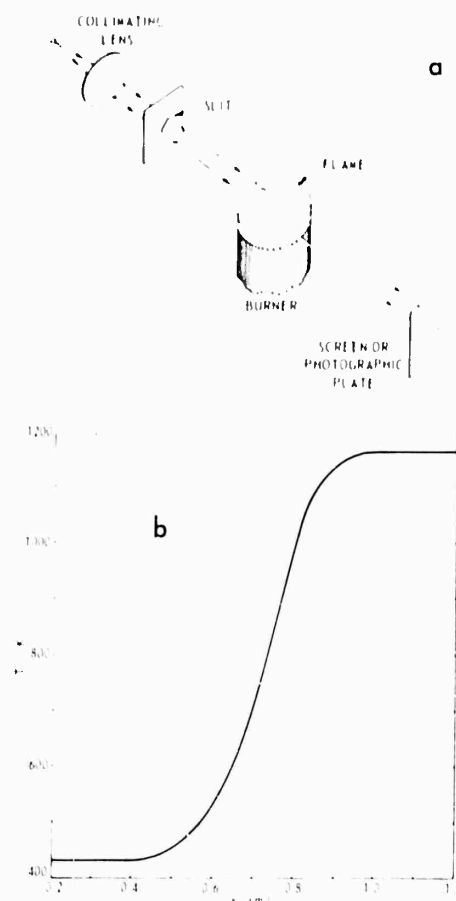
Fig. III-10   INCLINED SLIT METHOD OF DETERMINING TEMPERATURE
DISTRIBUTION

a - Schematic Diagram
b - Temperature Distribution Obtained by Method

93

fining slit, a burner, and a photographic plate receiver upon which
the measurements of slit deflection are made. The measured deflec-
tions can be interpreted as density and temperature using equations
10 a-d. The precision of the method is good. The techniques, theory,

and sources of error have been critically discussed in a survey (Ref. 33) and a definitive monograph (Ref. 31).

$$\frac{dn}{dZ} = -\frac{D}{Y}\frac{1}{\cos \phi} \qquad (10a)$$

$$n = \int_0^Z \frac{dn}{dZ}\, dZ \qquad (b)$$

$$\epsilon = \epsilon_0 \frac{n - 1}{n_0 - 1} \qquad (c)$$

$$T = \frac{P}{\epsilon R} = \frac{(n_0 - 1)}{(n - 1)}\frac{P}{\epsilon_0 R} \cdot \qquad (d)$$

COMPARISON OF METHODS FOR DETERMINING TEMPERATURE PROFILES AND SOME VALUE JUDGMENTS

A number of methods for determining temperature profiles have been discussed here and used in practice. Each technique possesses some advantages (Table III-3), but the most useful ones have been the thermocouple traverses and the inclined split method. Three direct comparisons of the various techniques have appeared in the literature. Thermocouple measurements have been compared with aerodynamic determinations and the pneumatic probe method (Ref. 42) (Fig. III-11b); with spectroscopic measurements (both in absorption and emission) (Ref. 10) (Fig. III-11c); and with the inclined slit technique (Ref. 40) (Fig. III-11a). The other techniques have usually been checked by comparison with calculated adiabatic flame temperatures. Agreement between the different methods is generally good. The techniques are compared in Table III-3.

94

Thermocouple measurements have been one of the most useful techniques. They combine high precision and spatial resolution with ease of measurement. The three principal problems are the emissivity correction, and spatial shift due to aerodynamic wake, and elimination
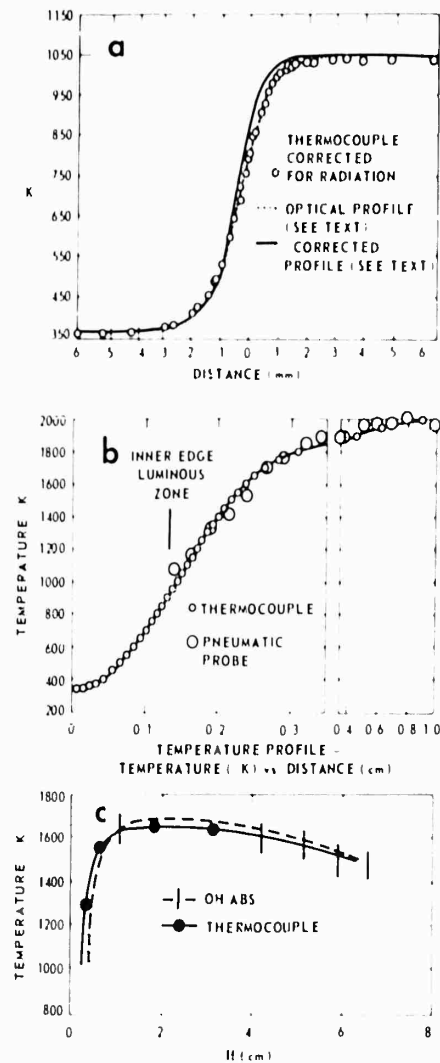
Fig. III-11   COMPARISONS AMONG VARIOUS METHODS OF MEASURING FLAME
TEMPERATURE PROFILES

       a - Comparison Between Pneumatic Probe Method and
          Thermocouple Method (Ref. 42).
       b - Comparison Between the Inclined Slit Method and
          Thermocouple Method (Ref. 40).
       c - Comparison Between Absorption Spectroscopic Method
          and the Thermocouple Method (Ref. 10).

95

of catalytic recombination on the thermocouple surface. Measurements are limited by the materials used, but for many systems this is not a problem.

Inclined slit method is also a widely used techinque. It has the advantages of reasonable precision and spatial resolution and ease of measurement, and has the virtue of not disturbing the flame. It provides an absolute position reference in the flame front and is amenable to instantaneous measurements. The sensitivity of the technique drops off with temperature, but to compensate for this, there is no particular upper limit. Difficulties include moderately complicated data reduction and the requirement of average molecular weight information.

Aerodynamic measurements for the derivation of temperature offers only limited precision and spatial resolution. It is principally useful as a cross check on the more precise measurements and to establish reference coordinate surfaces in the flame.

Pneumatic probe measurements are of moderate precision and spatial resolution and have the advantage of offering a method for directly connecting composition and temperature measurements. Problems include the effects of the probe on the flame and a drop off of sensitivity with temperature. The upper limit for such measurements is set by materials and the problem of making corrections for the changes brought about by radical recombination in the probe.

Emissivity and spectroscopic measurements offers good precision of measurement but only limited spatial resolution. They have the advantage of not disturbing the flame, although for optical pyrometry it is necessary to introduce an emitter and problems may arise. The principal problems are non-equilibrium emission, the restriction to relatively high temperature regions, and, in the case of spectroscopic measurements, the relatively high cost of the equipment.

96

X-ray absorption measurements offer moderate precision (about 2%) and spatial resolution (0.1 cm). Its use has been limited because the apparatus is not common in combustion laboratories.

Interferometry offers good precision and spatial resolution and the advantage of not disturbing the system. It is difficult to apply in very steep gradients but the technique is well complimented

by inclined slit measurements. This type of measurement has been held back by the cost of the equipment, although recently interferometers of modest cost have appeared (Ref. 31).

APPENDIX

FABRICATION OF SMALL THERMOCOUPLES

Flame structure work requires the use of rather small thermocouples in the range from 10^{-2} cm - 10^{-4} cm diameter. Because of the high temperatures involved these couples are generally made of noble metals using such pairs as Pt-Pt, 10% Rh, and Ir-Ir, 40% Rh (Table III-II). In addition, it is often necessary to coat them with silica or ceramic layer to reduce the catalytic effects on the flame.

The wires are available commercially and are suitable for thermometry in a wide range of sizes from 0.1 inch in diameter to 10^{-5} inch in diameter. The smaller wires are Wollastan wires which have a silver jacket some four or five times the platinum metal wire. This is a great convenience in handling the smaller sizes and can be readily removed by the cautious application of nitric acid which dissolves silver but not the platinum. Some caution is required because the smaller wires can easily be broken by the weight of a drop or the forces of surface tension. Strong (Ref. 18) discusses the manufacture and handling of such wires.

The platinum couples have reasonable mechanical strength down to about 2×10^{-3} cm diameter and irridium couples down to about 1×10^{-3} cm diameter and they can be handled and welds tested for strength by a gentle tug. Below this point they become so fragile that a strong breath will break them (rigidity drops off with the fourth power of diameter).

98

Because of this fragility and to avoid vibration problems, it is desirable to mount the small thermocouples on heavier wire supports. A number of designs have been used; the main requirement is that the couple be supported under light tension so that the leads extend a reasonable distance along an isothermal surface. Thus the heat losses due to lead conduction will be negligible. A word of caution: Although

present thermocouple wires are generally excellent, wires are occasionally found with a point of strain or nonuniformity which can act as a spurious couple falsifying the readings. It is wise to test the mounted couple by connecting it to a potentiometer and passing a microflame along the support wires. No EMF should be generated except when the hot gas passes over the thermocouple junction itself. This is an excellent test for conduction losses along the leads. If the spurious EMF is due to mechanical strains the wire can be annealed; otherwise it should be discarded.

The fabrication of couples consists of two operations: welding of the junction and coating of the couple with ceramic. Two techniques have been successfully used in welding small thermocouples: Electric welding and flame welding. A simple electric welding system (Fig. III-12) is very useful, particularly for non-noble metal couples which are easily oxidized down to 0.0075 cm. Techniques have been described (Ref. 43) which permit the welding of couples as small as 0.001 cm diameter, but the apparatus is moderately complex compared with the flame welding technique for small noble metal couples illustrated in Fig. III-14.

In flame welding the smaller wires should be butted together by a micromanipulator so that they are bent slightly by compression. Thus, when the flame melts the lower of the two wires, the wires are

Fig. III-12 SCHEMATIC DIAGRAM OF WELDER FOR SMALL THERMOCOUPLE WIRES

99

WIRE SIZE	MATERIAL	LENGTH	MATERIAL	LENGTH	WELD TECHNIQUE	CAPACITY	VOLTAGE
			IRON CONSTANTAN				
.21.	IRON	1.8	CONSTANTAN	1.8	TYPE A	24 4.	4'5
2.305	IRON	1.8	CONSTANTAN	1.8	TYPE A	4 1.	35. 45.
2.304	IRON	1.12	CONSTANTAN	1.12	TYPE A	2 t	35. 4%
.303	IRON	1.16	CONSTANTAN	1.16	TYPE A	1.5 2	35. 4%
.302	IRON	1.64	CONSTANTAN	1.64	TYPE A	.3 1	35. 4'5
.301	IRON	1.64	CONSTANTAN	1.64	TYPE A	.2	2'5 3.
.3855	IRON	1.64	CONSTANTAN	1.64	TYPE A	.1	25.
			COPPER CONSTANTAN				
.305	Constantan Short		COPPER	1.8	TYPE B	63	125
.304	1 to 4.d.am		COPPER	1.4	TYPE B	32	125
.303	1 to 4.d.am		COPPER	1.3.	TYPE B	12	125
.302	1 to 4.d.am		COPPER	1.16	TYPE B	3.'	125
			CHROMEL ALUMEL				
.1.	CHROMEL	1.16	ALUMEL	1.8	TYPE B	6.	35
.305	CHROMEL	1.16	ALUMEL	1.8	TYPE B	1	3.1
.304	CHROMEL	1.16	ALUMEL	1.8	TYPE B	t	3.1
.303	CHROMEL	1.12	ALUMEL	1.16	TYPE B	.'	1.1
.302	Short 1 3.d.am		ALUMEL	1.16	TYPE B	1.3	3.5
.301	Short 1 3.d.am		ALUMEL	1.16	TYPE B	t	2.3.
			CHROMEL CONSTANTAN				
.21.	CONSTANTAN	1.16	CHROMEL	1.8	TYPE B	60	4.00
.305	CONSTANTAN	1.32 1.16	CHROMEL	1.16 1.8	TYPE B	2.8 12	5.00 5.0
.304	CONSTANTAN	1.32 1.16	CHROMEL	1.16 1.8	TYPE B	'	3.0
.303	CONSTANTAN	1.32	CHROMEL	1.32	TYPE B	2.8	3.00
.302	CONSTANTAN	1.32	CHROMEL	1.16		1.8	3.0
			PLATINUM PLATINUM 1. RHODIUM				
.1	PLATINUM						
	12% RHODIUM	1.16	PLATINUM	1.16	TYPE A	1.3	25.

Fig. III-13 CONDITIONS FOR WELDING VARIOUS THERMOCOUPLE COMBINATIONS

forced together in a junction; this is a good indication of the time
to remove the flame.   If the flame is applied too long after the initial
weld the couple will be burned.

The couple can now be mounted on a suitable support (see Fig.
III-14) by welding.   Since the support wires are larger than the thermo-
couple the usual method is to wind it onto the support.   The thermo-
couple can then be drawn taut by carefully bending the support frame.

100

The most satisfactory general coating found in our experience is silica.* This can be applied to a couple as small as 0.001 cm diameter in a uniform layer as thin as 0.0001 cm using the flame plating technique shown in Fig. III-14. The principle is to
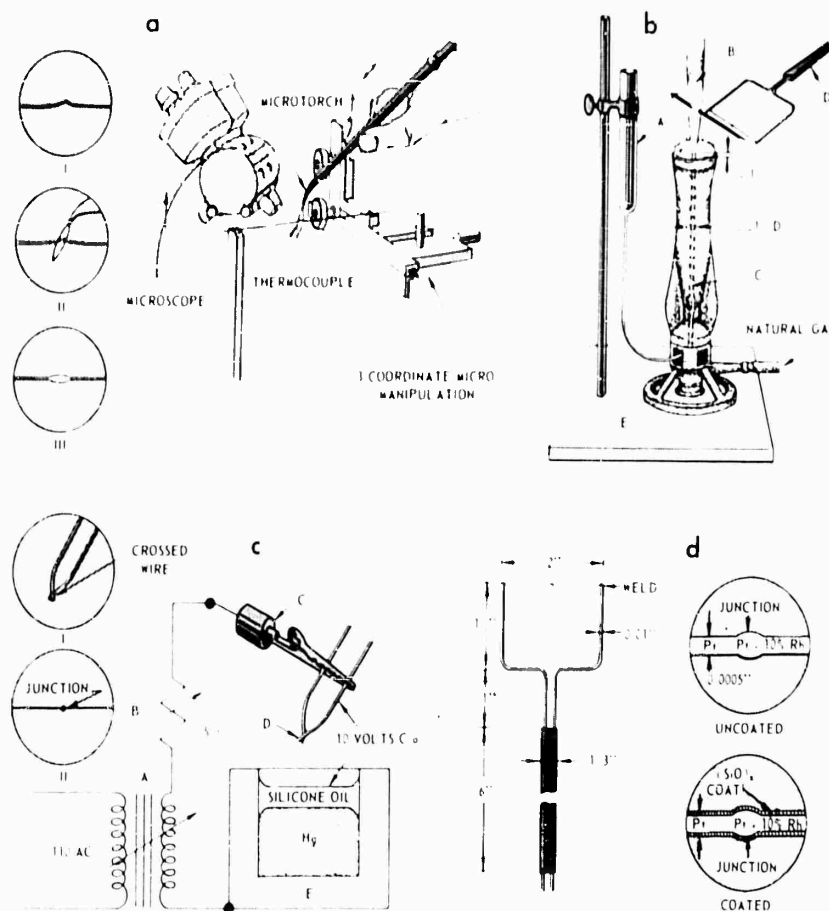
Fig. III-14   TECHNIQUES FOR MANUFACTURING SMALL THERMOCOUPLES

a - Flame Welding of Noble Metal Thermocouples.
b - Electric Welding of Base Metal Thermocouples.
c - Flame Plating Noble Metal Couples with Silica.
d - Diagram of Thermocouple Support and Idealized Thermocouple.

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* The recommended silicone compound is dimethyl siloxane, but most silicone oils (e.g., DC 703 diffusion pump oils) are also satisfactory.

use a small silica producing flame and allow the particles to coat
the couple by slowly passing it through the flame. The recommended
temperature of 1850°C (Ref. 9). The correct conditions can usually
be found experimentally by testing with a wire and examining the test
piece under a microscope. A satisfactory coating should have the
appearance of fine porcelain under direct illumination. The coating
should be adherent enough so that it can be rubbed with the finger
without coming off (do not test the final couple this way). Other
ceramic coatings have been described in the literature (Ref. 8).

Some typical examples of the outputs of some other high
temperature thermocouples are shown in Fig. III-15.
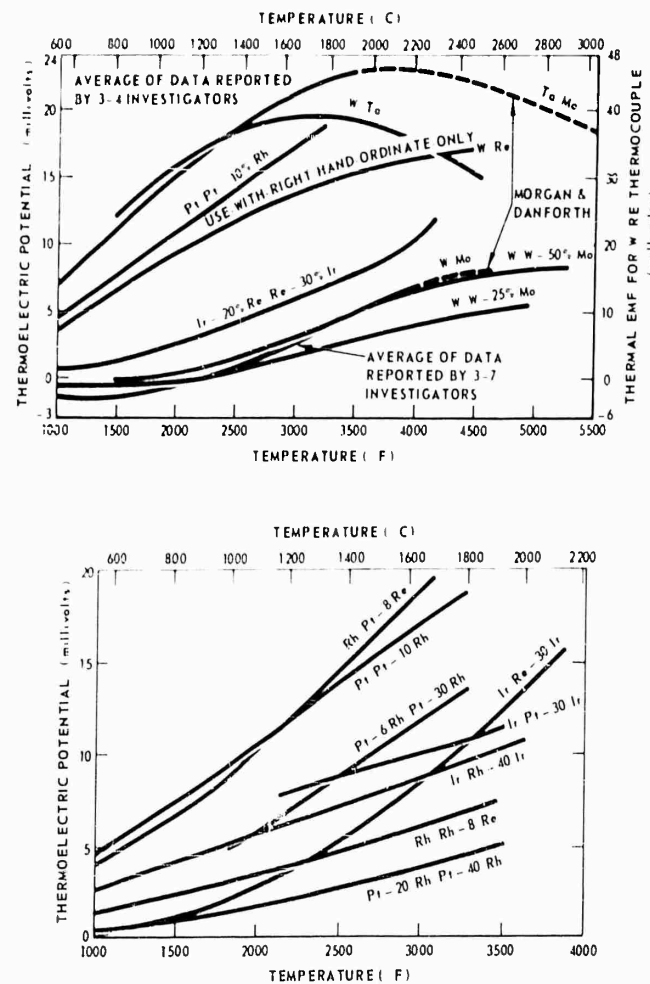
Fig. III-15 THERMOCOUPLE COMBINATIONS

102

TABLE III-4   CHAPTER III SYMBOLS

a - Area (cm^2)

D - Flame width (cm)

I - Intensity of X-ray beam (counts per second)

k - Constant

m - Mass (g)

$\bar{M}$ - Average molecular weight (g per molar volumes)

$\dot{m}$ - Mass flow (g cm^2 sec)

n - Refractive index

N - Moles (g M)

P - Pressure (dynes cm^2)

R - Molar gas constant (82.7 cc-atm °K)

T - Temperature (°K)

v - Velocity (cm sec)

V - Volume (cm^3)

Y - Path length (cm)

' - Ratio of Specific heats

ξ - Beam deflection (cm)

θ - Angle

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104

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IV

DETERMINATION OF COMPOSITION OF STABLE SPECIES IN FLAMES

Compositions in flame fronts provide the most interesting information for chemists and chemical engineers. These composition measurements must be associated with positions to be meaningful. This is often only given in qualitative terms (unburned, intermediate, or burned gases), but for quantitative work precise position determinations are required (see Chapter VI). The evaluation of chemical rate local gas velocity, requires the local composition, its first and second derivatives with respect to distance, local temperature, and local gas velocity together with appropriate diffusion coefficients.

MOLECULAR SPECIES IN FLAMES

Individual particles in a gaseous system are considered molecules from the standpoint of kinetic theory, but it is common to classify them as atoms, molecules, free radicals, or ions. All of these species are present in flames. A typical distribution of species in a flame would be: ordinary molecules, 1; radical species, 10^{-2}; and charged species, 10^{-7}. It is also convenient to classify molecules as reactants, intermediates, and products.

In common usage the term molecule refers to a polyatomic species having no electrical charge or unpaired electron spins. A molecule consisting of a single atom is referred to as an atom; a molecule or atom which is electrically charged is referred to as an ion; a molecule with unpaired electron spins is called a free radical. With atomic species, this latter distinction although significant, is often not made (occasionally the term unstable atom is used). More extensive discussions of the properties of atoms, molecules, radicals, and ions can be found in elementary chemistry texts.

107

References are on pages 137 and 138.

This chapter will deal with the determination of the concentration of the stable species (i.e., those stable to sampling). These species can be determined by straightforward sampling and analytical techniques. The unstable species, radicals, and ions require special techniques which will be discussed in the following chapter.

COMPOSITION VARIABLES

In flames and other flow systems, two composition variables are commonly distinguished composition (the mass of a species per unit volume) and species flux (the mass of a species passing through a unit area in unit time). A compilation of the more commonly used units and their conversion factors is given in Ref. 17. Experimentally, composition is the measured variable and flux the derived variable. The relation between them in a one-dimensional system is given by Eq. 1:

$$G_i \quad \frac{v}{M_i} \quad X_i - D_{i,j} \; v \quad dX_i \; dz \tag{1}$$

In this equation

D is the binary diffusion coefficient (cm^2 sec),

G is the fractional mass flux (g cm^2 sec),

M is molecular weight (g mole),

v is velocity (cm sec),

X is concentration (mole fraction),

z is distance (cm), and

 is density (g cc).

The subscripts i and j are species indices.

108

Concentration is an inherently positive, intensive quantity. Flux is also an intensive quantity, but it may either be positive or negative; usually it is a positive quantity. In a three-dimensional system flux is a vector while concentration remains intensive, i.e., a scalar. In a one-dimensional system with no concentration gradient, these variables are numerically identical when expressed in normalized units. Flames, however, are far from this limiting behavior, and the effects of molecular diffusion make two variables differ widely (Fig. 4-1).
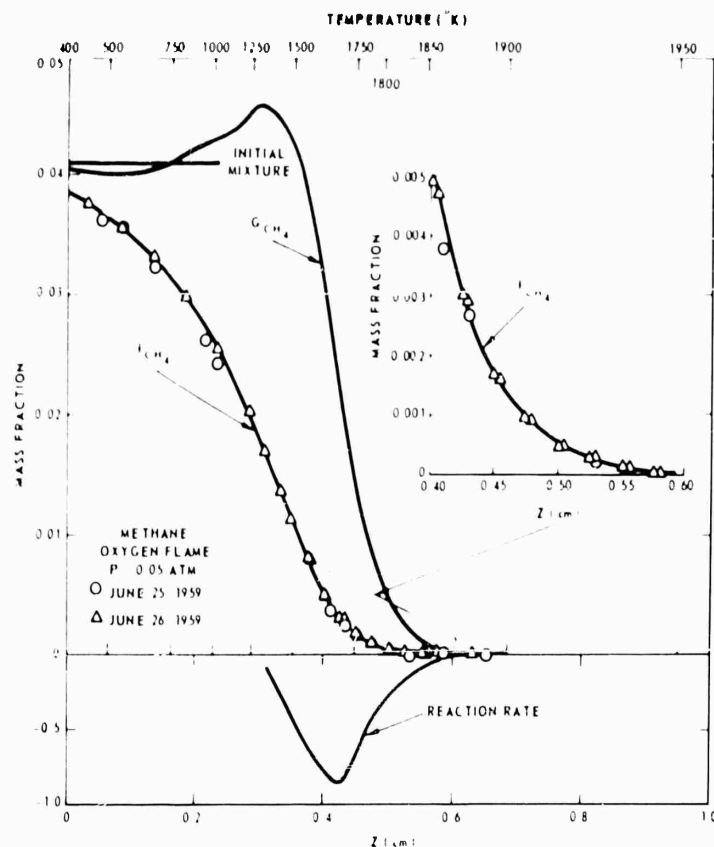
Fig. IV-1   COMPOSITION PROFILE OF METHANE IN A METHANE-OXYGEN FLAME

Experimental points from two successive days runs are
plotted to show reproducibility of data.   Mass fraction
is plotted as a function of distance (cm) and tempera-
ture ($^\circ K$).   Fractional mass flux derived from these
data is plotted to show the strong effect of molecular
diffusion.   Reaction rate (moles/cc/sec) derived from
the data is plotted.

DETERMINATION OF THE CONCENTRATION OF STABLE SPECIES IN FLAMES

109

Concentration in flame systems is usually determined by one
of two techniques: (1) probe sampling followed by analysis, and (2)
in situ analysis by spectroscopic methods.   Each technique has ad-
vantages and has been used in flame studies.   Most studies of stable
species have made use of probe sampling.   The reason is that spectro-
scopic techniques can not be applied to all species.   Therefore, probe

sampling and analysis will be discussed in this chapter and in situ
spectroscopy will be discussed in the following chapter on the determina-
tion of unstable species, since its advantages make it a more widely
used technique.

PROBE SAMPLING

Micro-probe sampling is a straightforward process - the
sample is withdrawn, quenched, and analyzed. Although there are a
number of problems, most of these have been solved by the use of the
quartz microprobe and mass spectrometer or other micro-analytical
technique (Ref. 1). Such a probe withdraws only a few micrograms of
sample per second and does not disturb a flame visibly (Fig. IV-2).

Fig. IV-2 PHOTOGRAPH OF QUARTZ MICROPROBE ENTERING A QUARTER
ATMOSPHERE PROPANE AIR FLAME (4.20 C_3H_8; 95.8 Air)(mole %)

(Ref. 18)

The contoured nozzle and large pressure drop used effectively quenches
the flame reactions so that a reliable sample reaches the analytical
instrument. Sampling with cooled probes at stream velocity has not

proven satisfactory because it is not possible to quench the fast flame reactions completely (Ref. 2) and the flame is disturbed by bulky cooled surfaces. On the other hand, in engines where the scale is larger, such probes are very useful (Ref. 3).

A probe sampling system consists of a probe, connecting lines, and an analytical system. Samples can either be withdrawn in batches and subsequently analyzed or the analytical instrument can be part of the sampling system. Diagrams of two typical systems are shown in Fig. IV-3.
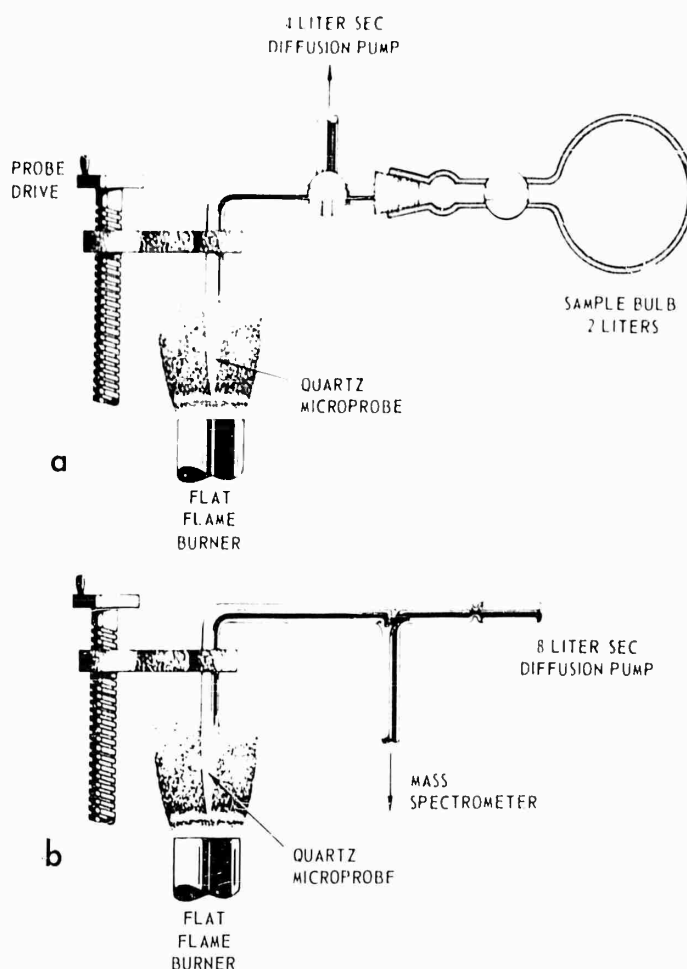
Fig. IV-3   SCHEMATIC DIAGRAM OF TWO PROBE SAMPLING SYSTEMS

a - Batch Sampling of Flames
b - Continuous Flow of Flames

111

The Design and Construction of Sampling Probes

Sampling probes are designed to produce a minimum of disturbance in the flame. This disturbance arises both from sample withdrawal and from the bulk of the probe itself. A probe must also allow rapid decompression and withdrawal of the sample to a cool region outside the flame. These objectives can both be accomplished by use of tapered quartz microprobes with small sonic orifice inlets (Fig. IV-4). Tapers between 15° and 45° are generally satisfactory. The connecting tubing is chosen to handle the inlet mass flow from the orifice at a pressure which assures a five to ten-fold pressure drop across the inlet orifice. The exact size of tubing is not critical since the disturbance to the flame is determined by the taper of the tip rather than the size of the tube.
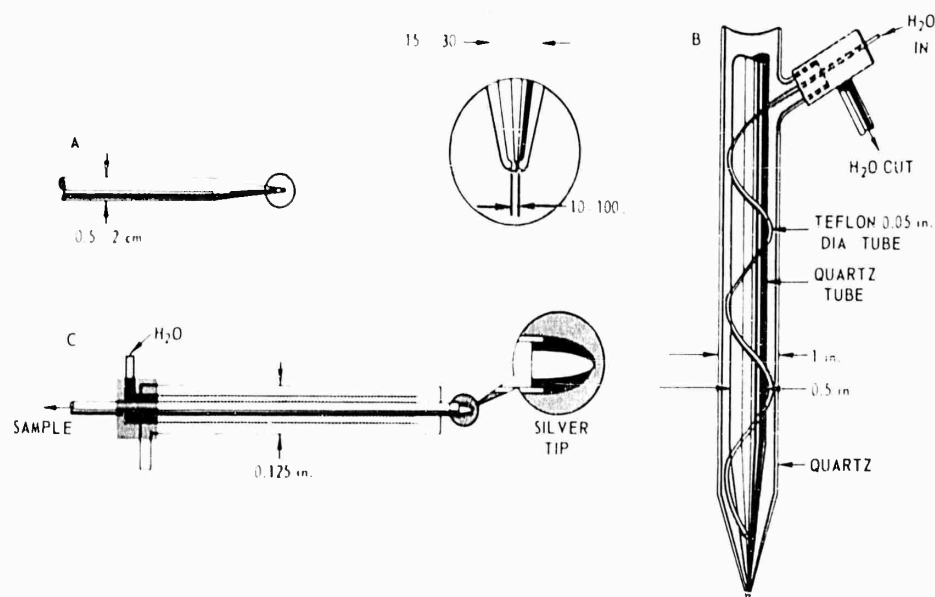
Fig. IV-4 TYPICAL MICROPROBES

a - Uncooled Quartz Microprobe.
b - Water Cooled Quartz Microprobe.
c - Water Cooled Metal Microprobe.

The flow through the orifice of a microprobe can be estimated using Eq. (2). The mass flow is chosen to be the smallest yielding -a satisfactory sample. The connecting tubing size can be chosen using Eq. (3).

$$Q \quad k \, d_o^{\,2} \, c \, T^{-1/2} \tag{2}$$

$$Q \quad [(P_i/n)^2 - P_s^{\,2}] \, \frac{d_t^{\,4}}{L} \tag{3}$$

In these equations:

Q   volume flow per second through the probe (cc/sec).

k   a number indicating the ratio between the effective area of an orifice and the geometric area. It is dependent on the boundary layer and hence is a function of the mean free path in the gas and the Reynolds number. For very large orifices it approaches unity, for the small orifices used in probes it ranges around 0.5.

d_o diameter (cm).

T   temperature (°K).

c   a function of the average molecular weight and ratio of specific heat of the sample (see Table I of Chapter I).

    a function of the viscosity of the sample (see Table I of Chapter I).

L   length of tube (cm).

P   pressure (atm).

Subscript i   refers to inlet conditions.

Subscript s   refers to conditions at the analytical instrument or sampling bulb.

n   pressure ratio across the sample orifice. (Since this pressure drop controls the quenching of the sample it is usual to choose n between five and ten.

113

The usual requirements are a few micrograms flow per second. For flames in the fractional atmosphere region this can be obtained with orifices in the range from five to fifty micron radius. Such probes can be readily fabricated and sized using the techniques described in Appendix 1.

The diameter chosen should also be large compared with the mean free path in the hottest (i.e., least dense) part of the flame or sampling biases will occur. The problems of sampling with orifices small compared with mean free path are discussed in the section on low pressure sampling.

Batch Sampling and Continuous Flow Sampling

Samples can be taken in batches using suitable sample bottles or introduced directly into the analytical instrument with a continuous flow arrangement (Fig. IV-3). Batch sampling does not require an instrument directly connected with the apparatus and samples can be analyzed at leisure, but it is difficult to obtain reliable analyses of polar species, particularly water. In some cases this can be avoided by use of Teflon or polyethylene-lined sample bottles.

Where absorption is a problem the best solution is a continuous flow system. The absorbing surfaces ultimately come to equilibrium with the sample and the material reaching the analytical instrument is identical with that entering the probe. For example, with Teflon lines only a few seconds were required to reach equilibrium with a typical water ladened sample, while under comparable conditions a glass and metal system required a number of minutes to reach equilibrium. One further precaution is necessary. The system must be continuum flow throughout (i.e., tube diameters large compared with the mean free path), and the pump must be isolated by a choking orifice or by a capillary of sufficient length so that back diffusion from the pump is negligible.* This is necessary because molecular separation occurs in the Knutson flow regime and diffusion pumps show a different pumping speed for each component of a mixture. This would bias the sample and analysis. A typical flow sampling system used in connection with a mass spectrometer is shown in Fig. IV-3.

114

The pumping speed required for a flow system depends on the probe size and pressure in the sampling lines, but a small laboratory diffusion pump of a few liters per second at twenty-five microns is usually adequate. With batch sampling, pumping speed is of secondary importance, but a good ultimate vacuum is necessary ($< 0.1\mu$).

ANALYTICAL TECHNIQUES

The primary requirement for flame studies is the handling of small samples at low pressures. Probe sampling rates range between 0.001 and 0.1 cm^3-atm/sec, and batch samples can be conveniently collected over periods up to 15 minutes.

Four techniques have been used to analyze flame samples: (1) Orsat or PV analysis, (2) mass spectrometric analysis, (3) gas chromatography, and (4) infrared spectroscopic analysis.

Orsat Analysis

Orsat analysis makes use of the gas laws and the physical and chemical properties of the gases being studied. The sample size is determined by measuring pressure and volume at constant temperature. Then the sample is separated into its components by suitable physical or chemical operations and the size of each fraction determined by measuring its P-V product (Fig. IV-5).
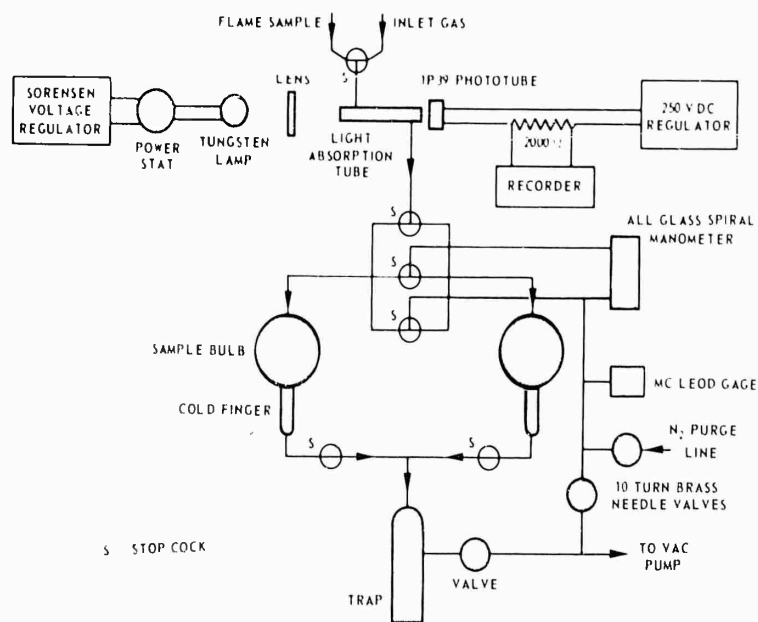

Fig. IV-5   ORSAT ANALYSIS FOR STUDY OF HYDROGEN-
                  BROMINE FLAMES (Ref. 4)

Bromine is determined by light absorption,
hydrogen is determined by freezing out bromine
and HBr with liquid nitrogen and HBr is de-
termined by difference.

115

* See explanation of Eq. (4) on following page.

The criterion for negligible diffusion is that the tube be long compared with the ratio of diffusion coefficient to the gas velocity (Eq. 4).

$$L \cdot \cdot D/v \qquad (4)$$

In this equation

- L is the tube length (cm)
- D is the diffusion coefficient (cm^2/sec). A typical value at room temperature is $0.25P^{-1}$ where P is the pressure in atmospheres.
- v is the average linear velocity of the gas (cm sec). This is calculated by dividing the volumetric flow at the pressure in the sampling line by the area of the line.

This system is simple, inexpensive, and requires only a few cc-atm samples. It is an absolute method. Under favorable circumstances, traces as small as a few parts per million can be detected.

The technique is slow and requires manipulation by an experienced operator. Given enough time mixtures of almost any complexity could be analyzed. It is only practical to analyze mixtures of moderate complexity, however, if less than an hour can be alloted to an analysis. The components must have appreciable vapor pressure at room temperature or adsorption will compromise the analysis, hence polar species and species with low vapor pressure must be avoided.

Orsat analysis has been applied in studies of the H_2 - Br_2 flame (Ref. 4) and the afterburning region of the propane-air flame (Ref. 5). Separations were obtained by differential freezeout.

The idea of physical or chemical separation can be applied to flow systems, provided the sample can be withdrawn at a suitable pressure or compressed by a pump (Ref. 6).

116

Mass Spectral Analysis

Mass spectrometry has been the most versatile and useful analytical technique for flame gases. Two types are available commercially: (1) the conventional magnetic deflection spectrometer, (2) the "time of flight spectrometer."

Magnetic Deflection Mass Spectrometry---Mass spectrometry
is based on the observation that with controlled electron bombardment,
a molecular species will produce a reproducible spectrum of ions which
can be separated from one another by accelerating them with an elec-
tric field through a magnetic field. In practice, the sample is in-
troduced through a molecular leak and bombarded by an electron beam
from a heated filament. The resulting ions are accelerated by a set
of electrodes in a crossed magnetic field (see Fig. IV-6). The radius
of curvature of the ion path is a function of the charge to mass ratio,
or "mass number" as it is commonly called. Therefore by use of colli-
mating slits, ions with a particular charge to mass ratio can be se-
lected. The current which they generate upon impinging on a target
electrode provides a signal which is proportional to the partial pres-
sure of the molecular species parent to the ion. The resolution or
minimum fractional mass difference which can be separated varies from
one mass unit in thirty for simple commercial instruments to one mass
unit in 10^{5} for isotope spectrometers. Resolution and high sensitivity
are purchased at the expense of simplicity, cost, and versatility. For
most flame work the simpler commercial instruments are satisfactory.
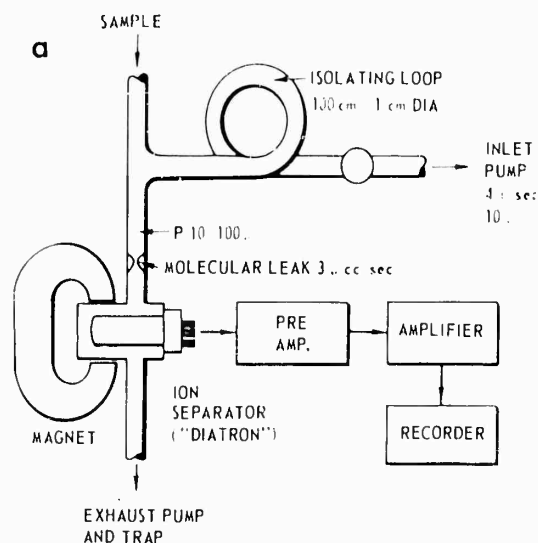
Fig. IV-6   MAGNETIC DEFLECTION MASS SPECTROMETER (CEC 620-10).

    a- Schematic Diagram of Flow System and
        Spectrometer.

117

ELECTRONIC DRAWER

b

SAMPLE INLET
CONNECTIONS

PREAMP HEAD

MAGNET

CHARCOAL TRAP

DIFFUSION PUMP

POWER CABLE

WATER LINES

CABINET FLOOR LOCK

c

ANODE

FILAMENT

CHARGED PARTICLES OF MASS
— NO IN REGISTER
▨ LIGHTER PARTICLES
▨ HEAVIER PARTICLES
--- ELECTRONS FROM
FILAMENT TO ANODE
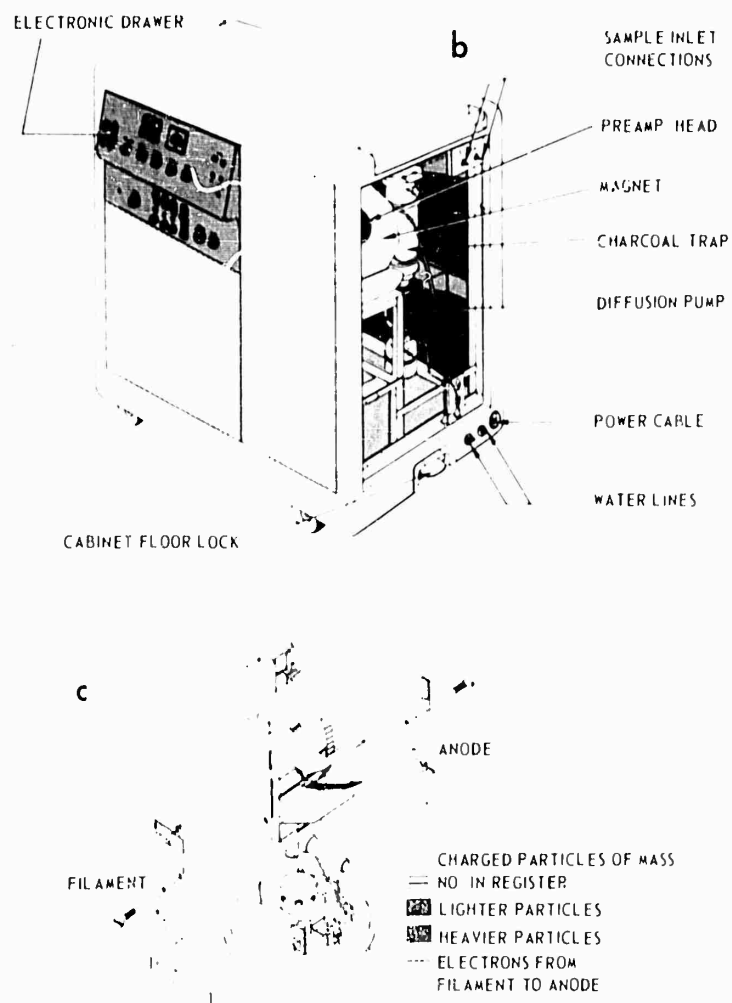
Fig. IV-6   b - Picture of Spectrometer.
             c - Diagram of Ion Separation Tube ("Diatron")

There are a number of good books on mass spectrometry (Refs. 7 and 8); a short discussion of the analysis of flame gases is given in Appendix B.

118

Time of Flight Spectrometers---Time of flight spectrometers differ from magnetic deflection instruments in that ion separation is obtained in time rather than space (Ref. 9). This is accomplished by forming and accelerating the ions with a pulsed field and allowing them to drift to the sensing electrode. Since the kinetic energy of an ion accelerated by a field depends only on its charge and the field and not on the mass, it is clear that for ions of a given charge the velocity and hence the time taken to transverse the drift space (Fig. IV-7) will be inversely proportional to the square root of the mass of the ion. Commercial instruments cover the "mass unit" range from 1-4000 with a resolution of about 1-600. One of the principal advantages of this type of spectroscopy is extreme rapidity. A complete spectrum can be obtained every 10^{-4} sec (10,000 cps). Under these conditions the spectrometer has a dynamic range of 1-1000 and a precision of about 5%. Higher precision and sensitivity can be obtained

Fig. IV-7 SCHEMATIC DIAGRAM OF TIME OF FLIGHT MASS SPECTROMETER

(BENDIX MODEL 12)

119

by averaging a large number of spectra with an electronic analog comparator. This technique trades speed for precision so that spectra can be obtained only in times of the order of minutes rather than fractions of milliseconds. Sensitivities comparable with other types of mass spectrometers can be attained $(1:10^9)$.

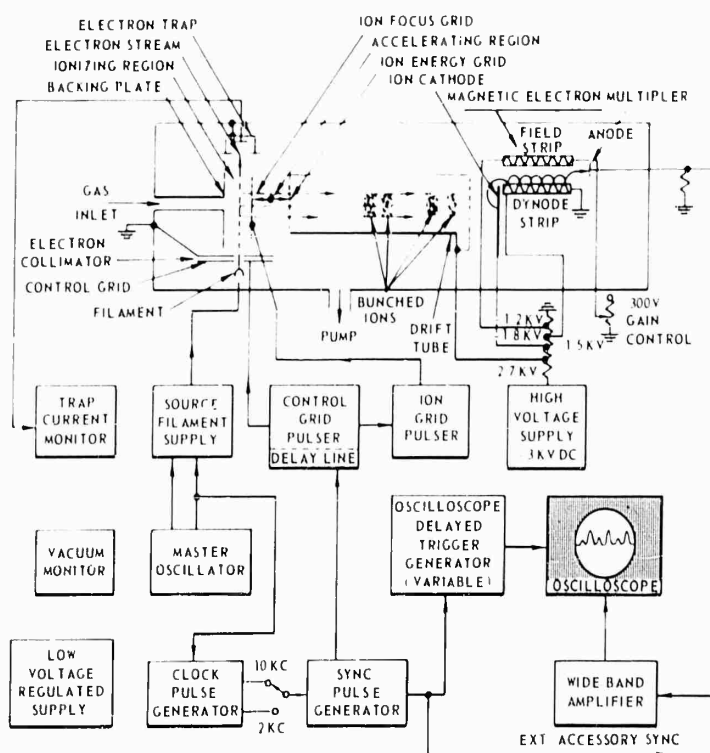One of the interesting advantages of the oscilloscope-type of presentation is that individual molecular species have characteristic patterns which can be readily recognized in the compact picture given on the oscilloscope face. This Gestalt recognition of spectra is useful for qualitative analysis.

Chromatography

Chromatography has advantages for analysis of flame gases: (1) high selectivity - with a suitably chosen column even isotopic molecules and optical isomeres can be separated: (2) high sensitivity - using the beta ray-type detector and flame detectors it is claimed that a trace as small as one part in 10^9 can be detected (Ref. 10); (3) analytical accuracy as good as the detection scheme (1 - 2 per cent); (4) small sample size (1 - 10 cc-atm); (5) moderate rapidity - the time taken for an analysis depends upon conditions, but a typical time is of the order of 20 minutes.

A chromatograph consists of a column packed with a suitable adsorbant, a flow system, a sample introduction system, and a sensing element (see Fig. IV-8). If a spatially well-defined sample is introduced into such a flow system with a carrier gas, the components will show residence times which depend on their adsorptive properties. The more heavily adsorbed materials will have the longest residence times. Thus, if the column is long enough, the components of the sample will be separated and individual species will leave the tube at different times. This reduces the original multicomponent analysis problem to a series of analyses of binary mixtures.

120

The column consists of a tube ranging from 3 to 300 feet long. It is packed or lined with an adsorbing agent suitable for the system to be studied. There is no universal column and complex samples require use of several columns in parallel or series. Tempera-
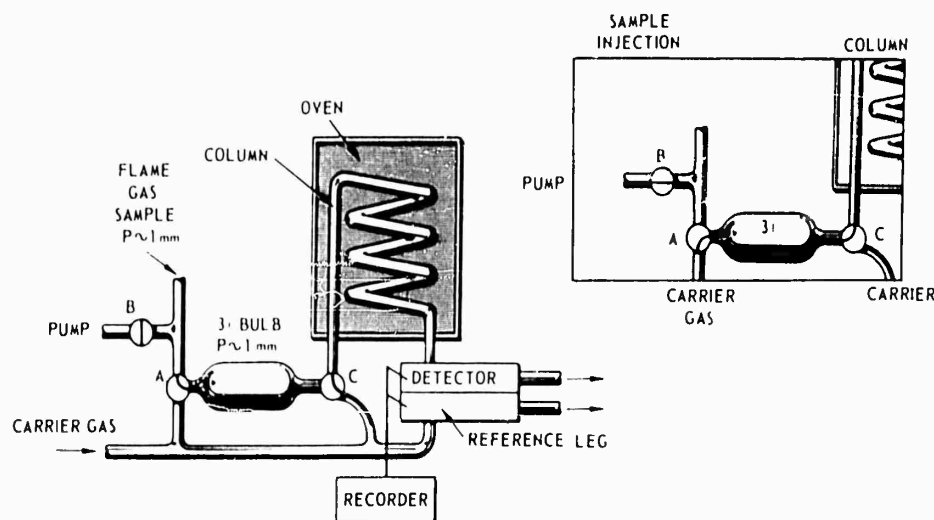
Fig. IV-8   SCHEMATIC DIAGRAM OF GAS CHROMATOGRAPH MODIFIED FOR TAKING
LOW PRESSURE GAS SAMPLES FROM FLAMES

Stopcocks are set in the position for collecting sample
and running chromatograph.   Insert: Stopcock Positions
for Injection of Sample.

ture variation can also be used.   Adsorbing agents range from "molecu-
lar sieves" to commercial detergents.   A very interesting column is
the Gollay-type consisting of an open capillary with coated walls.

Detection can be made by any of a number of techniques:
thermal conductivity, ionization detectors using beta-rays or flames,
density balances and even mass spectrometers (Ref. 11), although be-
cause of the expense of the mass spectrometer, it is more realistic
to view the chromatograph as an adjunct to the mass spectrometer.   The
combination of chromatograph and T.O.F. mass spectrometer is a power-
ful analytical tool whose use in flame studies will undoubtedly be
useful.

121

Adsorption Spectroscopy

Spectroscopy offers a convenient analytical tool for flame
studies: a number of good texts discuss the theory and practice (Refs.
12 and 13).

The variable measured is the loss of beam intensity due to sample insertion. The relation between absorbed light and composition is given by Eq. (5).

$$P_i = \frac{\ln (I_o / I)}{a_i (P,T) \ L} \qquad X_i = P_i / P \qquad (5)$$

In this equation

P is pressure (atm),

I is light intensity,

L is the length of the light path,

a_i (P,T) is the extinction coefficient.

In general it is necessary to deal with single lines of low strength; otherwise, absorption is not proportional to concentration. The extinction coefficient is a function of concentration and temperature which for species more complex than diatomic molecules must be determined empirically. Any region of the electromagnetic spectrum might in principle be used for analysis, but only two regions, the infrared and the ultra-violet, have proven useful for flame work. The sample size required for commercial instruments is often inconveniently large for flame studies where only a few cc atm can be collected over a reasonable sampling period. This difficulty can be overcome by using special cells of minimal volume; and by using multiple pass optics which reflect the beam through the cell a number of times (about ten-fold increase in sensitivity can be had by this technique), or by in situ spectrometry (Fig. IV-9).

122
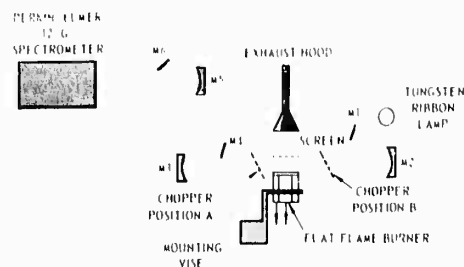
Fig. IV-9 SCHEMATIC DIAGRAM OF OPTICAL ARRANGEMENT FOR INFRARED SPECTROSCOPY OF FLAMES (Ref. 26)

M1, 4, and 6 are plane mirrors. M2, 3, and 5 are f4 spherical mirrors with 29.4 cm radius of curvature.

Interpretation of the Sample

The results obtained from a probe sample study of a flame are a set of composition profiles. Relating the sampling positions to those in the undisturbed flame is discussed in Chapter 6. The first problem is: What is the relation of the sample composition to the flame composition in the absence of errors? This question has been studied both theoretically and experimentally (Ref. 14). It was concluded that if the stream velocity was low compared with the speed of sound and the sink strength was reasonable that the sample would be representative of the composition at the point of sampling (see Fig. IV-10). The effective point of sampling is displaced a few probe-diameters ahead of the probe tip.
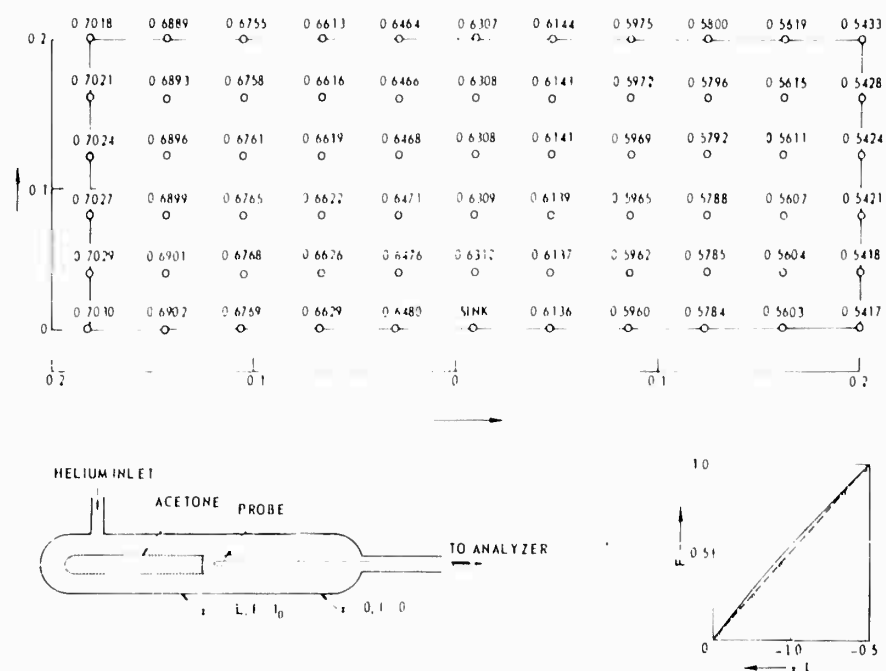
Fig. IV-10   DISTURBANCE OF CONCENTRATION STRUCTURE BY A PROBE SINK
(Ref. 14)

a – Theoretical Model; Two Dimensional Concentration
     Field with a Point Sink Solved by the Method
     of Relaxation.
b – Experimental Verification on a One Dimensional
     System, the Linear Concentration Gradient above
     the Surface of a Pool of Acetone Confined in a
     Long Tube and Evaporating into an Atmosphere
     of Helium. Line theoretical; points experimental
     values.

The second question is: How much does a probe disturb a flame? It is convenient to classify the disturbances as aerodynamic, thermal, and chemical.

Aerodynamic flow in a flame front is disturbed both by the wake of the probe and the sample withdrawal. These effects tend to cancel and a small tapered probe introduced along the streamlines from the hot side of the flame gives no visual disturbance. The distortion introduced by probes has been discussed by Rosen (Ref. 15), who uses a disc sink model. He concludes that the flow disturbance drops off rapidly with distance and will be less than 5% on the axis at ten probe-diameters downstream. In a typical case, this point would be 0.01 cm ahead of the probe. This general behavior has been confirmed experimentally (Ref. 16), (Fig. 14-10). The usual probe has a 10 to 20 micron orifice and withdraws a few micrograms per second (Refs. 17 and 18). This aerodynamic disturbance is not serious, although it limits resolution and location of the effective position of sampling.

A probe represents a heat sink which can disturb the flame by reducing temperature and enthalpy in the region being sampled. This can be important with cooled probes, although in many parts of flames even this is permissible. With an uncooled quartz probe, radiation is the primary heat loss mechanism. Quartz has a very low emissivity ($\cdot$ 0.02) and at 2000°K in the region of the tip, rough calculations indicate that less than 1% of the sample enthalpy would be extracted prior to sampling. This would lower the temperature by less than 20 K. Since the effect varies at T^4, it would be less than 1°K at 1000 K and negligible below this point. The qualitative correctness of these calculations has been confirmed by measurements of the surface temperature of a quartz probe. The measured temperature was only 50°K below the gas temperature in a 2000°K flame (Ref. 16).

A probe is a solid surface in an otherwise gaseous system. Its presence could either accelerate or inhibit the flame reactions. Quartz probes show very little catalytic activity and on general grounds one would expect surface catalysis to diminish in importance as the temperature rises. This is because the mechanism of catalysis is to provide a low energy path around the activation energy barrier for a reaction. In flames the reactions are generally of low activation energy and the temperature is high so that the energy barrier

124

is small. What small effects do appear are leveled by the action of lateral diffusion. This leveling action has been discussed in relation to sample withdrawal, and since catalysis usually represents a sink which is small compared with sample removal one would not expect to observe significant distortion of the sample due to surface catalysis of the probe. Recombination can often be visualized by the hot spots which appear on dirty probes, but are absent on clean, acid-washed quartz. The reproducibility of results with various probes and the consistency of the analysis of the flame structure data confirms the unimportance of these effects.
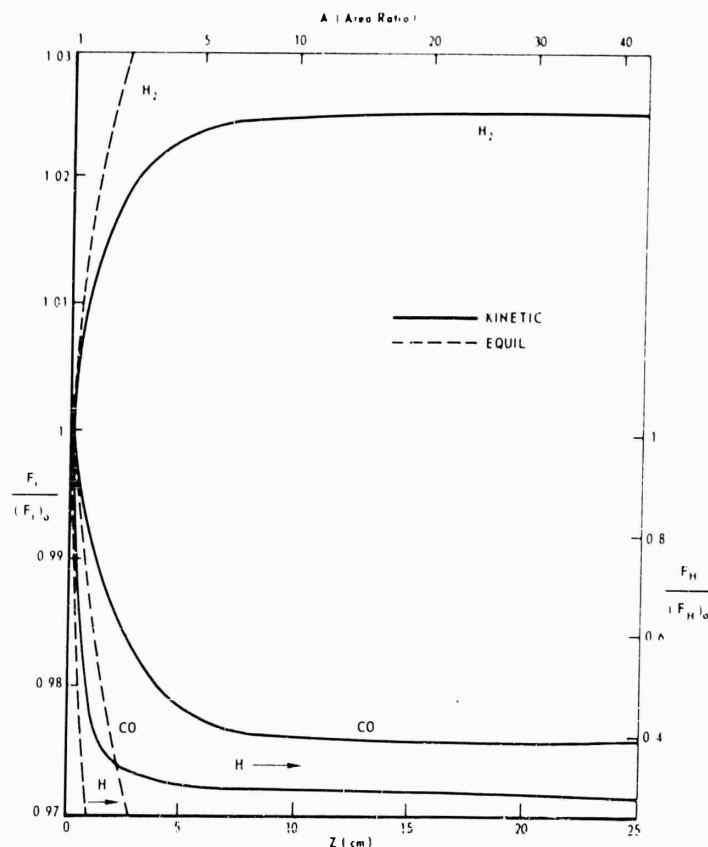

Fig. IV-11 FROZEN AND EQUILIBRIUM FLOW IN A SUPERSONIC NOZZLE

125

A third problem is disturbance of the composition in the probe and lines before the sample reaches the analytical instrument. Chemical changes are considered in the paragraph on quenching and physical changes in the paragraph on adsorption.

The quenching of chemical reaction is the most important requirement of a probe. In a typical flame front of thickness 1 cm, with a burning velocity 75 cm/sec, reaction half-lives are as short as 100 microseconds. Reaction rate usually depends quadratically on pressure and burning velocity. This sets one of the limitations on the flame systems which can be quantitatively studied by these techniques (Fig. IV-11).

Quenching is accomplished by pressure and temperature drop due to expansion of the sample into the probe. The slowing of reaction is cumulative, and it can be seen intuitively that if the rate of pressure and temperature drop due to adiabatic expansion is rapid compared with the reaction rates, the sample composition will be quenched or "frozen." These considerations have been put in a quantitative form by Bray (Ref. 19).

In practice, bimolecular reactions as short as a few tens of microseconds should be frozen by probes used in flame sampling. This conclusion is substantiated by experimental studies which have yielded reproducible kinetic data for reactions of this speed (Refs. 20-23).

Two other problems remain: catalytic reactions on the inside walls of the probe, and fate of the free-radical and atomic species withdrawn by the probe.

The reasons for believing that catalytic reactions are unimportant in the flame proper have already been stated. Within the probe these reasons are less compelling but wall reactions are probably still unimportant, because of short residence times and the inertness of the quartz walls. Gas absorption, which is the precursor to wall reactions, will be very low on the hot surfaces, and on the cool surfaces it would make little difference. Experimentally, it has been shown that passing a combustible gas mixture at these pressures through a tube with walls heated to flame temperatures does not result in measurable reaction (Ref. 16).

126

The question of the fate of the radicals and atoms sampled by the probe is a separate one. Their equilibrium concentrations are negligible at room temperature, and reaction rates are so high that even with rapid sampling they persist only a few centimeters beyond the probe inlet. The normal analytical system only detects the re-combined species. The neglect of radicals is one of the major sources of error in probe sampling studies. Normally being of the order of one per cent, this can be higher in high temperature flames where radicals are important species. The reactions within the probe are generally wall recombinations chain reactions are usually unimportant, thus the stable species concentrations are only affected by the addi-tion of recombination products. The problem of radicals in sampling probes is discussed further in the section on scavenger sampling.

A final source of error is adsorption of the sample on walls. This biases the sample composition of polar species. The problem can be avoided by using a continuous flow sampling system where conservation considerations dictate that the sample reaching the instrument must ultimately reach the inlet composition. The rate at which the true value is approached depends on the wall material.

SAMPLING UNDER EXTREME CONDITIONS

In the previous discussion, it was presumed that the sam-pling occurred under moderate conditions of pressure, temperature, and stream velocity, and that the system was in a steady state. The data discussed in this book were obtained in this region (Fig. IV-13). How-ever, it may be possible to extend the techniques.

High Pressure

127

Sampling at high pressures provides no particular diffi-culties insofar as quenching and sample size are concerned; spatial resolution is the major problem. Flame front thickness varies in-versely with pressure (see Chapter VI). Therefore, to maintain reso-lution, it is necessary to reduce the orifice diameter. This approach

is limited by three factors: (1) The smallest orifices which can be conveniently produced in quartz probes are a few microns in diameter. (Holes smaller than this are capillaries rather than orifices and have poor quenching characteristics.) (2) It is impractical to position a probe much closer than a micron. (3) The available sample drops quadratically with orifice diameter and only increases linearly with pressure. Therefore, for comparable conditions of resolution, a high pressure flame will produce a smaller sample. This is not usually a problem.

Since an orifice must be several hundred times smaller than the flame thickness to obtain reasonable resolution, the first factor will limit the studies to flame fronts thicker than a few tenths of a millimeter. This limit (10^{-4} cm) corresponds roughly to that attainable with a good micrometer. Sample size provides no problem if the analytical instrument is a mass spectrometer, but if less sensitive analytical systems are used this limitation must also be considered.

Low Pressures

Probe sampling in flames at low pressure is not limited by orifice, sample size, or positioning, but the question of quenching must be carefully examined. Using a mass spectrometer it would be possible to study flames in the micron region by introducing the sample directly into the ion chamber. By using a diffusion pump in series with the probe even lower pressures could be studied. At low pressures, the sampling orifice usually is small compared with the mean free path, and the lower molecular weight species will pass through more easily than higher species. This will bias a batch sample according to Eq. (6). In a flow system this bias can be calibrated out.

128

$$X_{i \text{ true}_{d \cdot i}} = X_{i \text{ sample}} (\overline{M}/M_i)^{1/2} . \tag{6}$$

Further, the sample is derived from an area one mean free path from the orifice within the boundary layer around the probe and may not be typical of the main system.

High Temperatures

Sampling with uncooled quartz probes is limited by the softening point of quartz (2000 K). It is possible to work in flames which are hotter than the softening point because radiation cools the probe.

Uncooled probes can be used in gases at almost any temperature by operating at reduced pressure. The rate of heat transfer to the probe is proportional to the product of the coefficient of thermal conduction (which is pressure independent) and the boundary layer gradient of temperature (which is inversely proportional to the mean free path in the gas and hence directly proportional to pressure). The usefulness of this approach is limited by the problems discussed under low pressure sampling. Cooled probes can be used in systems which combine high temperature and pressure or which require cooled walls for sampling.

Non-Steady State Systems

The problems of sampling in a time varying system are primarily those of interpretation. Two cases can be readily interpreted: the first is that of variations which are slow compared with the response time of the analytical instrument (and or sampling time). The second is where one has a knowledge of the time dependence of mass rate flow of the sample and a statistical interpretation is possible.

SUMMARY

Microprobe sampling appears to give substantially correct values for local composition in flames. The data are reproducible (see Fig. IV-1) and do not depend on probe size, sampling pressure, or the presence or absence of cooling. Where a direct comparison can be made with known values, such as equilibrium gases, and the inlet fluxes, the probes are found to sample composition accurately (Refs. 1, 16, and 17). Conservation of the fluxes of all atomic species is obtained upon analyzing the data (Refs. 23-25). The chance of accidental agreement with this type of analysis is small since it involves not only the composition measurements and their first two derivatives, but also the associated temperature, velocity, and diffusion coefficients.

It is possible to identify a number of elementary reactions in flames and derive kinetic constants using these data (Refs. 20-22). The most serious source of error is the neglect of radical concentrations which are usually of the order of a per cent (Chapter V).

130

APPENDIX A

CONSTRUCTION OF QUARTZ MICROPROBES

Quartz tubing is the best material for the construction of
microprobes. It is available in a wide range of sizes and possesses
excellent mechanical and thermal properties. Sizes up to 1 cm can be
easily worked using ordinary glass blowing equipment (oxygen-propane
or natural gas flame). A discussion of quartz handling can be found
in Strong (Ref. 27). Two precautions should be observed in handling
the material: (1) Glasses should be worn to protect the operator's
eyes; and (2) A well ventilated room should be used.

The five steps in pulling microprobes are illustrated in
Fig. IV-12.

The taper should not be pulled by hand while it is being
heated (see step 1); the force of gravity is sufficient to draw the
taper out. Circular symmetry should be insured by using two torches
and by rotating the tubing slowly. The taper and wall thickness can be
controlled by judicious heating and control of the pulling weights. Thin
walled tubing can also be drawn using these techniques.

When the tube has been reduced below 0.5 mm o.d., the drawing
weight should be reduced; a microtorch or pair of microtorches substi-
tuted for the glass blowing torch, and the process viewed with a low
power microscope. Glasses need not be worn for this operation since
the glass of the microscope protects the eyes. The drawing procedure
is essentially the same as used in rough drawing except that more care
must be taken. The taper should be drawn beyond the expected size to
be used.

131

The drawn tube is notched with a broken edge of fine ceramic[*]
at a point such that the hole will be 2 to 3 times the required final
orifice diameter. This operation requires some practice since it is
difficult to judge wall thicknesses. The tube is broken off by apply-

[*]Suggested by A. Gordon of NOTS, China Lake, California.

ing pressure with a fine quartz fiber. The cut should be examined to make sure it is clean and normal to the axis of the probe.

To allow the formation of a properly shaped orifice it is desirable to grind some of the excess wall from the tip of the tube. This can be done by hand with a fine Arkansas stone using xylene, water or some other lubricant, or with some care on a high speed, fine carborundun wheel. The latter method is much more rapid but requires

132
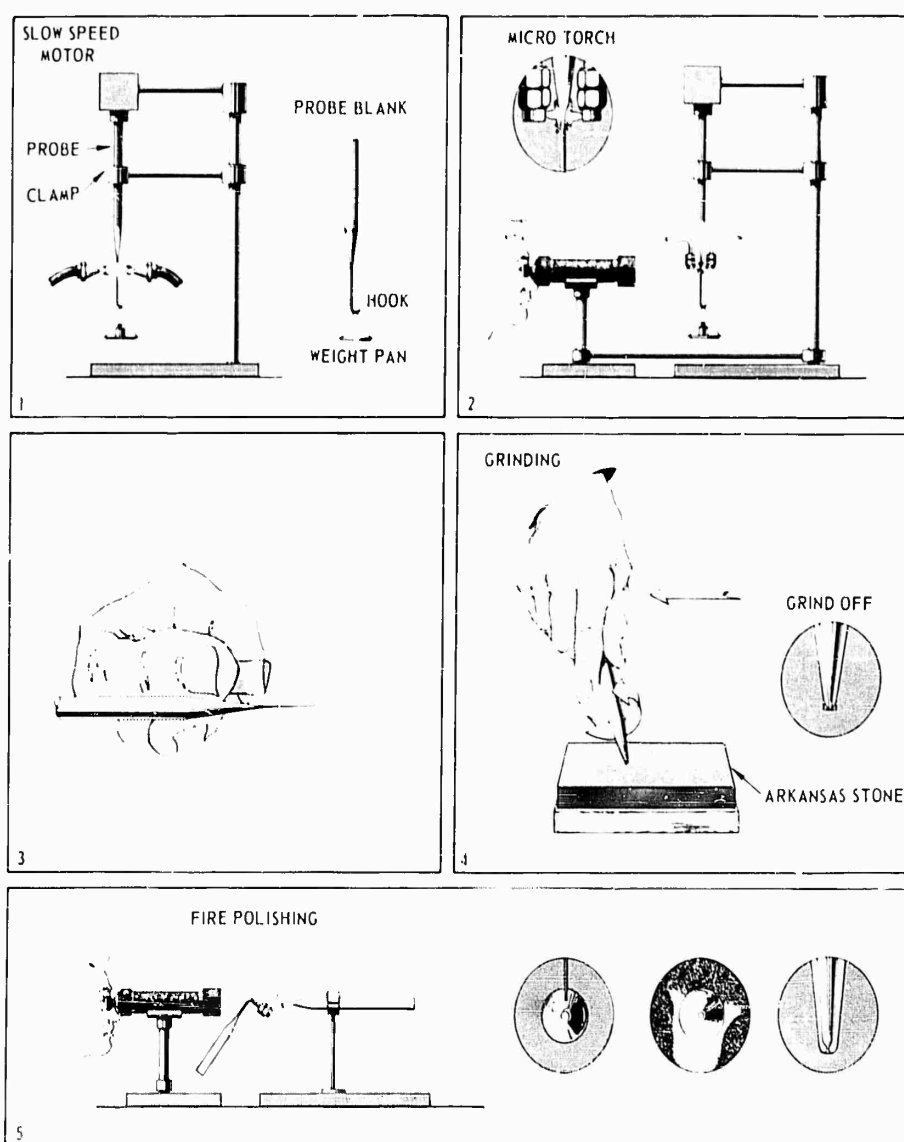
Fig. IV-12   CONSTRUCTION OF QUARTZ MICROPROBES

(Ref. 17)

some practice, and care must be exercised to protect the operator from breakage. The resulting tip should be examined under a microscope to see if it is uniform. Before proceeding the tube should be thoroughly cleaned with acid and rinsed with distilled water.

The final orifice is formed by fire polishing. This is done under a microscope. With careful manipulation, the orifice diameter can be controlled to 20%. A wire of the diameter to be formed is mounted in the microscope field together with the probe tip, as indicated in Fig. IV-12. The microflame is then slowly brought in contact with the tip. As the quartz softens, the dark orifice surrounded by glowing quartz will be seen to slowly contract. When the proper diameter is reached the flame is withdrawn and the orifice freezes rapidly through radiation cooling.

The resulting orifice should look like the final picture in Fig. IV-12. Its size should be checked by a traveling microscope and/or by its flow rate under fixed pressure conditions. If it appears satisfactory, it should be cleaned with nitric or hydrofloric acid and stored in distilled water. Probes of varying types can be made using these techniques. Some examples are given in Fig. IV-4.
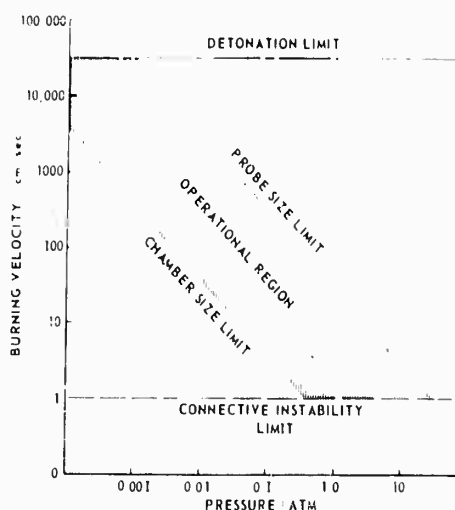
133

Fig. IV-13   LIMITATION OF MICROPROBE SAMPLING STUDIES OF FLAME FRONTS

Burning velocity (cm/sec) vs. pressure (atm). Limitations provided by (1) the formation of detonations (burning velocity exceeding the speed of sound), (2) flame stability (convective velocities comparable to flame velocities), (3) apparatus size (larger than 1 meter), and (4) minimum probe size (10 microns) (probe must be small compared with flame front).

APPENDIX B

MASS SPECTRAL ANALYSIS OF HYDROCARBON OXYGEN FLAME GASES

The analysis of the flame gases obtained from hydrocarbon-oxygen flames is straightforward, but complicated. The mixtures consist of hydrocarbons, traces of oxygenated intermediates such as formaldehyde and methyl alcohol, carbon monoxide, hydrogen, water, carbon dioxide, oxygen and inert gases. This differs from the analyses usually discussed in the literature in involving substantial amounts of oxygen and oxygen containing compounds. "Carburized filaments" (Ref. 7) are undesirable because of the reaction of oxygen with the carbides to form spurious carbon monoxide. This problem is best avoided by using a rhenium filament which forms no stable carbides or by running with a clean tungsten filament.

In analyzing a spectrum it is necessary to make some reasonable choice of expected species. All species of any quantitative importance should be included although the smaller the number chosen the easier the analysis will be. A common approximation which is valid for most hydrocarbon flames is to assume (1) no hydrocarbons higher than in the incoming gas, (2) no oxygenated compounds except formaldehyde (possibly methyl alcohol), (3) no nitrogen compounds other than elemental nitrogen.

This choice should be checked for consistency by analyzing some typical spectra in detail showing that all of the observed peaks are quantitatively accounted for. This procedure is described in some detail for the case of hydrocarbon mixtures (Ref. 7). Having established the qualitative makeup of the mixtures to be analyzed a characteristic mass peak is assigned to each species. This should preferably be its strongest mass peak and uninterfered with by other species. Where it is possible to assign unique mass peaks which no other species of the mixture possesses, the analysis is trivial since the partial pressure

134

is the peak height (corrected for background) multiplied by the sensi-
tivity factor obtained by calibrating the instrument. The mole fraction
is the partial pressure of the species divided by the sum of all of the
partial pressures.

In general more than one species contributes to a given mass
peak. Fortunately the contributions of each species are additive so
that the observed peak height is the sum of the product of the partial
pressures of the contributing species multiplied by their respective
sensitivity factors.

$$h_i = \sum_j p_j k_i{}^j \quad .$$

One such equation can be written for each mass peak measured
and a mass peak measured for each species expected. This constitutes
N linear algebraic equations with N unknown partial pressures. These
equations can be solved for the partial pressures and mole fractions
can be calculated from the relation:

$$X_i = p_i / \sum_i p_i \quad .$$

If a machine and programmers are available, this is a straight-
forward problem of matrix inversion which digital machines do excel-
lently well. For those less affluent, the problem of hand computation
is not as formidable as the solution of ten (or more) simultaneous
equations. In practice, only a few interferences occur (i.e., only a
few off diagonal elements occur in the determinant), and generally, the
spectrum of a low mass molecule will not interfere with that of a
higher mass molecule. Thus, by solving the equations in order, starting
with the highest molecular weight species, it will be found that most
interferences will be from species of higher molecular weight than the
one being calculated whose partial pressures have been previously
calculated. Thus, in a mixture of a dozen components of flame gases
from methane, only one pair of simultaneous equations need be solved.
With a little experience and a hand calculator, analysis of ten-fifteen
component mixtures can be done in 20 to 30 minutes. The equations used
to analyze the methane-oxygen flame are given in Table IV-1 as an example.

135

Mole fractions of a sample can be determined by solving the determinental equation given below for the partial pressures of the species

$$P_i = \frac{\Delta_i}{\Delta} \qquad\qquad X_i = P_i \, \Sigma_i P_i$$

$K_i^{\,p}$ — Mass spectrometer sensitivity for species i on mass p (divisions of response per unit of partial pressure).

P_i — Partial pressure of species i.

X_i — Mole fraction of species i.

Δ — Sensitivity factor determinant given below.

Δ_i — Determinant formed by replacing the ith column by the measured peak heights.

TABLE IV-1

DETERMINANT FOR THE ANALYSIS OF MASS SPECTRAL
DATA ON METHANE-OXYGEN FLAME GASES

Mass	H_2	CH_4	H_2O	CO	OCH_2	O_2	A	CO_2
2	$K_{H_2}^2$	$K_{CH_4}^{2+}$	$K_{H_2O}^{2+}$	0	$K_{OCH_2}^{2+}$	0	0	0
15	0	$K_{CH_4}^{15}$	0	0	$K_{OCH_2}^{15*}$	0	0	0
18	0	0	$K_{H_2O}^{18}$	K_{CO}^{18*}	$K_{OCH_2}^{18*}$	$K_{O_2}^{18*}$	0	$K_{CO_2}^{18*}$
28	0	0	0	K_{CO}^{28}	$K_{OCH_2}^{28}$	$K_{O_2}^{28**}$	0	$K_{CO_2}^{28}$
30	0	0	0	K_{CO}^{30}	$K_{OCH_2}^{30}$	0	0	$K_{CO_2}^{30*}$
32	0	0	0	0	$K_{COH_2}^{32*}$	$K_{O_2}^{32}$	0	0
40	0	0	0	0	0	0	K_A^{40}	0
44	0	0	0	0	0	0	0	$K_{CO_2}^{44}$

[*] Isotopic species which is normally negligible.
[**] Interference due to CO formed by reaction of oxygen with carbided filaments or carbon deposits on ion chamber walls.
[+] Recombination peaks normally, but not always, negligible.

136

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138

V
DETERMINATION OF
CONCENTRATION OF UNSTABLE SPECIES IN FLAMES

Unstable species can be divided into two general categories:
free radicals (i.e., unpaired electron species) and ions (i.e., charged
species). This represents a convenient division since different ex-
perimental techniques are required for the two types. Unstable species
are important in flame processes, but have not been studied as com-
pletely as stable species because of the difficulties involved. They
are usually present only in low concentrations (10^{-2} - 10^{-8} M. F.),
and are too reactive for conventional sampling and analytical tech-
niques.

Although these species are generally called unstable they
are not necessarily or usually unstable in the thermodynamic sense.
What is meant is that they are unstable under normal laboratory condi-
tions, and so reactive that they cannot be successfully sampled or
isolated.

DETERMINATION OF THE CONCENTRATION OF ATOMS AND FREE RADICALS

Free radical species play an important role in the chemistry
of flames and these odd electron molecules enter into virtually every
important flame reaction. A few radical species, notably molecular
oxygen and the oxides of nitrogen and chlorine, are stable under nor-
mal conditions and can be handled by conventional sampling and analyti-
cal methods, but most radical species are so reactive under normal con-
ditions that they require special precautions for sampling and analysis.
This problem is not unique to flame studies although in conventional

kinetic studies, it is avoided by use of the "steady state approxima-
tion" (Ref. 1), which allows the derivation of radical concentrations
from measurements on stable species. In the case of flames there is
considerable doubt as to the applicability of this principal (Refs. 2
and 3), and the problem must be considered an experimental one. A
number of techniques have been developed recently for determining radi-
cal species concentration and although some difficulties remain, sig-
nificant progress has been made.

The techniques can be divided into two categories: in situ
techniques and sampling techniques.

MASS SPECTROMETRIC TECHNIQUES

The mass spectrometer has been used extensively for studies
of radicals produced in flames and other systems. An early discus-
sion of the possibilities of such a system is given by Aston; more
recent work has been by Stevenson, Robertson, Ingold, Lossing, Foner,
and others (Refs. 4 and 5). A successful spectrometer is shown in
Fig. V-1.

There are three major problems in these studies: (1) intro-
ducing the radicals into the ionization chamber of the spectrometer
without reaction: (2) differentiating the radicals from the parent
molecular species: and (3) calibration of the spectrometer. In flame
structure work, there is a fourth problem of minimizing the distur-
bance of the flame. This latter problem has not been seriously
attacked because early workers were interested in the radical species
themselves rather than flame structure.

Three techniques have been used to introduce the sample into
the spectrometer ionization chamber: (1) molecular beams: (2) fast
flow; and (3) pin holes. The most satisfactory of these is a molecu-
lar beam consisting of molecules which have made no collisions either
with one another or with the walls (Ref. 5), (Fig. V-1). With such
a system, radicals could only be affected by internal rearrangements.
Less sophisticated inlet systems utilizing rapid flow and non-
catalytic walls have been used successfully in the study of slowly

140
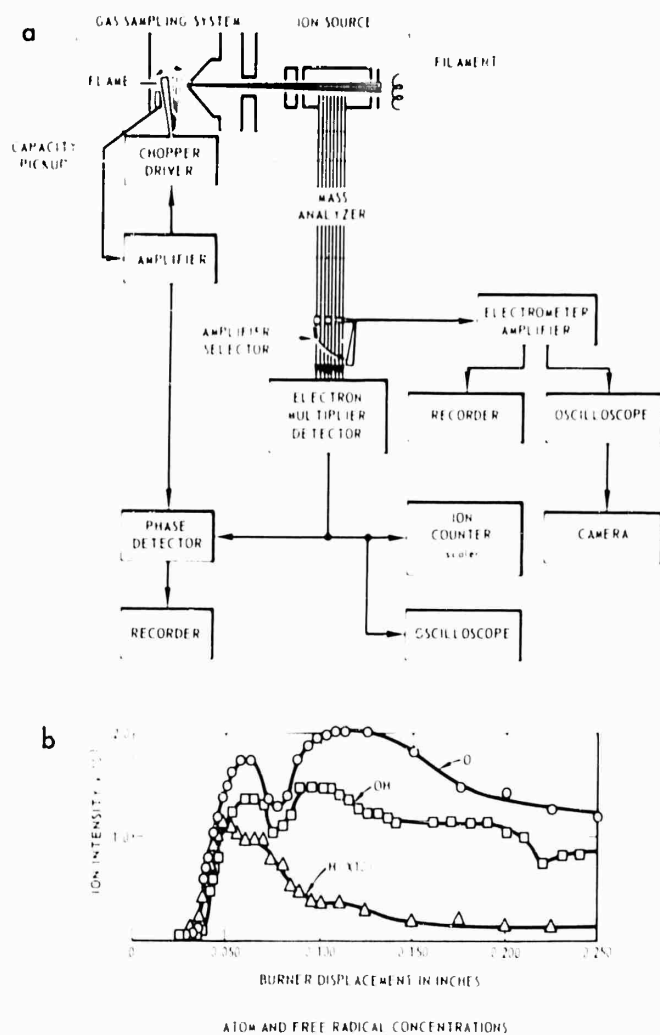
Fig. V-1 FREE RADICAL MASS SPECTROMETER (Ref. 5)

    a. Schematic Diagram.
    b. Atom and Radical Profile for a Hydrogen-Oxygen
        Diffusion Flame.

141

reacting radicals, but it is necessary to justify the inlet system
with each new study. Pin hole inlets introducing a sample directly
into the spectrometer ionization chamber avoid molecular collisions
since ion chamber pressures are very low, but two problems remain.

First, the sample is actually taken from the boundary layer and may not be typical of the system, and second, unless pumping speeds are extremely high the radicals remain in the ion chamber long enough to make a number of wall collisions. Proper design can remove many of these problems.

The second problem in free radical mass spectrometry is that of the interference from stable species. In general, radicals are trace species and the molecule parent to a radical will be present in high concentrations. Since the parent possesses all of the peaks characteristic of the radical (with at least one additional peak of its own), the radical spectrum must be inferred by difference. This greatly reduces sensitivity and an accurate knowledge of the spectrum of the molecule parent is necessary. This problem can be minimized by adjusting the ionizing voltage between the appearance potentials of the molecule and radical species. This is usually possible because radicals are more easily ionized than ordinary molecules. Unfortunately, two other problems appear: (1) the ionization cut off is not sharp because of the molecular velocity distribution due to the high temperature of the electron source, and some interference still remains; and (2) reducing the ionization voltage reduces the probability of ionization of all species, and this in turn reduces the sensitivity of the spectrometer. In a typical case, this will be a factor of $10^2 - 10^1$. Since the signal to noise ratio is not affected as strongly, some of this loss can be regained by the use of sensitive detectors such as ion multipliers. In spite of these difficulties, systems of this type have been successful and much information on radicals, in particular bond strengths, has been obtained.

The calibration of the spectrometer for absolute concentration measurements is best made by using a source of radicals of known concentration. However, this is usually not possible and some other method must be used. One can calibrate using a system which is simple so that radical concentrations can be obtained by difference, e.g., a diatomic molecule and its dissociated atom. If the total pressure in the system is known and the sensitivity of the spectrometer for the parent molecule is known, then the partial pressure of the atom will be the difference between the total pressure and the partial pressure of the molecule as measured by the spectrometer. From this information and the response of the spectrometer to the radical

142

species, the sensitivity can be calculated. The precision of this method is poor if the radical concentration is low or if the pressure measurements are unsatisfactory. Once such a calibration is accomplished, however, the spectrometer can be used on complex systems.

Calorimetric Methods

The classic method of determining atom concentrations is by calorimetry. If the heat of recombination is known and a known sample size can be introduced into a calorimeter then the radical concentration can be deduced from the temperature rise of the system. The work on atoms involved platinum or platinum coated calorimeters (Ref. 6), while oxygen atoms involved silver calorimeters (Ref. 7).

Calorimetry has a number of advantages: (1) the equipment is moderate in cost; (2) the method can be absolute; (3) good spatial resolution can be attained using thermocouples or other probes. There are certain serious disadvantages: (1) the method is not selective since any one of several radicals or excited species will generate heat. There are a number of coatings for which claims of selective recombination have been made, but in a complex system this is open to grave doubts (see, for example, Ref. 8). (2) The efficiencies of coatings both catalytic and non-catalytic are not as satisfactory as previously supposed (e.g., Wise (Ref. 9) states that platinum which was supposed to give H atom recombination at every collision actually may be only 10% efficient, and silica which was supposed to be relatively non-catalytic has been found by Linnett to possess a high temperature coefficient for recombination (Ref. 10)). (3) Calculation of the effective sampling region for such a probe is difficult. These factors would induce serious errors in calorimetric measurements made under the unfavorable conditions which occur in flame studies. The spectrometer must be capable of resolving individual rotational lines; otherwise the integrated absorption coefficient will be too low. Generally a grating spectrometer is used.

In spite of these difficulties, these techniques in the form of a double thermocouple have been used to study O atom concentrations in the recombination region of a hydrocarbon flame (Ref. 11)

143

and the method has recently been extended by Rossner (Ref. 12) to the analysis of supersonic streams using silica probes — one coated with Pt and one uncoated (Fig. V-2). This elegant work is satisfactory for electric discharges with simple chemistry, e.g., diatomic gases.
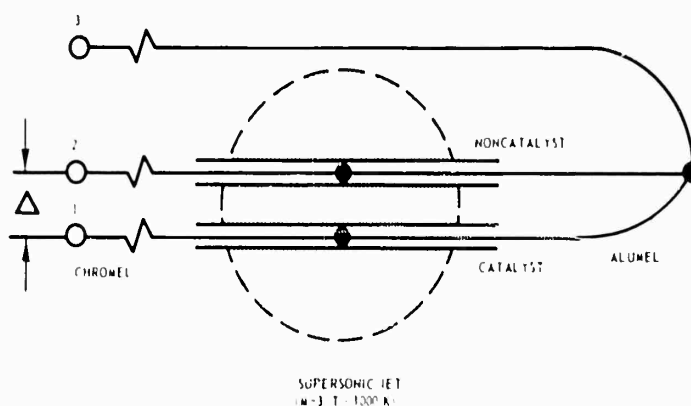
Fig. V-2   DIAGRAM OF CATALYTIC PROBE FOR DETERMINING
ATOM CONCENTRATIONS
(Ref. 12)

In Situ Absorption Spectroscopy

Ultra-violet absorption spectroscopy has been used to study radical concentrations in flames (Refs. 13 and 14). The technique is particularly favorable for the study of Hydroxyl radical, and can perhaps be extended to other radicals. The experimental setup is quite simple (see Fig. V-3). Focusing optical systems have been used rather than collimated light systems. This reduces the spatial resolution, but is necessary to obtain sufficient light intensity with the available sources.

The requirements for accurate measurements using an optical probe are:

144

1. A flame is available whose isocompositional surfaces lie parallel and are linear. Several types of flame geometry are suitable for such measurements, but the flat screen flame is the most obvious choice, and has been used most often. The cylindrical flame, however,

offers another geometry well adapted to such measure-
ments.

2. The beam and flame surface must be accurately aligned.

3. The path length in the flame gases must be known.

4. The beam should be no wider than the flame being meas-
ured and should be no thicker than the required resolu-
tion.

Making measurements in a flame by optical techniques gen-
erally involves knowing the effective path length in the flame. This
is a difficult problem both because of the edge effects in most
burners and because in many flames the reacting gas column expands as

OPTICAL SCHEMATIC

XBO 162 L_1 S   BURNER L_2

LIGHT FILTER   MONOCHROMATOR

a

STOICHIOMETRIC $CH_4 - O_2$

O FLAME AT p 3 TORR, \ 3.2 m sec
△ FLAME AT p 8 TORR, \ 1.2 m sec
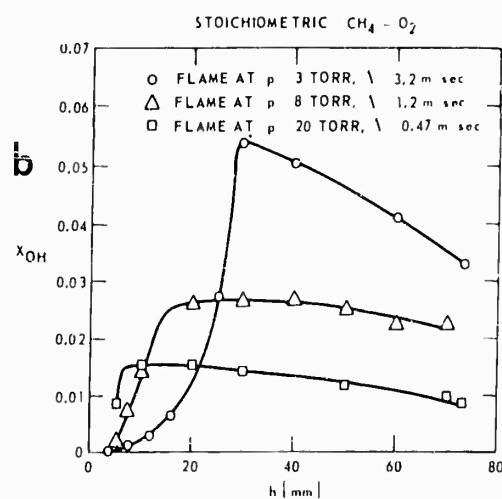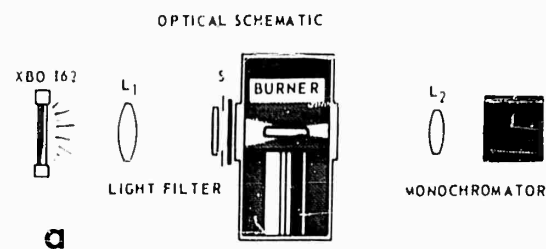□ FLAME AT p 20 TORR, \ 0.47 m sec

b

x_{OH}

h [mm]

Fig. V-3 APPARATUS FOR STUDYING IN SITU OH CONCENTRATIONS IN FLAMES

a - Schematic of Optical Arrangement.   (Ref. 13)
b - OH Profiles for Several Stoichiometric Methane-
    Oxygen Flames.

reaction progresses, making it necessary to know this value at each point at which measurements are made.

The bending of the light beam due to refraction provides a serious source of error in high-pressure flames. It is not so serious in low-pressure flames, since both the density and the gradients are reduced by lowering the pressure. In general this refraction should not exceed the desired resolution.

Searches have been made for free radical absorptions in flames in the infrared region, but up to the present no successful studies have been reported.

Paramagnetic Resonance Spectroscopy

Radicals are odd electron molecules and show absorptions associated with the free electron spin. Recently, apparatus has been developed of sufficient sensitivity for studying radicals at relatively low pressures. The technique is particularly valuable because the sensitivity is calibratable and directly proportional to the number of odd electrons. It has been used for flame studies of hydrogen atom concentration (Ref. 15); but spatial resolution is rather poor ($\sim$ 5 cm).

Emission Spectroscopy

Recently, Sugden and his co-workers have studied the emission of traces of alkali metal salts in flames (Refs. 16 and 17). They have shown that the intensity of emission of the resonance lines which are proportional to the concentration of free alkali metals can be related with the concentrations of the radicals H and OH because their hydrides and hydroxides are stable under flame condition and exist in equilibrium with the radicals. This technique is only useful in regions where the metal-radical reactions are rapid compared with the change in atom or radical concentrations. This has been shown to be the case in the slow recombination region which follows most flame systems. Since recombination reactions must be three-body recombinations they are usually slow.

146

In a typical case the emissivity of Na and Li are compared (see Fig. V-4). The relative brightness of Li is diminished in the presence of OH since it enters into an equilibrium Li + OH $\rightleftharpoons$ LiOH.
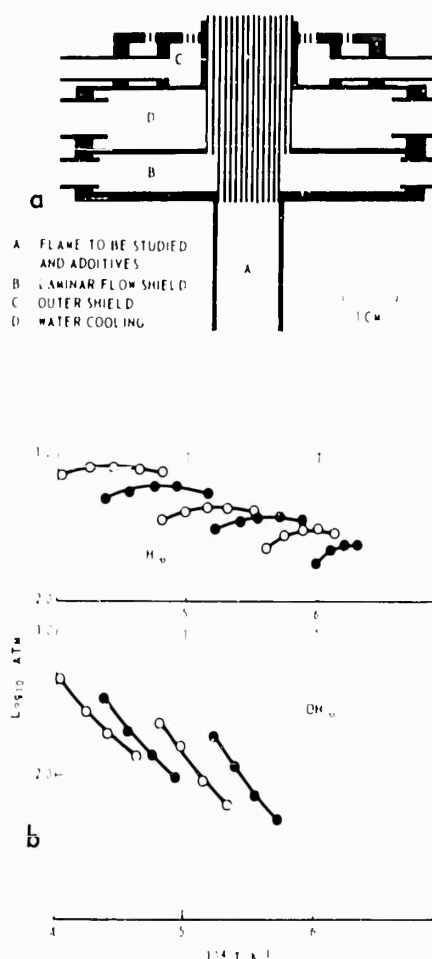
Fig. V-4   ATOM CONCENTRATIONS MEASURED BY USE OF RESONANCE
            RADIATION IN FLAMES   (Ref. 16)

            a - Schematic of Burner.
            b - H and OH in the Reaction Zone for Various
                Families of Flames Estimated from Short
                Extrapolations of CuH and Sodium Continuum
                Measurements Respectively.

147

This is in turn a function of the temperature through the equilibrium constant. The reference sodium emission is unaffected by OH because

NaOH is unstable at flame temperatures. The sodium emission[*] provides a thermometer for the system (see Chapter III). Other salts can be used with other radicals, e.g., CuH. The amounts of salt required are quite small ($1:10^5$) and the disturbance of the flame is slight. Further, Sugden was able to show that in this region that all of the bimolecular reactions connected with the radicals are fast compared with the recombination reactions and that in this region the radicals will be in an equilibrium with one another although out of true thermal equilibrium. Thus, the measurement of one radical concentration in this region allows the others to be inferred from equilibrium calculations.

Another useful emission for radical studies is the "oxygen afterglow." This characteristic greenish glow is associated with the reaction $O + NO \cdot NO_2$. It can be shown that this emission is proportional to the oxygen atom (and NO) concentration and since in this system the NO is regenerated so rapidly that it can be considered to be constant the emissivity provides a measure of O atom concentration. Although it requires calibration, this can provide a convenient measure of relative oxygen atom concentration (Ref. 18). The O atom - NO, NO_2 reactions are discussed in more detail below.

Exchange Methods

The rates of a number of elementary reactions are well enough known that they can be used to estimate radical concentrations from isotopic exchange rates. The most commonly used materials are deuterated compounds. Tritiated compounds could also be used. H and O concentrations can be inferred from the rates of reaction of D_2O and N_2O (Refs. 19 and 20). It should be noted that a correction should be made for the effect of deuterium substitution on the rate itself, since the rate may be as much as 40% slower than the corresponding H reaction.

$$H + D_2O \rightarrow HD + OD \tag{1}$$

$$N_2O + O \rightarrow 2NO \tag{2}$$

148

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[*]In the reaction zone the excess emission of Na* can be correlated with the reaction $Na + H + OH \rightarrow Na* + H_2O$ and CuH* with $Cu + H \rightarrow CuH*$ (Ref. 17).

Since the concentrations of the deuterated compounds must be determined by sampling and analysis (usually by mass spectrometry) some precautions must be observed in avoiding wall exchange after sampling. For water the exchange on glass walls can be so rapid that a few seconds exposure is sufficient to show measureable exchange.

Scavenger Probe Sampling

Radical concentrations can be determined by a technique which combines microprobe sampling with chemical scavenging. This technique is of interest because it offers the possibility of high spatial resolution (determined by the orifice size) and because it provides some insight into the radical recombination processes occurring in probe sampling studies. The operation depends on the fact that after sampling by a microprobe radical concentrations are in "frozen flow" sufficiently long for mixing with a secondary stream. If this secondary stream consists of a species which reacts quantitatively with a particular radical, then the original concentration of the radical can be deduced by analyzing the resulting product. An example of the process is the determination of oxygen atoms by the reaction $O + NO_2 \rightarrow NO + O_2$. It is extremely rapid and quantitative and has been well studied because it is used for the gas phase titration of oxygen atoms (Ref. 7). In the presence of only a small excess of NO_2 the NO concentration is in a one to one correspondence with the initial O atom concentration.

The apparatus consists of a large cooled quartz microprobe with provision for scavenger injection (Fig. V-5).

The requirements for this method are that the sample be taken under frozen flow conditions (Ref. 21); that the reaction be quantitative and faster than any other reaction (gas phase or surface) which the radical can undergo; and that no other radical in the system undergoes a rapid competing reaction. These requirements limit the applicability of the method; but satisfactory analyses can be made in a number of cases (Table V-1), using quite simple apparatus (Refs. 22 and 23) (Fig. V-5).

149
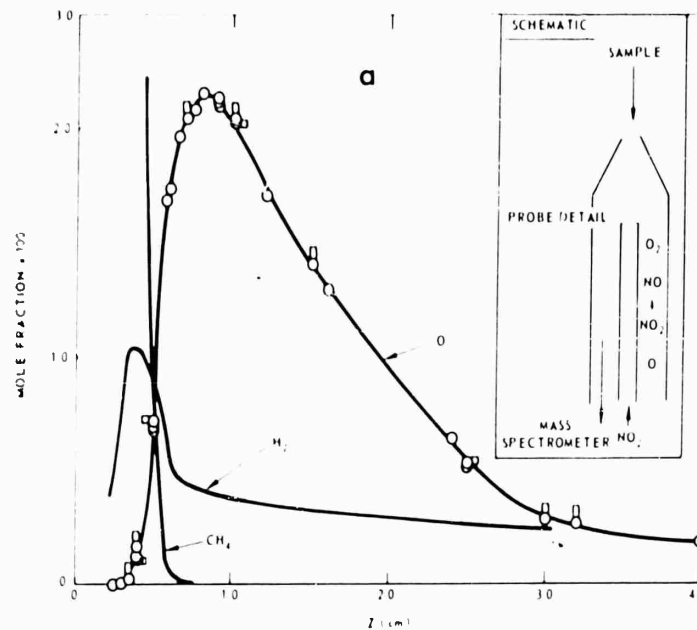
Fig. V-5   SCAVENGER PROBE TECHNIQUE FOR DETERMINING RADICAL
CONCENTRATIONS IN FLAMES

a - O Atom Concentrations in a Methane-
Oxygen Flame Determined by Scavenger
Probe Technique. (Ref. 23). H_2 and CH_4 curves
in the same flame are added for comparison.

DETERMINATION OF CONCENTRATIONS OF CHARGED SPECIES IN FLAMES

Charged particles were first associated with flames by Volta
who demonstrated that electrostatically charged bodies could be dis-
charged by brushing them with a flame.   Many advances have been made
since this qualitative observation, but the source and role of ions
in flames is still a subject of debate.   It is well established that
ions are produced in the primary reaction zones of flames probably by
radical reactions.   These ions are formed in considerable excess over
the concentrations to be expected from thermal equilibrium considera-
tions and hence are referred as being produced by "chemionization."

Over-all, the flame is electrically neutral and there is
little separation of charges even in the reaction zone.   The flame can
be considered as a dilute plasma ($\sim 10^{-7}$ mole fraction or 10^{12} elec-

150
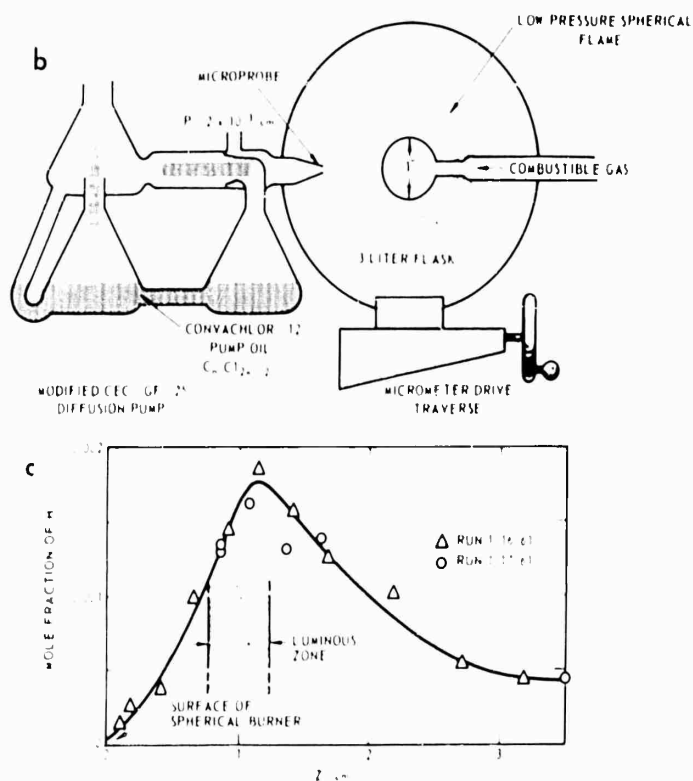
Fig. V-5   b - Schematic of Apparatus for Determining H Atom
(Cont.)   Concentration.
            c - H Atom Concentration in a Methane-Oxygen Flame.

trons/cc atm).   The negative particle is usually (though not always)
the electron while the positive particles are generally complex ions.
This is to be expected because few molecules possess energy levels
stable enough for an added electron (i.e., show a positive electron
affinity) whereas the loss of an electron (to form a positive ion)
rarely decreases molecular stability unless the electron is one of the
bond electrons.   Experimentally the determination of ion concentrations
is considered a difficult problem although it might be pointed out that   151
ions are the only species which could be determined in such low concen-
trations.

IDENTIFICATION OF CHARGED SPECIES IN FLAMES

The initial qualitative problem in flames is to determine the identity of the ions being produced. The early work (Ref. 24) centered on measurements of ion mobility and conductivity, established that the positive ions had mass (to charge ratio) in the molecular range and a mobility at atmospheric pressure of 1 cm sec per volt cm gradient; while the negative carrier had a charge to mass ratio and a mobility a thousand times greater. Clearly these were ordinary molecular ions and electrons. Hall effect measurements confirmed this ion mobility ratio and conductivity (or absorption) measurements in the radio frequency and microwave region confirmed the existence of free electrons in flames. Recently, direct mass spectrometric studies have allowed identification of a number of the molecular ions.

Ion Mobility

The conductivity of a flame can be measured directly by inserting two electrodes applying a potential and measuring the resultant current. Unfortunately this simple experiment yields complicated and often irreproducible results. These rough measurements do allow an estimate of the ion concentration providing the ion mobilities and average mean free paths can be estimated. Ion mobilities have been determined in flames by measuring the voltage gradient which would allow ions to propagate against the flame gas stream. Alkali metal ions lend themselves to this measurement because their course can be easily followed by the emission of the neutral metal atoms which are in equilibrium with the ion (the ions do not show visible emission in flames). The mobility is simply given by the ratio of the limiting voltage gradient at which the sodium glow does not propagate to the calculated flame gas velocity.

152

A related measurement on flames is the velocity induced by an electric field. Since the ionic concentrations are low the induced velocities are quite small. This is usually determined by measuring the resulting pitotstatic pressure. Neglecting the contribution of the negative carrier because of its inefficiency in momentum transfer it

can be seen that the induced flow is in the direction of the negative electrode. The pressure induced even by strong fields (10^4 v/cm) are only a few millionth of an atmosphere. They have been measured directly using an ingenious pressure balance devised by Weinberg (Ref. 25), (Fig. V-6).

ELECTRODES   SCALE

PISTON

BALANCE

PARAFFIN OIL
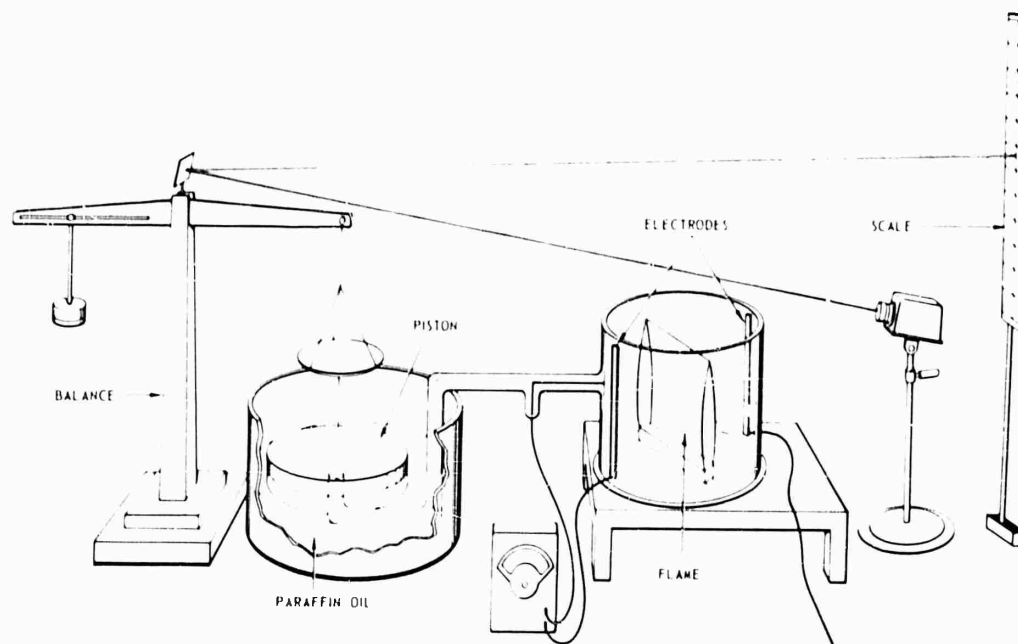
FLAME

Fig. V-6 PRESSURE BALANCE FOR MEASURING PITOTSTATIC PRESSURES CAUSED BY ELECTROSTATIC ACCELERATION OF IONS FROM A FLAME (Ref. 25).

Hall Effect

Hall effect measurement on flames indicates that the major carrier in flames is a free electron. In Hall effect studies measurements are made of the voltages induced at right angles to a current flow crossed by a magnetic field. This voltage is a function of the difference in mobility between the positive and negative conductors. The modification of the theory to apply to flow systems such as flames is discussed by Wilson (Ref. 24) and the apparatus and some measurements are described.

153

Collision Cross Sections

Since flames are very dilute plasmas, most collisions of ions are with neutral molecules, and collision frequencies are of the same order as molecular collision frequencies. Collision cross sections can be estimated by assuming that ion diameters are the same as the corresponding molecules, and that the electron diameter is small compared with other colliding species. Collision diameters for ordinary molecules can be found in Ref. 26. In highly ionized systems the idea of collision diameter loses much of its meaning because the electrostatic interactions important in ion-ion and ion-electron collisions are long range.

It is possible to determine electron molecule collision cross sections in flames by measuring the width of the cyclotron absorption frequency. This has been done for a number of flames (Ref. 27). For magnetic fields of a few kilogauss these absorptions lie in the microwave region (50 milomegacycles).

Mass Spectrometry

The best technique for determining the identity of ions in flames is direct mass spectrometry which has been developed to the point where reasonably reliable identifications can be made and quantitative studies of ion concentration profiles are possible with reasonable resolution in low pressure flames (Refs. 28 and 30).

The apparatus required (Fig. V-7) is similar to that used in ordinary mass spectrometry with the modification that no electron gun is necessary to produce ions. Instead a sampling orifice and a set of focusing electrodes are required. Considerable care must be devoted to the design of the sampling inlet and pumping system. In the case of the sampling inlet, it is desirable to operate in continuum flow so the sample is not biased by the probe boundary layer conditions which are much lower in temperature than the flame being sampled. It is necessary to maintain molecular flow conditions inside the spectrometer (mean free path large compared with the apparatus) to avoid
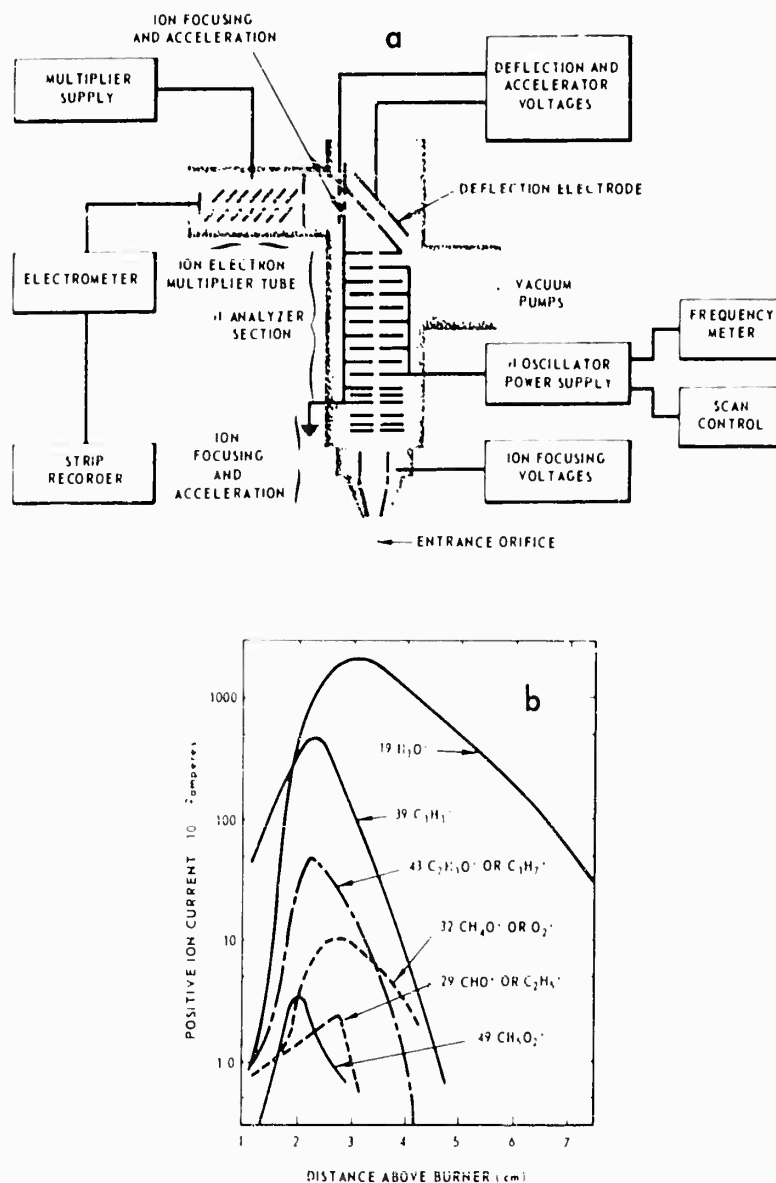
154

Fig. V-7   DETERMINATION OF ION CONCENTRATIONS BY MASS SPECTROMETRY.

      a - Schematic of Apparatus.
      b - Ion Profiles for an Acetylene Oxygen Flame
         $(P = 2.5$ mm Equivalence Ratio 0.66) (Ref. 30).

155

producing spurious ions. In the analyzing chamber the focusing voltages
are high and secondary ions could be easily produced if multiple col-
lisions were allowed.

Any of several types of mass spectrometer can be used - magnetic deflection, time of flight, or radio frequency. An interesting form of rf spectrometer has been used in ion studies. It is essentially a small linear accelerator which is related to omegatron spectrometers in the same way that the giant linear accelerators and cyclotrons of nuclear physics are related. The principle of this type of spectrometer is that ions of only one single mass can stay in phase with the accelerating electrodes at a given frequency. For normal ion mass to charge ratios and electrode spacing (~ 1 cm) this frequency is a few tens of megacycles. Using this type of instrument it has been possible to identify a number of the ion species in flames and determine their spatial distribution (Refs. 28 and 30), (Fig. V-7).

DETERMINATION OF THE SPATIAL DISTRIBUTION OF CHARGED SPECIES IN FLAMES

Four techniques have been used to determine the spatial distribution of charged species in flames. (1) The Langmuir probe, which measures dc resistance; (2) the rf probe which measures energy dissipation in the microwave region; (3) the photographic technique; and (4) the ion sampling mass spectrometer. The first two techniques measure electron concentrations; the first and third can measure either electrons or positive ions, but do not distinguish between positive ions. The fourth technique allows the direct measurement of individual positive ion concentrations.

The Langmuir probe was one of the earliest methods for studying ion concentrations in flames. Using this technique it is ideally possible to measure ion or electron concentration and effective electron temperature (Refs. 30 and 31).

The apparatus consists essentially of large area and a small area electrodes (Fig. V-8). For a given applied voltage the current is limited by the arrival of ions (or electrons) at the surface of the small electrode. The current is proportional to the area of the electrode. If the small electrode is positive the current is limited by and proportional to the electron concentration. If the small electrode is negative the current is limited by and proportional to the positive ion current. The area ratio between small and large electrodes must be

156

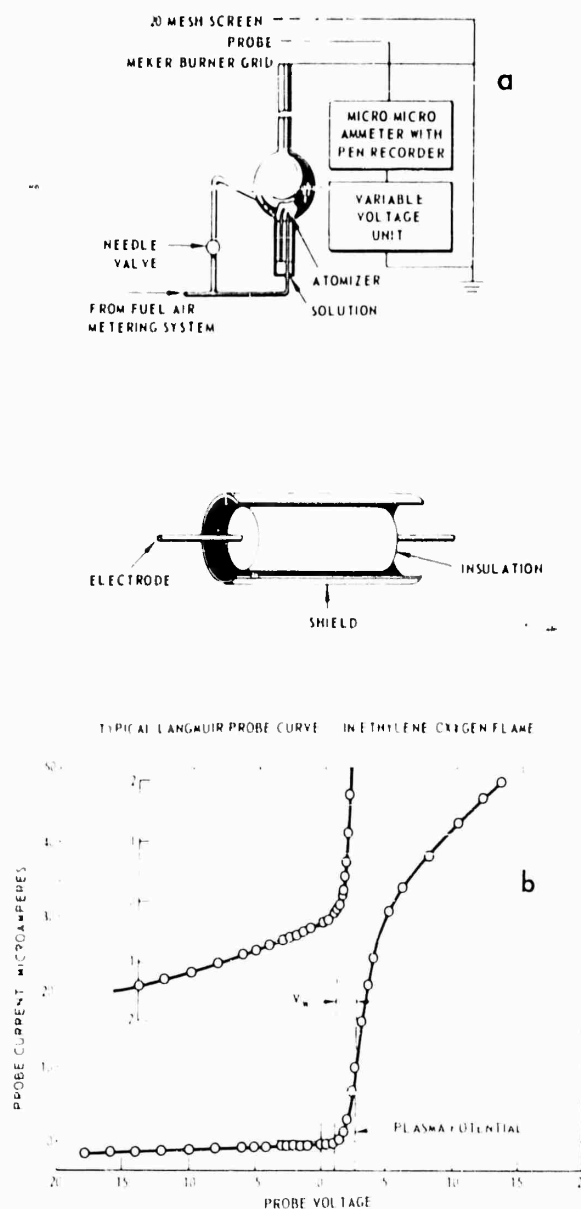Fig. V-8 THE LANGMUIR PROBE TECHNIQUE FOR STUDYING ION AND ELECTRON
CONCENTRATIONS IN FLAMES (Refs. 30, 31).

a - Apparatus for Studying Ionization in Flames.
b - Diagram of Langmuir Probe.

157

very large if the limiting electrode is positive, because of the high
mobility of the electron. Complications in interpretation stem from
the electrode size which affects the gradient and the plasma potential
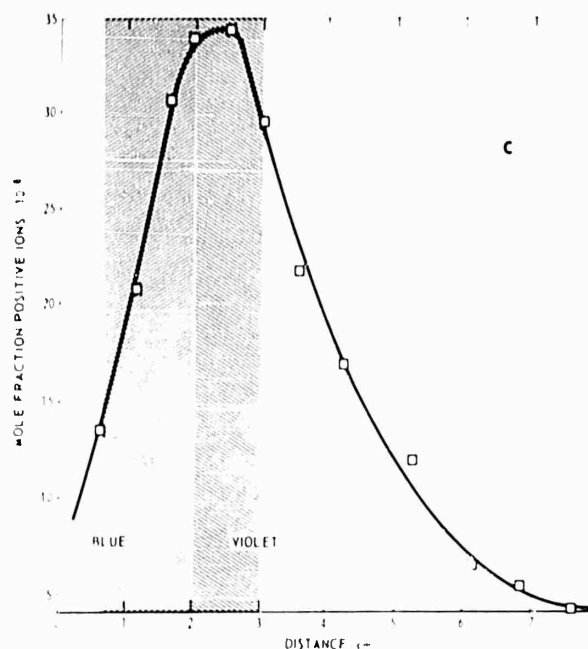
Fig. V-8   e-   Typical Langmuir Probe Curve in Ethylene-Oxygen
(Cont.)   Flame (P = 2.6 mm of Hg).

which develops around an electrode immersed in a plasma. The technique
has been criticized because of the disturbance to the system being
studied; but with reasonable care useful results can be obtained in
systems with spatial resolution which could be obtained by no other tech-
nique (Fig. V-8). The techniques are similar to those of polarography
in solutions of electrolytes (Ref. 32).

        The energy of alternating electric fields of frequency higher
than a few megacycles can only be absorbed by free electrons. This is
because ionic particles are too massive to respond. By the time they
start to move the field is in the opposite direction pushing them the
other way. This method for studying electron concentrations has the
advantage of not disturbing the system. The disadvantages are low
spatial resolution and difficulties in determining exact path lengths
and absorption coefficients. The equipment used depends on the fre-
quency employed. In the 30 megacycle region a resonant loop coupler

158

is employed (Ref. 33), (Fig. V-9), while the kilomegacycle region wave-
guide horns can be used to direct the microwave energy in a relatively
narrow beam (Ref. 34). The higher the frequency used, the higher the
attainable spatial resolution.
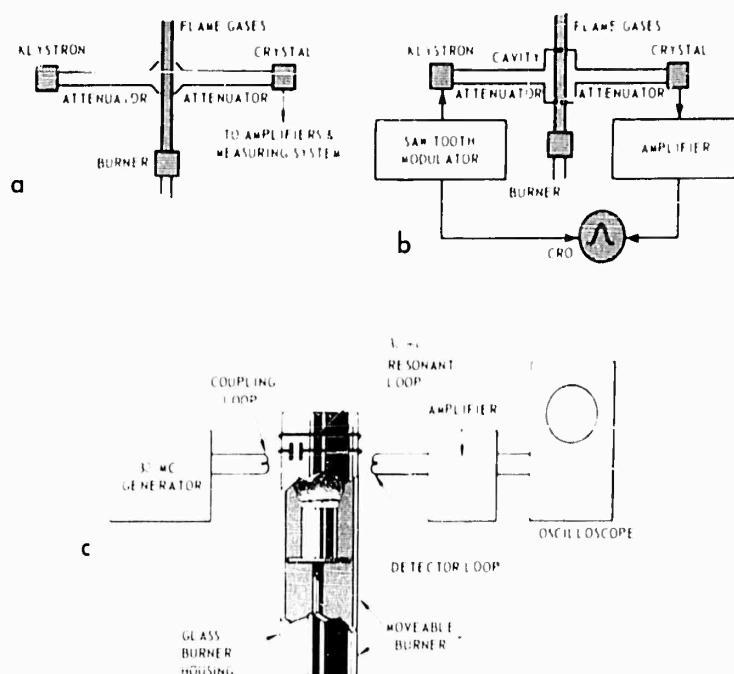
Fig. V-9   THE DETERMINATION OF ELECTRON CONCENTRATIONS IN FLAMES
BY RADIO FREQUENCY ABSORPTION

a - Direct Attenuation Apparatus for Studies in
    Microwave Region.   (Ref. 34)
b - Resonant Cavity Apparatus for Studies in Microwave
    Region.   (Ref. 34)
c - Resonant Loop Method for Studies in RF Region.
                             (Ref. 33)

159

A photographic method has been used by Weinberg (Ref. 35) to
determine the spatial distribution of ions in flames. It makes use of
the fact that at ordinary pressures, high ion velocities can be induced
by fields which are well below electrical breakdown. These velocities
are large compared with the stream velocities and therefore, by using
a uniform normal field, the ions will strike the withdrawal electrode
at a position only slightly different from its coordinates of origin.
By use of a matrix of electrodes, in contact with a photographic paper

or film, the current density distribution in a flame can be determined. The matrix has the dual purpose of protecting the photographic paper from exposure to the light of the flame and of increasing sensitivity by concentrating the current at a point. The resulting data has the appearance of a half-tone print. A very fine matrix can be made by casting a wire brush in plastic and machining the resulting block into a flat plate. With Ilford C2iP paper a sensitivity of 0.2 coulombs per cm^2 was realized with standard development. Some considerable improvement might result from the use of new ultra high sensitive films. In typical experiments, flame "exposure times" were of the order of 15 minutes.

Very interesting individual ion profiles have been measured in flames using a sampling probe and the ion mass spectrometer (Fig. V-7). This detailed type of information will no doubt play an important role in determining the kinetics of ion reactions in flames.

MEASUREMENTS OF CHARGE PRODUCTION RATES IN FLAMES

When detailed electron and individual ion profiles become available it will be possible to determine the net rates of production for the various ionic species in the flame in the same manner as is used to determine the production rates of stable species. The equations are similar (Eq. 3) to those used with stable species, differing only in the substitution of ambipolar for ordinary diffusion coefficients. This is necessary because the electron diffuses rapidly compared with the positive ions and since electrostatic forces are large the two diffusions are coupled. The species conservation equation for an ion is:

$$D_a \nabla^2 n_f - v \frac{dn_f}{dz} - \gamma n_f^2 + q = 0 \tag{3}$$

where

160

D_a = ambipolar diffusion coefficient (cm^2/sec)

n_f = molar concentration of ion (moles/cm)

γ = recombination rate

q = formation rate

Over-all charge generation can be measured directly in a
number of cases by placing a flame front of simple known geometry in a
"saturation" electric field which extracts the ions as rapidly as they
are formed. This approach has been applied successfully to the study
of flat diffusion flames (Ref. 25). There are some complications
associated with the effective geometry and perturbing effects of the
ion wind developed; and only over-all charge generation is measured.
A further limitation with certain flames is that so many ions are formed
that before the saturation level is attained secondary ionization occurs
so that no plateau occurs in the current versus voltage curve. The
apparatus for such studies is simple - consisting of a suitable burner,
a set of electrodes and appropriate current and voltage measuring
devices, so that the technique may well be worth exploiting in simple
systems where a quantitative interpretation might be possible.

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162

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163

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164

VI

DISTANCE MEASUREMENTS IN FLAMES

INTRODUCTION

The intensive properties vary substantially from beginning to end of a flame front; therefore, to avoid ambiguity it is necessary to associate a position with each local measurement. Since most of the flames which have been studied are a few millimeters thick, precise distance measurements are necessary for quantitative work. Associating local intensive properties with distance measurements is also important because the quantitative interpretation of flame structure data requires use of spatial derivatives (Ref. 1). In determining chemical kinetic information, for example, both first and second derivatives of the composition data are necessary; while in determining rates of heat release, first and second derivatives of temperature are used. The development of a precise method for measuring position in flames is a necessity. The method must allow location of the physical position of the probe. The designation probe is used here in the general sense to include not only composition probes, but also thermocouples, particle tracers, and light beams. In addition it is necessary to evaluate the absolute relation of the measurements to one another. The precision required for position determination depends on the thickness of the flame region to be studied and the desired resolution. It is desirable to study as thick a flame front as possible. Flame thickness can be controlled by varying pressure and burning velocity.

The resolution requirements depend not only on the thickness of the region to be measured, but also on the number of independent determinations which are required. In flames, this problem is intensified because the reaction zone only occupies a fraction of the region over which composition and temperature change (Fig. VI-1). Ten inde-

165
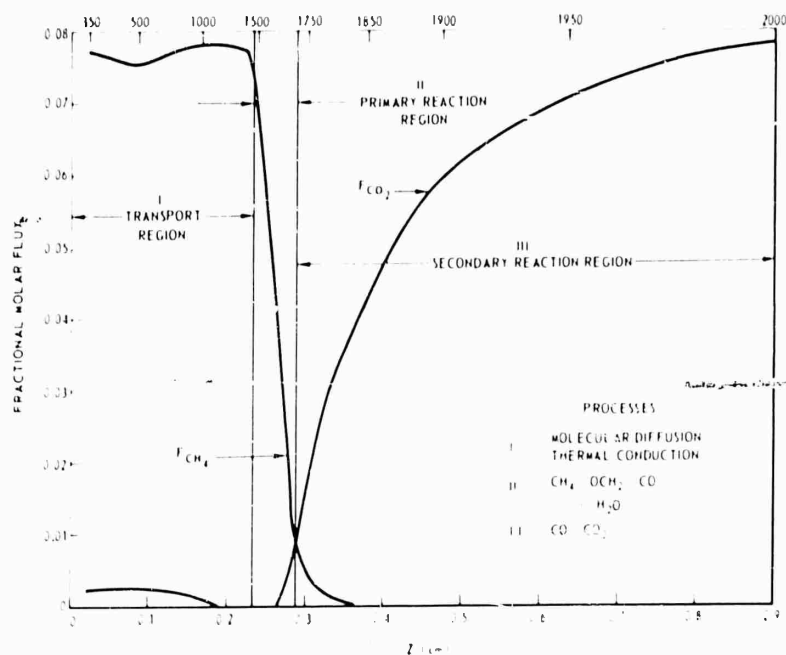
Fig. VI-1   REGIONS IN A PREMIXED METHANE-OXYGEN FLAME.

Fractional molar flux of methane and carbon dioxide
are plotted as a function of distance (cm) (and
temperature) (°K). Note that there are two separate
reaction zones and the narrowness of the primary
reaction region.

pendent determinations of rate have a reasonable minimum number. If one
per cent measurements are desired, then the measuring instrument should
have a least count and reproducibility better than 1/1000 of the thick-
ness of the flame front (Table VI-1). Since a significant second deriva-
tive is also required for each station, the sampling depth of the probe
should be small compared with 1/10 of the thickness of the reaction
region (Appendix A). If these requirements are met, it should be
possible to make significant measurements of flame front structure.

166

RELATIVE POSITION MEASUREMENT

The measurement of distance is fundamental to science; it
involves comparison between distance in the system being studied and a

Table VI-1

CONDITIONS FOR OBTAINING TEN SEPARATE DETERMINATIONS
OF RATE IN A FLAME FRONT[*]

Thickness	Minimal Burner Diameter	Spatial Reproducibility	Resolution Required	Maximum Probe Dimension
0.1	1	2×10^{-3}	10^{-2}	10^{-3}
1	10	2×10^{-2}	10^{-1}	10^{-2}
10	100	2×10^{-1}	1	10^{-1}

[*]All quantities are given in centimeters.

standard distance. The ultimate standard for scientific work has been
the standard meter of Paris; though in recent years the more accurate
reference provided by interferometric measurements of the wave length
of a certain Kr line has been adopted. The English system of units
(of the U.S.) is tied to the metric system by a legal definition which
specifies that 1 in. 2.54 cm.

Position measurements in flames can be one of three types:

1. "Dead reckoning" in which a probe is advanced by a
   calibrated micrometer drive and the distance measured
   directly.

2. Visual measurements in which a telescope and cross hairs
   are sighted on the probe, and the movement is measured
   by a micrometer drive attached to the telescope system.

3. Photographic techniques in which measurements are made
   on a negative or print.

167

DEAD RECKONING METHOD

Most of the probes used in studying flame structure are pro-
vided with some type of mechanical drive for convenience in movement
and reproducing positions. If the drive is a micrometer or provided

with a calibration, the displacement of the probe can be measured
directly. Some problems arise with such systems, such as alignment of
the probe drive with the axis of the flame, mechanical hysteresis, and
errors due to differential thermal expansion. If care is taken to
minimize these errors, direct measurements can be made with a precision
of the order of 2×10^{-4} cm.

An ideal probe drive is rigid, easily aligned, has negligible
positional hysteresis, possesses sufficient mechanical advantage to drive
the probe easily against vacuum or pressure, and has a distance scale
which can be easily and precisely read. Systems of this type can be
readily designed, but for economic reasons it is wise to use as many
commercially available parts as possible. Drives are available with
three levels of precision:

1. The machinist's milling-machine carriage provides a
     rugged linear drive with 2 in. of travel and a repro-
     ducibility better than 0.001 in. Its two primary dis-
     advantages are its clumsiness and the lack of a direct
     measuring scale. The latter problem can be solved by
     using a dial micrometer for the direct measurements.

2. A second commercially available drive can be furnished
     by the machinist's micrometer. Micrometers are avail-
     able to read directly in either English or metric units.
     Several designs are available with lengths of travel
     ranging from 1/4 to 1 in.; travel greater than this is
     not commonly available. (The so-called 2- or 3-in.
     micrometer normally has a 1-in. travel, and is used
     for measuring distances from 1 to 2 in., from 2 to 3 in.,
     and so forth.) Two levels of precision are available:
     direct reading to 0.001 in., allowing estimates of
     2×10^{-4} inch, and direct reading to 0.0001 in., allow-
     ing estimates of 2×10^{-5} in. The cost of the instrument
     depends on the precision; the 0.001-in. micrometer costs
     around \$10.00, while the 0.0001-in. instrument is priced
     around \$75.00.

Micrometers have two disadvantages when used as probe drives:
The spindle (Fig. VI-2) is smaller than many of the probes commonly
used, and the spindle rotates as well as translates.

168

DIAL MICROMETER

MICROMETER

LATHE MILLING ADAPTOR
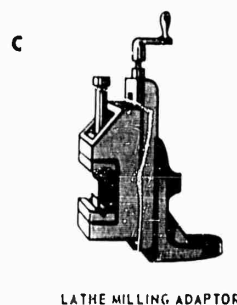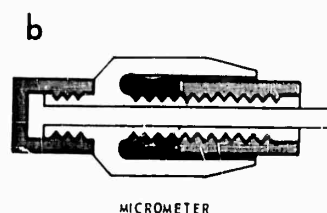
Fig. VI-2   COMMERCIALLY AVAILABLE POSITIONING AND MEASURING DEVICES

        a - Machinist's Micrometer.
        b - Machinist's Dial Micrometer.
        c - Lathe Milling Adaptor (Linear Traverse).

Where an uncalibrated drive mechanism is available, it is often convenient to make measurements using the commercial dial micrometers (Fig. VI-2). They are available in the same ranges of travel and precision as the ordinary micrometer and read in either English or metric units. They are about twice as expensive as the ordinary machinist's micrometer.

169

CATHETOMETER METHOD

It is often desirable to view the probe directly and measure its position in relation to the burner or luminous region of the flame. These measurements are best accomplished by use of a cathetometer. The ordinary laboratory cathetometer has a precision of 0.1 mm, but optical comparators are available with which a precision of a few microns can be obtained in routine measurements over distances as great as 30 cm.

In flame studies the primary sources of error are not the distance measurements themselves, but the aberrations and errors in locating the object being measured. Discussion of several sources of error follows:

Alignment

One obvious source of error is misalignment of the axis of the cathetometer and the axis of the flame. The error is a function of the sine of the angle between the two coordinate systems. Since it is easy to align a system vertically (or horizontally) with a machinist's level, this error can generally be reduced to below one part in a thousand.

Vibration

Since the optical lever arm in such systems is moderately long, vibration can be a problem; however, the presence of vibration can be easily detected through the movement of the telescope image, and normally can be reduced to tolerable levels with little difficulty. In especially difficult circumstances the use of a vibration-free plat-form may be necessary.

170

Optical Aberrations

The optical aberrations of the telescope are normally not a source of error, since it is used as a null instrument and alignment

is always made on the center of the cross hairs. It is sometimes necessary to use a horizontal cross hair. Under these conditions alignment of the cross hair is important and good optics are necessary. Most commercial telescopes are satisfactory for such work.

More serious than telescope aberrations are those due to windows, and density gradients in the flame itself. Good windows can usually be obtained by careful selection of commercial plate glass. Distortions due to density gradients in the flame result in errors of the order of a few microns in tenth-atmosphere flames; however, the displacement depends quadratically on the pressure, and can provide a serious source of error in higher-pressure flames.

PHOTOGRAPHIC METHOD

In many cases it is necessary, or more convenient, to photo-graph the system and make measurements on the resulting negative or print. In designing a photographic measurement system, one should first decide on the size of field to be covered, then the required resolution, the maximum allowable distortion, the available object brightness, and the required exposure times. These requirements allow a rational basis for the choice of lens, shutter, magnification ratio, film size, resolution, and speed.

Lens

A lens should be chosen with respect to the size of field to be covered; thus if the field is of the order of an inch in diameter, a 35 mm camera lens is suitable. If a 4-in. field is required, a 4 x 5 in. camera lens is necessary. The resolving power of the lens should be as good or better than the minimum distance increment required in the measurement; the maximum tolerable distortion determines the quality of lens required. The lens speed, or f/ number (ratio of focal length to diameter) should be determined by image brightness, exposure time, and film speed. For a given quality of lens (resolution and distortion), the higher the f/ number, the lower the cost, and lenses of highest resolution can only be obtained with moderate f/ number. It is

171

desirable to have an image which is bright enough for visual monitoring, and it should be remembered that the brightness drops off quadratically with magnification ratio.

Only the best of lenses have resolution exceeding 100 lines per millimeter (will resolve two lines spaced 1 100 of a millimeter apart in the image plane). Most lenses give their best performance when operated at moderate apertures (f 5 to f 8). Often if an enlarged image is desired it is best to reverse the lens, since lenses are normally designed to operate with a large field and small image, while in flame work the opposite condition is often desired. Image distortion by even a good lens usually will exceed 1 per cent in the peripheral field outside the central 15 cone. Special lenses designed for oscilloscope photography are commercially available. They possess characteristics desirable for flame photography, namely high magnification ratio, high aperture, excellent resolution, and flat field. These designs are excellent, but this excellence is purchased by specialization: such lenses have good characteristics only when operated under specified conditions. Distortion can be corrected by calibration, but this is usually too time-consuming to be worthwhile. The resolution of camera lenses that must cover a wide field of view is much inferior to that of the traveling microscope of the optical comparator, which operates on its optical axis. For this reason one can more easily achieve high precision with the optical comparator than with photographic techniques. On the other hand, photography provides a permanent primary record of information.

Shutters

172

There are two common types of shutters, the Compur shutter, which operates either between lens elements or directly behind the lens, and the focal-plane shutter, which consists of a slit in a curtain which is passed in front of the film. The Compur shutter exposes the whole film simultaneously. For moderate size lenses (2-cm diameter) it is available in speeds up to 1/1000 sec, and up to 1/50 sec for large lenses (5-cm diameter). The speeds marked on such shutters are effective exposure times and are shorter than the true open interval. This is because, for shorter intervals, opening and closing times of the shutter become appreciable.

A focal-plane shutter usually takes between a fifth and a
twenty-fifth of a second to travel across the face of the film, and
events faster than this will not be exposed simultaneously, although
effective exposure times as low as 0.001 sec can be obtained with any
size of lens. This type of distortion is intolerable for some flame
work. Special rapid shutters, such as Kerr cells and Faraday cells,
have been designed which allow exposure times as short as a fraction
of a microsecond (Ref. 2).

In addition to the problem of exposure times, synchronization
is often a problem; that is, either the camera is to be set off at the
same time as an event, or vice versa. Most camera shutters provide
special synchronizing contacts for such work, and commercial solenoid
shutter releases can be obtained. With techniques of this type it is
feasible to obtain synchronization to the nearest millisecond. Closer
synchronization requires special instrumentation.

Film

Film size should be chosen to match the magnification and
field size. The resolution should be chosen to correspond to re-
quired spatial accuracy in the field. The speed of the film should be
chosen to match the image brightness and exposure times available.
Table VI-2 gives a summary of information on some common film types.
More detailed information can be obtained by consulting manufacturers'
manuals. Cut film is often more satisfactory than roll film or pack
film because it can give a limited number of pictures.

Shrinkage can be a problem which in the worst case will vary
with region and direction. Moderate care will reduce these distortions
below one per cent, and they have no effect on the resolution of the
film. If extreme precision is required, glass plates can be used to
avoid the shrinkage problem.

173

For determining positions the higher the contrast, the easier
are the measurements. Therefore, it is desirable to use film of the
maximum contrast and develop it for high contrast. Film with almost
any resolution can be obtained commercially, but high resolution is
normally purchased at the expense of film speed, since a minimum of one

Table VI-2

SOME FAST FILMS AND THEIR DEVELOPMENT

FILM	DEVELOPER	TIME (min.)	TEMP. (°F)	Fog-D	GAMMA	ASA	RESOLUTION (lines/mm)	TYPE
Polaroid	Self developed	0.2	Room			3000		4 x 5
Royal X*	DK50	10	70	0.41	1.00	3000	40	35 mm
ID-2*	Dektol	5	70	0.67	1.04	2400		35 mm
Isopan Record*	X500	12	75	0.59	1.16	2210		35 mm
Tri X (1959)*	Dektol	7.5	70	0.56	0.86	1920		35 mm
Superior-4	Supermix (GE X-ray)	7	70	0.64	0.90	1920		35 mm
Photoflur (green sens.)	Liq. X-ray (Kodak)	7	70	0.36	1.66	1180		35 at
Tri X (improved)*	UGF	10	70	0.41	1.02	1030		35 mm
Shell burst*	Dektol (stock sol.)	7.5	70	0.375	1.60	775		35 mm
Royal Pan	DK50	7	70				50	4 x 5
Panatomic X	DK50	7	70				65	4 x 5
Contrast Process Ortho	D-20	15	70				125	4 x 5

*Taken from Ref. 2, p. 80.

174

or two quanta of light are required to activate the photographic grain, which itself limits resolution.

Where immediate information is desired, Polaroid film can be used with development times as short as 10 sec. Adapters are available for using this film on any standard camera.

Film Reading

Film can be measured directly to 10^{-2} cm with a steel scale and low power reading glass. For more precise measurements an optical comparator and microscope can be used. The errors in this type of measurement are dominated by film resolution and reproducibility. With very good glass plate negatives, readings reliable to 5-10 microns can be obtained. A more convenient method of reading film is to have an enlarged print made, which can be measured with sufficient accuracy using a scale. This has the disadvantage of multiplying the errors, and of lowering either the contrast, resolution, or both. With care the resolution of this technique can also approach 5-10 microns.

The detailed problems of optical design and photographic techniques are beyond the scope of the present treatment. The interested reader is referred to specialized works on photography (Ref. 2), optics (Ref. 3), and photomicroscopy (Ref. 4).

ABSOLUTE POSITION MEASUREMENT

In addition to measuring one position relative to another, it is also necessary to establish an absolute coordinate system in the flame so that measurements of different types can be associated, and successive measurements compared and interrelated. This problem is twofold: to establish a reference surface or point in the flame front that will serve as an origin for the measuring system; and to establish the relation between the measured probe coordinates and the coordinates of the sample taken; thus, the congruency between the various profiles is established. The first problem is straightforward; the second is involved.

175

ORIGINS FOR COORDINATE REFERENCE

An ideal coordinate origin should be accurately observable, and bear a fixed spatial relationship to the flame front. Several possibilities suggest themselves: (a) the luminous zone of the flame, (b) the burner screen or edge, or (c) a fixed thermocouple in the incoming gas stream. Each of these origins has been used; the best reference is probably provided by a fixed thermocouple.

Luminous Zone

The luminous zone is a region whose edges or maximum luminosity points can be located with reasonable precision. It does bear a fixed relationship to the flame front structure,and would provide an ideal reference surface if the edges were sufficiently well defined. Unfortunately, luminous regions usually fall short of this ideal by almost an order of magnitude. For example, the luminous region of the methane-oxygen flame can be located reproducibly to about 100 microns, while the reproducibility of the measurements is about 10 to 20 microns. Since the thickness of the luminous region (and hence the sharpness of the reference boundary) possesses the same dependence on pressure and burning velocity as the main flame structure, it appears that there are probably no conditions (for hydrocarbon flames) under which the luminous region could serve as a reference for quantitative work.

Burner Surface or Edge

If the flame remains fixed in space, as it must for meaningful measurements, a point on the burner could serve as the reference point or surface for the coordinate origin. The burner provides a very satisfactory reference during a single run, but for intercomparing runs it is less satisfactory, since this requires reproducing conditions of flow, pressure, initial temperature, and burner cooling with the same precision as they are held during a run (better than one part in a thousand). Although this is not impossible to do, it is difficult, since it involves control of room temperature, cooling water, and

purity of materials. On successive days, with identic room and water temperatures and using the same gas cylinders, excellent reproducibility can be obtained (Fig. IV-1), but such consistency depends on factors considered outside easy control. Controls could be set up by putting the burner in a housing, thermostating the burner and incoming gas, and cooling water to a tenth of a degree. However, this is unnecessary for most work since a fixed thermocouple provides a reference which is satisfactory and independent of these minor variations.

Fixed Thermocouple Reference

The most satisfactory coordinate reference is provided by a fixed thermocouple. This is usually a small (- 25-micron) thermocouple of chromel-alumel. Since it is placed in the low temperature region of the flame ahead of the reaction zone, the thermocouple can be made of materials with high thermoelectric power and need not be coated with silica.

In the region of initial temperature rise (the first few hundred degrees) the temperature gradient is very steep, and a small movement of the flame corresponds to a substantial temperature change. For example, in the tenth-atmosphere methane-oxygen flame, the gradient is 5000 cm, which means that a two-micron movement corresponds to a one-degree temperature change. Such a thermocouple serves two purposes: it provides a positional reference in the flame, and it provides a very sensitive detector of flame movement or oscillation. The latter is particularly important, since measurements can be no better than the spatial stability of the flame. With such a reference the small corrections for daily variation of flame position can be made using the known temperature profile. These variations usually amount to no more than 25-50 microns--that is, 10-20°K--and the correction is probably reliable to a few microns.

177

CONGRUENCY OF FLAME PROFILES

Since the interpretation of flame structural data depends upon the relation between the variables and their derivatives, it is

necessary to obtain congruence between profiles from the various types of measurements. This is not a straightforward problem because the effective position of sampling does not correspond exactly to the physical position of the probe (Fig. VI-3). A probe withdraws a sample a few diameters upstream of its physical position, while a thermocouple distorts the flame velocity profile locally so that it tends to sample
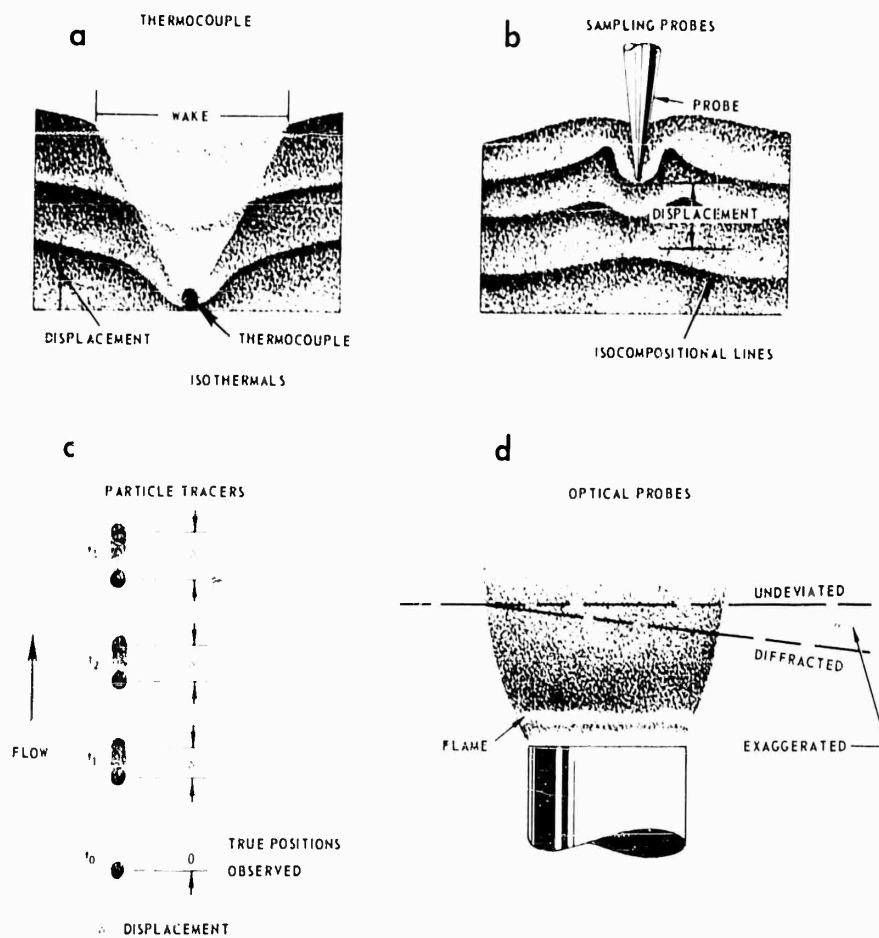

Fig. VI-3   DISPLACEMENT OF FLAME STRUCTURE MEASUREMENTS DUE TO
             INTERACTION BETWEEN FLAME AND PROBE.

             a - Thermocouple Distortions of Flame Fronts (Aero-
                 dynamic Wake).
             b - Sampling Probe Distortions of Flame Fronts (Effect
                 of Sink).
             c - Particle Tracer Errors (Aerodynamic Lags Due to
                 Acceleration).
             d - Optical Probe Deviations (Due to Schlieren Effects).

a temperature downstream from its apparent position; particles tend
to lag the gas flow so that particle position measurements are upstream
of their true positions. The orders of magnitude of these displace-
ments are known, but the phenomena are too complex for quantitative
estimates to be made. Sampling probes have been studied by Westenberg,
Raezer, and Fristrom (Ref. 5) with the conclusion that the position
represented by the sample is only one or two probe diameters downstream
of the probe tip. Friedman (Ref. 6) estimates that the wake displace-
ment due to a thermocouple is four or five bead diameters. Studies by
Walker (Ref. 7), (Fig. VI-3a) on the wakes behind small wires indicate
that this estimate is of the right order of magnitude. Fristrom (Ref. 8)
has estimated the displacement of a velocity profile due to accelera-
tional lags; for 5-micron particles in a propane-air flame front 3 mm
thick it would be of the order of 50 microns. Optical probes show dis-
placements due to schlieren effects, although as previously mentioned,
these are quite small for low-pressure flames. For example, at 1/10 atm
the displacement is less than 20 microns in a methane flame 5 in. in
diameter. These estimates indicate that in the case of 1/10 atm CH_4-O_2
flame the relative displacements between the several types of profiles
can be several tenths of a millimeter. This uncertainty is serious
since it represents some 20 per cent of the flame thickness.

Several methods are available for resolving these difficulties.
The most obvious one of estimating the displacements and correcting for
them only allows alignment of profiles to within one or two tenths of
a millimeter. For many purposes, this method is not sufficiently accu-
rate and other techniques must be used to obtain congruency. The
best method at present is to derive temperature profiles from the
measurements and align these profiles (Fig. III-11). The profiles are
of varying precision and resolution, but it is felt that this technique
allows alignment to about one to two per cent of the flame thickness
(Appendix A).

Either the conservation laws of energy or matter could be
used as a criterion of best fit of the various profiles. For example,
a choice between several trial alignments could be made on a basis of
the standard deviation from constancy of energy or of mass flux, or,
for that matter, any individual atomic species flux conservation could
be used. Unfortunately the results from this rather tedious calcula-
tion are not overly sensitive to displacement of the profiles.

179

A flame can be completely described by a set of absolute composition profiles and an area-ratio curve. Therefore, with a symmetric flame whose area ratio can be calculated from the geometry, only a single probe measurement of composition would be necessary. This would avoid alignment problems, since it would only be necessary to determine the relation between the sampling position and the geometric position.

In the case of the two symmetric flames which have been realized in practice, the spherical (Ref. 9) and cylindrical flame (Ref. 10), the radii of curvature are large compared with flame front thickness, and the errors due to displacement of the sample position are unimportant. This approach is the most promising one for flame studies in which such symmetric flames can be obtained (Ref. 11).

STABILITY, REPRODUCIBILITY, AND SPATIAL RESOLUTION

The reproducibility of distance measurements in flames is primarily determined by the stability of the flame, since the reproducibility of the measuring instruments is high. The spatial stability of the flame in turn is controlled by the precision of flow regulation. This is discussed in Chapter I along with general design problems. If flow is controlled to better than one part in a thousand and ambient temperature to $0.5°K$, and the pressure is adjusted with the same precision, then the flame will stay in place to about $1/1000$ of the flame front thickness (~ 5 microns in the typical case discussed). As was mentioned previously this stability is best measured by inserting a small thermocouple in the early region of the flame where temperature gradients are steep. The thermocouple allows the detection of drifts or slow oscillations of the flame with amplitudes as low as a few microns. The importance of stability to precision measurements can not be overstated; it is an absolute necessity.

180

Spatial reproducibility and resolution are separate concepts. The first implies that if a probe is moved, the property being measured will change reproducibly. It is limited only by the precision of the probe drive and the stability of the flame; it is independent of probe dimensions. Resolution, on the other hand, implies the ability to measure a true second derivative. This is only possible over a region

which is larger than the sampling region. Spatial reproducibility always exceeds the resolution usually by an order of magnitude.

The reason for the difference is that a probe sample represents an average of the property being measured over the sampling region. The average will change reproducibly with movements which are small compared with the dimensions of the sampling region, and if the second (spatial) derivative is small, a valid determination of the property and its first derivative can be obtained. If the second derivative is important, however, errors will occur (Fig. VI-4). An example is given by the monitoring thermocouple, which is twenty-five microns in diameter, yet shows a valid spatial reproducibility of the order of a few microns. The resolution of such a thermocouple is probably no better than fifty or a hundred microns.

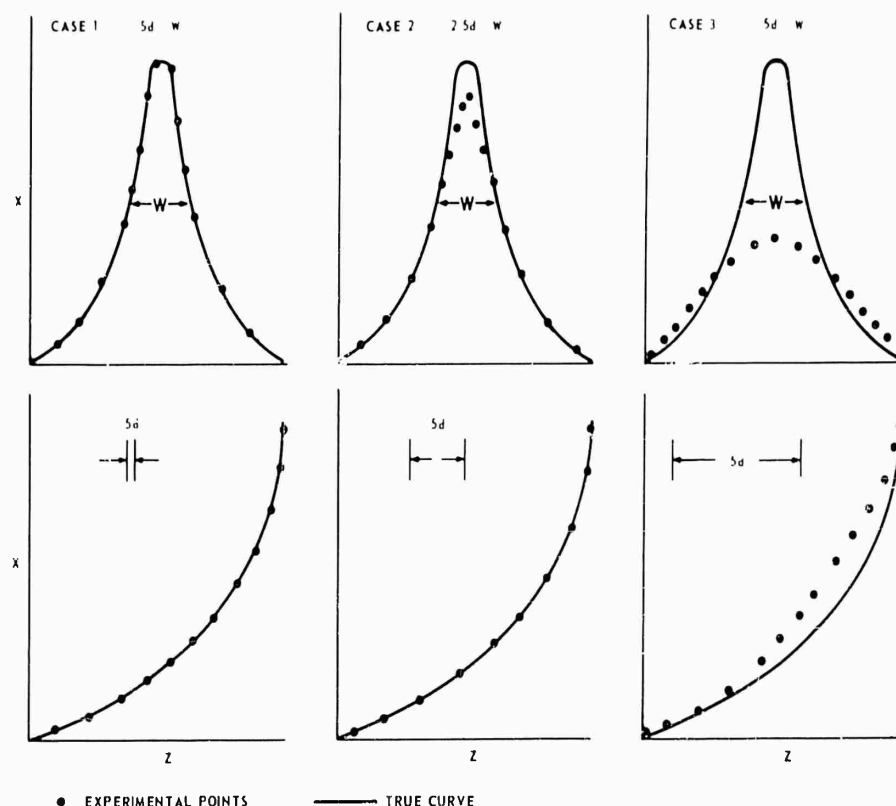● EXPERIMENTAL POINTS   —— TRUE CURVE

Fig. VI-4   ERRORS IN MEASURING PROPERTIES DUE TO FINITE PROBE SIZE

Upper Curves Property Passing Through a Maximum.
Lower Curves Property Monotonically Increases.

181

POSITION DETERMINATION IN MORE THAN ONE DIMENSION

The techniques which have been described can be generalized
to include measurements with more than one coordinate. The photograph,
for example, allows measurements in two dimensions, and a two-coordinate,
probe-drive comparator can be used to make cathetometer measurements in
two dimensions. Three-dimensional measurements can in principle be
made by using a third measuring axis at right angles to the other two
measuring axes. Under these conditions the question of depths of focus
of optical systems and identification of objects in the two planes of
measurement become considerable problems.

182

APPENDIX

FLAME FRONT THICKNESS AND DURATION

The assignment of a thickness or duration to a flame front is a convenient method of characterization. This is an approximation because the ideal flame extends exponentially to plus and minus infinity (Ref. 12). In the case of a simple flame this problem can be surmounted by choosing the distance between 5% and 95% temperature rise (e.g., Ref. 12) by the graphical definition of Fig. VI-5a or some similar arbitrary method. The laboratory flame is even more complex, however. For example, hydrocarbon flames have four definable thicknesses: (1) the pre-reaction transport region; (2) the primary reaction zone; (3) the secondary reaction region of carbon monoxide; and (4) the radical recombination region. The first two regions are strongly coupled together and are not greatly affected by external flow such as ducting, flame geometry, etc. Regions (3) and (4) are not as strongly coupled with the transport processes and do not show the same invariance with changes of flame geometry and flow. They are better considered as homogeneous reactions initiated by the primary flame reactions. Around atmospheric pressure, the carbon monoxide reaction and radical recombination region are approximately contiguous.

Theoretical analysis indicates that the relative thickness of the transport regions and reaction zones of a flame consisting of bimolecular reactions should remain in the same ratio as pressure is changed and that the thickness is inversely proportional to pressure (Ref. 13). In other words, the reaction takes a certain number of collisions to go to completion and the structure of a flame if measured with a scale proportional to mean free path would be independent of pressure.

183

The first two regions of the hydrocarbon flame correspond reasonably well to such a model if one neglects the influence of the following regions (3) and (4) on the grounds that the gradients are an
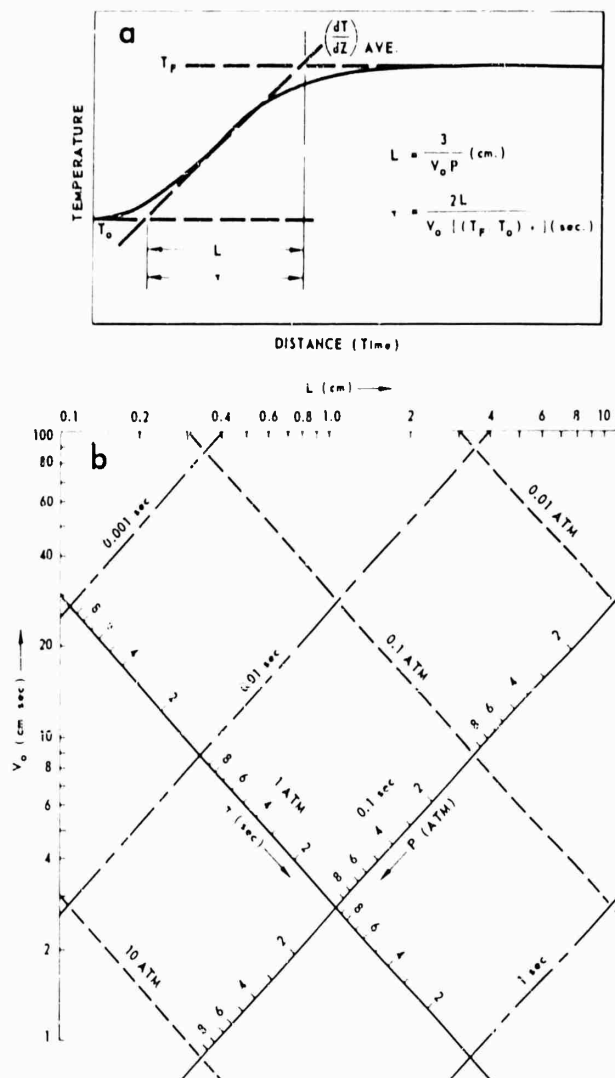
Fig. VI-5   FLAME FRONT THICKNESS AND DURATION

    a - Graphical Definitions of Thickness and Duration.
    b - Relation Between Bruning Velocity, Pressure, Flame
        Front Thickness, and Duration.   Values are nominal
        for a typical hydrocarbon air or oxygen flame.

184

order of magnitude lower than those in the primary region so that the
effect of the following reaction zones should be minor.   The importance
of the interaction of the radical recombination region should drop off
with pressure since it involves three body reactions and its charac-

teristic thickness should increase with the three halves power of inverse pressure (Ref. 13). Thus with very low pressure flames, the thickness of this region will become very great relative to the primary reaction zone and its effect on the primary region,which can only come about through diffusion or thermal conduction,will diminish with the decreasing gradients in this region and approach zero as the pressure is decreased without limit. Conversely, as the pressure is increased the interaction between the primary reaction zone and radical recombination region should increase. This interaction tends to lower the radical concentration in the reaction zone; it may set an upper pressure limit for radical driven flames of the type commonly studied.

For the reasons given above, we have chosen to identify flame front thickness with the sum of the transport and primary reaction region as defined graphically in Fig. VI-5a. The true primary reaction region is generally a quarter of this thickness. This thickness is convenient for making estimates of the spatial resolution required to study a particular flame. Since the other regions are thicker, any technique which is adequate for the study of the primary zone will be adequate for the other regions.

The principal advantage of this thickness is our ability to make reasonable rough estimates of it since it depends inversely on burning velocity and pressure. Equation (1) gives a reasonable empirical relation which is applicable to hydrocarbon-air and hydrocarbon oxygen flames in the range below ten atmospheres.

Since the major part of this thickness is the transport region whose thickness is proportional to the effective diffusion coefficient or thermal conductivity, this relation can also be applied to hydrocarbon flames with other diluents by making an appropriate correction proportional to the ratio of effective diffusion coefficient (or thermal conductivity) to that of oxygen (or nitrogen). For the same reason, the relation applies approximately to any flame in which the primary reaction region is narrow compared with the transport zone. The equation provides a lower limit for flame front thickness. The last two approximations apply to the transport zone thickness and in applying the estimates to other systems, it is advisable to remember that the relation of transport zone to reaction zone will also vary.

185

In hydrocarbon flames this thickness can be represented em-
pirically by Eq. (1)

$$L \approx 3 \, v_o^{-1} \, P^{-1} \tag{1}$$

where L is the flame thickness as defined by Fig. VI-5a (cm); v_o is
the burning velocity (cm/sec); and P is the pressure (atm). It corre-
sponds roughly to the sum of the transport and primary reaction zone
and is about four times the thickness of the primary reaction zone.
As would be expected, since the reactions are bimolecular and the major
part of the zone is controlled by transport, this thickness scales
proportionally to inverse pressure and burning velocity; and is approxi-
mately, although slightly larger than the thermal conduction thickness,
calculated from the temperature profile upstream of a heat source.

Duration, τ, is defined by Eq. (2) as the thickness divided
by the average velocity.

$$\tau \approx \frac{2L}{v_o \, (T_f/T_o + 1)} \tag{2}$$

The relations between pressure, burning velocity, flame
front thickness, and duration are summarized for typical hydrocarbon
flames in Fig. VI-5b.

186

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187

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