MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

SIXTH QUARTERLY TECHNICAL SUMMARY REPORT
1 January - 31 March 1963

ARPA Order No. 23-62, Amendment 28
Project Code No. 9100

M.R.I. Project No. 2551-P

For

Director
Advanced Research Projects Agency
Washington D. C.

(Contract No. Nonr-3599(00))

MRI   MIDWEST RESEARCH INSTITUTE

MIDWEST RESEARCH INSTITUTE

MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

by

Thomas A. Milne

SIXTH QUARTERLY TECHNICAL SUMMARY REPORT
1 January - 31 March 1963

ARPA Order No. 23-62, Amendment 28
Project Code No. 9100

M.R.I. Project No. 2551-P

For

Director
Advanced Research Projects Agency
Washington D. C.

(Contract No. Nonr-3599(00))

PREFACE

This report was prepared for the Advanced Research Projects Agency under ONR Contract No. Nonr-3599(00) monitored by Dr. Ralph Roberts, Head, Power Branch, ONR. The report describes the application of a one atmosphere molecular beam sampling system to gaseous mixtures and flames with metal additives.

The research staff consists of Dr. Thomas A. Milne, project leader, and Dr. Frank T. Greene. Mr. George Vowels has carried out many of the mass spectrometer studies. Discussions with Mr. Gordon E. Gross have been very helpful.

Approved for:

MIDWEST RESEARCH INSTITUTE

Sheldon L. Levy, Director
Mathematics and Physics Division

7 May 1963

TABLE OF CONTENTS

SUMMARY

Further studies of the "mass separation" phenomena, observed in aerodynamic molecular beams, are reported for a variety of 1 per cent solutes in solvents of H_2, N_2 and CO_2 at one atmosphere. To a first approximation the mass separation favors the heavier molecules by the first power of the molecular weight, for a mass spectrometer detector, independent of the solvent or the chemical nature of the solute species. The flame systems $CO-O_2$, $C_2N_2-O_2$ and $CO-N_2O$ are being applied to equilibria where hydrogen would interfere. Sampled gases from a $CO-O_2$ flame with 1 per cent Cl_2 added showed only Cl atoms, as predicted, with no recombination to Cl_2 during sampling.

I. INTRODUCTION

In the last quarterly report[1] we described in some detail an aerodynamic molecular beam sampling system capable of measuring small partial pressures of unstable, reactive and condensable species from one atmosphere flames. One particularly interesting feature of the sampling system was the large observed "mass separation" effect, in which the heavier components of mixtures were concentrated in the final molecular beam. A preliminary experiment with BCl_3 added to a H_2-O_2 flame demonstrated the ability to extract the species Cl, HCl and HBO_2 in approximately the right proportions.

Having demonstrated the qualitative feasibility of mass spectrometer sampling of metal containing flames, we have spent the last quarter in preparing for temperature measurements in flames, in obtaining suitable nonhydrogen containing flames and, principally, in studying the molecular weight dependence of the "mass separation" effect. This work is described in the following sections.

II. SAMPLING OF PERMANENT GASES AND MIXTURES AT ONE ATMOSPHERE

A. Simple Gases

The general behavior of our aerodynamic molecular beam system, as described in the fifth quarterly report[1], seems consistent with the behavior reported in the most recent papers by Fenn[2,3] and Scott[4,5] in their studies of the generation of intense molecular beams. It is not yet clear whether, at the conditions of our maximum beam intensity, the sampled gas is passing through a shock wave in front of the skimmer or second orifice, but if so, a large proportion of the original direct motion of the gas is still preserved.

A theory has been developed[5,6] which predicts the molecular beam intensity to be expected under certain idealized sampling conditions at high pressure.
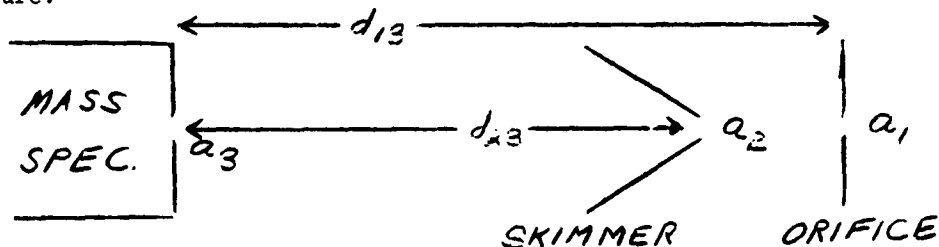

Fig. 1 - Schematic of Geometry of Sampler Orifice System.

Assuming shock-free, isentropic expansion from the first to the second orifice and no collisions after leaving the second orifice (molecular flow) and for beam Mach numbers at the second orifice of 3 or more, the following expression is obtained.

$$I = \frac{a_2 n_o c_o M}{\left[1+\frac{1}{2}(\gamma-1)M^2\right]^3}(3+\gamma M^2)\frac{a_3}{2\pi d_{23}^2}$$

where

	I	is the beam flux in molecules per second at the detector slit
a_2 and a_3		are the areas of the second orifice and the detector slit
	d_{23}	is the distance of the detector slit from the second orifice
	n_o	is the number density of molecules upstream of the first orifice
	c_o	is the speed of sound upstream of the first orifice
	γ	is the specific heat ratio
	M	is the Mach number at the second orifice

The idealizations of the theory plus the lack of knowledge of the actual conditions in experimental sampling systems make it impossible at present to predict reliably beam intensities in real situations.

A problem of particular interest to thermochemists is that of the dependence of beam intensity from a Knudsen cell on pressure in the cell when the mean free path of gas becomes small compared to the orifice diameter. The limiting behavior at high pressure, with properly designed slits and geometry, should approach that predicted above. In the molecular flow range, the intensity is given simply by[7]:

$$I = \left(\frac{k P_o a_1}{\sqrt{mT}}\right)\left(\frac{a_3}{d_{13}}\right)$$

where a_1 is the area of the first orifice, d_{13} is the distance of the detector slit from the first orifice, and m is the molecular weight of the species. In both limiting cases, I is proportional to pressure. However, one startling difference is that for molecular flow the intensity is proportional to a_1, the area of the first orifice (provided the second slit does not geometrically limit the beam), whereas in the aerodynamic flow regime, the intensity varies with a_2, the second orifice area and should be independent of the first orifice area for a given Mach number. Thus, if one attempted to predict the intensity versus P_o curve for a fixed system of slits, the result would depend on the relative size of the first and second slits among other things. This behavior has been verified qualitatively in

our measurements of I versus P_0 for argon gas using two different orifice sizes, but all other orifices and dimensions remaining essentially unchanged.

In Table I are shown the pertinent dimensions of the sampler in the two cases.

TABLE I

DIMENSIONS OF SAMPLER SYSTEM

	Orifice Dia. (in.)	Skimmer Dia. (in.)	Orifice-Skimmer Dist. (in.)	Orifice-Detector Dist. (in.)	Pressure Upstream of Orifice
Small orifice	0.002	0.010	3/16	~ 16	~ 1μ
Large orifice	0.0088	0.010	1/2	~ 16	~ 25μ

In Figs. 2 and 3 are shown the observed pressure dependence of intensity for H_2 , He and Ar with the small orifice. Also shown in Fig. 3 is the same dependence for argon with the large first orifice. These runs with different orifice sizes were made several weeks apart, the large orifice was conical rather than flat, the Mach numbers may have been different in the two cases, and no correction for scattering has been made with the larger orifice so that an absolute comparison of intensity at either end of the pressure range is not too meaningful. What is significant is the marked transition observed for the large orifice case from molecular flow to the high pressure behavior. The almost straight line dependence with pressure over the whole range for the small orifice is, of course, fortuitous, this comparison serving mainly to show how the behavior can vary with choice of slit sizes.

These curves illustrate just one of the complications that are going to arise in attempts to operate Knudsen cells at pressures well beyond the free molecule flow region. In studying equilibria at a constant pressure and temperature, however, where only relative intensities of species are required, this complication disappears and one needs only to be concerned about the relative sampling sensitivity as a function of molecular weight and perhaps chemical nature, size, and shape of the molecules. Such effects are the ones of concern in our flame studies and are discussed in the next section.
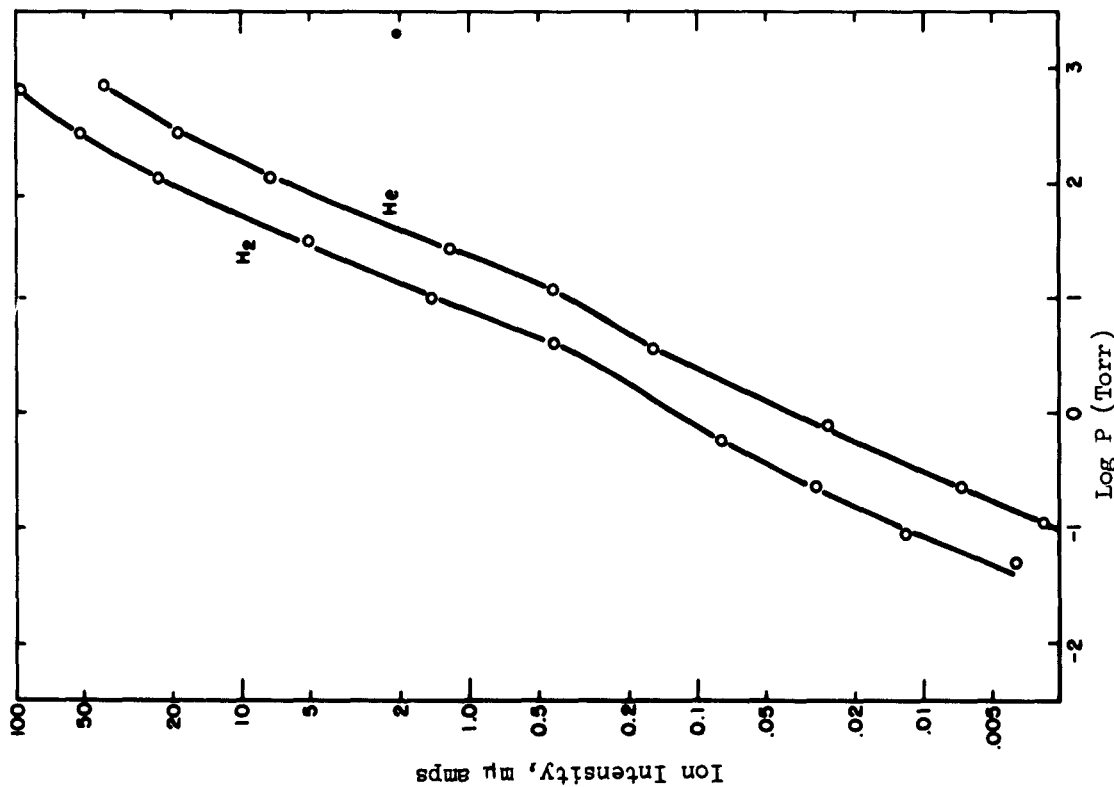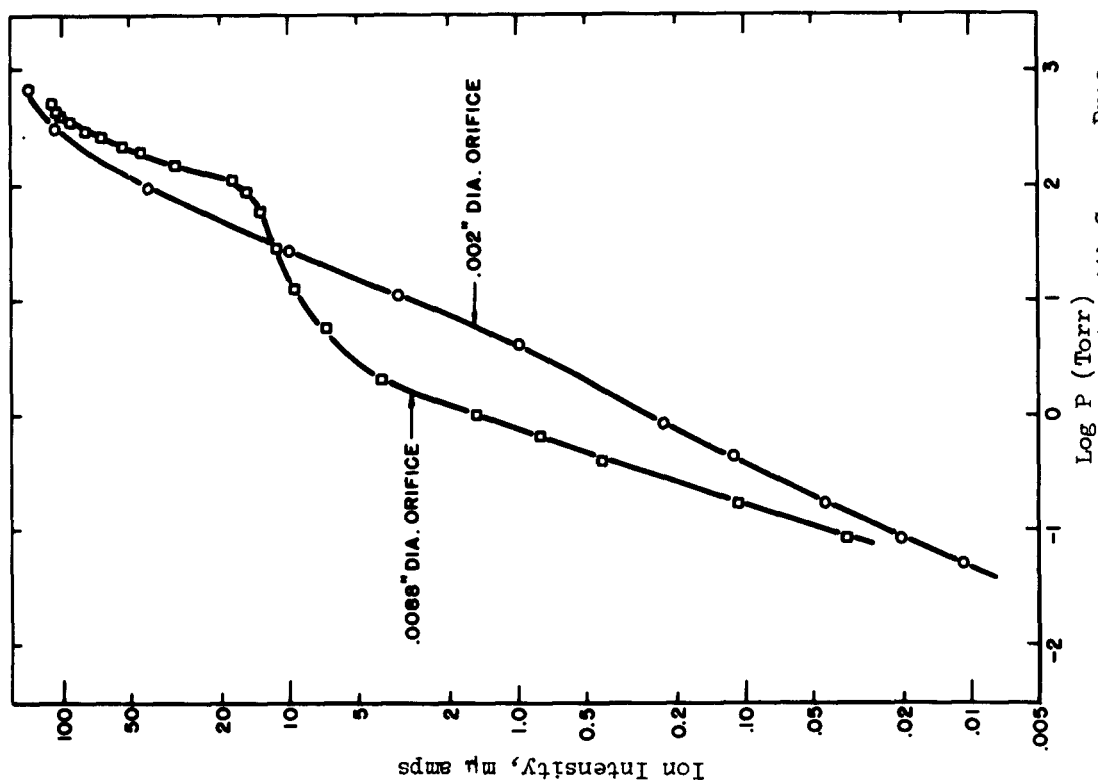
Fig. 3 - Variation of Ion Intensity with Source Pressure from Molecular flow to Continuum flow 0.002" and 0.0088" Orifice. Argon.

Fig. 2 - Variation of Ion Intensity with Source Pressure from Molecular flow to Continuum flow for 0.002" dia. Orifice H_2 and He.

B. Mixtures of Gases

We previously reported beam sampling results for a number of binary mixtures, showing enrichment of the heavier component in every case. This enrichment varied roughly with the ratio of molecular weights. In the last quarter, we studied more systematically the "mass separation" effect for solvent gases containing small percentages of different molecules. This situation approximates what we will be dealing with in flames when studying equilibria involving small concentrations of added metals.

In past work on mass separation[8,9,10] gas has been sampled from various portions of the jet by a probe not unlike our second orifice, the total gas coming through the orifice collected, and its composition compared either with the starting composition or with the remaining gas from the jet. In our sampling system, the mass spectrometer analyzes only that gas coming through in a very small solid angle molecular beam.

In preliminary work we simply compared the mass spectrum of the beam with the spectrum when the original gas mixture was bled indirectly into the ion source. This procedure is questionable, however, since the relative response of the machine to gases introduced in these two different ways might well be different. The quantities of gas in the beam were too small to collect and introduce into the ion source through the same permanent gas inlet as the starting mixture. Therefore, it was decided to calibrate the mass spectrometer for the various gases by performing Knudsen runs with each different gas at a series of pressures low enough so that scatter-free molecular flow occurred from the first orifice. The same geometry was maintained in all these comparisons. Typical plots of ion intensity versus pressure are shown in Fig. 4. In general, the plots were linear from 1,000 μ down to 100 μ or less and the slopes were computed for each species and taken as a measure of the sensitivity of the mass spectrometer for that species. Duplicate runs established a reliability of the slopes of ±10 per cent for the rare gases.

Following these calibrations a number of mixtures of gases were made up in a stainless steel tank of about 8 liters volume to a pressure of about one atmosphere. The gases were allowed to mix for several hours and beam experiments were carried out in which relative intensities were measured for each component. Repeat runs over the pressure range of 700 - 400 Torr gave agreement to ±10 per cent.

There are a number of variables besides molecular weight which might affect mass separation, such as orifice-to-skimmer distance, pressure, nature of solvent and nature and concentration of solute species. In the present experiments we used a rather small orifice, 0.002 in. diameter, which gives a
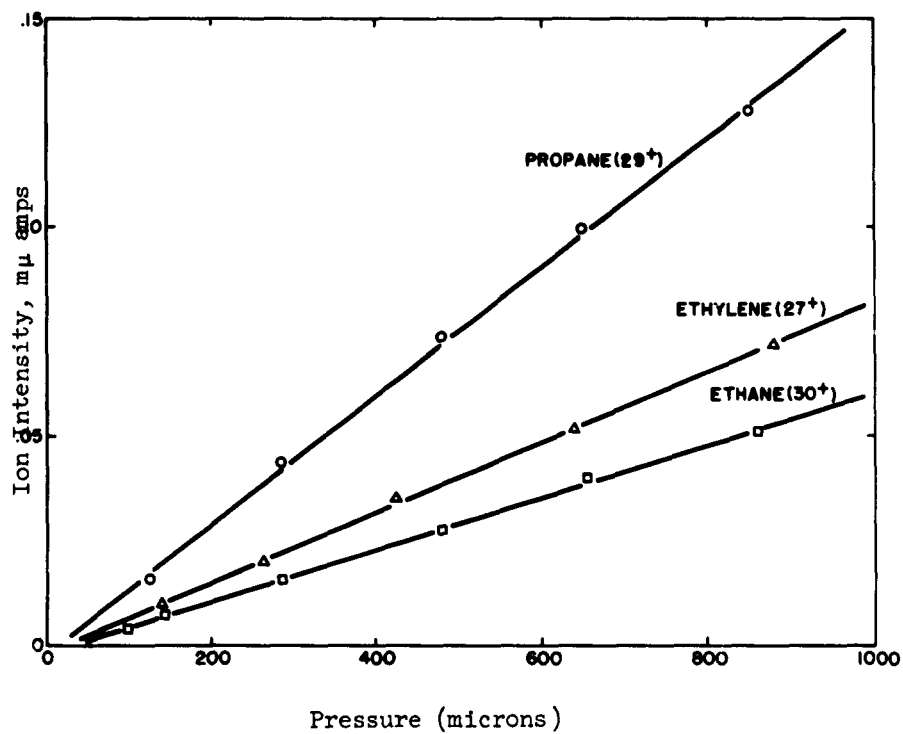
Fig. 4 - Variation of Ion Intensity with Source Pressure
in Knudsen Calibration Runs on Pure Gases.

good scatter-free beam at pressures up to one atmosphere. Orifice-to-skimmer distances of 1/8 in. and 1/2 in. gave identical results as did measurements at pressures of 700 to about 400 Torr. The mixtures used are tabulated in Table II.

TABLE II

MIXTURES USED IN MASS SEPARATION EXPERIMENTS

	Solvent	Solutes (about 1% each)
Mixture A, Fig. 5	H_2	He, Ne, Ar, Kr
Mixture B, Fig. 6	N_2	He, Ne, Ar, Kr
Mixture C, Fig. 7	CO_2	He, Ne, Ar, Kr
Mixture D, Fig. 8	N_2	H_2, He, CH_4, C_2H_6, C_3H_8, C_4H_{10}, O_2, Ar, CO_2, CF_3Cl, CCl_4

The data on mass separation were treated in the following manner. A calculated intensity (in arbitrary units) for each species was obtained by multiplying the partial pressure of the species in the tank by the slope obtained from the low pressure calibration runs. Next, the actually observed intensities were divided into the calculated intensities to give a (calc/obs) ratio for each species. If there was no mass separation these ratios should all be the same and if we choose one species, say the solvent, and normalize it to unity, then every (calc/obs) ratio should be unity. Actually, the ratio (calc/obs) was smaller the higher the molecular weight in almost every case, indicating an enrichment of the heavier species in the beam. The ratios,

$$\alpha = \frac{(calc/obs) \text{ solute}}{(calc/obs) \text{ solvent}} \quad ,$$

were then plotted versus the ratio of molecular weights, $\dfrac{\mu \text{ solvent}}{\mu \text{ solute}}$

The results are shown on a log-log plot in Figs. 5, 6, 7 and 8. The solid lines indicate the slope the plot would have depending on the molecular weight dependence of the mass separation effect.

good scatter-free beam at pressures up to one atmosphere. Orifice-to-skimmer distances of 1/8 in. and 1/2 in. gave identical results as did measurements at pressures of 700 to about 400 Torr. The mixtures used are tabulated in Table II.

TABLE II

MIXTURES USED IN MASS SEPARATION EXPERIMENTS

	Solvent	Solutes (about 1% each)
Mixture A, Fig. 5	H_2	He, Ne, Ar, Kr
Mixture B, Fig. 6	N_2	He, Ne, Ar, Kr
Mixture C, Fig. 7	CO_2	He, Ne, Ar, Kr
Mixture D, Fig. 8	N_2	H_2, He, CH_4, C_2H_6, C_3H_8, C_4H_{10}, O_2, Ar, CO_2, CF_3Cl, CCl_4

The data on mass separation were treated in the following manner. A calculated intensity (in arbitrary units) for each species was obtained by multiplying the partial pressure of the species in the tank by the slope obtained from the low pressure calibration runs. Next, the actually observed intensities were divided into the calculated intensities to give a (calc/obs) ratio for each species. If there was no mass separation these ratios should all be the same and if we choose one species, say the solvent, and normalize it to unity, then every (calc/obs) ratio should be unity. Actually, the ratio (calc/obs) was smaller the higher the molecular weight in almost every case, indicating an enrichment of the heavier species in the beam. The ratios,

$$\alpha = \frac{(\text{calc}/\text{obs}) \text{ solute}}{(\text{calc}/\text{obs}) \text{ solvent}} \quad ,$$

were then plotted versus the ratio of molecular weights, $\dfrac{\mu \text{ solvent}}{\mu \text{ solute}}$

The results are shown on a log-log plot in Figs. 5, 6, 7 and 8. The solid lines indicate the slope the plot would have depending on the molecular weight dependence of the mass separation effect.
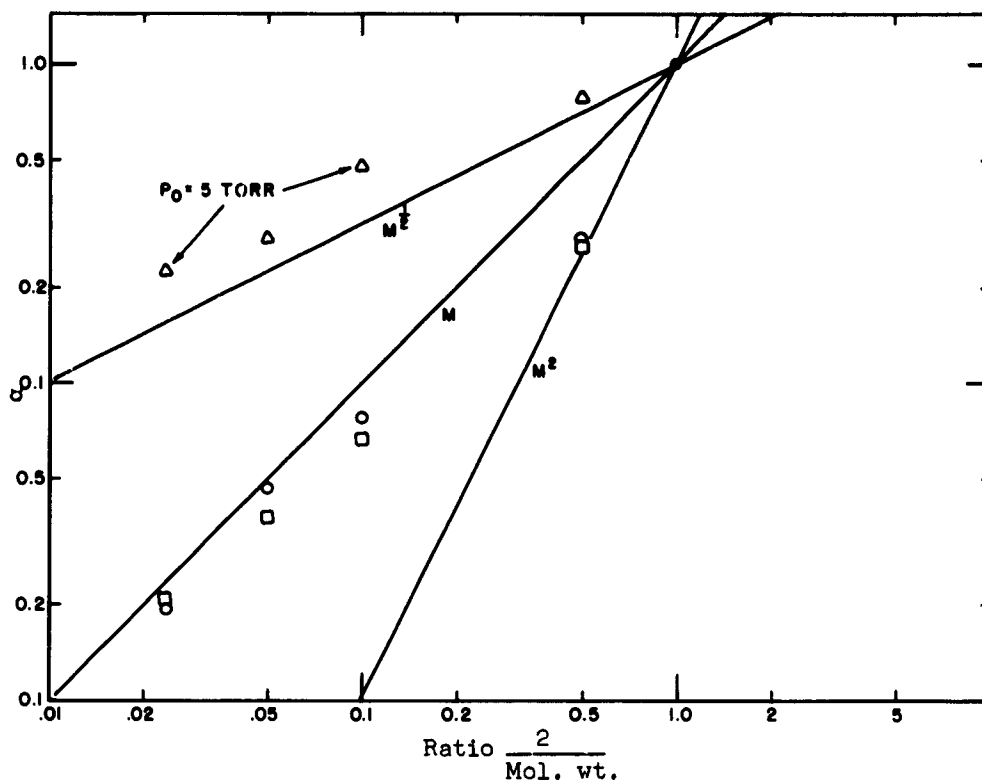
Fig. 5 - Mass Separation of He, Ne, Ar and Kv in H_2 at One Atmosphere and at Five Torr.
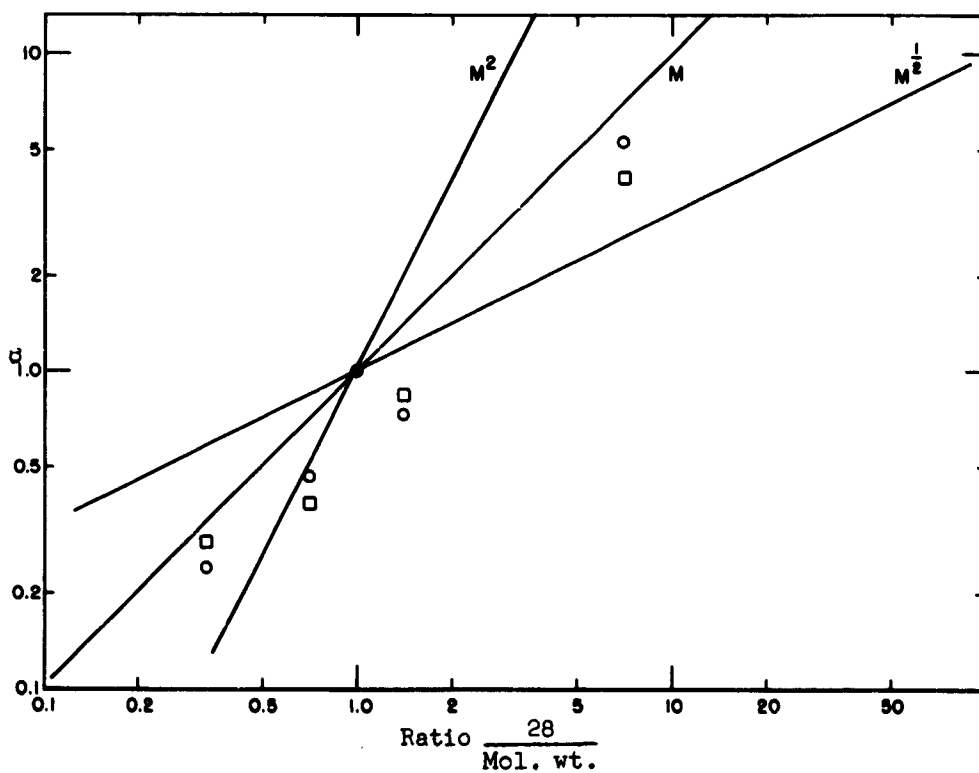

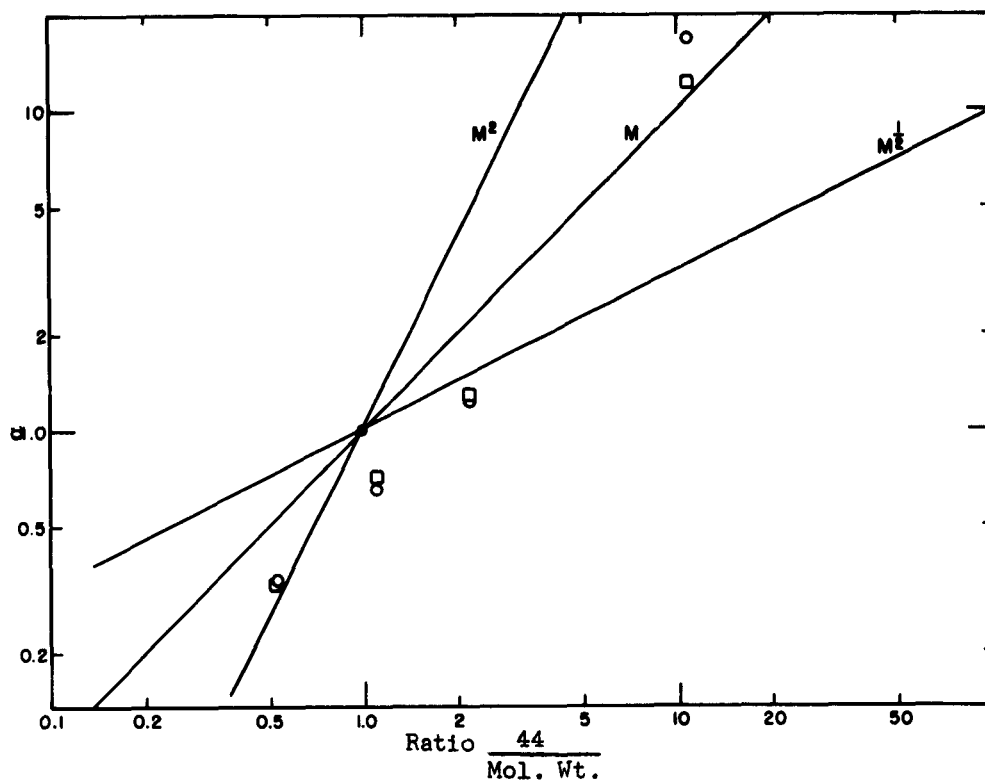Fig. 6 - Mass Separation of He, Ne, Ar and Kr in N_2 at One Atmosphere.

Fig. 7 - Mass Separation of He, Ne, Ar and Kv in CO_2 at One Atmosphere.
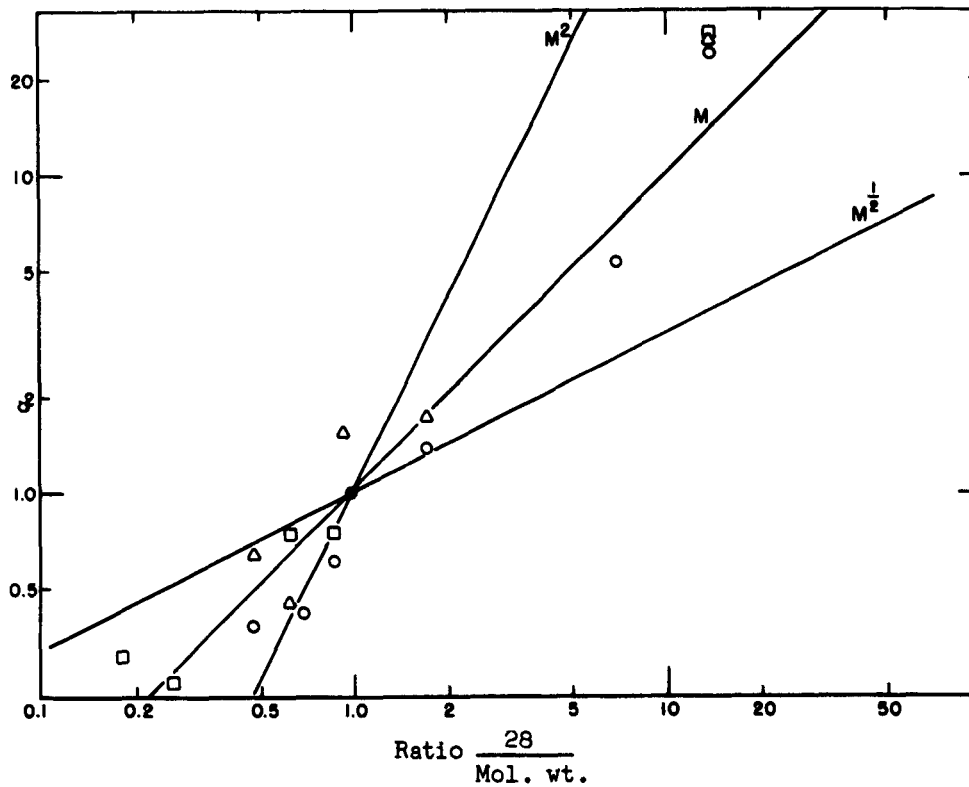

Fig. 8 - Mass Separation of H_2, He, CH_4, C_2H_6, C_3H_8, C_4H_{10}, O_2, Ar, CO_2, CF_3Cl and CCl_4 in N_2 at One Atmosphere.

Several features can be discerned in these plots. First, and most important, the data fall along a line whose slope is the same as that shown for a first power of molecular weight dependence. Second, within the rather bad scatter of points, the dependence of α on M seems to be reasonably independent of the chemical nature of the species, although the rare gases seem to fall slightly below the solvent and other solutes. To a first approximation then, good to about $^{\pm}25$ per cent, one can write $p_x = k\ I_x^{+}/M_x$, at constant temperature. This is to be contrasted with ordinary molecular flow sampling from a Knudsen cell for which $p_x = k\ I_x^{+}$ at constant temperature.

Much study remains to fully understand the behavior of mass separation and its dependence on the many variables in the aerodynamic molecular beam system. For instance, we have implicitly assumed above that in the supersonic beam all species have the same velocity when they enter the mass spectrometer ion source. To the extent that the heavier molecules are actually moving slower, their ionization probability will be higher and an apparent mass separation will result.

For the practical purpose of carrying out thermochemical studies in flames on other high pressure sources we feel the above data supply a sufficiently reliable mass correction, at least until the need for precise species pressure ratios arises. We will carry out mass separation studies with the inert gases in the actual flames to be used as solvents for metal addition, to verify that the same behavior is obtained.

III. FLAME STUDIES

The development of the high pressure sampling system has now progressed to the point that it should be quantitatively tested to determine whether satisfactory "quenching" is being obtained from the flames of interest. This can best be accomplished by sampling systems of known thermochemistry. Some of the problems involved in preparing for such testing are the measurement of the flame temperature under the actual conditions of the experiment, the introduction of the material to be studied into the flame, and the production of a chemical environment in the flame which is consistent with the species to be studied.

A. Temperature Measurements

A number of methods have been used to measure flame temperatures. These include thermocouple methods, total radiation methods, the line reversal method and a variety of spectroscopic methods. For our present work the line

reversal method has been chosen since it gives both good reliability and relative speed and simplicity. Although it can give erroneous results due to abnormal excitation (this is also true of the spectroscopic methods), this should not be a problem in the burnt gas region where equilibrium is generally achieved. Equipment for line reversal temperature measurement has been assembled and tested. We will now set up flames and simulated experimental conditions and measure temperature profiles through the burnt gas region.

B. Non-hydrogen Containing Flames

Obtaining a suitable chemical environment for studying a given species will not usually present much of a problem. The principal case in which difficulty may be expected is that in which an anhydrous or otherwise H_2 free flame is required. The anhydrous flames we have considered are those of $CO-O_2$, N_2O-CO, and $C_2N_2-O_2$. The N_2O-CO and O_2-CO flames were studied and found to burn without unreasonable difficulty even though preliminary mass spectroscopic analyses indicated a negligible quantity of H_2 in the oxidizer and fuel. Analyses for H_2O have not been carried out yet, but its partial pressure is expected to be quite low. A small quantity of C_2N_2 has also been obtained, and the $C_2N_2-O_2$ flame will be studied in the near future.

C. Additives in Flames

A few preliminary experiments testing the quenching efficiency of the high pressure sampling system have been carried out. About one per cent Cl_2 was introduced into a $CO-O_2$ flame, and the Cl radicals observed. No Cl_2^+ ions were detected, indicating that no appreciable recombination had occurred during the sampling process.

IV. FUTURE WORK

During the next quarter the major effort will be expended on actual flame systems. Mass separation effects of rare gases in flames will be determined to verify that the first power of the molecular weight enrichment holds for flames under our actual sampling conditions. Temperature and partial pressure profiles will be obtained for flames with and without additives and, in general, a systematic study of the flame parameters affecting flame sampling of known systems will be undertaken. In addition we will attempt to look qualitatively at several systems where new species or species of unknown thermo-chemistry may be expected. Chief among these will be aluminum in high partial pressures of H_2O at high temperatures.

REFERENCES

1. Milne, T. A., "Mass Spectrometric Study of Metal-Containing Flames," *Fifth Quarterly Technical Summary Report*, 1 October - 31 December 1962.

2. Deckers, J., and J. B. Fenn, *Rev. Sci. Instr.*, 34, 96 (1963).

3. Fenn, J. B., and J. Deckers, "Molecular Beams from Nozzle Sources," *Project Squid Technical Report*, PR-104-P.

4. Scott, J. E., Jr., and J. E. Drewry, "Characteristics of Aerodynamic Molecular Beams," *Project Squid Technical Report*, UVA 2-P.

5. Parker, H. M., A. R. Kuhlthau, R. Zapata, and J. E. Scott, Jr., "Rarefied Gas Dynamics," Pergamon Press, 69 (1960).

6. Kantrowitz, A., and J. Grey, *Rev. Sci. Instr.*, 22, 328 (1951).

7. Ramsey, N. F., "Molecular Beams," Oxford Univ. Press (1956).

8. Becker, E. W., et al., *Z. Naturforsch.*, 10a, 565 (1957) and 12a, 609 (1957).

9. Waterman, P. C., and S. A. Stern, *J. Chem. Phys.*, 31, 405 (1959) and 33, 805 (1960).

10. Reis, V. H., and J. B. Fenn, Report No. FLD-7, Princeton Univ., Mechanical Engineering Department, May 1962.