UNCLASSIFIED

AD NUMBER
AD439401
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited.**
FROM: **Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; MAR 1964. Other requests shall be referred to Defense Advanced Research Projects Agency, Washington, DC 20301.**
AUTHORITY
darpa per dtic form 55

THIS PAGE IS UNCLASSIFIED

MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

TENTH QUARTERLY TECHNICAL SUMMARY REPORT
1 January - 31 March 1964

Contract No. Nonr-3599(00)
ARPA Order No. 23-63, Amendment No. 38
Program Code No. 4910

MRI Project No. 2551-P

MAY 18 1964

For

Director
Advanced Research Projects Agency
Washington, D. C.

MIDWEST RESEARCH INSTITUTE

MIDWEST RESEARCH INSTITUTE

MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

by

Thomas A. Milne
Frank T. Greene

TENTH QUARTERLY TECHNICAL SUMMARY REPORT
1 January - 31 March 1964

Contract No. Nonr-3599(00)
ARPA Order No. 23-63, Amendment No. 38
Program Code No. 4910

MRI Project No. 2551-P

For

Director
Advanced Research Projects Agency
Washington, D. C.

This research was sponsored by the Chemistry Office of the Advanced Research Projects Agency under ARPA Order No. 23-63, Amendment No. 38, and monitored by ONR under 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 Mr. Roland Jackel and Dr. Ralph Roberts of the Power Branch, ONR. The report presents a summary of our current view of the high pressure sampling process and some experimental results on quenching equilibrium in flames.

The research staff consists of Dr. Thomas A. Milne, Project Leader, Dr. Frank T. Greene, and Mr. George Vowels. Dr. William Glauz, Mr. Fred Rollins, Mr. Lyle Taylor, and Mr. Bob Blackburn have contributed to this program through discussions.

Approved for:

MIDWEST RESEARCH INSTITUTE

Sheldon L. Levy, Director
Mathematics and Physics Division

12 May 1964

em

TABLE OF CONTENTS

SUMMARY

A summary is given of the present model of beam formation in high pressure sampling and of the effects associated with the process. Results of stable product analyses in CH_4-O_2-Ar flames and of a study of the dissociation of Cl_2 in CO-O_2-Ar flames are presented. Both studies showed successful quenching from 1-atm. flames.

I. INTRODUCTION

Although the experimental work during the last quarter has consisted mainly of actual temperature measurements and sampling of flames, the picture of the sampling process has been somewhat clarified. We have, therefore, taken the opportunity in this quarterly to summarize briefly our model of the high pressure sampling process and to correct certain observations made in previous quarterly reports. Two papers, which have been written for meetings and subsequent publication, give details of this picture. These are available as preprints. The results obtained in sampling flames for stable products and free radicals are also described, as are our future plans.

II. THE HIGH PRESSURE SAMPLING PROCESS

Our sampling system, which has been described in detail elsewhere,[1,2] consists of three differentially pumped stages between the sampling orifice and the ion source of a Bendix time-of-flight mass spectrometer. One improvement, currently being routinely used, consists of a vibrator-pulsed beam and detection system operated at 10 cps. This permits us to detect beam signals when the "random gas-to-beam" ratio is greater than 100. Table I summarizes the pumps, dimensions, and pressures for typical operation of the sampler. With this system, molecular beams with intensities of the order of 1×10^{17} molecules/cm^2/sec are obtained at 10 cm. from the sampling orifice.

The process of beam formation from high pressures has received considerable attention recently from aerodynamicists and others interested in obtaining very intense molecular beams.[3-8] It is generally accepted that the gas expands through the first orifice in continuum flow to form a supersonic jet. The second orifice is situated somewhere in this supersonic stream, and beam behavior can therefore be considerably altered by the relative positions of the two orifices and by the presence of shocks, both in the jet structure itself and at the second orifice. Our recent studies[9] indicate that under the usual conditions employed in our sampling system, the expansion behind the first orifice goes over into molecular flow well before the second orifice is reached, thus minimizing aerodynamic interactions with this orifice.

TABLE I

BEAM SYSTEM GEOMETRY AND OPERATING CONDITIONS DURING SAMPLING OF ONE ATMOSPHERE FLAMES

Stage	Pumps	Distance Beam Travels (cm.)	Typical Pressures (Torr)	Inlet Orifice or Slit
1	1,500 ℓ/sec oil diffusion pump	0.05-1.0	2-10 x 10^{-3}	0.12 mm. diam. hole in 90° cone
2	100 ℓ/sec oil diffusion pump	5.0	2 x 10^{-5}	0.25 mm. diam. hole in 60° cone
3	10 ℓ/sec Hg diffusion pump	23.0	3 x 10^{-6}	0.50 x 9 mm. slit
4	mass spec. ion source 400 ℓ/sec Hg diffusion pump	2.5	1 x 10^{-6}	0.75 x 12 mm. slit

The following simple picture is suggested as a first approximation to describe the sampling history of the gas. The gas along the center line, which ultimately forms the molecular beam entering the mass spectrometer, expands isentropically to quite large Mach numbers before going over into molecular flow. Calculations by Owen and Thornhill[10] for gas of specific heat ratio, $\gamma = 1.4$, and by Sherman[11] for several γ's, relate the jet Mach number to the distance from the orifice in orifice diameters. For a given γ , the results are independent of source pressure and temperature, stage one pressure, molecular weight, and orifice diameter. Mach number determinations with small nozzles or orifices have verified the calculations up to Mach numbers of 10 to 12, where apparent departures begin to occur, depending on pressure level.[4]

The expressions for beam intensity in an aerodynamic molecular beam, which were given originally by Kantrowitz and Grey[12] and modified by Parker et al.[13] and which we referred to in our previous work,[1] appear not to be applicable in our situation. When molecular flow exists at the second orifice, the Parker model of uniform parallel flow across the skimmer at Mach M and a sudden transition to molecular flow beyond the skimmer is clearly inappropriate. In fact, it is expected that the beam intensity under such conditions would be independent of skimmer area (provided line-of-sight from source to detector is not restricted by the skimmer) and dependent on first orifice area, instead of the reverse as is shown by eq. (1) in Ref. 2.

For the fall-off in density along the axis of the "free jet", the expansion of interest in sampling, Sherman[11] gives high Mach number limiting expressions as follows:

$$\rho/\rho_{\text{source}} \simeq \frac{A}{(\ell/r)^2}$$

Where A is a constant that depends on the effective γ of the gas being sampled and equals 0.632 for a γ of 5/3[11] and 0.350 for a γ of 7/5; ℓ is the distance from the sampling orifice and r is the radius of the sampling orifice. This limiting behavior is being used to develop a more realistic expression for beam intensity in supersonic beams when the transition to collisionless flow occurs well ahead of the skimmer. Since the Mach number is a known function of distance for the continuum part of the beam formation process and since the standard equations for isentropic expansion in flowing systems apply, we can obtain the T , P , density, collision frequency, or any property of interest for the gas during this part of the expansion. If at some point we assume a transition to molecular flow, where no further changes in the states of the molecules can occur, then we can make predictions as to what may happen during sampling.

Two major effects have been characterized in such a beam formation or sampling process, apart from the various parametric effects of system dimensions, scattering, etc. The effects are mass separation and polymer formation, and both can be explained nicely in terms of the above picture. Mass separation has been treated in our earlier work and refers to the phenomenon in which the composition of a gas mixture, going through the second orifice and finally ending up in the supersonic molecular beam, is usually depleted in the lighter components. Fenn[4] has recently attributed many of the observed separation effects to shock waves. We have found that the separation effect varies as the first power of the molecular weight, and is consistent with other evidence that shocks are not significant under our sampling conditions. It therefore appears that the simple molecular flow model of Waterman and Stern,[14] which predicts a first power of molecular weight dependence in the beam, applies to our results.

For sampling studies, we have verified the relation between observed

$$I_{x+} = k_x P_x (M.W.)_x$$

ion intensity in the mass spectrometer and species partial pressure and molecular weight (to within ±30 per cent) for a variety of species, concentrations, solvents and temperatures at 1 atm.[2] The effect decreases with pressure, but is still appreciable at several Torr. The importance of this relationship in quantitative sampling is clear.

The second effect, the occurrence of polymers in beams from high pressure sources, has also been reported by us in some detail.[15] As will be apparent from the quenching considerations below, as a gas expands from high pressure, its temperature drops so rapidly, relative to its pressure, that the gas may become supersaturated at some stage of expansion and a homogeneous nucleation process will ensue. The nucleation or condensation process will be arrested by the continued expansion to molecular flow, and in practice a surprising array of polymers will often be observed in the mass spectrum of the supersonic molecular beam. The relative extent of polymer formation observed in various gases can be qualitatively explained by considering the variation with γ in expansion rate and cooling, and by initial departures from saturation.

In some cases the polymers make up an appreciable fraction of the total. Thus, for H_2O or D_2O saturated argon at room temperature, the ratio of monomer ion to dimer ion is only about 4. Pure argon initially at 5 atm., and room temperature gives a few per cent Ar_2^+.

In identifying species in flames, such polymerization may occur for more strongly bound clusters than the primarily van der Waal's species shown in Table II. Thus, with condensible species the occurrence of dimers or higher polymers may be an artifact of the expansion process in the manner described. This process may also account for some of the ions of polymers observed in direct sampling of ions from high pressure flames.[16,17]

Accepting the simple picture of sampling and beam formations just presented, one can look at the history of the gas as it expands into molecular flow. For a thin circular orifice with sonic conditions existing uniformly across the effective diameter of the orifice (about 0.8 of the actual diameter) and assuming that the flame gases behave in expansion as a gas of constant γ, we can calculate T, P and stream velocity as e function of distance using the Owen and Thornhill relation between Mach number and distance. The second part of Table II summarizes the results for gases of $\gamma = 1.4$ (diatomic molecules with no relaxation of vibration and no heat effects due to shifting chemical equilibria) expanding from 1 atm. and 2500°K through a 0.12 mm. diameter orifice.

The time scale of the expansion is seen to be extremely short with very rapid temperature and pressure drop. Reactions with reasonably large activation energies would be expected to be rapidly quenched. As an example, the reaction $CO + OH \longrightarrow CO_2 + H$, known to control the conversion of CO to CO_2 in hydrocarbon flames, would be effectively quenched with a composition very near its value prior to sampling. The reaction $H + H_2O \longrightarrow H_2 + OH$, though somewhat faster, would still appear to be quenched readily. Radical recombination reactions and condensation reactions will be much slower initially, but being third-body reactions, they will be accelerated by decreasing the temperature, and will be quenched essentially by running out of collisions. The polymers mentioned above, however, are proof that such reactions can occur to an appreciable extent in some cases.

The above considerations of the expansion from the sonic condition at the throat of the sampling orifice to molecular flow lead to optimism that most species can be successfully quenched from 1-atm. flames. This part of the sampling process seems to be the one most usually considered in discussing quenching. Actually, however, the gases, in going from their undisturbed flow in front of the orifice to the sonic condition at the throat, experience a substantial cooling and pressure drop (apart from effects due to physical and thermal interaction of the flames with a cooler orifice of finite size). Thus, a typical burnt gas composition at 2500°K will be cooled to 2100°K at one-half the initial pressure simply in expanding to sonic flow. Therefore, this part of the expansion must also be considered.

TABLE II

AXIAL EXPANSION HISTORY OF A GAS DURING FORMATION OF A SUPERSONIC MOLECULAR BEAM

(Initial conditions: 1 atm., 2500°K, $\gamma = 1.4$,
0.0125 cm. orifice diameter, and
molecular weight 28)

Distance in Orifice Diameters from Throat of Orifice	Mach No.	Temp. (°K)	P (atm.)	Stream Velocity (cm/sec x 10^{-5})	Time from Orifice Throat (μsec.)
-2.0	0	2500	1.0		
-1.75	0.125	2495	0.99	0.12	-0.66
-1.5	0.25	2470	0.96	0.253	-0.40
-1.0	0.5	2380	0.84	0.497	-0.14
-0.5	0.75	2245	0.69	0.725	-0.090
0	1.0	2083	0.53	0.93	0
+0.5	1.6	1650	0.24	1.33	+0.067
1.0	2.6	1074	0.050	1.73	0.114
2.0	3.9	625	0.0075	1.97	0.19
4.0	5.6	350	0.00096	2.11	0.31
6.0	6.8	245	0.00029	2.17	0.43
8.0	7.8	190	0.00012	2.19	0.55
10.0	8.8	152	0.000055	2.20	0.66
	∞			2.26	

An approximate idea of the nature of the expansion to sonic conditions can be obtained from the simple point sink model by assuming incompressible flow. At two orifice diameters from the orifice, which is the closest to the orifice that this model seemed to be reliable, there is virtually no change in the gas properties. For the remaining distance, a linear change of the Mach number is assumed, since this appears to approximate the kinetically worst case. The results of these calculations are given in the first half of Table III. It can be seen that the entire expansion from the time that the temperature and pressure first begin to change, is complete in 1.5 to 2 μsec. This rate should be sufficiently rapid to satisfactorily quench most reactions.

TABLE III

RESULTS OF STABLE PRODUCT SAMPLING IN TWO CH_4-O_2-Ar FLAMES AT ONE ATMOSPHERE

Flame		Temp. (°K)	Composition, Partial Pressures in Atm.					
			H_2	H_2O	CO	O_2	Ar	CO_2
A $1CH_4$-$2O_2$-8Ar (avg. of 6 runs)	Meas.	2368	0.50	(16.4)*	1.81	1.95	(71.3)	9.23
	Calc.	2490	0.85	16.4	2.13	1.22	71.3	6.78
C $1CH_4$-$2.4O_2$-8Ar (avg. of 3 runs)	Meas.	2371	0.44	(16.13)	1.33	5.55	(69.2)	9.08
	Calc.	2485	0.45	16.13	1.26	3.91	69.2	7.39

Flame	Temp.	$K_{eq.}$ for $CO + \frac{1}{2}O_2 \longrightarrow CO_2$		$K_{eq.}$ for $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$	
		Meas.	Calc.	Meas.	Calc.
A	2368	36.4	56.0	234	316
C	2371	28.9	56.0	151	316

---

* Values in parentheses are calculated.

III. FLAME SAMPLING RESULTS

A. Stable Products

Continuing our systematic study of the factors affecting the ability to representatively sample 1-atm. metal-containing flames, we have studied the stable products in a number of CH_4-O_2-Ar flames. One such flame, a stoichiometric CH_4-O_2-Ar flame burning at about 2588°K, was reported in the last quarterly. We have obtained results on this and several other flames, including more detailed temperature measurements, during the past quarter.

Results for the two flames most thoroughly studied are shown in Table III. The agreement is felt to be satisfactory for both equilibria, the differences being as easily attributable to analytical calibrations as to failure to quench. A number of cooler and leaner flames were also studied, the results of which are shown in Table IV. Column (1) gives the composition of the unburned gases, column (2), the measured temperatures, and columns (3) and (4), the measured and calculated equilibrium constants for the equilibrium $CO + \frac{1}{2}O_2 \longrightarrow CO_2$. The results are seen to become progressively worse the cooler and leaner the flame (a single run on a CO-O_2-Ar flame is also shown). In these flames the CO concentration is obtained by correcting for the fragmentation pattern of CO_2, as determined from a room temperature calibration using a pure CO_2 beam. This involves an appreciable correction when the CO concentration is small.

The error in the experimental result is in the direction of too much apparent CO in almost every case. There are three possible reasons for this, each of which is being explored. First, there may be entrainment of N_2 in the inner flame in spite of quite extensive sheathing. Second, there may be incomplete combustion of the CO even 1 cm. beyond the reaction zone. Third, and most intriguing, the cracking pattern for CO_2 may change substantially from room temperature to the 2000° - 2370°K in the flames shown in Table IV. Support for this postulate is shown in the last column of Table IV, where the raw $44^+/28^+$ data are shown for each flame. The ratio seems to approach a limiting value of 5 to 6, compared to a value of 11 for room temperature CO_2. Stevenson[18] has reported substantial changes in the cracking pattern of CH_4 and more complicated molecules over a much smaller temperature range. The molecular beam source should prove valuable in carrying out studies of fragmentation patterns as a function of temperature.

TABLE IV

MEASURED CO-CO_2 EQUILIBRIA IN FLAMES

Flame	Composition (CH_4:O_2:Ar)	Measured Temperature (°K)	$CO + \frac{1}{2}O_2 \longrightarrow CO_2$ K_{eq} Experimental	K_{eq} Theoretical	$44^+/28^+$
Cooler ↓					
A	1:2:8.0	2368	36.4	56.0	3.6
A-1	1:2:8.7	2310	46.0	80.0	4.0
A-3	1:2:11.2	2173	47.7	200.0	5.4
Leaner ↓					
C	1:2.4:8	2371	28.9	56.0	4.4
D	1:2.9:7.4	2352	25.0	64.0	5.0
E	1:4.7:6.3	2249	13.7	120.0	5.4
G	1:8.6:0	2209	8.6	155.0	5.1
	(CO:O_2:Ar)				
CO-1	1:0.5:2.5	1784	79.5	5,600	7.8
Room Temperature - Pure CO_2		-	-	-	11.0

In view of the reasonable agreement in those cases where the stable products are all present in reasonable quantities, it seemed most profitable, as far as quenching studies are concerned, to go on to systems containing reactive species. One of the simplest test systems is the CO-O_2-Ar flame with a small amount of Cl_2 added. Preliminary results on this system were reported earlier.[1] We have now obtained more reliable data using sheathed CO-O_2-Ar flames. This flame was burned on a sheathed burner made by corrugating thin steel shim stock and rolling it into concentric cylinders. The flame and equilibrium presented certain problems. It was necessary to burn rather cool CO-O_2-Ar flames, and these were hard to stabilize with no hydrogen added other than that in the tank gases being used (less than 0.1 per cent). Furthermore, the Cl_2 inhibited the flames noticeably so that concentrations of 1 per cent or less were used, causing only a slight bulging of the otherwise flat reaction zone. During Na line-reversal temperature measurements, in which Na was introduced by passing the O_2 and Ar over molten NaCl, no Cl_2 could be present since it suppressed the atomic Na concentration to unusable values. With the low Cl_2 concentrations studied, however, temperature errors should be small.

Table V shows results of the Cl_2 dissociation study in three stoichiometric $CO-O_2-Ar$ flames at different temperatures. The relative cross-sections of Cl_2 to Ar have not yet been determined; the partial pressures of the chlorine species were calculated relative to argon, using cross-sections estimated as follows: $Ar:Cl:Cl_2 = 1:1:2$. Mass separation and fragmentation corrections were also made. The equilibrium constants obtained for the two hotter flames agree with the literature values as well as can be expected considering the probable error in the flame temperatures and cross-sections. Since the above method of treating the observed ion intensities is what will have to be done in studying completely unknown high temperature species, the agreement is encouraging.

Several more attempts have been made to detect the free radicals OH and O in H_2-O_2 and $CO-O_2$ flames, respectively, but so far without definitive results. It would be surprising if we failed to quench O atoms, in view of our success with Cl atoms, and a more detailed search is being undertaken.

TABLE V

CHLORINE EQUILIBRIUM IN A $CO-O_2-Ar$ FLAME

Temp. (°K)	P_{Cl_2}	P_{Cl}	$K_{experimental}$	$K_{literature}$
1784	4.8×10^{-4}	3.2×10^{-3}	0.021	0.086
2018	1.4×10^{-4}	8.6×10^{-3}	0.53	0.63
2152	1.4×10^{-4}	1.1×10^{-2}	0.94	1.60

IV. FUTURE WORK

The study of quenching ability will continue using F, Cl, and perhaps Br in the $CO-O_2-Ar$ flames. Tests with the HCl dissociation equilibria will also be made in H_2-O_2 flames. A concerted attempt to sample the free radicals O and OH will be made this quarter. Studies of the H atom would be more difficult by an order of magnitude due to the substantial mass discrimination effect with such a light species. Also this quarter we will pursue the quantitative sampling of condensible metal species in simple systems. A few tests will be run to resolve the question of the anomalous $44^+/28^+$ results in the $CO-CO_2$ equilibria.

REFERENCES

1. Milne, T. A., "Mass Spectrometric Study of Metal-Containing Flames," First through Ninth Quarterly Technical Summary Reports (1961-1964).

2. Greene, F. T., J. Brewer, and T. A. Milne, J. Chem. Phys., 40, 1488 (1964).

3. Scott, J. E., Jr., and J. E. Drewry, "Proceedings of Third International Symposium on Rarefied Gas Dynamics," Paris, June 1962 (Academic Press, 1963), p. 516. See also Bier, K., and O. Hagena, ibid., p. 478, and Fenn, J. B., and J. Deckers, ibid., p. 497.

4. Reis, V. H., and J. B. Fenn, J. Chem. Phys., 39, 3240 (1963).

5. Becker, E. W., and W. Henkes, Z. Physik, 146, 320 (1956).

6. Valleau, J. P., and J. M. Deckers, Can. J. Chem., 225 (1964).

7. Ko, Denny Ru-sue, "Drag of a Two-Dimensional Strip Normal to Hypersonic Near Free Molecule Flow," Report No. AS-64-4, Institute for Engineering Research, University of California, Berkeley, California, January 30, 1964.

8. Patterson, G. N., "Mechanics of Rarefied Gases and Plasmas," UTIAS Review No. 18, Institute for Aerospace Studies, University of Toronto, March 1964.

9. Greene, F. T., and T. A. Milne, "Mass Spectrometric Sampling of High Pressure-High Temperature Sources," to be published in Advances in Mass Spectrometry, Vol. III.

10. Owen, P. L., and C. K. Thornhill, Aero. Res. Council (U.K.), R & M No. 2616 (1948) (unpublished).

11. Sherman, F. S., Private communications to J. B. Fenn.

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

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

14. Stern, S. A., P. C. Waterman, and T. F. Sinclair, J. Chem. Phys., 33, 805 (1960).

15. Greene, F. T., and T. A. Milne, *J. Chem. Phys.*, *39*, 3150 (1963).

16. Green, J. A., and T. M. Sugden, Ninth Symposium (International) on Combustion, Academic Press, p. 607 (1963).

17. Van Tiggelen, A., "Ion Production and Concentration in Flames," University of Louvain, Second Annual Summary Report for Aeronautical Research Laboratory, USAF, May 1962.

18. Stevenson, D. P., *J. Chem. Phys.*, *17*, 101 (1949).