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MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

SECOND QUARTERLY TECHNICAL SUMMARY REPORT
1 January - 31 March 1962

ARPA Order No. 23-61, Amendment 17
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))

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by

Thomas A. Milne .

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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 early test results on a differentially pumped sampling system for one-atmosphere flames.

The research staff consists of Dr. Thomas A. Milne, project leader, and Dr. Jerome Brewer, who were assisted in the experimental work by Mr. George Vaughn and Mr. George Vowels. Useful discussions and guidance from Dr. Sheldon Levy and Mr. Gordon Gross have also contributed greatly to the program.

T.A.M.

Approved for:

MIDWEST RESEARCH INSTITUTE

Sheldon L. Levy, Director
Mathematics and Physics Division

30 April 1962

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SUMMARY

The differentially pumped apparatus for sampling one-atmosphere sources, described in the first quarterly report, has been completed and initial studies carried out. A usable molecular beam has been attained, originating from the second orifice, but its intensity is much lower than the maximum value predicted. In the present system, the gas expanding from the first orifice as a supersonic beam appears to be completely randomized before reaching the second orifice and very fast reactions, at least, cannot be quenched in sampling from one atmosphere.

I. INTRODUCTION

In the First Quarterly Report,[1] we described the experimental approach to be used to obtain thermodynamic information on metal-containing species in flames. In that report we discussed the reasons for studying one-atmosphere reacting systems and presented a schematic of the differentially pumped sampling system to be used for initial experiments.

The pumping speeds, orifice dimensions and over-all geometry were chosen to give expansion from one atmosphere to a pressure such that molecular flow could begin at the second orifice and a collision-free beam travel from there into the mass spectrometer. The work of Nutt, et al.,[2] served as a guide in predicting the conditions necessary for the molecular flow part of the apparatus. The processes occurring in the expansion from one atmosphere are less readily predictable and form a part of our current investigation. The details of our first apparatus and the results obtained with it are described in the next section, while future plans are outlined in the last section.

II. RESULTS AND INTERPRETATION

During the last quarter we have assembled the differentially pumped sampling system for one-atmosphere reactions, including the auxiliary equipment for measuring and controlling pressures in each stage and aligning of the several orifices and slits required. Experimental results have been obtained with this equipment on the simplest possible systems--noncondensible and condensible nonreacting gases such as argon and CO_2.

The differential pumping and transition to a molecular beam is accomplished with four pumping stages, each separated by an orifice or slit, all of which are in optical alignment. The orifice sizes, distances between orifices, and pressures obtained in typical runs are listed in Table I.

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[1] First Quarterly Technical Summary Report, "Mass Spectrometer Study of Metal-Containing Flames," 1 October - 31 December 1961, ARPA Order No. 23-61, Amendment 17, Project Code No. 9100, Contract No. Nonr-3599(00).

[2] Nutt, C. W., Botterill, J. S. M., Thorpe, G., and Penmore, G. W., _Trans. Far. Soc._, 55, 1500 (1959).

TABLE I

ORIFICE SIZES, GEOMETRY AND PRESSURES IN TYPICAL OPERATION OF DIFFERENTIALLY PUMPED SAMPLING SYSTEMS

Orifice or Slit No.	Size (in.)	Distance from Electron Beam in Mass Spec. (in.)
1	0.00645 dia. x 0.002 thick	12
2	0.00838 dia. x 0.002 thick	9
3	0.030 x 0.5 x 1/4 thick	5-3/4
4	0.030 x 0.5 x 1/4 thick	4-1/2

Stage No.	Typical Pressure (Torr)(argon)	Pumping Speed and Pump
0	760	Source, Manostatically controlled
1	8.2×10^{-2}	DK-90, 53 cfm Mech. Pump
2	4×10^{-5}	PMC-115, 110 1/sec Oil Diff. Pump
3	4×10^{-6}	1M2B, 10 1/sec Hg. Diff. Pump
4	1×10^{-6}	Mass Spec., 180/1/sec Hg. Diff. Pump

The choice of orifice sizes was dictated by the pumping speeds available and by the slits which form an integral part of the ionization source of the Time-of-Flight Mass Spectrometer. The last two slits were made with large L/R to take advantage of the low Clausing factor for random gas effusion through these slits while leaving the main molecular beam unaffected. A gain in beam-to-background effusion ratio close to that predicted from Clausing factors was observed experimentally as the slit thicknesses were increased. The choice of distances between slits and their shape was not based on any optimum design in these first experiments but was dictated largely by the geometry of the exit pipes leading to the exhaust pump, valves and traps. It was felt that results obtained with such an arbitrary arrangement might be of interest as representing the worst conditions that might occur if one uncritically designs and operates a simple differentially pumped sampler for one-atmosphere sources.

As can be computed from the data in Table I, molecular flow should occur from orifice No. 2, giving a scatter-free molecular beam. Such a beam has been obtained with argon and CO_2 at one atmosphere as confirmed by shutter dependency and variation of background pressures in the various stages. The beam intensities with argon and CO_2 were about the same when allowance is made

for the different response of the mass spectrometer to the two gases. The intensity of the molecular beam was such that a minimum partial pressure of 1×10^{-4} atm. could be quantitatively measured in the one-atmosphere gas. In the case of the argon, however, the shutter-dependent beam signal was accompanied by a very large signal due to background gas effusing into the mass spectrometer from the third stage. This background gas amounted to 80 per cent of the total contribution to the argon peak, but did not invalidate quantitative measurements on the shutter-dependent part of the signal (the shutter was placed midway in stage 2). Such an effect was not observed with CO_2 due to the much lower background pressures caused by the condensation of CO_2 on the liquid nitrogen cold trap placed in stage 2.

It is very difficult to predict a priori what fraction of the random gas effusing from stage 3 will contribute to the ion signal since the fraction pumped away by the mass spectrometer before passing through the ionizing electron beam is unknown. However, the results indicate that an appreciably faster pump would be desirable in this last stage.

With the arrangement of slits described above, it was found that the beam intensity and the pressures in each stage were a function only of the pressure in stage 1, regardless of whether the gas from the one-atmosphere source entered through orifice No. 1 when it was aligned or badly misaligned or whether it was bled in at the side of stage 1 through a needle valve. This indicates, not surprisingly, that the ordered motion of the supersonic jet of gas which initially emerges from orifice No. 1 is effectively dissipated by the long distance in background gas through which it must travel, or by shock waves set up somewhere between the two orifices.

In perhaps the severest test that could be devised for the ability of the present system to quench an equilibrium at one atmosphere, the system $N_2O_4 \rightleftharpoons NO_2$ was sampled. At one atmosphere and 298°K, the fractional dissociation of N_2O_4 is only 0.19. At 10^{-4} atm. the value is about 0.9987 so that if no effective quenching of the dissociation occurs during the expansion to the second orifice, then very little N_2O_4 would be detected in the molecular beam. The kinetics of this dissociation make it one of the most rapid known, and the present sampling system was incapable of freezing a measurable amount of N_2O_4; no species attributable to it were observed in the mass spectrometer.

III. FUTURE WORK

The results with the sampling system as described above can be summarized as follows:

a. A reasonably collision-free, shutter-dependent molecular beam has been obtained from one-atmosphere sources, but for noncondensible gases the ratio of beam-to-background gas is much higher than desirable.

b. The sensitivity of the system and mass spectrometer is such that the limiting partial pressure of species that can be detected in a one-atmosphere source is about 1×10^{-4} atm.

c. The gas expanding into the first stage appears to be completely randomized by the time it reaches the second orifice and no quenching of a very fast dissociation equilibria was obtained.

To improve the situation in (a), two approaches are being considered. First and simplest, one can use larger pumps in stages 2 and 3. Second, simple tests are under way to try to modulate the molecular beam by means of a shutter operating at frequencies of the order of 100 cycles/sec. This would lead to an ac signal coming out of the mass spectrometer electrometer output which could then be separated from the dc output due to all sources of gas other than the molecular beam. Such a technique is complicated in the case of the Bendix Time-of-Flight mass spectrometer because the normal unmodulated output is itself made up of 10,000 pulses of ions per second so that capabilities of this technique are uncertain. In either event, the present ratio of beam to random gas is sufficient to allow continued study of other parameters, as described below, while investigating the above changes.

The sensitivity mentioned above in (b) is lower than the most optimistic value that could be predicted by several orders of magnitude-- another indication that the expanding gas in stage 1 is completely randomized by the time it reaches orifice No. 2. This sensitivity can be improved by placing the second orifice much closer to the first orifice. This will also affect the ability to quench equilibria, mentioned in (c).

During the next quarter we will make changes in the position and shape of orifice No. 2 relative to orifice No. 1, with the corresponding changes in the other slits and dimensions, so that a molecular beam will always be present downstream of orifice No. 2. Such changes will be guided

by the work of Kantrowitz and Grey,[3] Kistiakowski and Slichter,[4] and Zapata, and co-workers.[5]

The best design of sampling system that emerges from the above study will then be tested by investigating, as far as is practical, a series of simple equilibria with rates of reaction covering a range from quite slow to very fast. The kinds of equilibria of interest in our ultimate investigation of metal-containing flames will involve condensation and may present entirely different quenching problems than simple homogeneous equilibria.

The results of the program outlined above will determine whether one-atmosphere flame studies are practical or whether reduced pressure flames, with the corresponding greater ease of sampling, must be used.

[3] Kantrowitz, A., and Grey, J., The Review of Scientific Instruments, 22, 328 (1951).

[4] Kistiakowski and Slichter, ibid., 333 (1951).

[5] Zapata, Parker and Bodine, "Rarefied Gas Dynamics," Supplement 1 of Advance in Applied Mechanics, pp. 67-81, Academic Press, 1961.