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Comprehensive Mechanisms for Combustion Chemistry:
An Experimental and Numerical Study with Emphasis on Applied Sensitivity Analysis

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Prepared by:

Frederick L. Dryer
Principal Investigator
Professor

Richard A. Yetter
Co-Investigator
Research Scientist

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Mechanical and Aerospace Engineering
School of Engineering and Applied Sciences
Princeton University
Princeton, New Jersey 08544-5263

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Abstract

This research program is an integrated experimental/numerical effort to study pyrolysis and oxidation reactions and mechanisms for small-molecule hydrocarbon structures under conditions representative of combustion environments. The experimental aspects of the work are conducted in large diameter flow reactors, at pressures from one to twenty atmospheres, temperatures from 550 K to 1200 K, and with observed reaction times from 10^{-2} to 5 seconds. Gas sampling of stable reactant, intermediate, and product species concentrations provide not only substantial definition of the phenomenology of reaction mechanisms, but a significantly constrained set of kinetic information with negligible diffusive coupling. Analytical techniques used for detecting hydrocarbons and carbon oxides include gas chromatography (GC), and gas chromatography/Fourier Transform Infrared spectrometry (GC/FTIR) for off-line analyses. Non-Dispersive Infrared (NDIR) and FTIR methods are utilized for continuous on-line sample detection of light hydrocarbons, carbon oxides, oxygenated species, and water. Laser induced fluorescence and resonance absorption measurements of OH have also been performed in an atmospheric pressure flow reactor (APFR), and a variable pressure flow (VPFR) reactor has been developed specifically to accommodate optical measurements of radicals and highly reactive molecular intermediates.

The numerical aspects of the work utilize zero and one-dimensional pre-mixed, detailed kinetic studies, including, path, elemental sensitivity gradient, and feature sensitivity analyses. The program emphasizes the use of hierarchical mechanistic construction to understand and develop detailed kinetic mechanisms. Numerical studies are utilized for guiding experimental parameter selections, for interpreting observations, for extending the predictive range of mechanism constructs (by comparison with literature data from other kinetic experiments), and to study the effects of diffusive transport coupling on reaction behavior in flames. Modeling using well defined and validated mechanisms for the CO/H_2/Oxidant systems and perturbations of experimental oxidations by small amounts of additives are also used to derive absolute reaction rates and to investigate the compatibility of published elementary kinetic and thermochemical information.

Over the last three years, this program has made significant progress on a number of problems These include: 1) Continuing development of a comprehensive experimental data base for the oxidation of the $CO/H_2/O_2$ system; 2) Development and continuing refinement of a comprehensive kinetic mechanism for the $CO/H_2/O_2$ system 3) Additional experiments on formaldehyde oxidation in the APFR, comprehensive mechanistic studies inclusive of flow reactor results and literature results from static reactors, shock tubes, and flames, and identification of elementary reactions needing further study; 4) A mechanistic study of previously acquired APFR flow reactor data on ethanol oxidation, including an estimation of the branching ratios for C_2H_5OH + X, X= OH, H and identification of elementary reactions needing additional study; 5) Completion and mechanistic evaluation of the first *insitu* optical diagnostic measurements of OH in the APFR; 6) Experimental determinations of the uni-molecular decomposition rate for 1,3,5-Trioxane at temperatures from 700 to 800 K; 7) Demonstration of seeded perturbation experiments on the moist CO oxidation in flow reactors as a means to determine elementary rate constants for specific reactions; 7) Determination of elementary rates for CH_4 + OH $\rightarrow$ CH_3 + H_2O at 1026 and 1140 K, and C_3H_6 + OH $\rightarrow$ products at 1020 K; 8) First experimental studies of the H_2/O_2 reaction system in the VPFR at conditions between the extended second and third explosion limits.

Continuing efforts are presently: 1) Publishing additional APFR measurements and mechanistic results on the complex dependence of the moist CO oxidation rate on oxygen concentration; 2) Extending previous efforts on methanol oxidation by additional experimental efforts in the VPFR to twenty atmospheres, with subsequent mechanistic studies inclusive of the previous and new flow reactor data, as well as literature results from shock tubes, static reactors and flames; 3) Experimentally and numerically studying the H_2/O_2 $CO/H_2O/O_2$, $CO/H_2/O_2$ reaction systems at elevated pressures in the VPFR to 15 atmospheres; 4) Adapting prior OH resonance absorption measurements utilized in the APFR to the VPFR; 5) Developing a lamp-based resonance absorption approach to measure CH_3.

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I. Program Overview

The assembly and validation of detailed kinetic mechanisms is an important aspect of developing understanding of chemical processes occurring in combustion systems. The resulting mechanisms provide useful tools in determining what elementary reactions require further study, in acting as bench marks against which simplified empirical chemistry (needed for complex reacting flow modeling) can be developed and tested, and in evaluating the interactions of chemistry and transport phenomena in simple one-dimensional systems. Moreover, comprehensive mechanisms (Westbrook and Dryer, 1981, 1984), evaluated and validated over large ranges in pressure, temperature, and equivalence ratio are necessary in simulating combustion environments. This is especially so for small hydrocarbon and hydrocarbon oxygenates (up to C_4 species), since their reactions often dictate the overall radical pool characteristics and contribute significantly to the pressure dependence of the reaction mechanism.

I.A. Introduction

The role of this project is to provide an interface for fundamental elementary chemical kinetic, thermochemical, and chemical dynamic research with the needs generated by combustion systems applications. The principal transfers to the combustion community involve: 1) the supply of "building blocks" for the reaction chemistry needed to model conventional fuel combustion/emissions chemistry; 2) tools to determine which elementary processes are important; 3) bench marks for semi-empirical chemistry model development and testing; and 4) mechanisms to study interactions of chemistry and transport in simple one-dimensional configurations. The principal transfers to the fundamental science community have been, through kinetic systems studies, to define in relative terms which elementary process/reaction/thermochemical parameters need to be better characterized to achieve accurate predictive kinetic modeling.

The work follows a "hierarchical" approach to detailed kinetic studies (Westbrook and Dryer, 1981) by considering increasingly complex models as composites of smaller systems. These systems are studied in a comprehensive manner (by considering a wide range of conditions and comparison with numerous experimental sources over those wide ranges of parameters), and then the results of such studies are utilized as the "base mechanism" for the next, more complex system. With the exception of pre-mixed laminar flames themselves (in which chemical kinetics are strongly coupled with diffusive transport), no single experimental technique provides either the elementary or composite chemical kinetic data which are required for mechanism development and validation over the range of parameters important in combustion. Thus, data from several sources, such as shock tubes, flow reactors, and static reactors, as well as flames, are necessary for performing the task. The "comprehensive" character of such an approach depends strongly on the available elementary and mechanistic kinetic data, and thus as additional data become available, revisions and updating of constructs are important at each mechanistic level. The specific

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experimental contribution to these endeavors made by this program is the generation of data on mechanistic behavior through the use of flow reactor approaches.

Over the past thirty years, flow reactors at Princeton (Crocco, et al., 1957) have been an evolving and important source of pure chemical kinetic information for the pyrolytic and oxidative behavior of various molecular structures at atmospheric pressure and near 1000 K. Typically, quasi-steady flows of reacting mixtures, highly diluted in nitrogen, are produced, and quenched gas samples are withdrawn at various reaction times. Subsequent gas chromatographic and non-dispersive infrared analyses lead to definition of stable reactant, intermediate and product concentration data as a function of reaction time. During the last fifteen years, the Princeton atmospheric pressure flow reactor (APFR) (Dryer, 1972; Yetter, et al., 1991a) has been a principal source of mechanistic data for CO/H_2/Oxidant mixtures, alkanes (through octane), alcohols (through C_4), aldehydes (through C_2), and aromatics (through 1-methyl-naphthalene; Shaddix, 1993), as a result of the efforts of both this group and that of Glassman (Dryer and Glassman, 1978; Brezinsky, 1985; Glassman, 1987; Dryer, 1991). Flow reactor data have provided not only phenomenological insights into mechanisms for pyrolysis and oxidation, but have been a source of information for validation of proposed detailed kinetic mechanisms.

I.B. Program Accomplishments and Directions

This section summarizes recent efforts of this program which have appeared in the archival literature since 1990. Appendix A of this progress report contains a collection of the published abstracts. A collection of archival publications is forwarded as an attachment to this report.

Considerable effort has been devoted to comprehensive mechanism development for the $CO/H_2/O_2$ oxidation system, which characterizes the base description of the hydrogen/oxygen radical pool interaction for larger mechanisms (Yetter, 1985; Yetter, et al., 1991a, 1991b; Roesler, et al., 1993). Parametric experiments in an atmospheric pressure flow reactor were conducted to develop a detailed characterization of the reaction system at temperatures from 852-1138 K (Yetter, et al., 1991a). Model predictions have been compared against shock tube and these and other various types of reactor data which collectively encompass the temperature range 823-2870 K. Perturbations of this reaction system by small amounts of hydrocarbons have also been studied as a means of elucidating specific elementary reaction processes (Yetter, 1985; Yetter and Dryer, 1992).

The underpinnings of these studies have been the development of refined APFR experimental techniques, which recently included the first measurements of [OH], (Linteris, 1990; Linteris, et al., 1991a, 1991b), as well as advances in and application of elementary/feature sensitivity analyses to the study of reaction mechanisms (Yetter, et al., 1984, 1985), kinetic/diffusive coupling (Smooke, et al.,1989; Vadja, et al., 1990; Mishra, et al., 1991; Hochgreb and Dryer, 1992b), and extraction of elementary rate information from complex reaction data (Yetter, et al., 1984, 1985, 1989; Yetter and Dryer, 1992). Through

this work, a comprehensive detailed mechanism for $CO/H_2/O_2$ kinetics has been developed which spans static reactor, flow reactor and shock tube conditions near atmospheric pressure. The development of this mechanism has also been critical to other programs which have subsequently studied the inhibition of the moist CO oxidation (Roesler, et al., 1992a, 1992b) by HCl.

A similar analysis has recently been completed for CH_2O oxidation (Hochgreb, 1991; Hochgreb and Dryer, 1992b). In this work, the oxidative-pyrolysis and oxidation of CH_2O (which adds interactions of CH_2O and HCO to the $CO/H_2/O_2$ system) were studied in the APFR (Hochgreb, 1991; Hochgreb, et, et al.,990; Hochgreb and Dryer, 1992a), at temperatures from 943-1045 K, and numerical predictions were compared with these data, as well as those from static reactors, shock tubes, and flames. Specific elementary reactions which need additional definition to improve model performance were identified. Ancillary efforts also produced a near-high pressure limit measurement for the decomposition rate of 1,3,5-Trioxane (Hochgreb and Dryer, 1992a).

As the next extension incorporating these sub-mechanisms, the oxidation (Norton, 1990; Norton and Dryer, 1989, 1990b) and the pyrolysis (Norton and Dryer 1990a) of methanol have been studied, adding the interactions of CH_3OH, CH_3O, and CH_2OH. The pyrolysis modeling efforts also considered shock and static reactor conditions (especially the branching ratios and relative importance of CH_3O and CH_2OH reaction channels). However, we chose to delay comprehensive modeling of the oxidation, pending completion of new flow reactor experiments on methanol oxidation at pressures to twenty atmospheres (Held, 1993).

In similar work Egolfopolous, et al., 1992a have recently completed a comprehensive modeling of our atmospheric pressure data, as well as their own premixed flame propagation data. This work constructed a methanol oxidation model by incorporating methanol reactions from our work (Norton, 1990) into earlier constructs (Egolfopolous and Law, 1990a, 1990b). However, the modeling efforts are open to question (Grotheer and Just, 1992), since the authors mistakenly used a rate expression for the reaction $CH_3 + OH \rightarrow CH_3O + H$ that actually refers to the low-lying channel $CH_3 + OH \rightarrow CH_2OH + H$. Combination of this rate with current thermochemical data for CH_3O, leads to a rate some two orders of magnitude greater than collision frequency for the reverse reaction ($CH_3O + H$). (This mishap was in part from a misleading listing of reaction parameters by Roth and Just, 1985, a further adoption of this error by Dagaut et al, 1988, and subsequent inclusion of the error in the developments by Egolfopolous, et al., 1990a, 1990b, 1992. Unfortunately, this error is also present in the recent review of Baulch, et al., 1992.) It appears that this error is important to matching the experimentally determined flame velocity and may also be the source of the questionable result that Egolfopolous, et al., 1992a must reduce the rate for $CH_3OH + OH \rightarrow CH_3O + H$ by a factor of three (from that of Hess and Tully, 1989) to obtain agreement with our flow reactor data.

Finally, the oxidation of ethanol (which adds not only C_2H_5OH and the C_2H_5O isomers, but

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CH₃CHO and C₂H₄ sub-mechanism components to those considered above) has been investigated in the flow reactor in some detail (Norton and Dryer, 1992). The specific issues addressed in this work point to the importance of the reaction branching ratios leading to the three reaction channels associated with the various C_2H_5O isomers, and the need for improved understanding of the acetaldehyde and ethene sub-models. The oxidation of several other oxygenates (n- and iso-propanol, t-butyl alcohol, methyl-tert-butyl ether) were also briefly studied (Norton and Dryer, 1990b). While these works did not consider comprehensive modeling of data from other sources, the results of these studies have also served as important examples of considering isomeric branching ratio effects on oxidation behavior and as experimental and mechanistic inputs to several other recent modeling studies (Egolfopolous, et al., 1992; Curran, et al., 1992; Dagaut, et al., 1992).

The above efforts, all associated with experiments in the APFR, have provided a significant part of the experimental base for developing mechanisms for larger hydrocarbons (see, for example the many works of Westbrook et al.) through hierarchical model construction (Westbrook and Dryer, 1981, 1984). The reactions of the above as well as other small molecules and their fragments strongly influence the mechanistic behavior of larger molecule pyrolysis and oxidation which are typically relevant to conventional combustion system performance and emissions. Yet, the extrapolation of atmospheric pressure chemistry (in general) to pressures which encompass those found in combustion systems (such as internal combustion engines) is severely complicated (Dryer, 1991; Vermeersch, 1991; Vermeersch, et al., 1991). A limited range of pressures has typically been studied in fundamental kinetics experiments, particularly in the 600 to 1100 K temperature range where pressure can considerably influence the relevant chemistry. At atmospheric pressure, the reaction times and temperatures over which the above mechanistic transitions often occur are low in comparison to adiabatic flame temperatures, and fall in a regime which is difficult to study using static reactors (reaction times very short; heterogeneous reactions and inhomogeneities present) or atmospheric pressure flow reactors (reaction times too long). However, as reaction pressure is increased, reaction times become considerably shorter (both from density effects and changes in mechanism). The importance of the pressure response of chemical kinetics in combustion systems emphasizes the need to understand more fully the interactions of molecular oxygen with hydrocarbon radicals, the reactions of simple olefins and oxygenates, and, especially, the reactions of HO_2 radicals. This chemistry is especially important in terms of the chemistry which affects autoigntion in and the molecular types and quantities of hydrocarbon emissions produced by combustion devices. Few experimental and numerical studies have addressed the effects of pressure on reaction systems at temperatures in the 600 to 1200 K range prior to 1990.

In 1987, under sponsorship of the Department of Energy, Office of Energy Conservation Utilization Technologies (ECUT), we first conceived of a new variable pressure flow reactor (VPFR) to provide data on combustion chemistry of large molecules (>C₄), simple reference blends of pure components, and full-distillation-range mixtures characteristic of conventional fuels. The principal motivation of this work was to elucidate the autoigntion and emissions chemistry for spark ignition engine applications, both in the above

temperature range, and for conditions inclusive of the cool flame chemistry regime. This project also provides experimental data for others pursuing detailed numerical modeling of large molecule oxidation kinetics (e.g. Westbrook, Pitz, and their colleagues) as well as those interested in semi-empirical description of two-stage ignition processes. Actual construction was initiated in March of 1989, supported by ECUT (and later by the Office of Industrial Technology, Advanced Energy Concepts Division, OIT/AECD), the University, and industry (Mobil Research and Development Corporation), with initial operations commencing in May of 1990, and the facility has continued to evolve since that time. The design concepts for this reactor are more fully described elsewhere (Vermeersch, 1991; Vermeersch, et al., 1991), and the present characteristics of the experimental facility, including recent modifications, are briefly described here in Appendix B.

As a result of this ongoing development, we proposed in our renewal for the present effort (1989) that our future work in this program (on small molecule and oxygenate kinetics) should take directions toward encompassing a significant range of pressures. As part of this effort, we also desired to build a foundation for more routine use of *insitu* optical diagnostics in quantifying radical and other reactive species. Coincidental with the DOE/BES APFR experimental work described above and its interpretations, we have pursued these new directions.

The operating characteristics of the VPFR were initially demonstrated through experimental studies of hydrogen/oxygen (jointly supported by DOE/BES and DOE/OIT), methane, and n-butane (Vermeersch, 1991; Vermeersch, et al., 1991). (Other research conducted on behalf of DOE/OIT is reported elsewhere (Dryer, 1992)). Preliminary comparisons of H_2/O_2 measurements with predictions using our original model suggested that the H_2/O_2 subset of the $CO/H_2/O_2$ comprehensive mechanism of Yetter, et al., 1991b, was reasonably predictive at high pressures (to 9 atm.) under stoichiometric conditions (Vermeersch, et al., 1991). Recently, we have been extending these published studies on the H_2/O_2 system in the VPFR to a larger range of pressures, temperatures, and equivalence ratios. We have also been developing an expanded experimental data base on $CO/H_2/O_2$ to 15 atm. (Kim, 1993), and we have completed experimental studies on methanol oxidation over a range of stoichiometries, to 20 atm. pressure (Held, 1993).

We have, since the inception of this program, strongly supported the notion that kinetic information could be enhanced by judicious measurement of some of the key radical concentrations profiles in specific flow reactor experiments. *Insitu* optical measurements of highly reactive molecular intermediates which sampling processes may affect is also of similar importance. The efforts we have put forth on *insitu* optical diagnostics studies of OH in the APFR were well-conceived (Linteris, 1990; Linteris, et al., 1991a, 1991b) but comparatively difficult ones in this configuration (a source of much delay in achieving results). This experience has led to the novel configuration of the VPFR in which we will make future measurements. The substantial apparatus modifications (the order of $200,000) we have pursued offer a significant improvement in potential for optical measurements.

Additional instrumentation necessary to apply optical diagnostic radical measurements of [OH] in the VPFR were part of the previous renewal proposal for this program (1989), but reductions in funding level precluded support of this part of the proposed work. We considered this issue important enough to use our own limited discretionary resources to develop most of the hardware to accommodate *insitu* laser resonance absorption measurements of [OH] in the VPFR. Unfortunately, an unexpected laser system failure, prevented optical diagnostic measurements of OH as part of these studies in the new facility. However, hardware is now fully in place for OH absorption studies and should be operable later this spring. We have also suggested approaches to measure CH_3 and HO_2. for which supplementary funding from DOE/BES has recently been provided (Septmber, 1992). These approaches are briefly described in Appendix B.

Progress on much of the research stemming from recent investigations in the VPFR is currently unpublished, and these efforts are briefly summarized below.

I.C. Recent (Unpublished) Work

This section briefly describes work presently underway on extending the data base for the H_2/O_2, $CO/H_2/O_2$, and methanol oxidation systems. The H_2/O_2 and $CO/H_2/O_2$ reaction mechanisms form the foundation on which all hydrocarbon oxidation reaction mechanisms are constructed (Yetter, et al., 1992). Uncertainties in these mechanisms can therefore propagate through and significantly affect the validations of more complex mechanisms. It is therefore important in the development of hydrocarbon mechanisms that a well developed, validated mechanism be used. We have to date postponed further work on extending the pressure range over which the formaldehyde oxidation is investigated, pending further developments on supplying formaldehyde vapor to the VPFR. Instead, we have pursued extending investigations of the methanol oxidation system to higher pressures. Numerical modeling efforts are simultaneously being pursued on all of the systems.

I.C.1 New Results on the H_2/O_2 System

Significant prior efforts have developed the most comprehensive $CO/H_2/O_2$ reaction mechanism available in the literature (Yetter, et al., 1991b). As a result of the new range of pressures available in the VPFR, new opportunities have existed to expand the experimental characterizations of this system to conditions more similar to those found in energy conversion devices. As noted above, some initial experiments on the H_2/O_2 system were performed during the development of the VPFR (Vermeersch, 1991; Vermeersch, et al., 1991). These early studies were limited (in terms of the conditions that could be studied and the species which could be measured) by the developing state of VPFR gas heating facilities and the analytical sampling system. As described in Appendix B, the VPFR system is now fully functional, with a much more extended operating envelope, and a full complement of on-line and off-line extractive sampling techniques. (*Insitu* optical methods will be available later this calendar year.)

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Additional experiments have been underway on both the H_2/O_2 and $CO/H_2O/O_2$ systems (Kim, 1993) since early 1992. This work can be best characterized in the context of the H_2/O_2 explosion limits shown in Figure 1. (The classical explosion limits are the solid lines.) The second limit is due to the competition of the $H + O_2 \rightarrow OH + H$ branching versus the $H + O_2 + M \rightarrow HO_2 + M$ chain terminating reaction. The third limit is a thermal limit with some small amount of branching due to additional reaction paths available through formation of H_2O_2 and its subsequent decomposition. The experimental initial conditions for H_2/O_2 experiments conducted thus far are shown on Figure 1 as circles, where we have varied the initial temperature, stoichiometry, and in particular the pressure. The experimental data were then compared to model predictions using the $CO/H_2/O_2$ mechanism developed by Yetter et al, 1991b.

Experiments were first conducted at fixed mole fractions of reactants, and initial temperature at various pressures for equivalence ratios of 1 and 0.25. The stoichiometric data are shown in Figure 2. The 3 atmosphere data lie near the "extended" second explosion limit and thus show the transition from slow to fast reaction (from self-heating) as the system goes from nearly straight chain character to chain branching. Kinetically, this is due to the competition of the chain branching $H + O_2 \rightarrow O + OH$ and the terminating $H + O_2 + M \rightarrow HO_2 + M$ reactions. As the pressure is further increased, the $H + O_2 + M \rightarrow HO_2 + M$ reaction dominates the branching reaction so that the overall reaction rate is steady. From this graph, the pressure dependence of the slow reaction was found to be proportional to $P^{0.56}$.

In a second set of experiments, the effect of oxygen addition on the "extended" second explosion limit behavior was investigated. Figure 3 shows the hydrogen mole fraction as a function of reaction time for the same hydrogen mole fraction and initial temperature as Figure 2. For the stoichiometric case, a transition from slow to fast reaction is again clearly evidenced. Increasing the oxygen content is observed to have two effects. First, the system no longer exhibits crossing of the extended second limit although the same heat release occurs. This result occurs because the additional oxygen concentration increases the explosion temperature. Secondly, the oxygen addition increases the overall rate of the slow reaction; this increase was found to be proportional to $X_{O2}^{0.6}$. Sensitivity analysis and reaction flux calculations indicate increased importance of rates involving H_2O_2 and HO_2. The reactions $H_2O_2 + H \rightarrow HO_2 + H_2$, and OH attack on H_2O_2 and HO_2, are most likely responsible for the decreased amount of branching in the system and the increased rate of the slow reaction. The classic work of Lewis and von Elbe, 1951 examined the effect of changing the equivalence ratio on the second explosion limit by varying the total pressure of static reactor experiments. Upon careful consideration, it is clear that their data is dominated by the pressure effect rather than the oxygen addition effect. Thus, this work appears to be the first to clearly show the effect of oxygen addition on the second explosion limit in a isobaric, adiabatic, nitrogen-diluted system.

Another set of experiments has examined the effect of varying the initial temperature on the kinetics between the third and "extended" second explosion limits. Experiments were

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performed at 6 atmospheres, an equivalence ratio of 0.30 and initial temperatures between 881 K and 934 K. Figure 4 displays the natural logarithm of the normalized H_2 mole fraction as a function of reaction time. At 934 K, the data shows a rapid, but steady reaction. What is interesting about this plot is that the system shows a high overall activation energy (around 100 - 120 kcal/mole) at the low temperatures. This is especially evident in experiments with initial temperatures of 881 K and 887 K. The system reacts very slowly initially and then abruptly transitions into a much faster chemistry as the exothermicity of the reaction drives the system into a different chemical regime. Numerical modeling work indicates this abrupt transition is accompanied by a peak in the H_2O_2 concentration. After this peak, H_2O_2 is noted to decompose rapidly into OH radicals, thus explaining the rapid reaction. This behavior was noted by Lewis and Von Elbe as characteristic of third explosion limit behavior. Work in progress is investigating whether this phenomena can be seen at higher pressures and lower temperatures. If this is the third explosion limit, it would the first such data ever reported for fuel lean conditions and non-diffusive systems. Currently, the model offers a good description of the stoichiometric chemistry for the full pressure range studied (e.g. see Fig. 5). However, at fuel lean conditions where HO_2 and H_2O_2 chemistry is known to become more important, the model is too fast relative to the data. Additional modeling efforts will be necessary to determine which specific reactions are most likely the source(s) of this discrepancy.

I.C.2. New Results on the $CO/H_2/O_2$ System

The $CO/H_2/O_2$ system is also presently under study to examine the effect of pressure on the CO system from 3-6 atmospheres (Figs. 6, 7). The lines in these figures represent numerical calculations utilizing the mechanism of Yetter, et al., 1991b, but with an updated rate constants for $HO_2+ OH \rightarrow H_2O+O_2$ (Hippler and Troe, 1992), see discussion below. At 1038 K, and between 3 and 6 atmospheres (Figs. 6, 7), the effect of increasing pressure is to decrease the overall reaction rate. Preliminary work indicates this pressure dependence is proportional to $P^{-0.5}$. The transition behavior resulting from crossing of the explosion limit has been observed at 1038 K and 6 atmospheres (Fig. 7).

Efforts in progress are parametrically determining the effect of pressure, temperature and stoichiometry on this system as well. The model of Yetter, et al., 1991b is in good agreement with data at atmospheric pressure. However, at higher pressures and for all stoichiometries, the model is too fast relative to the data. This discrepancy is again ascribed to the increased importance of reactions involving HO_2, which are not well quantified in the literature. In addition, reaction flux and sensitivity analysis results suggest that the reaction rates for $CO + HO_2 \rightarrow CO_2 + OH$ and $CO + O + M \rightarrow CO_2 + M$ may be in error at the conditions of the new data.

Finally, other studies in our laboratory (Roesler, et al., 1992a, 1992b) have suggested that oxygen may have a counter-intuitive effect on the rate of moist CO oxidation and actually decrease its rate below approximately 1040 K at atmospheric pressure. To investigate the inhibition effect of oxygen and further validate the model, experiments were conducted over

a wide range of equivalence ratios at 1000 K. Indeed, excess oxygen was observed to significantly decrease the rate of CO oxidation (Fig. 8). The original model qualitatively predicted this trend, but under-predicted the extent of inhibition. Sensitivity and reaction flux analyses were used to pinpoint three reactions which might be in error. Using a new critically reviewed value for the rate of $HO_2+ OH \rightarrow H_2O+O_2$ (Hippler and Troe, 1992), the model was found to accurately predict the new inhibition data without affecting the previous validations. These results are fully detailed in Roesler, et al., 1993, a copy of which is available as an attachment to this document.

I.C.3. New Results on Methanol Oxidation

Methanol oxidation has been studied in several environments previously, including static and flow reactors , shock tubes and flames. All of these studies have either been in the high temperature regime, where $H+O_2$ branching is important, or at low (500-600 K) temperatures and pressures. For applications involving power generation, such as automotive engines, preflame reactions and pollutant formation reactions in crevices and quench zones and during exhaust processes take place at moderate temperatures and pressures well above atmospheric. In addition to its importance as a fuel, methanol and its primary radicals, methoxy and hydroxymethyl, are important combustion intermediates. In work in progress, we have for the first time obtained data on the oxidation of methanol at elevated pressure over the temperature range 750-1100 K.

Experiments were performed in the VPFR over a range of pressures from 1-20 atmospheres and temperatures from 1100-750 K, with the higher temperatures corresponding to the lower pressures. An equivalence ratio range from 0.4 to 2.5 was covered. The data from selected experiments at 10, 15 and 20 atmospheres are shown in Figures 9-14. The solid lines in Figs 9-13 correspond to current numerical modeling efforts, while the solid lines in Figure 14 are merely connecting experimental data points. These measurements represent the largest range of conditions over which methanol oxidation kinetics have ever been defined, and twenty atmospheres represents the upper limit at which data have ever been collected in flow reactors.
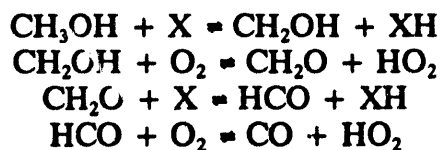
The stable species detected by FTIR were methanol, formaldehyde, carbon monoxide, carbon dioxide, water and formic acid. In the rich oxidation experiments, 1,2-ethanediol (ethylene glycol) was detected following the depletion of oxygen. The identification of formic acid and 1,2-ethanediol was confirmed by comparison with spectra obtained by bubbling nitrogen through liquid samples of the two species. The 1,2-ethanediol identification is somewhat tentative, as only one spectral feature was unobscured by the absorption spectra of other species. The quantities of these species are still being determined, but preliminary estimates yield values in the 50-100 ppm range for each. The measured total carbon data for the experiments without inclusion of these species are constant to within ±5%. The addition of these two species will not affect the carbon totals beyond this uncertainty. Based on comparisons with a preliminary model (see below) , hydrogen peroxide is expected in quantities of approximately 100-500 ppm. Attempts at locating a spectrum for hydrogen

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peroxide have thus far been unsuccessful in this system, due to FTIR interferences from methanol, water and formaldehyde

A small amount of carbon dioxide can be detected at the first data point. Extrapolation of the first few points back to the time of injection does not yield a zero result as is the case for other species. This effect was very pronounced in early experiments in which nearly 10% of the methanol was converted to carbon dioxide by the first data point. After this initial amount was formed, the carbon dioxide mole fraction remained essentially constant until late in the reaction. This phenomenon was eventually traced to cupric oxide and cuprous oxide (both effective oxidation catalysts) deposits on the walls of the mixer assembly from erosion of the anode of the arc plasma gas heater in use at that time. Replacing the contaminated mixer with a clean one and eliminating the use of the arc gas heater (Appendix B) have essentially removed the problem. However, since this effect did not occur with hydrocarbon fuels it is evident that methanol may be oxidized on surfaces fairly readily.

The lines in Figures 9-13 indicate results of a preliminary detailed chemical kinetic model. The computations were performed using zero-dimensional, isobaric and adiabatic conditions. The mechanism is derived from the two studies of Norton and Dryer, 1989, 1990a. Because the later publication included some different reaction paths and rate coefficients, the values from this reference were used preferentially. In addition, several pressure-dependent reactions had falloff coefficients calculated manually, while in this recent work, these parameters were fit with Lindemann mechanisms. The model reproduces the stoichiometric experiment reasonably well during the majority of the fuel consumption. In the later stages of the reaction, the model predicts a preferential oxidation of hydrogen over carbon monoxide, when the experiment indicates the reverse.

The performance of the model for the rich experiments is relatively poor. The initial stages of the reaction are too slow, but the primary difficulty arises upon the point of complete consumption of the oxygen. At this point the experiment indicates a decreased reaction rate with over 25% of the initial fuel remaining. The model actually predicts a fairly rapid reaction at this point. Examination of the reaction path fluxes provides an indication as to the cause. While oxygen is present, the reaction proceeds along the following sequence:

$$CH_3OH + X \rightarrow CH_2OH + XH$$
$$CH_2OH + O_2 \rightarrow CH_2O + HO_2$$
$$CH_2O + X \rightarrow HCO + XH$$
$$HCO + O_2 \rightarrow CO + HO_2$$

(X represents an active radical, primarily OH, H and HO_2 in these experiments)

This provides a reasonably steady rate of reaction, with the HO_2 radicals abstracting hydrogen from methanol and formaldehyde, and self reacting to form hydrogen peroxide, which then decomposes to provide two hydroxyl radicals. When the oxygen is depleted,

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reactions involving oxygen are no longer available, and no other reactions are present to compete with the decomposition of these two radicals. The end result is a very sudden increase in the H atom concentration coincident with the complete consumption of oxygen, which in turn yields a rapid increase in the overall reaction rate.

The experimental indication is that the fate of the hydroxymethyl (and perhaps also formyl) radical in the absence of oxygen is not solely decomposition. The elevated pressure (and thus concentration) and lower temperature relative to previous studies favors the possibility of radical-radical reactions. The presence of formic acid and 1,2-ethanedic s an indication of some possible routes. The combination reaction of hydroperoxyl and hydroxymethyl radicals would yield an excited complex which could decompose, yielding formic acid, H and OH, or could rearrange and decompose, giving formic acid and water. 1,2-Ethanediol is an obvious hydroxymethyl recombination product.

Current efforts are testing a revised mechanism against these other k etic data as well as flame data.

D. Summary

Significant advances have been made on numerous tasks over the duration of this reporting period. Some of the more important ones for future work are the development of a new facility to study chemical kinetics over a large range of pressure, and the progress made toward utilizing insitu optical diagnostics in conjunction with extractive sampling techniques. Development of these new facilities has been no small task, since very different engineering designs were pursued in developing the new VPFR. Even as experiments in this new facility have been conducted, significant engineering changes have occurred. We have now completed nearly all such developments so that a base facility is available in which to implement optical diagnostics. We believe these endeavors will add significant new knowledge concerning oxidation kinetics of small hydrocarbons and hydrocarbon oxygenates, especially under conditions where RO_2, HO_2 and H_2O_2 kinetic effects are prevalent.

II. References

Baulch et al. (1992). "Evaluated Data for Combustion Modeling", J. Phys. Chem. Ref. Data, 21 411.

Brezinsky, K. (1985). "The High Temperature Oxidation of Aromatic Hydrocarbons", Prog. Energy Combust. Sci., 12, 1.

Crocco, L., Glassman, I., and Smith, I.E. (1957). "A Flow Reactor for High Temperature Reaction Kinetics", Jet Propulsion, 12, 66.

Curran, H.J., Dunphy, M.P., Simmie, J.M., Westbrook, C.K., and Pitz, W. J. (1992). "Shock Tube Ignition of Ethanol, Isobutene, and MTBE: Experiments and Modeling", Twenty Fourth International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA. p. xxx. (to be assigned)

Dagaut, P., Cathonnet, M., Boettner, J.C., and Gallaird, F. (1988). "Kinetic Modeling of Ethylene Oxidation", Combust. Flame, 71, 295.

Dagaut, P., Boettner, J.C., and Cathonnet, M. (1992). "Kinetic Modeling of Ethanol Pyrolysis and Combustion", J. Chim. Phys., 89, 867.

Dryer, F.L. (1972). "High Temperature Oxidation of Carbon Monoxide and Methane in a High Temperature Flow Reactor", Ph.D. Thesis, Department of Aerospace and Mechanical Sciences, Princeton University, Princeton, NJ, March. Report Number AMS-T-1034.

Dryer, F.L. (1991), "The Phenomenology of Modeling Combustion Chemistry", to be published in **Fossil Fuel Combustion: A Sourcebook**, W. Bartok and A.F. Sarofim, eds., John Wiley and Sons, Inc.

Dryer, F.L. (1992). "Fundamental Studies of Fuel Chemistry as Related to Internal Combustion Engine Phenomena: The Chemistry of Autoignition", U.S. Department of Energy Report Progress Report on Grant No. DE-FG04-90A1-65450, November. Report No. 90AL65450-003.

Dryer, F.L. and Glassman, I. (1978). "Combustion Chemistry of Chain Hydrocarbons", Prog. Astronaut. Aeronaut. 62, 55.

Egolfopolous, F.N. and Law, D.K. (1990a). "An Experimental and Computational Study of the Burning Rates of Ultra-Lean to Moderately-Rich H_2/O_2 N_2 Laminar Flames with Pressure Variations", Twenty Third International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA. p. 333.

Egolfopolous, F.N. and Law, D.K. (1990b). "Experimental and Numerical Computational Determination of Laminar Flame Speeds: C_2-Hydrocarbons with Oxygen and Nitrogen", Twenty Third International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA. p. 471.

Egolfopolous, F.N., Du, D.X., and Law, D.K. (1992a). "A Comprehensive Study of Methanol Kinetics in Freely-Propagating and Burner Stabilized Flames, Flow Reactors, and Static Reactors", Combust. Sci. Tech., 83, 33.

Egolfopolous, F.N., Du, D.X., and Law, D.K. (1992b). "A Study on Ethanol Oxidation Kinetics in Laminar Premixed Flames, Flow Reactors, and Shock Tubes", Twenty Fourth International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA. p. xxx. (to be assigned)

Glassman, I. (1987). **Combustion**, (2nd Edition) Academic Press, Orlando, FL.

Grotheer, H-H, and Just, Th. (1992). Institut fur Physikalische Chemie der Verbrennung, Stuttgart, Personal Communication, July.

Grotheer, H-H., Kelm, S., Driver, H.S.T., Hutcheon, R.J., Lockett, R.D., and Robertson, G.N. (1993). "Elementar~ Reactions in the Methanol Oxidation System. Part I: Establishment of the Mechanism and Modeling of Laminar Burning Velocities", Int. J. Chem. Kin., In Press.

Hess, W.P. and Tully, F.P. (1989). "Hydrogen Atom Abstraction from Methanol by OH", J. Phys. Chem., 93, 1944.

Held, T.J. (1993). "A Flow Reactor Study of Methanol, Iso-butene, and Methyl Tert-Butyl Ether", Ph.D. Thesis, Mechanical and Aerospace Department, Princeton University, Princeton, NJ. In Preparation.

Hippler, H. and Troe, J. (1992). "Rate Constants of the Reaction $HO + H_2O_2 \rightarrow HO_2 + H_2O$ at T≥1000 K", Chem. Phys. Let., 192, 333.

Hochgreb, S. (1991). "An Experimental and Numerical Study on the Oxidation of Formaldehyde", Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ., April. MAE 1910-T.

Hochgreb, S., Yetter, R.A., and Dryer, F.L. (1990). "The Oxidation of CH_2O in the Intermediate Temperature Range (943-995 K)", Twenty Third International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA. p.171.

Hochgreb, S. and Dryer, F.L. (1992a). "Decomposition of 1,3,5-Trioxane", J. Phys. Chem., 96, 295.

Hochgreb, S. and Dryer, F.L. (1992b). "A Comprehensive Study on CH_2O Oxidation Kinetics", Combust. Flame, 91, 257.

Kim, Tae (1993). "The High Pressure Oxidation of H_2/O_2 and $CO/H_2/O_2$ in a Variable Pressure Flow Reactor", MSE Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ. In Progress.

Lewis B., and Von Elbe. G. (1961). **Combustion, Flames, and Explosions in Gases**, (Second Edition), Academic Press, NY.

Linteris, G.T. (1990). "Trace Radical Species Detection in a Turbulent Chemical Kinetic Flow Reactor Using a 180° Laser Induced Fluorescence Probe", Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, February. Report T-1878.

Linteris, G.T., Yetter, R.A., Brezinsky, K., and Dryer, F.L. (1991a). "Hydroxyl Radical Concentration Measurements in Moist Carbon Monoxide Oxidation in a Chemical Kinetic Flow Reactor", Combust. Flame, 86, 162.

Linteris, G.T., Brezinsky, K., and Dryer, F.L. (1991b). "A High Temperature 180 Degree Laser Induced Fluorescence Probe for Remote Trace Radical Concentration Measurements", Applied Optics Letters, 30, 381.

13

Mishra, M. Peiperl, L., Reuven, Y., Yetter, R.A., Rabitz, H., and Smooke, M.D. (1991). "On the Use of Green's Functions for the Analysis of Dynamic Couplings: Some Examples from Chemical Kinetics and Quantum Dynamics", J. Phys. Chem., 95, 3109.

Norton, T.S. (1990). "The Combustion Chemistry of Simple Alcohol Fuels", Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, January. Report T-1877.

Norton T.S. and Dryer, F.L. (1989). "Some New Observations on Methanol Oxidation Chemistry", Combust. Sci. Tech., 63, 107.

Norton, T.S. and Dryer, F.L. (1990a). "Toward a Comprehensive Mechanism for Methanol Pyrolysis", Int. J. Chem. Kinet., 22, 219.

Norton, T.S. and Dryer, F.L. (1990b). "The Flow Reactor Oxidation of C_1 - C_4 Alcohols", Twenty Third International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA. p. 179.

Norton, T.S., and Dryer, F.L. (1992). "An Experimental and Modeling Study of Ethanol Oxidation Kinetics in an Atmospheric Pressure Flow Reactor", Int. J. Chem. Kin., 24, 319.

Roesler, J.F., Yetter, R.A., and Dryer, F.L. (1992a). "The Inhibition of the $CO/H_2/O_2$ Reaction by Trace Quantities of HCl", Combust. Sci. Tech., 82, 87.

Roesler, J.F., Yetter, R.A., and Dryer, F.L. (1992b). "Detailed Kinetic Modeling of Moist CO Oxidation Inhibited by Trace Quantities of HCl", Combust. Sci. Tech., 85, 1.

Roesler, J.F., Yetter, R A., and Dryer (1993). "On the Dependence of the Rate of CO Oxidation on O_2 Concentration", Com?. as¹. Sci. Tech.. Submitted, Jan. 15, 1993

Roth, P. and Just, Th. (1985). "Kinetics of the High Temperature, Low Concentration CH_4 Oxidation Verified by H and O Atom Measurements", Twentieth International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA. p. 807.

Shaddix, C.R. (1993). "An Experimental Study of the High Temperature Oxidation of 1-Methylnaphthalene", Ph.D. Thesis, Dept. of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ.

Slagle, I.R., Park, J-Y, Heaven, M.C., and Gutman, D. (1984). "Kinetics of Polyatomic Free Radicals Produced by Laser Photolysis: 3. Reaction of Vinyl Radicals with Molecular Oxygen", J. Chem. Soc., 106, 4356.

Smooke, M.D., Rabitz, H., Reuven M., and Dryer, F.L. (1988). "Application of Sensitivity Analysis to Pre-mixed Hydrogen-Air Flames", Combust. Sci. Tech., 59, 295.

Vajda, S., Yetter, R.A., and Rabitz, H. (1990). "Effects of Thermal Coupling and Diffusion on the Mechanism of H_2 Oxidation in Steady Premixed Laminar Flames", Combust. Flame, 82, 270.

Vardanyan, I.A., Sachyan, G.A., and Nalbandyan, A. B. (1971). Combust. Flame, 17, 315.

Vermeersch, M.L. (1991). "A Variable Pressure Flow Reactor for Chemical Kinetic Studies: Hydrogen, Methane and Butane Oxidation at 1 to 10 Atmospheres and 880 to 1040 K". Ph.D. Thesis, Dept. of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ.

14

Vermeersch, M.L., Held, T.J., Stein, Y., and Dryer, F.L. (1991). "Autoignition Chemistry of n-Butane in a Variable Pressure Flow Reactor", SAE Transactions, 100, 645.

Westbrook C.K., and Dryer, F.L. (1981). "Detailed Chemical Kinetics and Combustion Modeling", Invited Paper, Eighteenth International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, p. 749.

Westbrook, C.K. and Dryer, F.L. (1984). "Kinetic Modeling of Hydrocarbon Combustion", Prog. Energ. Sci. Combust. 10, 1.

Yetter, R.A. (1985). "An Experimental /Numerical Study of Carbon Monoxide - Hydrogen - Oxygen Kinetics with Applications of Gradient Sensitivity Analysis", Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, June. MAE Report No. 1703-T.

Yetter, R.A., Eslava, L.A., Dryer, F.L. and Rabitz, H. (1984). "Elementary and Derived Sensitivity Information in Chemical Kinetics", J. Phys. Chem. 88, 1497.

Yetter, R.A., Dryer, F.L. and Rabitz, H. (1985). "Some Interpretive Aspects of Elementary Sensitivity Gradients in Combustion Kinetics Modeling", Combust. Flame, 59, 107.

R.A. Yetter, H. Rabitz, F.L. Dryer, R.B. Klemm, and R.G. Maki (1989). "Evaluation of the Rate Constant for Reaction OH + CH$_2$O: Application of Modeling and Sensitivity Analysis Techniques for Determination of the Product Branching Ratio", J. Chem. Phys., 91, 4088.

Yetter, R.A., Dryer, F.L., and Rabitz, H. (1991a). "Flow Reaction Studies of Carbon Monoxide/Hydrogen/Oxygen Kinetics" , Comb. Sci. Tech., 79, 129.

Yetter, R.A., Dryer, F.L., and Rabitz, H. (1991b). "A Comprehensive Reaction Mechanism for Carbon Monoxide/Hydrogen/Oxygen Kinetics", Comb. Sci. Tech., 79, 97.

Yetter, R.A. and Dryer, F.L. (1992). "Inhibition of Moist Carbon Monoxide by Trace Amounts of Hydrocarbons", Twenty-Fourth International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA. p. 757.

Yetter, R.A., Dryer, F.L., and Golden, D.M. (1992). "Combustion Kinetics for High Speed Chemically Reacting Flows", An invited Contribution to Major Research Topics in Combustion, ICASE/NASA Series, M.Y. Hussaini, A. Kumar and R.G. Voigt, eds., Springer-Verlag, NY. p. 309.

III. Figures

Classical $H_2 - O_2$ Explosion Limits, $\varphi = 1$

---- Extended Second Explosion Limit, $\varphi = 1$

● Experimental Initial Conditions, $\varphi = 0.3$

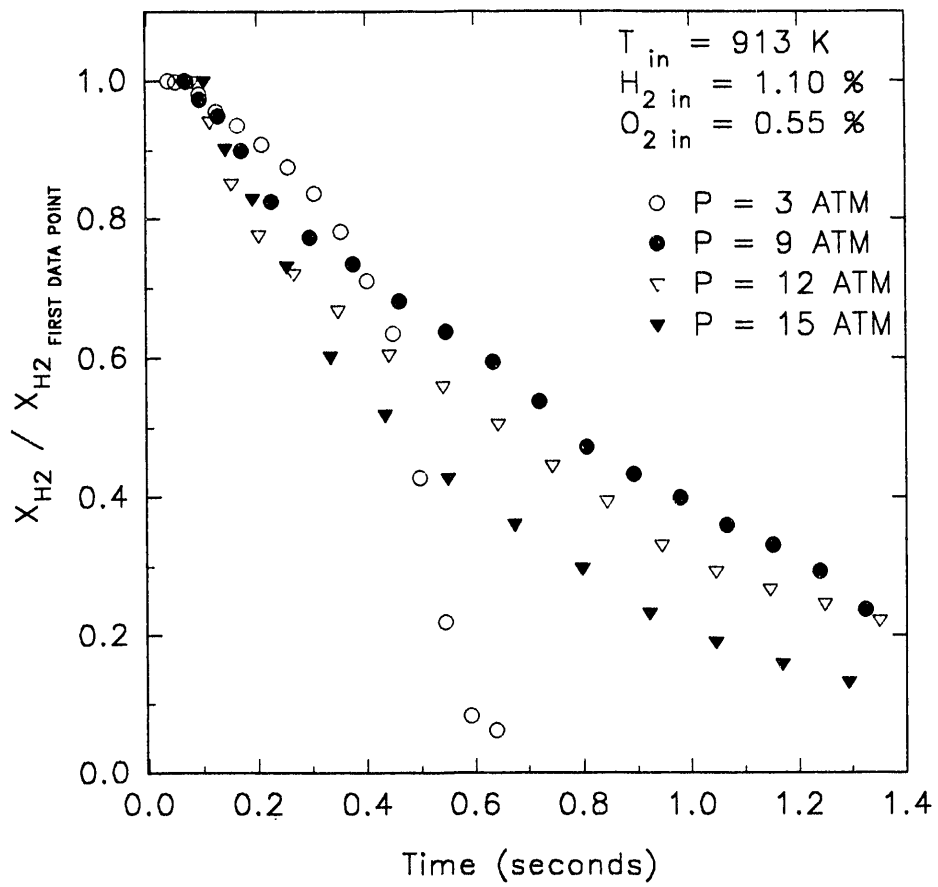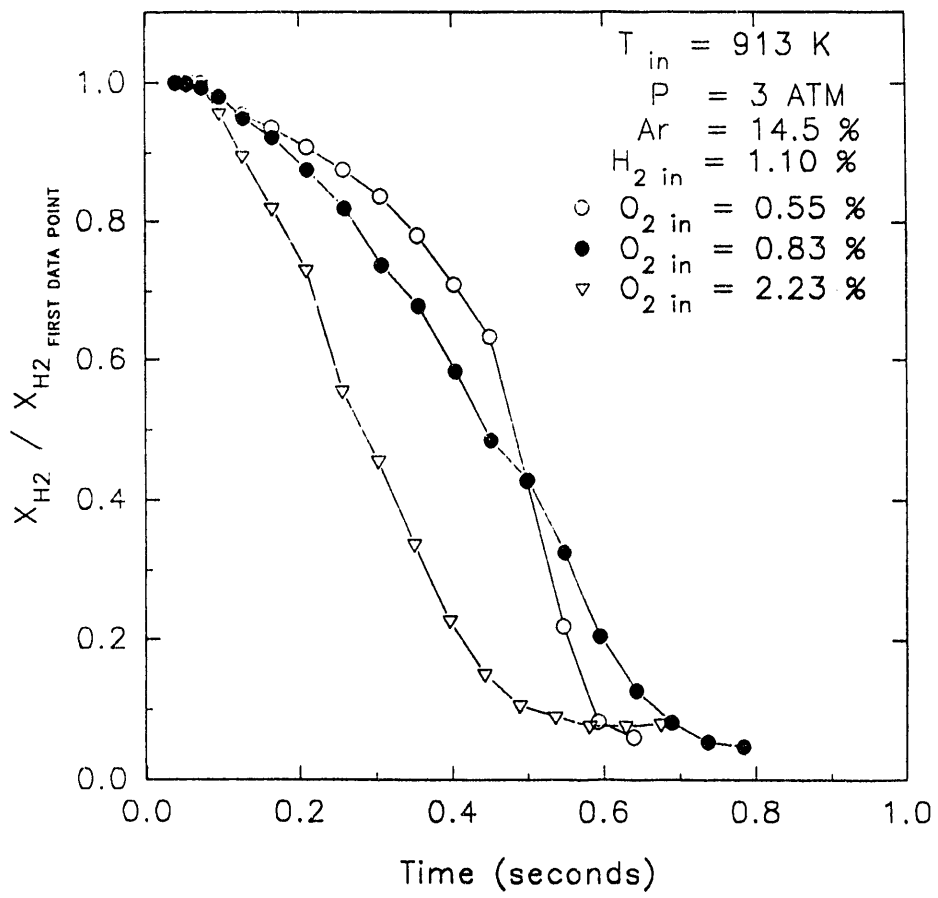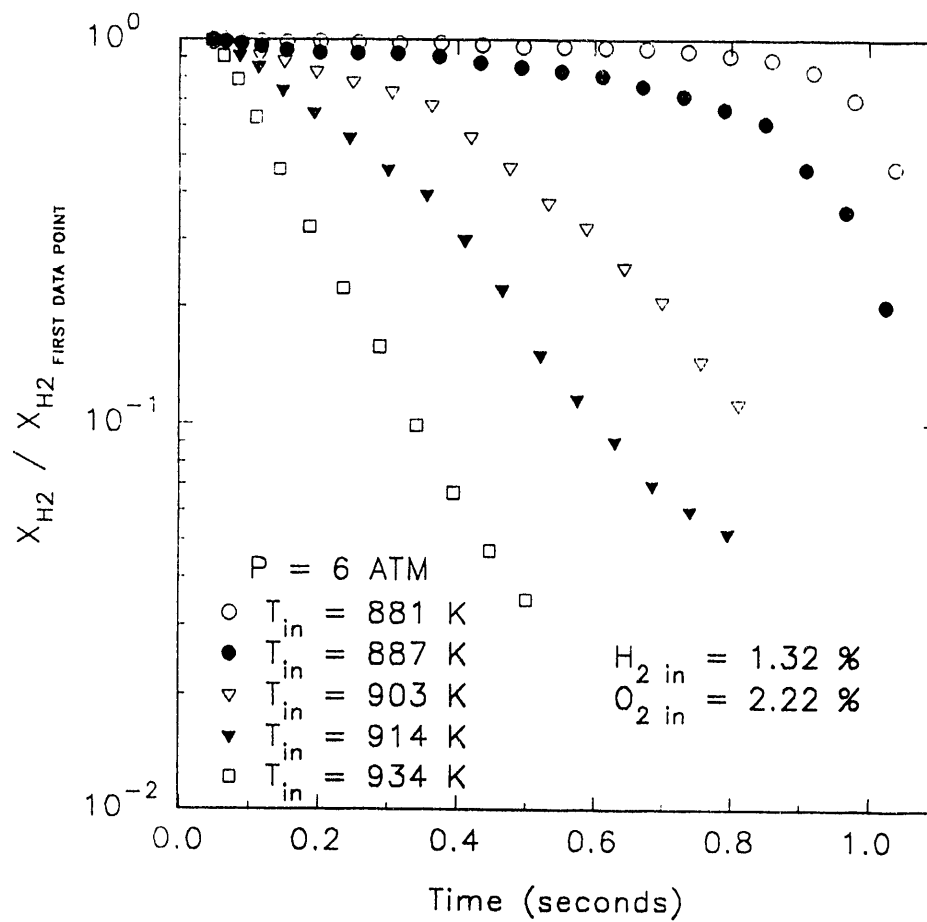○ Experimental Initial Conditions, $\varphi = 1$, $\varphi = 0.26$

Figure 1

Figure 2

T $_{in}$ = 913 K
P = 3 ATM
Ar = 14.5 %
H $_{2\ in}$ = 1.10 %
○ O $_{2\ in}$ = 0.55 %
● O $_{2\ in}$ = 0.83 %
▽ O $_{2\ in}$ = 2.23 %

Figure 3

Figure 4

Phi=1 P=15 ATM Ti=914K
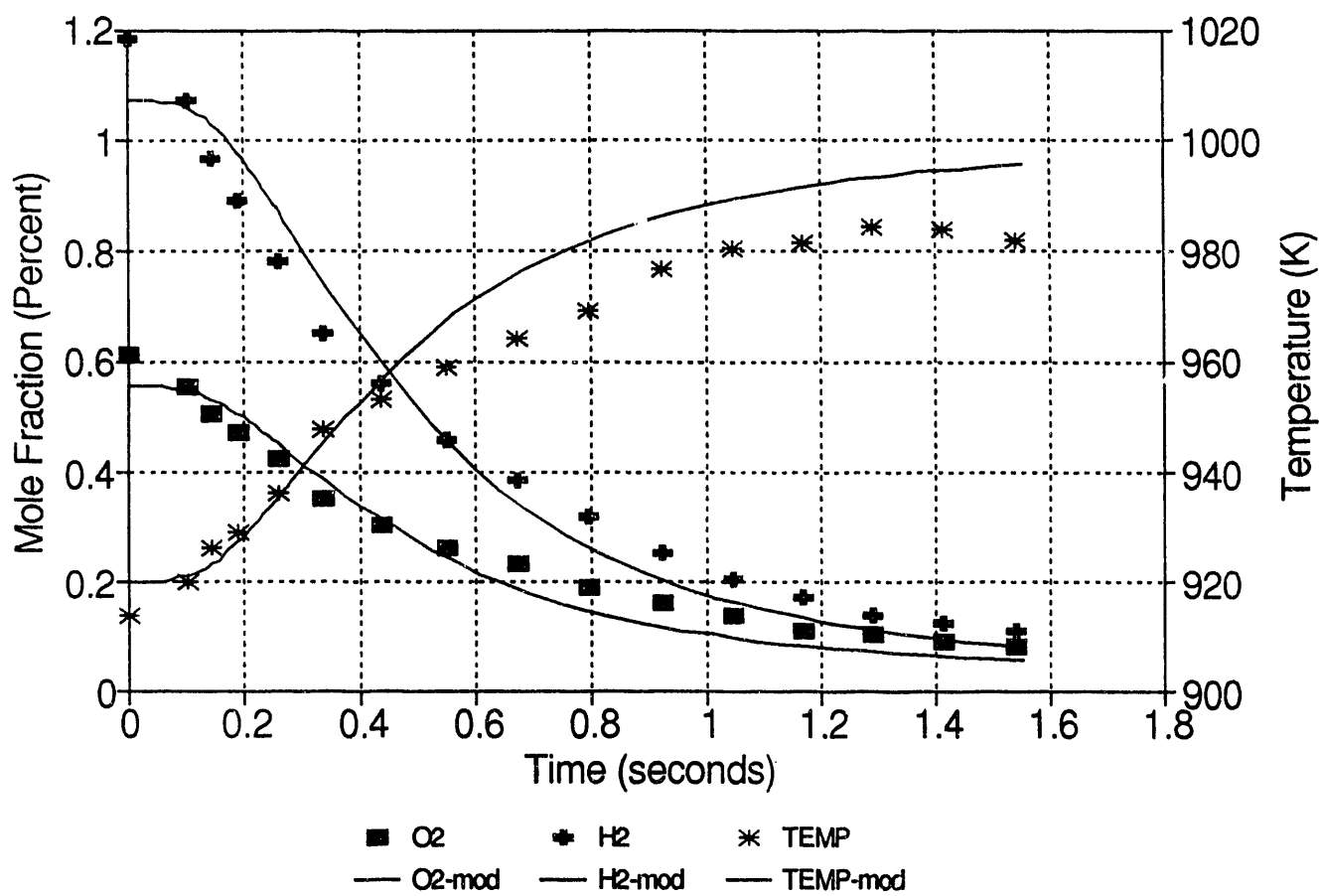
Figure 5

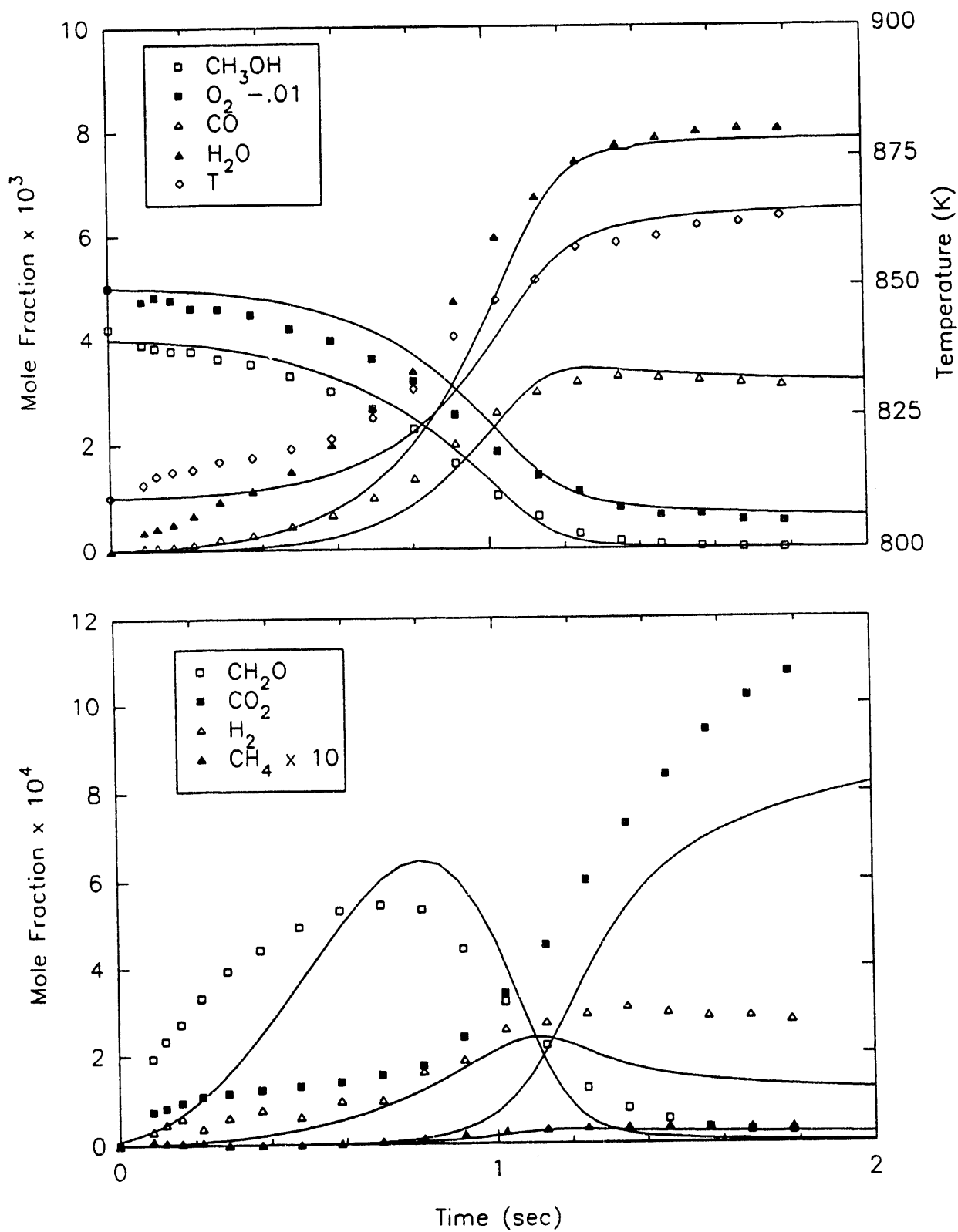PHI=1 P=3 ATM Ti=1038K H2O=0.65%
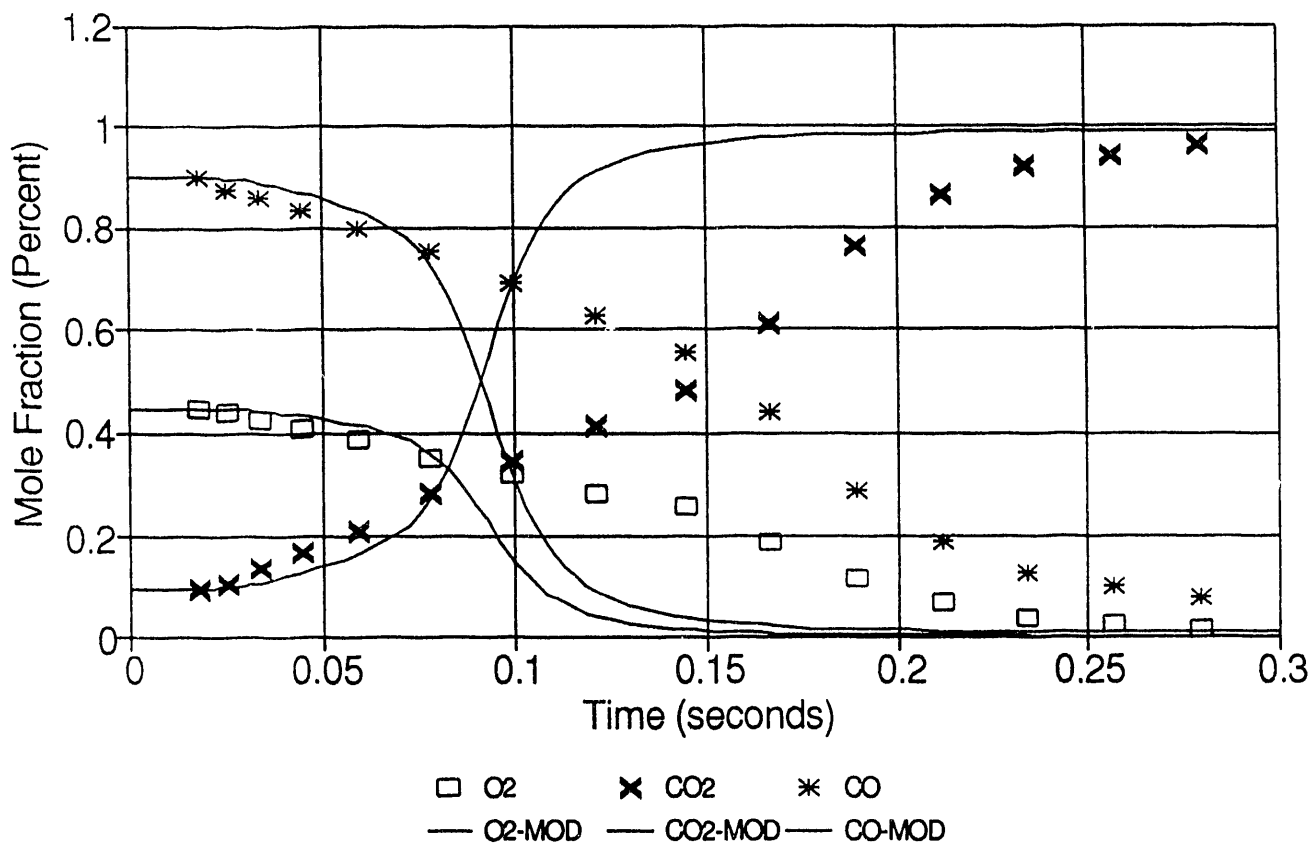
Figure 6
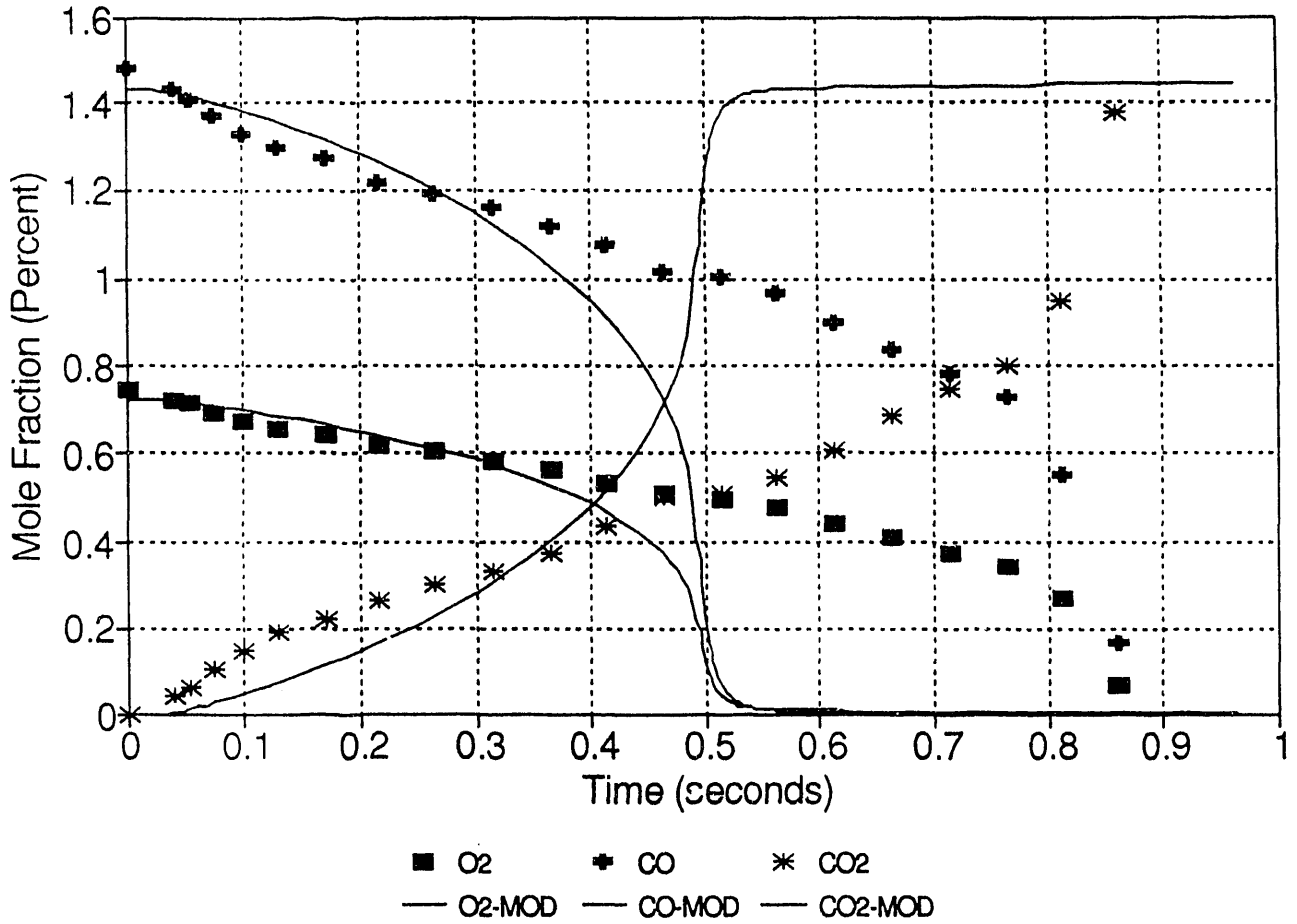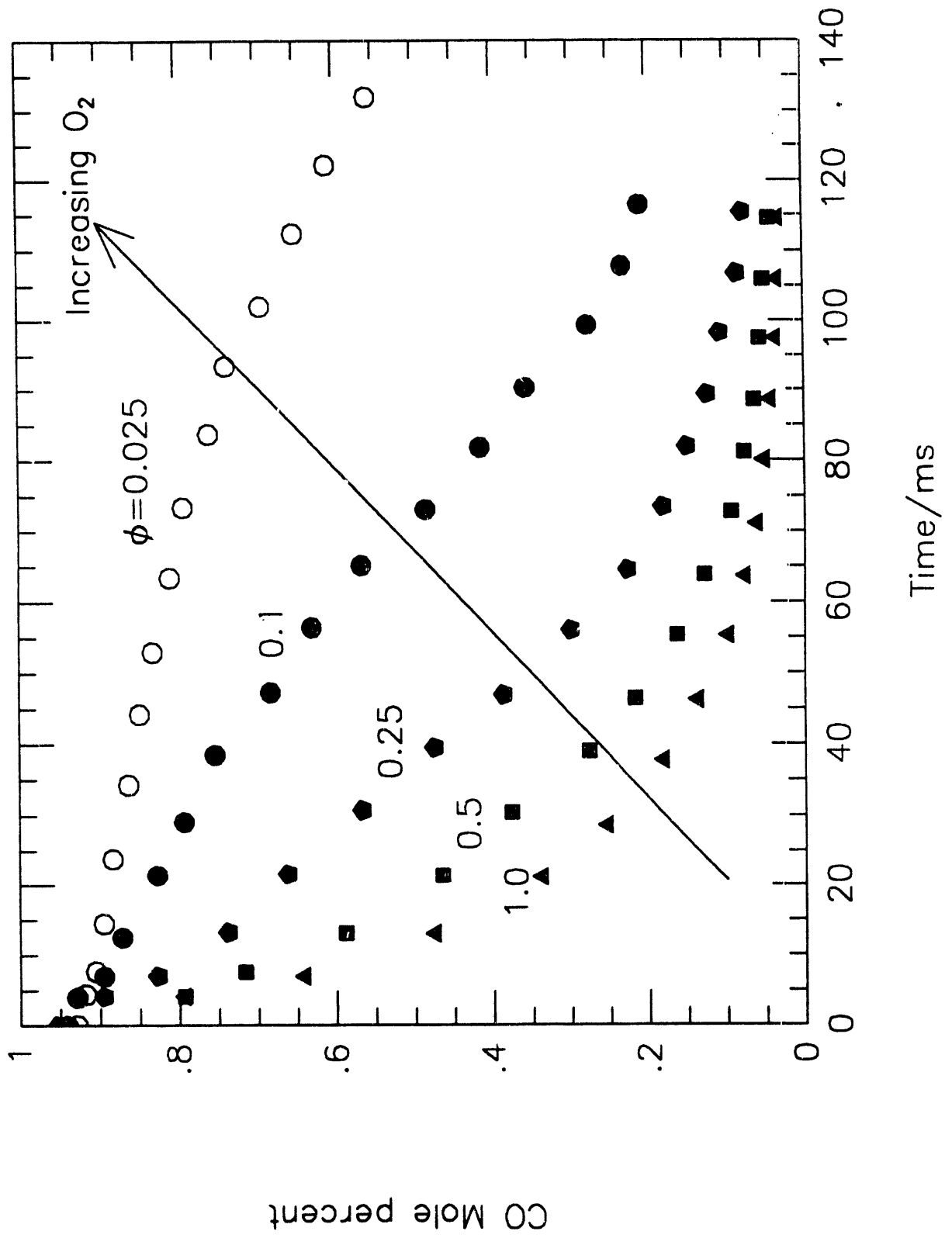
Figure 7

Figure 8

Methanol Oxidation

10 atm, T_i=810K, $X_{F,i}$=0.004, Φ=0.4

Figure 9

Methanol Oxidation

10 atm, T_i=810K, $X_{F,i}$=0.004, Φ=1.0

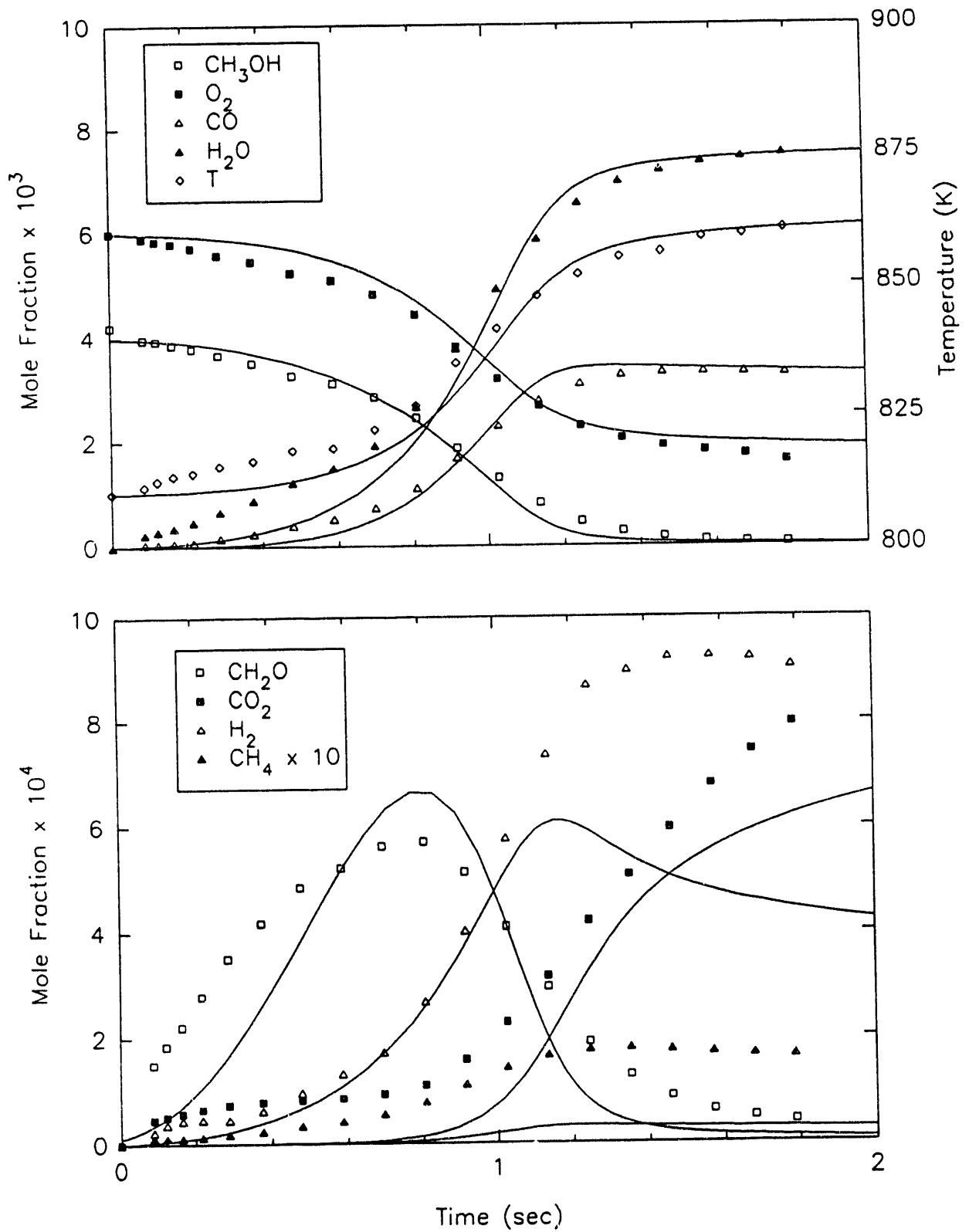Figure 10

Methanol Oxidation
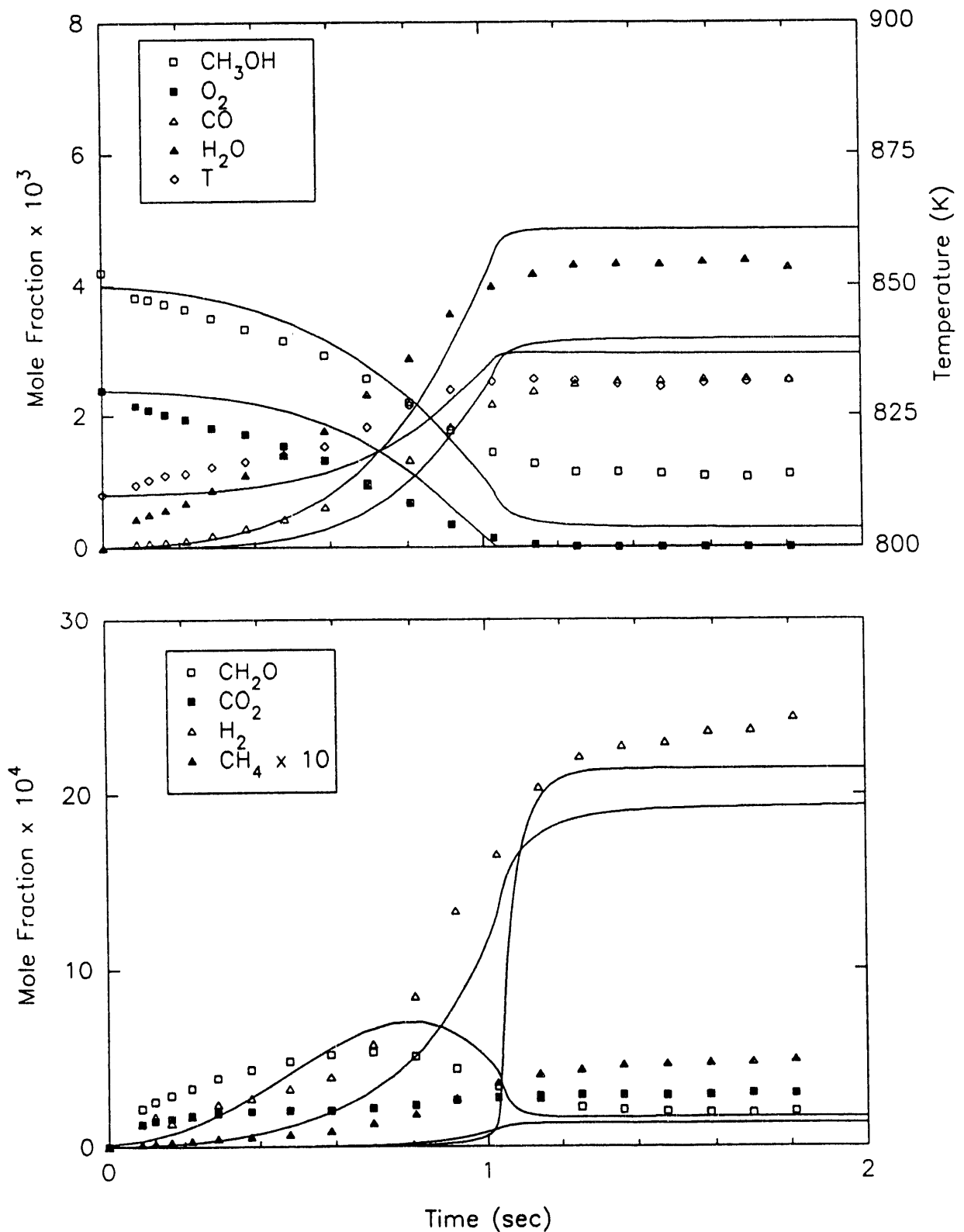
10 atm, T_i=810K, $X_{F,i}$=0.004, Φ=2.5

Figure 11

Methanol Oxidation

15 atm, T_i=783K, $X_{F,i}$=0.004, Φ=1.0

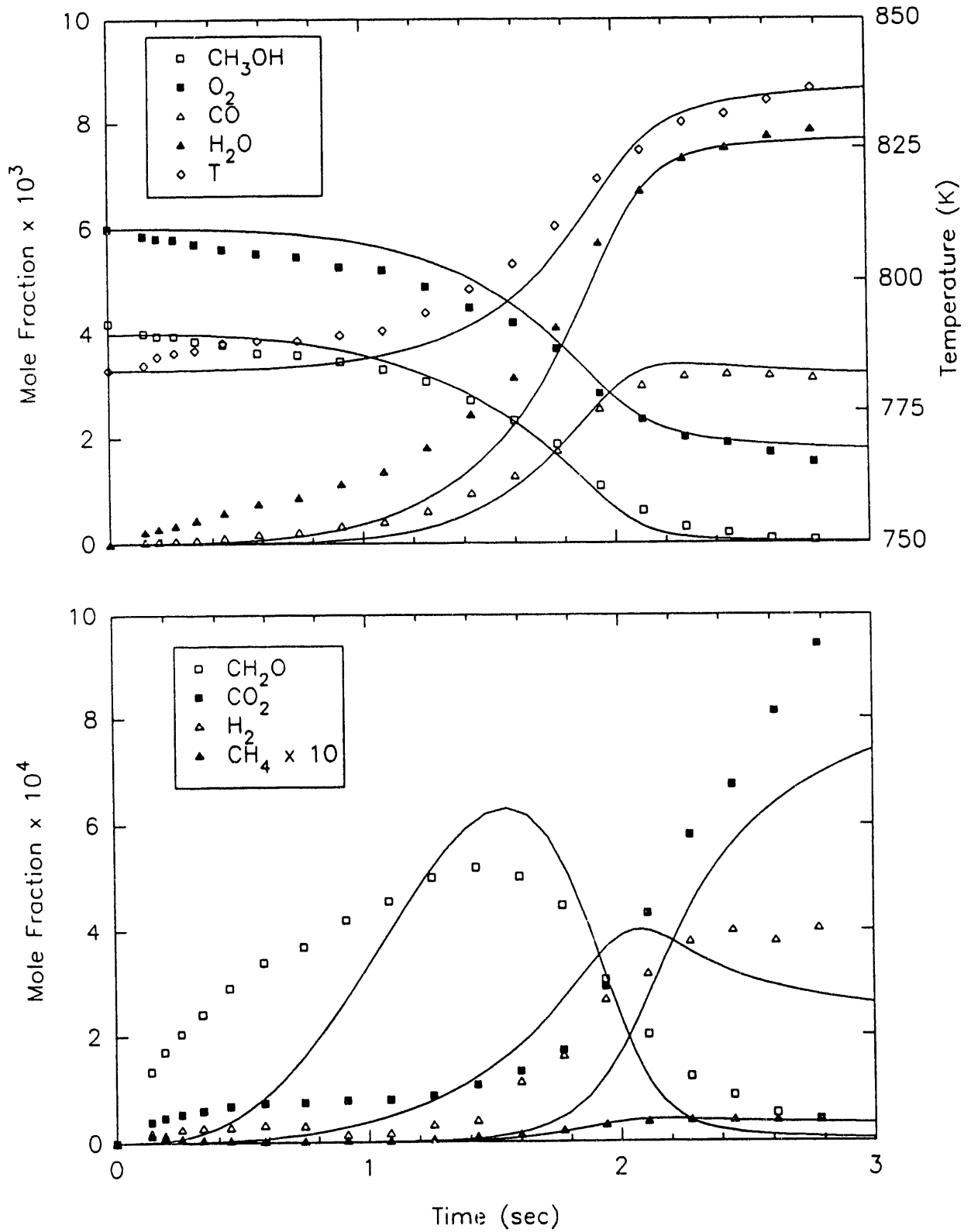**Figure 12**

Methanol Oxidation

15 atm, T_i=783K, $X_{F,i}$=0.004, Φ=2.5
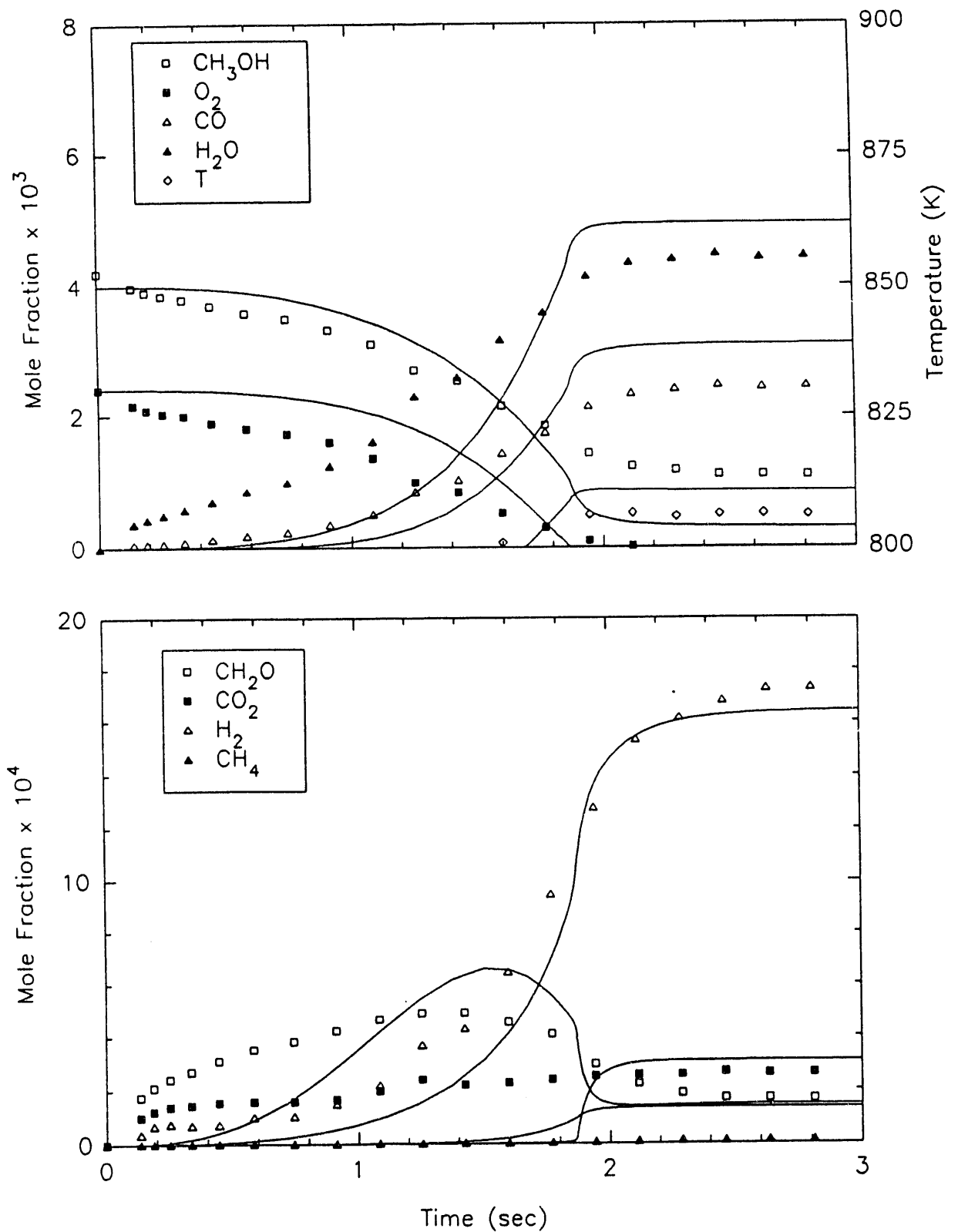

Figure 13

Methanol Oxidation

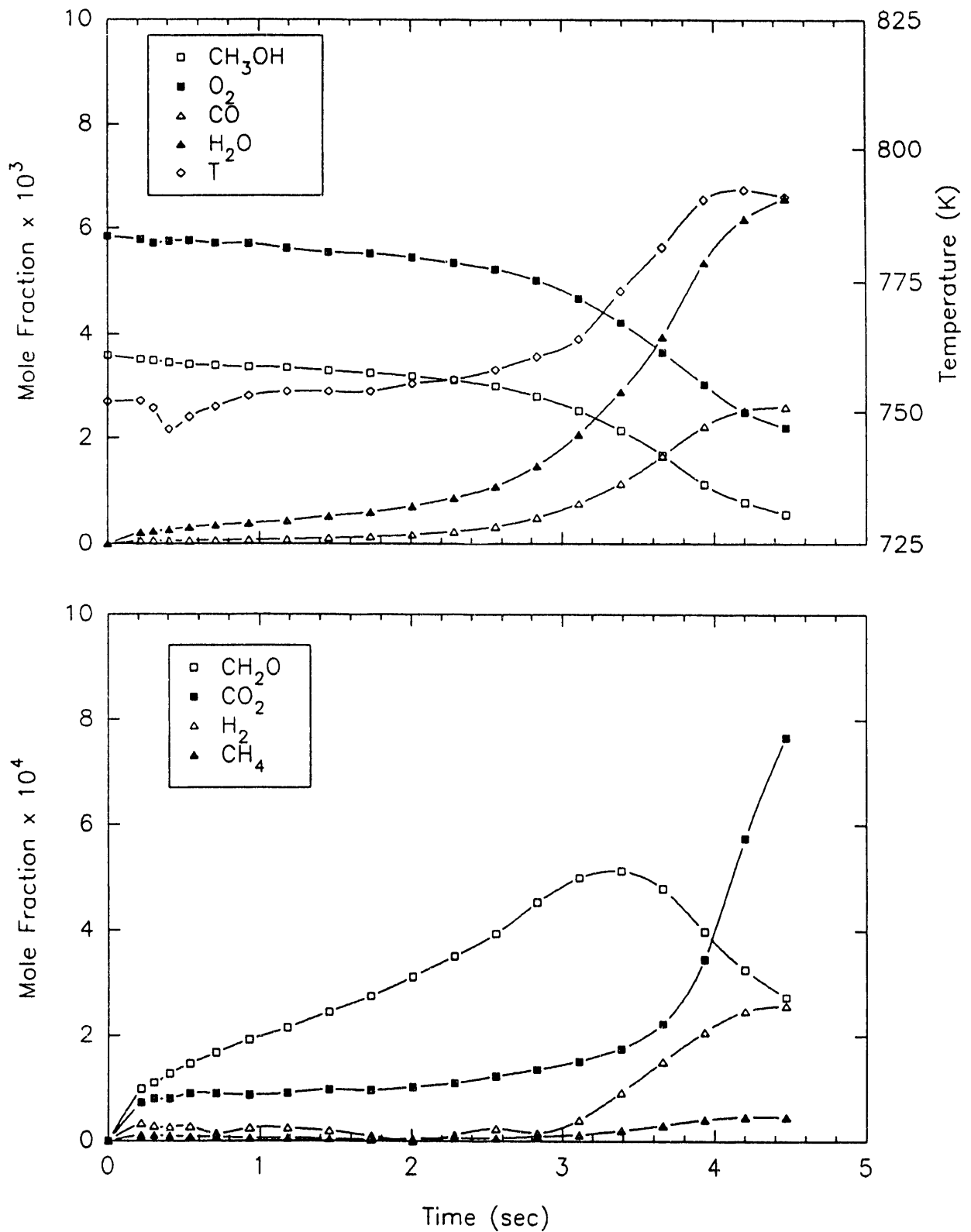## 20 atm, T_i=752K, $X_{F,i}$=0.0036, Φ=1.0

Figure 14

IV. Publications

IV.A. Publications and Theses, 1990 - Present

1. J.F. Roesler, R.A. Yetter, and F.L. Dryer, "On the Dependence of the Rate of CO Oxidation on O_2 Concentration", Comb. Sci. Tech., Submitted, Jan. 1993.

2. S. Hochgreb and F.L. Dryer, "A Comprehensive Study on CH_2O Oxidation Kinetics", Combust. Flame, 91, 257 (1992).

3. R.A. Yetter and F.L. Dryer, "Inhibition of Moist Carbon Monoxide by Trace Amounts of Hydrocarbons", Twenty Fourth International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1992. p. 757.

4. T.S. Norton and F.L. Dryer, "An Experimental and Modeling Study of Ethanol Oxidation Kinetics in an Atmospheric Pressure Flow Reactor", Int. J. Chem. Kin., 24, 319 (1992).

5. S. Hochgreb and F.L. Dryer, "Decomposition of 1,3,5-Trioxane", J. Phys. Chem., 96, 295 (1992).

6. R.A. Yetter, F.L. Dryer, and D.M. Golden, "Combustion Kinetics for High Speed Chemically Reacting Flows", An Invited Contribution to Major Research Topics in Combustion, ICASE/NASA Series, M.Y. Hussaini, A. Kumar and R.G. Voigt, eds., Springer-Verlag, NY, 1992. pp. 309.

7. S. Hochgreb, "An Experimental and Numerical Study on the Oxidation of Formaldehyde", Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ., April, 1991. MAE 1910-T.

8. F.L. Dryer, "The Phenomenology of Modeling Combustion Chemistry", Part 1, Chapter 3, in Fossil Fuel Combustion - A Sourcebook, W. Bartok and A.F. Sarofim, eds., John Wiley and Sons Inc., NY, 1991.

9. M.L. Vermeersch, T.J. Held, Y. Stein, and F.L. Dryer, "Autoignition Chemistry of n-Butane in a Variable Pressure Flow Reactor", SAE Transactions, 100, 645 (1991).

10. G. T. Linteris, R.A. Yetter, K. Brezinsky, and F.L. Dryer, "Hydroxyl Radical Concentration Measurements in Moist Carbon Monoxide Oxidation in a Chemical Kinetic Flow Reactor", Combust. Flame, 86, 162 (1991).

11. R.A. Yetter, F.L. Dryer, and H. Rabitz, "A Comprehensive Reaction Mechanism for Carbon Monoxide/Hydrogen/Oxygen Kinetics", Combust. Sci. Tech., 79, 97 (1991).

12. R.A. Yetter, F.L. Dryer, and H. Rabitz, "Flow Reaction Studies of Carbon Monoxide/Hydrogen/Oxygen Kinetics" , Combust. Sci. Tech., 79, 129 (1991).

13. G. T. Linteris, K. Brezinsky, and F.L. Dryer, "A High Temperature 180 Degree Laser Induced Fluorescence Probe for Remote Trace Radical Concentration Measurements", Applied Optics Letters, 30, 381 (1991).

14. T.S. Norton and F.L. Dryer, "The Flow Reactor Oxidation of C_1 - C_4 Alcohols", Twenty Third International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1990. p. 179.

15. S. Hochgreb, R.A. Yetter, and F.L. Dryer, "The Oxidation of CH_2O in the Intermediate Temperature Range (943-995 K)", Twenty Third International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1990. p.171.

16. G.T. Linteris, "Trace Radical Species Detection in a Turbulent Chemical Kinetic Flow Reactor Using a 180° Laser Induced Fluorescence Probe", Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, February, 1990. Report T-1878.

17. T.S. Norton, "The Combustion Chemistry of Simple Alcohol Fuels", Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, January, 1990. Report T-1877.

18. T.S. Norton and F.L. Dryer, "Toward a Comprehensive Mechanism for Methanol Pyrolysis", Int. J. Chem. Kinet., 22, 219 (1990).

IV.B. Pre-Prints, Abstracts, and Presentations, 1990-Present

1. S. Hochgreb and F.L. Dryer, "A Comprehensive Study of CH_2O Oxidation Kinetics", Fall Eastern States Sectional Meeting of the Combustion Institute, Cornell University, Ithaca NY, October 14-16, 1991. Extended Abstract.

2. J.F. Roesler, R.A. Yetter, and F.L. Dryer, " Effect of Oxygen Concentration on Moist CO Oxidation", Fall Eastern States Sectional Meeting of the Combustion Institute, Cornell University, Ithaca NY, October 14-16, 1991. Extended Abstract.

3. M.L. Vermeersch, T.J. Held, R.A. Yetter, Y. Stein, and F.L. Dryer, "A New Variable Pressure Flow Reactor (VPFR) for Kinetics Studies from 1 Atm. to 15 Atm.", Fall Eastern Sectional Meeting of the Combustion Institute, Orlando, FL, December 3-5, 1990. Extended Abstract.

4. M.L. Vermeersch, R.A. Yetter, Y. Stein, and F.L. Dryer, "A New Variable Pressure Flow Reactor: Reaction Studies on $CO/H_2/O_2$ Kinetics from 2-15 Atm. and 900 - 1200 K", Twenty Third International Symposium on Combustion, Orleans, France, July 22-27, 1990. Poster Session Presentation.

Appendix B.

The Princeton Variable Pressure Flow Reactor (VPFR)

Atmospheric pressure flow reactors (APFR's, e.g. Crocco, et al., 1957; Dryer, 1972; Yetter, et al., 1991a) typically provide data in a range of conditions not accessible to shock tubes and static reactors. The experimental apparatus described here was developed specifically to produce chemical kinetic information relevant to combustion/emission phenomena at pressures similar to those found energy conversion systems. The VPFR is unique in that the facility can access such a wide range of conditions: temperature (550 K < T < 1200 K); pressure (1 atm. < P < 20 Atm., Fig. 1). Wide ranges of stoichiometry can also be studied, from pure pyrolysis, to very oxygen rich conditions. As in earlier flow reactors, the reacting mixture is typically diluted in large amounts of pre-heated nitrogen such that mixtures are well outside those which might result in flammable and/or explosive conditions inside the reactor. (The effects of dilution can be studied and compensated for in reaction mechanisms much more directly than can the effects of pressure, temperature and equivalence ratio.) Dilution reduces the experimentally observed reaction rates from those found under higher concentration conditions (for example stoichiometric conditions in air). Thus, the reaction times evident in combustion systems (often less than a few milliseconds) are scaled by dilution to a range of reaction times from 10^{-2} to 5 seconds, all of which can be studied under quasi-steady conditions in the VPFR. By maintaining large convective rates for these dilute conditions, the effects of diffusive transport are typically negligible. Design concepts and details of the sysytem appear in Vermeersch, 1991; Vermeersch, et al., 1991; Held, 1993. What follows is a brief description of the current operating facility.

The VPFR operates quite differently from typical low pressure, fast-flow kinetic experiments. The flow is turbulent, but not fully developed; thus, the core of the flow is radially uniform. In low pressure fast flow systems (< 10 Torr), the flow is typically radially uniform due to high diffusivities. In this case, however, molecular collisional effects with the walls are expected to occur, and surface reaction rates can be comparable to those in the gas phase. Thus, corrections of results for wall reactions are required. At higher pressures, (10-50 Torr), the flow becomes laminar in character. As the flow field and species concentrations are radially non-uniform, radial diffusive effects cause significant effects on axial species concentrations. At still higher pressures, wall collisional effects are of minimal importance because the time for molecules to diffuse to and from the wall to affect the core flow are long, in comparison to the mean residence time of the flow in the reactor. As a result of the laminarized flow near the wall, this result can be true even with the presence of enhanced diffusivities from turbulence in the core flow. Seeley, et al., 1993 have recently studied elementary reactions of the chlorine atom near room temperature over a wide range of fast flow conditions, and at pressures from 2 to 760 Torr. At pressures greater than about 50 Torr, the flows were turbulent. It was shown that higher pressure, turbulent conditions yielded elementary rate constant values identical to those obtained from classical low pressure, fast flow experiments. Indeed, wall effects were also found to be absent at higher pressures, as expected. At the much higher pressures that the VPFR can accommodate, diffusivities are sufficiently reduced that reaction times as long as 5 seconds can be studied without incurring wall effects.

A second feature demonstrated by our own experimental results and those of Seeley, et al., 1993, is that in dilute turbulent flows, conditions can be produced where turbulence-chemistry coupling is also of minimal importance. This results from the fact that turbulence-chemistry coupling from temperature fluctuations is much more significant than from localized concentration fluctuations. Seeley et al.'s results, along with our own determinations of elementary rates (e.g. Hochgreb and Dryer, 1992a, Yetter and Dryer, 1992), suggest that the turbulence/chemistry coupling perturbations under our respective experimental conditions are within the uncertainties of the kinetic measurements themselves.

In the present reactor design, the diffusion times to the reactor walls are long in comparison to the observation times. Radial uniformity only exists in the "core" of the flow (surrounding the axis of the cylindrical flow). The flow is a "developing" one, with boundary-layer growth occurring at the reactor wall, over the length of the reaction region. To accurately define the relative times of various axial positions to one another and the mixing location, the axial velocity distribution is defined experimentally.

A novel design feature of the VPFR (in comparison to other flow reactors) is based on fixing the diagnostic sampling position, and moving the point of fuel injection relative to this location to vary the reaction time (Fig. 2). The approach is similar to that which is normally performed in the study of pre-mixed, laminar, one-dimensional flames, where the burner rather than the diagnostic sampling position is moved. This design accommodates not only very short gas sampling residence times to continuous, on-line diagnostic instruments (important for on-line measurement of low-stability molecular species such as aldehydes and other oxygenates), but simple optical access for *insitu* diagnostics at the sampling location. Crossed-beam optical access ports (normal to the flow direction) are positioned at the same location at which a hot water cooled, wall convection quenched, gas sampling probe and silica coated thermocouple probe are axially located.

The movement of the mixing position rather than the diagnostic location does introduce some significant engineering difficulties, however. The relative length of the reaction zone introduces significant coupling in terms of boundary heat transfer, particularly as the reaction occurring is not necessarily isothermal. In order to deal with these issues effectively, all experimental parameters are independently closed-loop controlled. These controls permit the initial reaction, wall boundary conditions, and reaction pressure to be reproduced accurately for each re-location of the mixer, relative to the diagnostic location.

The reactor walls, shown in Fig. 2, are preheated (by five individually closed-loop controlled electrical resistance heaters) to the desired initial reaction temperature. Oxidizer enters with a nitrogen carrier gas (flowing from left to right) which is heated (using methods described below) to the desired initial reaction temperature. Gaseous (or pre-vaporized liquid fuel), along with about 5-10% of the total nitrogen carrier flow, is injected into the carrier-oxidizer stream at the entrance to the mixer-diffuser (Fig. 3) through a multi-jet injector. The upstream carrier flow is directed outward to the reactor tube wall by a central baffle plate, and then radially inward through a gap between the baffle plate and the mixer-diffuser block. A large number of opposed jets of the pre-vaporized fuel/nitrogen mixture issue into this radial inward flow from the fuel injection probe. An opposed-jet stirring occurs at the entrance to the diffuser section, with a nominal turnover time of about 0.5% of the total reaction test time downstream of the diffuser.

The mixer-diffuser (Fig. 3) is approximately 45 cm long and is machined from a low porosity, silica foam block to an outside diameter about 1.2 mm less than the nominal 10.16 cm inside diameter of the cylindrical reactor duct. The interior contour of the diffuser section has a throat diameter of 2.5 cm and an expansion half-angle of 5 degrees. The central baffle plate upstream of the mixer-diffuser is made of fused silica to reduce any chemical surface effects which might occur in the mixing region.

A stepper-motor-driven mechanism inside the pressure boundary is used to position the mixer-diffuser (Fig. 4) by moving the fuel injector. Liquid fuels are pre-vaporized into nitrogen at the entrance to the fuel injector, which is designed such that fuel vapor residence times in the probe are very short in comparison to those to be studied in the reactor. Fuels with as high a latent heat of vaporization as methanol, carbon numbers as large as C_{12}, thermal stabilities as sensitive as n-octane, and surface catalytic sensitivities as high as those of methanol, have been pre-vaporized and injected into the reactor without noted reactions prior to reaching the mixer-diffuser. In fact, in other work, we have also shown that full-blend gasolines can be pre-vaporized with this same technique, without reaction prior to reaching the mixer-diffuser.

Initially, an arc plasma gas heater similar to that employed in the Princeton APFR (Yetter, et al., 1991a) was used to heat the main carrier gas flow entering the mixer-diffuser ($800 < T < 1200$ K; $1 < P < 3$ atm.). This

approach was supplemented with a ferrous alloy electric resistance heater to increase the pressure and temperature operational ranges of the VPFR ($550<T<940$ K; $1<P<20$ atm.). Recently, both of these methods have been replaced with a composite ferrous alloy/tungsten resistance heater, operating over the combined experimental ranges.

The pressure shell of the VPFR (Fig. 2, 4) is made of 12" Schedule 40 carbon steel pipe and is ASME code stamped for operation from full vacuum to 28 atm. and 245 K to 533 K shell temperature. As mentioned earlier, the pressure shell encloses not only the reactor section (including electrical resistance heaters and insulation surrounding the reactor duct), but also the positioning mechanism and fuel vapor injector which axially locates the fuel/carrier mixing section relative to the sampling position. This design results in very low thrust to move probes (due to pressure drop across flanges) and eliminates the need for critical dynamic seals. Since all flanges are at lower temperature, there is also no need for exotic materials of construction to be used for the pressure shell nor elaborate designs required to maintain pressure seals. The cylindrical reactor section in which kinetic measurements are performed is a 173 cm long, 2 mm wall thickness, 10.16 cm inside diameter, fused silica tube which extends from a Inconel mating flange at the fuel injection probe entrance to a similar mating flange located at the entrance to the exhaust port of the reactor shell. A maximum of about 115 cm and a minimum of 25 cm of axial distance from the throat of the mixer-diffuser section to the sampling position are possible.

In order to translate flow reactor position into reaction time, the mean velocity distribution along the centerline is measured under cold flow conditions using hot-wire anemometry. These measurements are related to experimental conditions through Reynolds number correlations. Figures 5, 6 show typical hot-wire measurements of axial and radial velocity distributions taken under cold-flow conditions over the range of Reynolds numbers available in the VPFR.

The flow reactor is operated as a steady, isobaric flow device and the time from mixing to sample position is varied by moving the mixer-diffuser assembly along the quartz test tube. At each location of the fuel injection probe, the heat transfer and sampling systems are given time to reach quasi-steady conditions, and then sampling and other diagnostic data are acquired. All of the independent experimental parameters (carrier, liquid/gaseous fuel, fuel injector nitrogen, oxidizer flows; carrier inlet, reactor wall temperatures; reaction pressure; mixer-diffuser location) are electronically monitored and independently controlled from a single microprocessor-based control station. The ability of the VPFR design to achieve rapid mixing of reactants and a quasi-steady initial reaction temperature are demonstrated in Fig. 7. Figure 7 shows the reaction temperature, CO and O_2 mole fractions as functions of residence time for experimental conditions under which little reaction proceeds (because there is very little moisture present). Figures 8 and 9 are photographs of the VPFR and the VPFR control facilities.

Sample Extraction and Analyses

We have shown through our numerical modeling work the simultaneous characterization of numerous stable species, through extractive sampling and analyses, are as important as radical species measurements in comparison with, and constraint of, mechanistic model constructs. It should be mentioned here that, sampling difficulties are much less than in flames because sampling temperatures, radical concentrations, and spatial gradients are much lower. A hot-water-cooled, wall-convection-quenched, stainless steel sample probe is mounted in the reactor end flange and is used to continuously extract and convectively quench a small portion of the reacting gases (Fig. 2, 4). The reaction temperature at the gas sampling location is measured with a silica coated Pt-13%Rh/Pt thermocouple. Calculated gas sampling quenching times have been estimated to be very short in comparison to overall reaction times (Dryer, 1972; Emdee, 1991). From the probe, the gas sample flow passes through heated sampling lines to gas-sampling storage valves and then through further heated transfer lines to a Nicolet Model 730 FTIR, to a continuous flow electrochemical analyzer for O_2, to continuous non-dispersive infrared (NDIR) analyzers for CO and CO_2, and to a

continuous selective detector for H_2. Data acquired by these instruments are forwarded to an analog-digital board interface and recorded on a microprocessor system.

The gas sampling and storage technique developed here at Princeton (Dryer, 1972; Euchner, 1981) is utilized to obtain samples which can be analyzed off-line. Gas sample storage valves are interfaced with gas chromatographs (GC) to determine complex hydrocarbon species. Discrete samples collected at various axial locations are analyzed on a Model 5890A Hewlett Packard gas chromatograph, equipped with column switching, cryogenic capabilities and both catalytic and non-catalytic flame ionization detectors. Typically, analyses have been conducted on both 25m PlotQ and 30m DB-5 columns (0.32mm i.d. each). This system gives excellent separation and quantification of C_1 through C_{20} hydrocarbons. The same technique will be utilized to interface with a new GC/FTIR facility recently awarded to Princeton as part of the DOE/URI program (Dryer, et al., 1992).

While off-line analyses are essential for large hydrocarbon structures, we have recently developed on-line FTIR-based techniques to determine small hydrocarbon and hydrocarbon oxygenates directly in extracted sample stream. This technique is especially useful for compounds which exhibit off-line storage and/or GC analytical difficulties (e.g., H_2O, CH_2O and CH_3CHO). On-line, continuous analysis, of the extracted sample stream using FTIR is unique and exclusive to this group's flow reactor studies, and this analytical approach has been developed by us and utilized extensively since 1990.
An on-line, Nicolet Model 730 FTIR is used to measure NO, NO_2, H_2O, CO, CO_2, small hydrocarbons ($<C_4$) and hydrocarbon oxygenates in the sampled stream. Species measurements also made with GC off-line analyses compare favorably with those obtained by FTIR. We have also shown that FTIR can be used to characterize particular "classes" of compounds in the sampled stream, such as aromatics, olefins, etc. The analyzer has a 0.5 liter, heated (100 C) multi-reflective gas cell with an optical path length of 8.6 m. A liquid nitrogen-cooled MCT-A detector is used to measure spectral absorbance with a resolution of 0.5 cm^{-1}. Multivariate least squares fit software is used for quantification of the spectral data. Calibrations for species are obtained by measuring absorbance for different concentrations of each compound in nitrogen (and in mixtures in nitrogen), or by comparing responses to that determined by conversion of the material to combustion products.

One of the most powerful attributes of FTIR is that H_2O can be measured. Along with the other on-line measurements noted above, a C-H-O atom conservation balance can be performed continuously on the sampled stream. All of the FTIR spectra are multi-scan-averaged (32 scans), and computer storage of the raw spectral data permit searches for additional information (and species), even after the experiment has been performed.

Insitu Optical Diagnostics

Seldom is diagnostic experience and application in various systems easily transferred from one situation to another, unless it involves nearly the same experimental conditions. For example, it can be argued that (unlike the case of the flow reactor) the measurement of substantial numbers of key stable and short-lived molecular species is not adequately defined in many other kinetic-mechanistic experiments at high temperatures, e.g. in high temperature shock tubes. The importance of performing such additional measurements as a means of improving the definition of important reaction processes is obvious. It is recognized, however, that the definition of these species *insitu* under such circumstances is inordinately difficult, and often not universally useful. Similarly, product measurements of various reaction channels in elementary kinetic experiments are often incompletely defined. Frequently, this result is not from a failure to recognize the importance of such measurements, but the significant challenges in performing them. Flames represent systems where an abundance of optical diagnostics can be brought to bear simultaneously, but again, it is only with mass-extractive methods that an abundance of species can be measured. Furthermore, the kinetic interpretation of these experimental observations are strongly influenced by diffusive transport

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of species and energy. The cogent point to be recognized, however, is that each of the experimental conditions and configurations mentioned above offer different challenges to the experimentalist and the available diagnostic techniques. This result emphasizes the significance of developing detailed kinetic mechanisms by considering a wide range of data sources and conditions, what we have referred to as "comprehensive" model development (Westbrook and Dryer, 1981). Further, the fact that in none of these situations is each and every important parameter able to be measured (without interferences) emphasizes the need to carefully formulate experimental conditions (through sensitivity studies, for example) such that important observations are well defined by what can be measured.

A continuing criticism of flow reactor work (here and at other laboratories) has been a perception that very little consideration, in general, has been given toward direct measurement of reactive intermediates. Well-established methods for extractive sampling and analyses (principally developed here at Princeton) are commonly utilized here and elsewhere in high pressure flow reactors. However, the use of optical diagnostics in such devices is presently limited to efforts here at Princeton. As noted earlier, we have recently published two papers which report measurements of OH in the APFR (Linteris, 1990; Linteris, et al., 1991a, 1991b). Measurements were obtained in a $CO/H_2O/O_2$ reaction using line resonance absorption (Linteris, et al., 1991a) and 180 degree laser-induced fluorescence techniques (Linteris, et al., 1991b), and the OH profiles (at mole fractions from 10^{-5} to 10^{-6}) were in close agreement with a priori predictions generated from a comprehensive reaction model we had previously developed (Yetter, et al., 1991a, 1991b). We do not consider this result fortuitous, but indicative that the careful, collective measurement of numerous stable species through gas sampling methods, over a well chosen set of experimental conditions, offers considerable constraints on the associated modeling parameters. Most importantly, these measurements showed that radial concentration deviations in [OH], as determined by fluorescence, were such that radial line-of-sight absorption would result in accurate quantification of the absolute axial concentration (Linteris, 1990).

The concentrations of radicals in CO, H_2 and hydrocarbon oxidation reactions at flow reactor conditions are typically different from one another, and from those present under flame and high temperature shock tube conditions (where similar multi-component mixtures are present). Some typical species which would be useful in our work include OH, HO_2, H_2O_2, and CH_3, and it is enlightening to note mole fractions of these species under several sets of experimental conditions typical in the VPFR. For example in a $CO/H_2O/O_2$ (1%/0.5%/0.5% in nitrogen) reaction at 1000 K and 6 atmospheres pressure, the predicted peak mole fractions of OH, HO_2, and H_2O_2 are $5x10^{-7}$, $1.2x10^{-6}$, and $1.1x10^{-7}$, with OH being further depressed by increased pressure. Atmospheric pressure conditions are discussed fully in Linteris, et al., 1991a., where OH mole fractions may be as high as $5x10^{-5}$. Under some ranges of initial conditions, this system can generate HO_2 mole fractions as high as $2-3x10^{-4}$. In methanol oxidation (0.4% CH_3OH, 0.6% O_2 in nitrogen) at fifteen atmospheres and 783 K (recently studied experimentally), the predicted peak mole fractions of OH, HO_2, and H_2O_2 are $2.5x10^{-9}$, $3.5x10^{-6}$, and $4.3x10^{-4}$ (CH_3 less than 10^{-10}). Finally, the predicted mole fractions of OH, HO_2, H_2O_2, CH_3 and HCO in an oxidation of iso-butene (0.3% isobutene, 1.8% O_2 in nitrogen) at 1140 K and one atmosphere at 50% fuel consumption are $7.7x10^{-9}$, $1.1x10^{-6}$, $1.2x10^{-7}$, $5.5x10^{-6}$, and 10^{-9}. Development and application of "universal" techniques which meet all of these requirements with quantitative capabilities the order of 50 to 100 greater than these peak values offer severe challenges, indeed. It should be clear that only in select, judicious experimental configurations and conditions can these species be quantified with accuracy sufficient to refine kinetic models at flow reactor conditions.

We have, since the inception of this program, strongly supported the notion that kinetic information could be enhanced by judicious measurement of some of the key radical concentrations profiles in specific flow reactor experiments. In situ optical measurements of highly reactive molecular intermediates which sampling processes may affect is also of similar importance. The efforts we have put forth on in situ optical diagnostics studies of OH in the APFR were well-conceived, but comparatively difficult ones in this configuration (a source of much delay in achieving results), and this experience has led to the novel configuration of the VPFR in which we will make future measurements. The substantial apparatus modifications (the order of

$200,000) we have pursued offer a significant improvement in potential for optical measurements. We consider that OH, HO_2, and CH_3 measurements in the VPFR, under some restricted experimental conditions, would contribute significant bench-mark measurements for mechanistic comparisons. Using our own discretionary resources we have developed the hardware to accommodate *insitu* laser resonance absorption measurements of [OH] in the VPFR. Additional instrumentation to measure CH_3 and HO_2 is presently being developed. Each of the measurement approaches are briefly described below.

The design of the VPFR greatly simplifies optical access and insitu optical diagnostic measurements at any reaction time within a single experiment. In the VPFR, the optical access consists of four ports at 90 degree radial positions. Because of the hazards involved in the design and operation of windows in high pressure environments, all optical signals are conducted to the interior of the pressure envelope surrounding the experiment by fiber optics. A small pressure vessel is connected to the main shell (Figure 10) and contains the fiber positioner, detector, beam splitter and a small chopper (Figure 11). The opposite port is equipped v. .th a flange attachment positioning a 1" mirror on a gimbal mount.

A Coherent 699-21 CW ring dye laser served as the light source for performing OH measurements. In order to access the near ultraviolet wavelengths, intracavity frequency doubling by a lithium iodate crystal is used. Because of the low conversion efficiency of doubling crystals, a large amount of power is required to generate a sufficient quantity of UV radiation. Thus, the CR-699 is optically pumped by a Coherent I-100/20 argon ion laser. This laser provides approximately 7.5W of optical power at 514 nm which is then converted into 2-4 mW of single frequency ultraviolet radiation by the CR-699.

The lasers are located in a separate laboratory adjacent to the VPFR, and the UV beam is coupled to a 20m length of 50 micrometer core silica fiber. A single detector (EG&G Photon Devices UV-444B with a PMI OP-27 amplifier) alternately detects the signal and reference beams, as in Figure 11. This arrangement allows for the detection of the difference in signal and reference intensities, which is more sensitive than simply detecting the individual beams and ratioing them. The sensitivity of this methodology is about one and a half orders of magnitude greater than that reported in Linteris, et al., 1991. Of special interest are CO oxidation studies seeded with small amounts of other reactants (such as hydrocarbons) and hydrocarbon oxidations themselves.

We have chosen OH resonant absorption on the $A^2\Sigma^+(v=0)$ to X^2 $(v=1)$ band at approximately 308 nm over the more commonly used technique of laser induced fluorescence (LIF) for two reasons. (The design of the VPFR facility, however, would accommodate this option.) First, the LIF measurement requires independent knowledge of the collisional quenching cross-section for the electronically excited OH radical. While efforts have been made to quantify this parameter, it is a strong function of the composition of the bath gas and pressure. Because the composition varies during the course of the reaction and the experiments are carried out over a range of pressures, it is difficult to obtain a quantitatively accurate measure of the concentration of OH using LIF.

Typically, experiments are carried out at a roughly constant initial mole fraction as the pressure is varied. Thus, the detection limit of a species of interest is more appropriately determined in terms of mole fraction, rather than concentration. This has the effect of increasing the sensitivity of the diagnostic as the pressure is increased due to the density effect. However, the increased density also increases the effects of pressure broadening on an absorption line profile, thus decreasing the line center absorption coefficient for a given concentration. These two effects are roughly compensating, and both absorption and LIF measurements are affected. However, the LIF signal is also reduced at higher pressures by increased collisional de-excitation. Thus, an absorption measurement maintains a roughly constant detection limit in terms of mole fraction, while the LIF technique should suffer an approximately linear degradation in detection limit with increasing pressure.

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For these two reasons, absorption was chosen as the initial optical diagnostic for VPFR experiments. However, the OH diagnostic described above could still be used in conjunction with LIF measurements to obtain valuable spectroscopic information (at radial locations as well). First, because simultaneous absorption and LIF measurements can be made, and stable gas species mole fractions are determined by conventional gas sampling, the effect of bath gas composition and pressure on quenching rates could be determined simply in a series of experiments. Also, once this information is obtained, along with broadening coefficients as a function of pressure and temperature, LIF could be used as a secondary diagnostic for OH, especially as the pressure increases such that the line width of the rotational line becomes comparable with the scanning range of the dye laser.

Absorption (since it is a line-of-sight measurement) is accurate only if the concentration (or mole fraction) of the species to be measured is constant over the optical path. Measurements in the APFR using a radially positioned LIF probe (Linteris, 1990) indicate that the OH concentration is constant to within experimental scatter over at least the central 90% of the reactor tube diameter (Figure 12). Because of the similarity of the two reactors with respect to geometry and flow field considerations, this result also applies to the VPFR.

The measurement of the OH radical is especially important for the work we have initiated (Yetter and Dryer, 1992; see progress report) on the study of elementary reactions involving HO_2 in seeded $CO/H_2/O_2$ reaction studies at high pressures. The measurement of OH in selected experiments, along with the stable species in these reactions, will significantly improve the kinetic definition of the reacting system and the estimation of O, H, and HO_2 in the reaction zone.

Methyl radicals and hydroperoxy radicals are of comparable importance to the combustion kinetic experiments we wish to pursue. For this reason, additional optical diagnostics, using the same optical porting as the OH measurements have been considered. We have proposed to measure CH_3 and HO_2 spectroscopically in the UV at 216.6 nm and between 210 nm and 230 nm, respectively. Hanson, et al., 1992 has recently demonstrated methyl radical measurements in shock tube experiments at 216.6 nm, but at considerably higher temperatures (≈ 2043 K). In experiments at much lower temperature (≈ 1300 K), Hanson et al. also detected HO_2 at 226.06 nm, but with some interferences from CO. Jemi-Alade, et al., 1992 have also studied HO_2 at 210 nm at ≈ 650 K, but with some interferences from H_2O_2. Hippler and Troe, 1992 used 230 nm for HO_2, since at this wavelength the absorption characteristics are nearly independent of temperature, Because absorption measurements do not typically require large amounts of incident light intensity, and poly-atomic radicals exhibit broad absorption bands, a conventional light source with a spectrograph detector should perform these measurements as easily and in a much more cost effective manner than laser-based diagnostics. A medium power xenon light source coupled to a fiber optic will be utilized as the UV source (and also could be used as a visible and NIR source). Instead of utilizing a signal detector inside the pressure boundary, the return beam will be focused onto another fiber optic coupled to an external 1/4 meter monochrometer/spectrograph (Figure 11). These more conventional optics can supply spectrographic information for the aforementioned radical, as well as several other species simultaneously. Because of the greater power stability of the conventional light source over that of a dye laser, the sensitivity of this diagnostic technique should be at least as great as a laser-based method. The obvious disadvantage is the lower spectral resolution of the spectrograph as compared to laser-based methods. This is not as important an issue with the broadened spectroscopic features of polyatomic species.

References

Crocco, L., Glassman, I., and Smith, I.E. (1957). "A Flow Reactor for High Temperature Reaction Kinetics", Jet Propulsion, 12, 66.

Dryer, F.L. (1972). "High Temperature Oxidation of Carbon Monoxide and Methane in a High Temperature Flow Reactor", Ph.D. Thesis, Department of Aerospace and Mechanical Sciences, Princeton University, Princeton, NJ, March. Report Number AMS-T-1034.

Emdee J.L. (1991). "An Experimental and Modeling Study of the High Temperature Oxidation of the Xylenes", Ph.D. Thesis, Dept. of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ. Report Number MAE-T-1900.

Euchner J.A. (1981). "A Study of the Oxidation of Toluene in a Flow Reactor", M.S.E. Thesis, Dept. of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ. Report Number MAE-1497-T.

Hanson, R.K., Bowman, C.T., and Davidson, D.F. (1992). "The Chemistry of Natural Gas Combustion and Pollutant Formation", 1992 Contractor's Review Project Advisor Group Meeting, Gas Research Institute, Chicago, IL, May 20-21.

Held, T.J. (1993). "A Flow Reactor Study of Methanol, Iso-butene, and Methyl Tert-Butyl Ether", Ph.D. Thesis, Mechanical and Aerospace Department, Princeton University, Princeton, NJ. In Preparation.

Hippler, H. and Troe, J. (1992). "Rate Constants of the Reaction $HO + H_2O_2 \rightarrow HO_2 + H_2O$ at $T \geq 1000$ K", Chem. Phys. Let., 192, 333.

Jemi-Alade, A.A., Lightfoot, P.D., and Lesclaux, R. (1992). "A Flash Photolysis study of the $HO_2 + HCHO \rightarrow H_2O_2 + HCO$ Reaction between 541 and 656 K", Chem. Phys. Let., 195, 25.

Linteris, G.T. (1990). "Trace Radical Species Detection in a Turbulent Chemical Kinetic Flow Reactor Using a 180° Laser Induced Fluorescence Probe", Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, February. Report T-1878.

Linteris, G.T., Yetter, R.A., Brezinsky, K., and Dryer, F.L. (1991a). "Hydroxyl Radical Concentration Measurements in Moist Carbon Monoxide Oxidation in a Chemical Kinetic Flow Reactor", Combust. Flame, 86, 162.

Linteris, G.T., Brezinsky, K., and Dryer, F.L. (1991b). "A High Temperature 180 Degree Laser Induced Fluorescence Probe for Remote Trace Radical Concentration Measurements", Applied Optics Letters, 30, 381.

Seeley, J.V., Jayne, J.T., and Molina, M.J. (1993). "Fast Flow Techniques of Gas Phase Kinetic Studies", Int. J. Chem. Kin., In Press.

Yetter, R.A., Dryer, F.L., and Rabitz, H. (1991a). "Flow Reaction Studies of Carbon Monoxide/Hydrogen/Oxygen Kinetics", Comb. Sci. Tech., 79, 129.

Yetter, R.A., Dryer, F.L., and Rabitz, H. (1991b). "A Comprehensive Reaction Mechanism for Carbon Monoxide/Hydrogen/Oxygen Kinetics", Comb. Sci. Tech., 79, 97.

Figures

Figure 1

Figure 2

Figure 3

Electric Resistance Heater

Arc Heater

Evaporator

Slide Table

Oxidizer Inlet

Fuel Injector

Optical Access Ports

Wall Heaters

Sample Probe
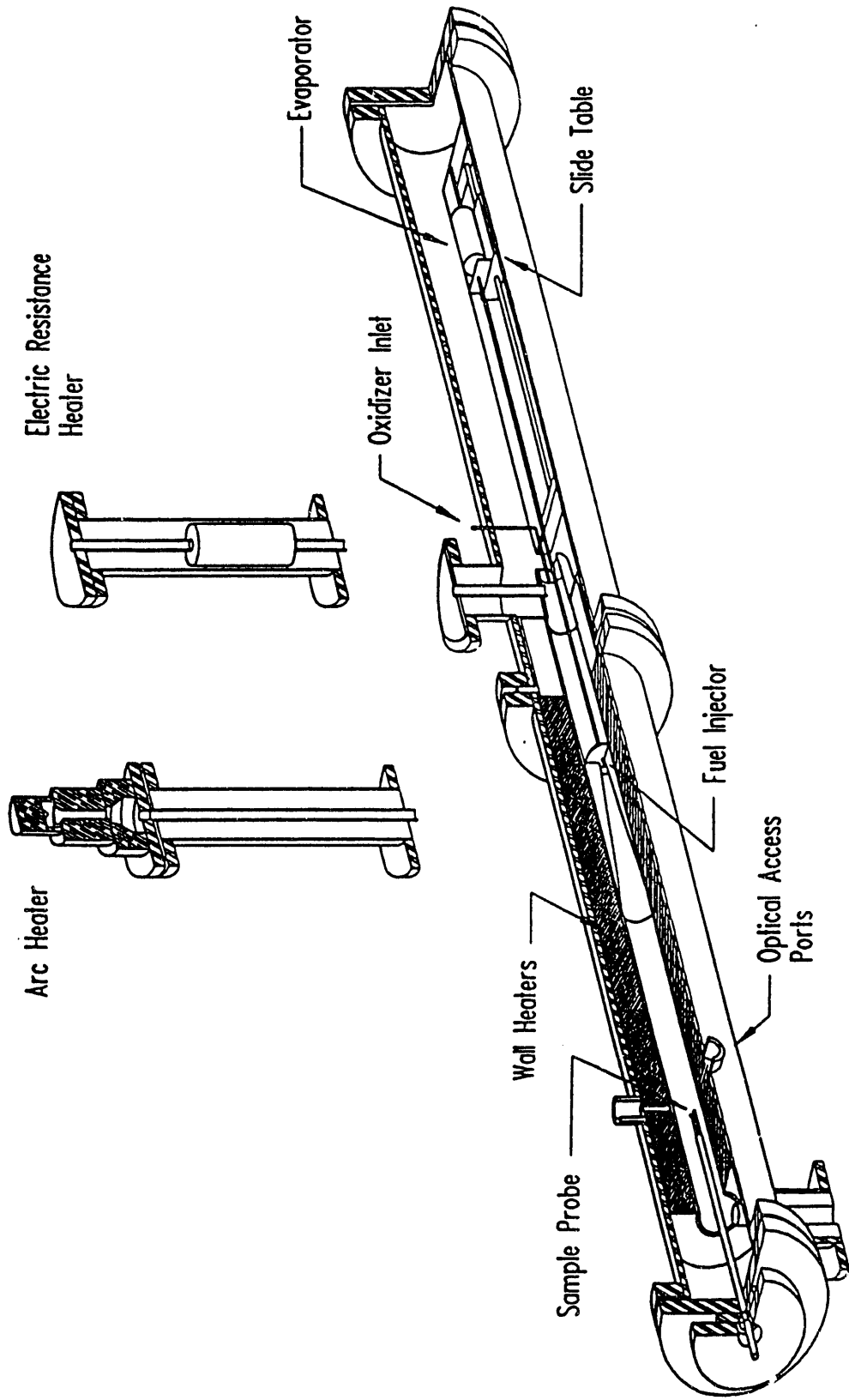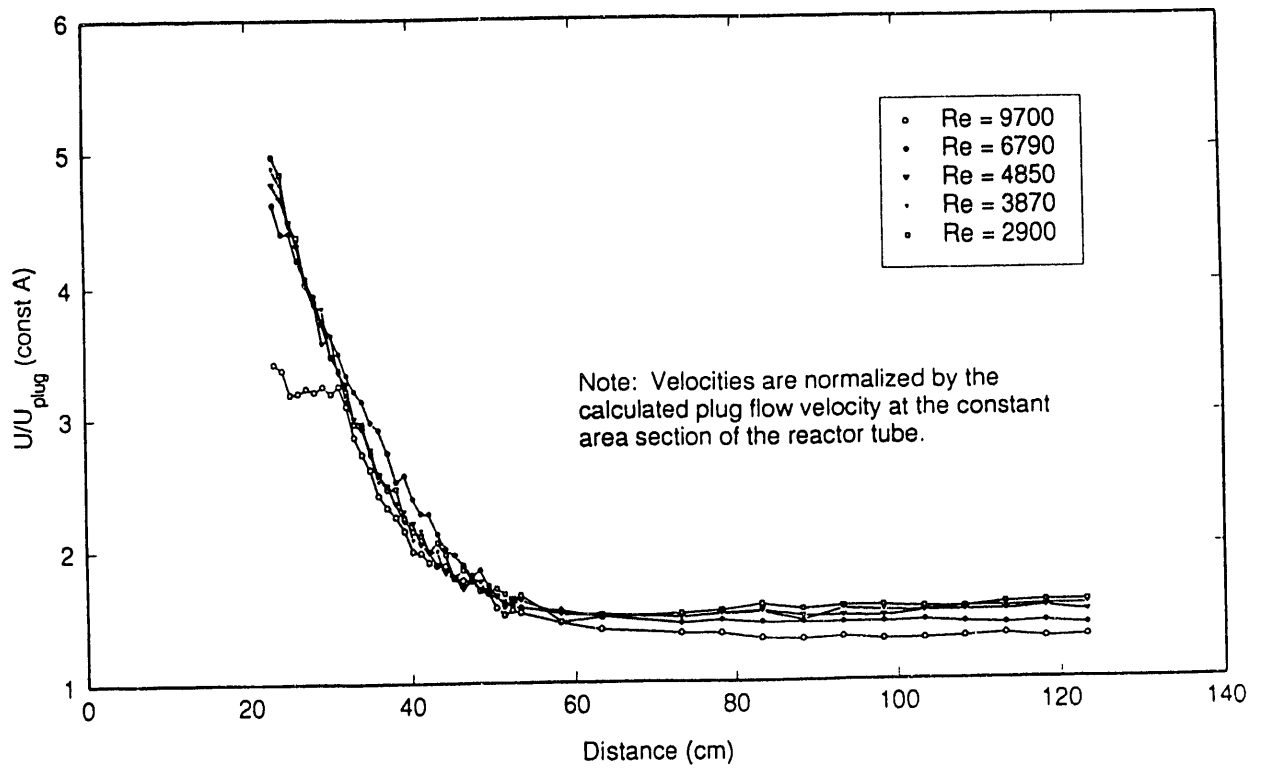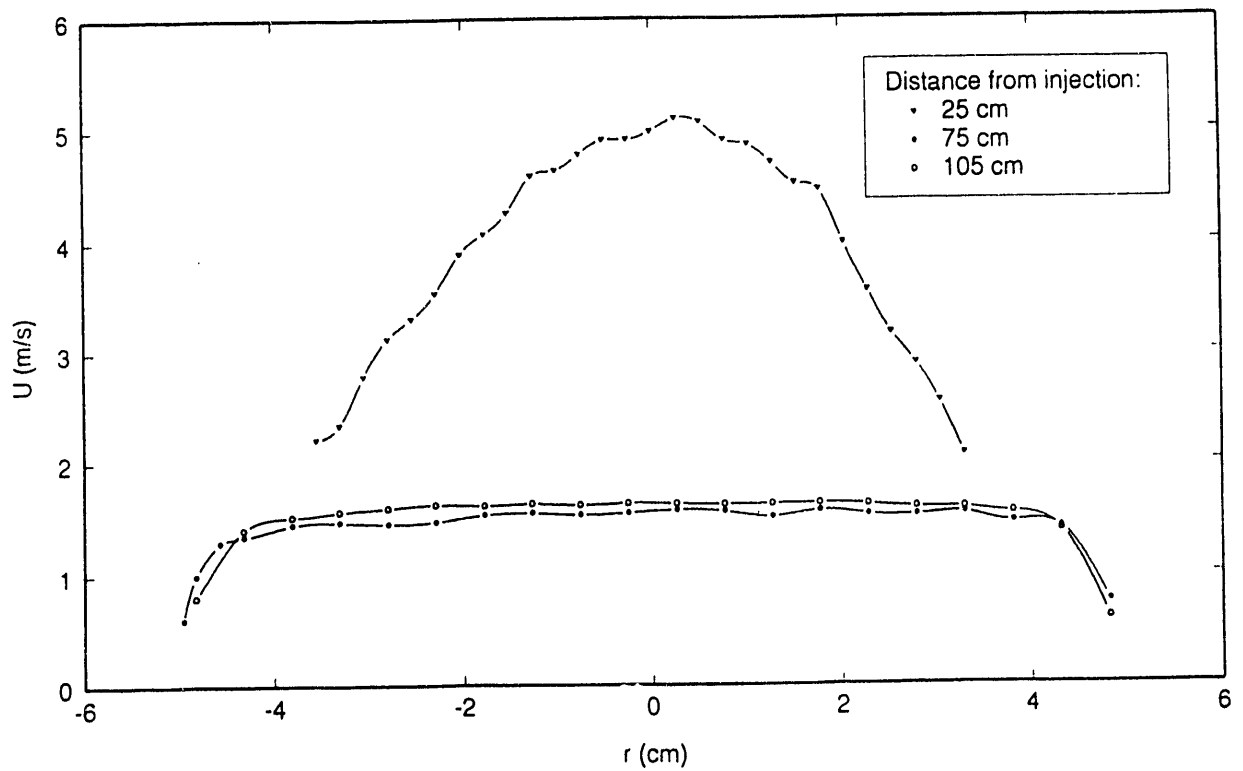
Figure 4

Figure 5

Figure 6
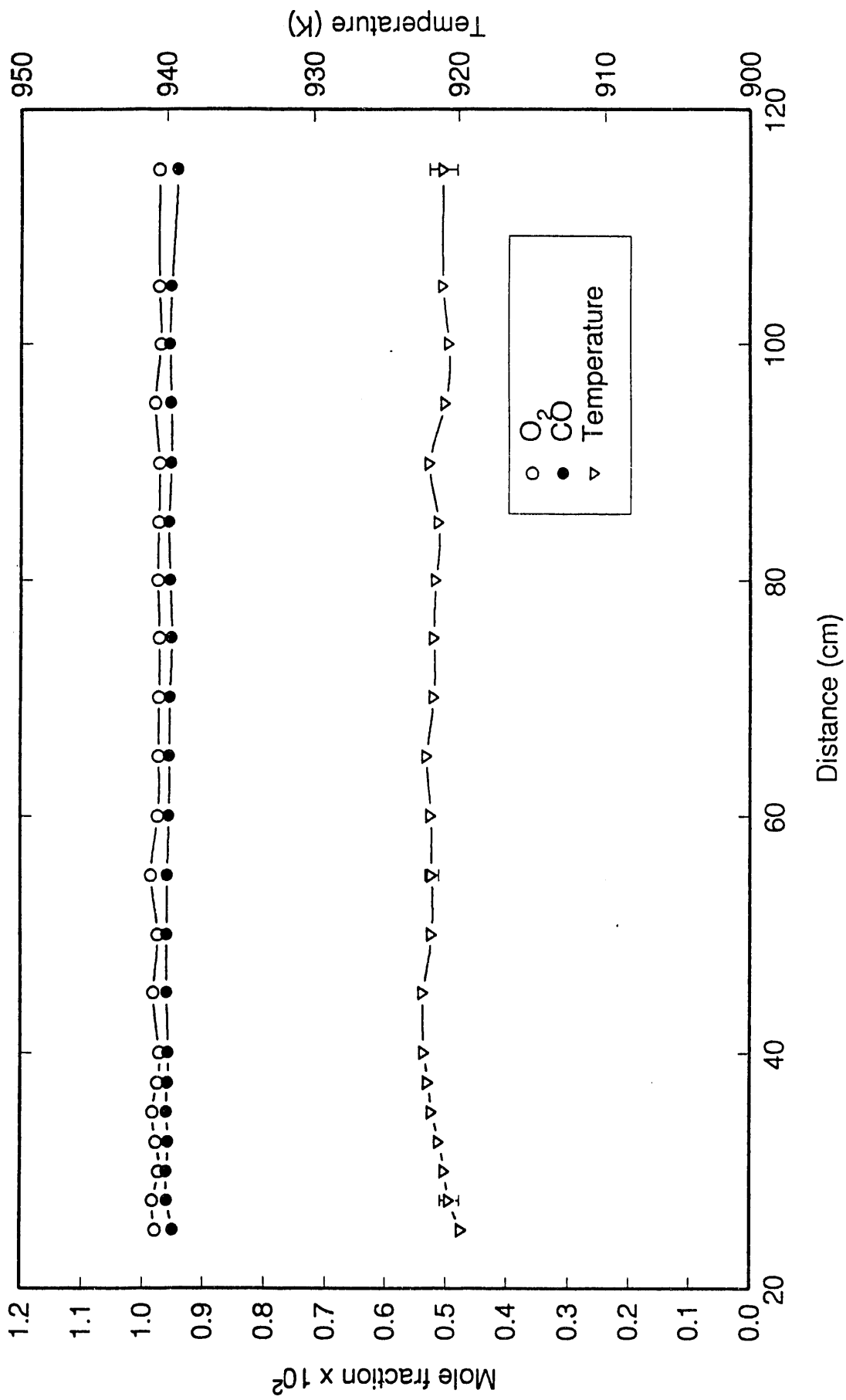
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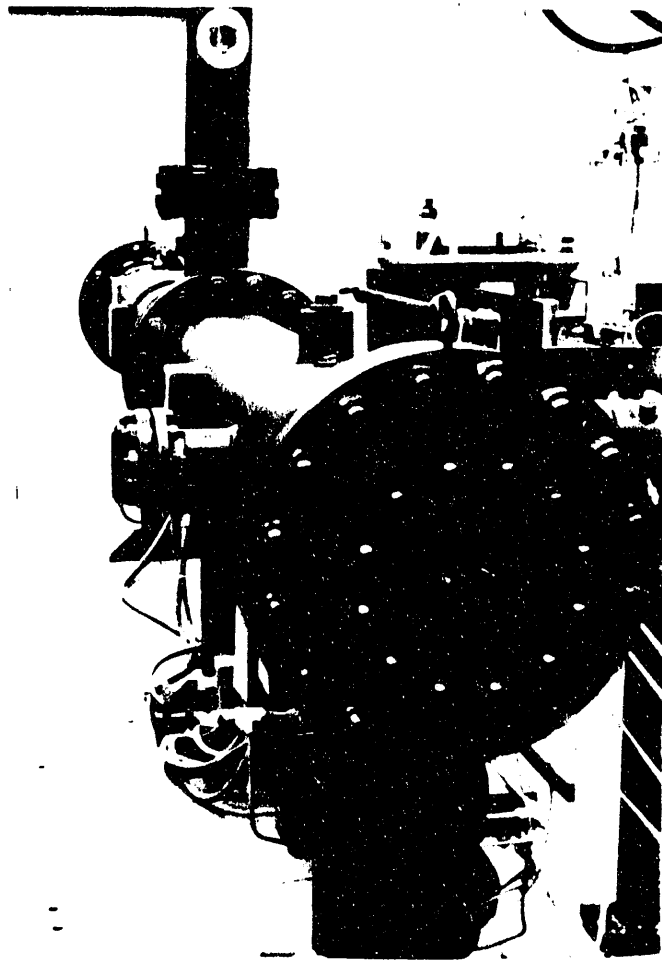
Figure 8

Figure 9

Figure 10

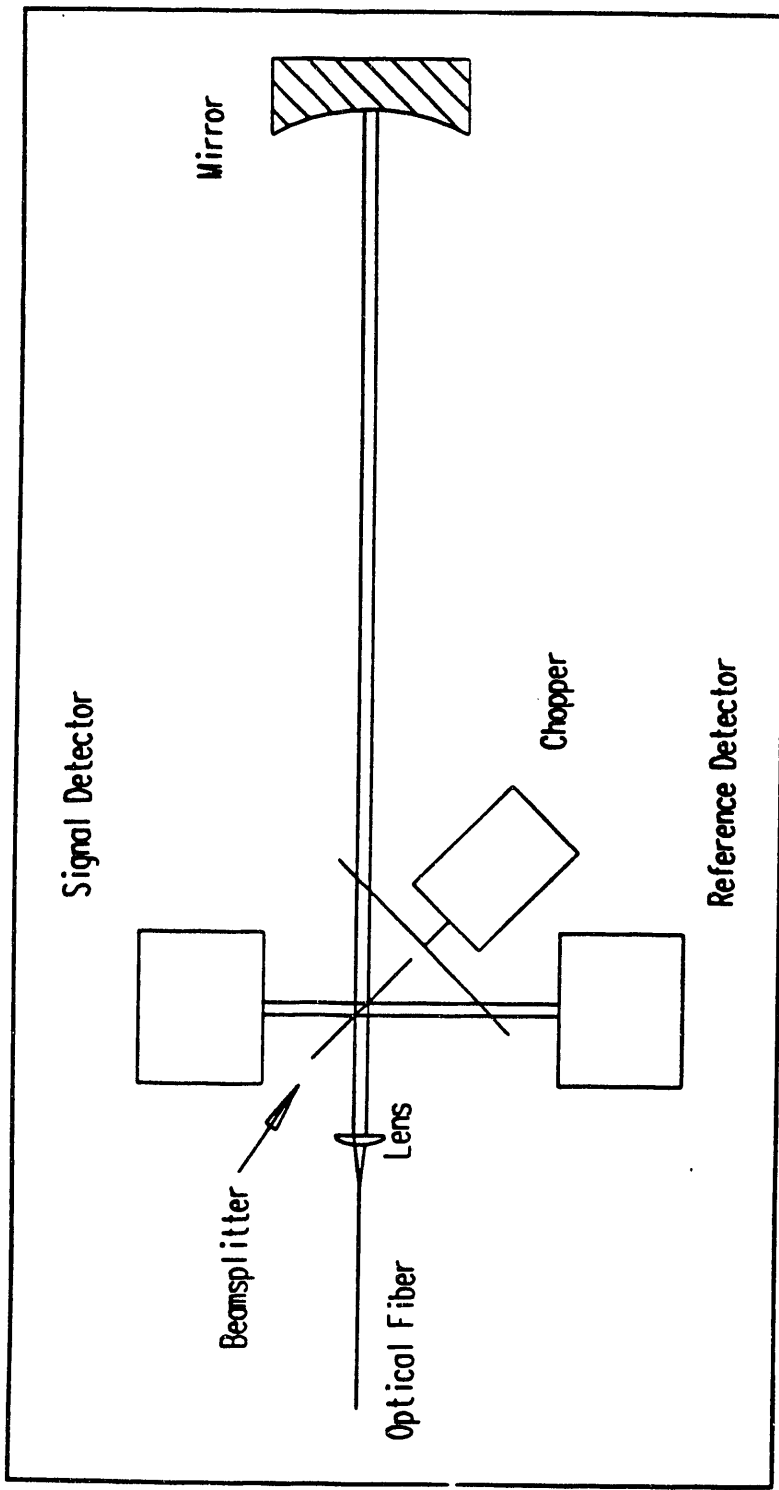Electrical and fiber optic feedthroughs
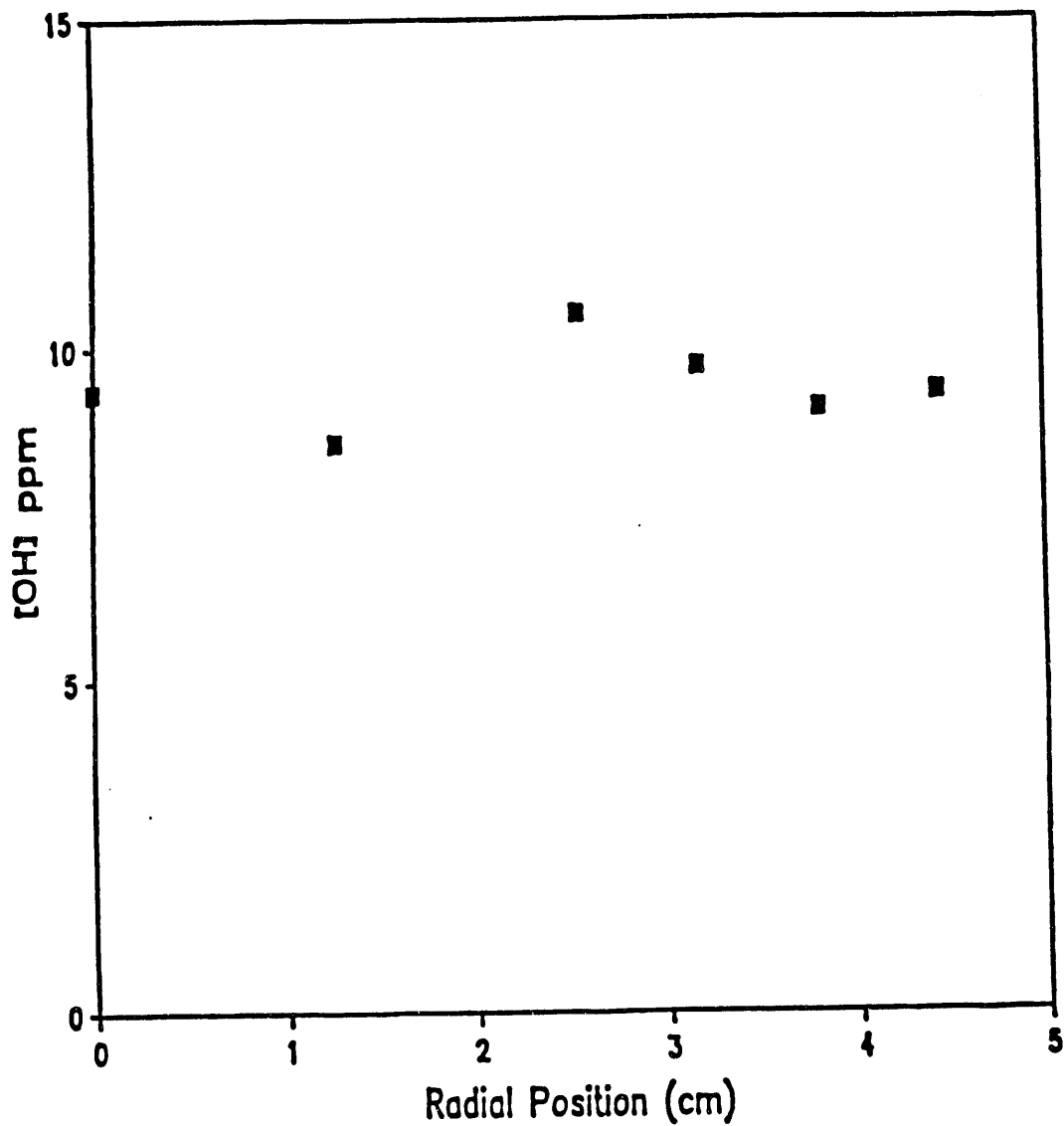
Quartz tube

Mirror
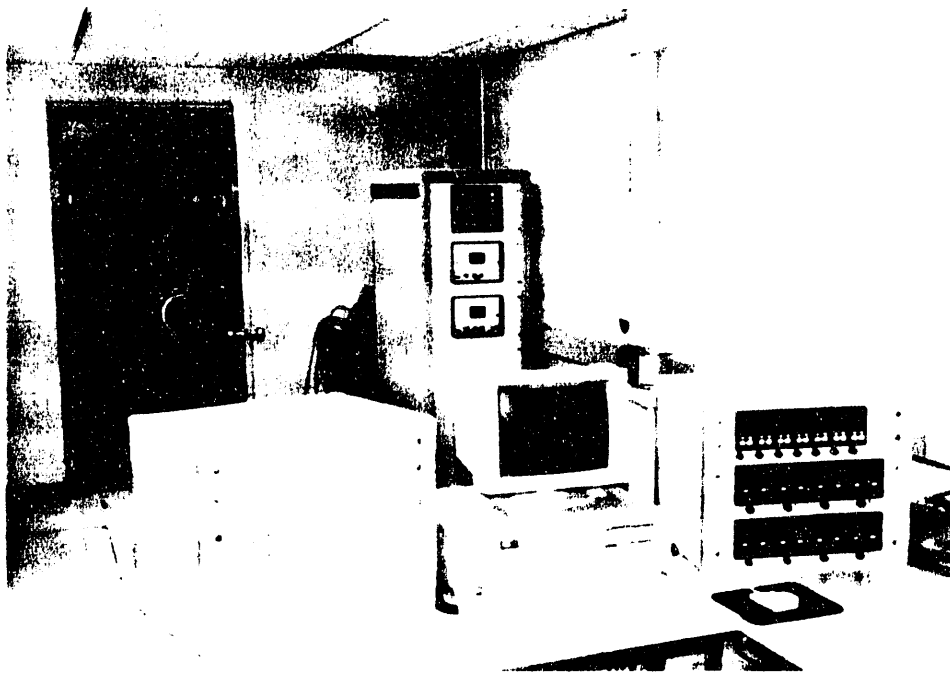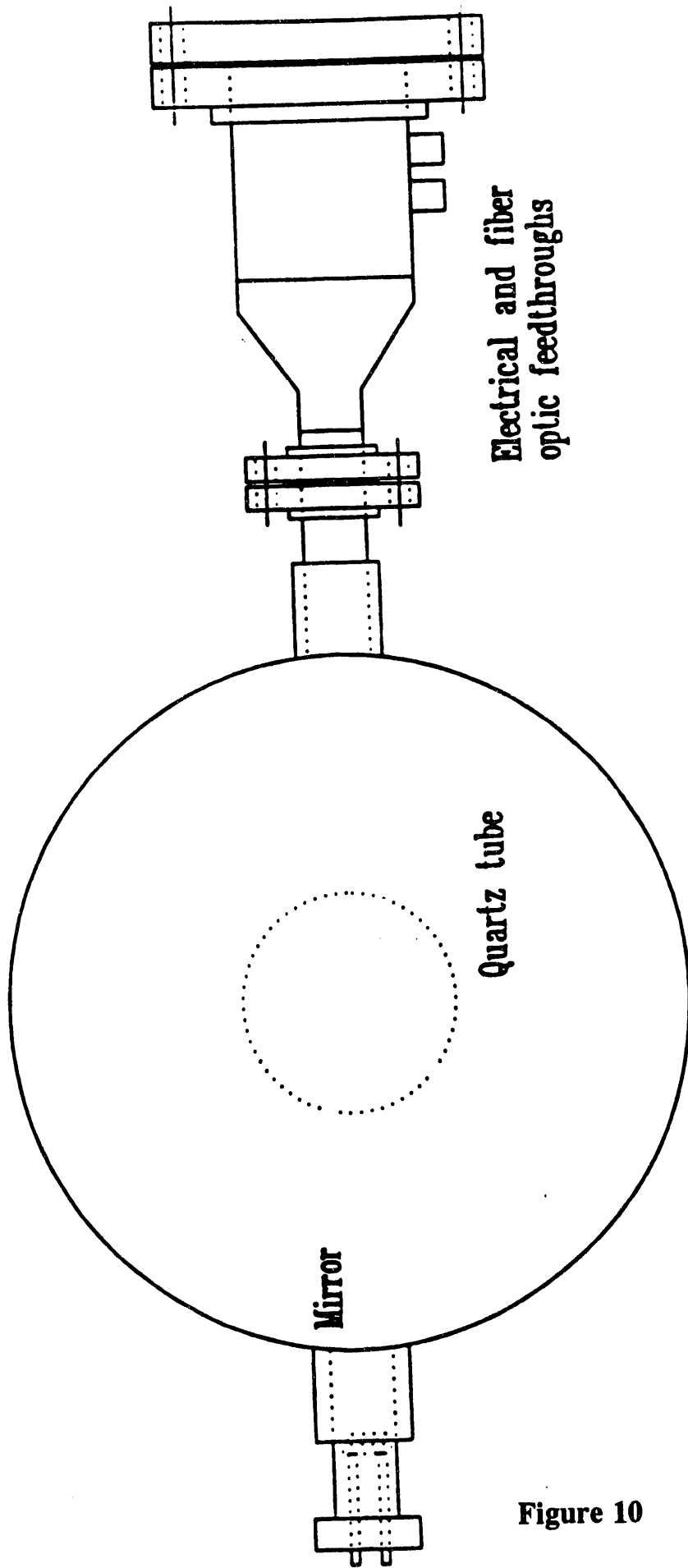
Figure 11

APFR Moist Carbon Monoxide Oxidation
Radial Distribution of [OH], 99 cm From Initial Mixing Location
Measured Using a Movable 180 Degree Laser Induced Fluorescence Probe
(Linteris et al., 1991)

$X_{CO} = 0.00849$, $X_{O2} = 0.00923$, $X_{H2O} = 0.00600$, T = 1115 K, Re = 9,980

Figure 12

END

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