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COMBUSTION CHEMISTRY OF CHAIN HYDROCARBONS

by

Frederick L. Dryer and Irvin Glassman

Aerospace and Mechanical Sciences Report #1350



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Abstract

→ The current understanding of the combustion chemistry of paraffin hydrocarbons is summarized. Emphasis is placed on reviewing the semi-empirical methods presently available for modelling alkyl hydrocarbon combustion. The anomalies inherent in some of the existing models and approaches to improve both qualitative and quantitative predictive capabilities are discussed. Modelling alkane combustion chemistry over extended ranges of equivalence ratio, pressure, and temperature, requires the consideration of sequential but partially overlapping processes: an initial period of induction phase chemistry; conversion of primary aliphatics to olefins, oxidation of the resulting olefins to carbon monoxide, and simultaneous oxidation of hydrogen produced in the hydrocarbon destruction. The conditions under which the induction phase chemistry can be neglected in modelling efforts is explored. HO_2 chemistry is found to be required in order to extend the applicability of detailed hydrogen/carbon monoxide/oxygen mechanisms to ranges of pressure and temperature normally used in practical combustion system modelling. Functional quasi-global kinetic expressions for alkane oxidation are discussed and errors in some published results on overall rate coefficients are clarified. Stress is given to the advantages of quasi-global kinetic modelling and the additional modifications required for these models to have greater applicability. ←



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Introduction

Numerical modelling may play an ever important role in our understanding of complex combustion systems. In this regard, then, accurate representation of combustion kinetics becomes a very necessary and important element in advancing the analytical tools required to guide development of hardware compatible with alternative fuels. Recent work has led to improved, conceptual understanding of high temperature hydrocarbon pyrolysis and oxidation chemistry. However, detailed modelling of hydrocarbon reaction systems other than methane has not been successful because of more complex kinetics (e.g., see Reference 1). Both the lack of understanding of the elementary reactions required to model these systems over extended ranges of temperature and pressure and the lack of accurate elementary rate data contribute to the problem. Furthermore, although it has been frequently demonstrated that relatively large systems of elementary reactions can be handled numerically, even in simplified fluid-mechanically coupled simulations, the numerical complexities and code size required to model real energy conversion systems with large detailed mechanisms remains prohibitive. Thus much of the modelling to date has employed some approximation to the chemical kinetics in order to predict the interactions of chemistry and fluid mechanics which result in energy release distributions and the rate of production of pollutants. This paper summarizes the available information from which realistic kinetic approximations for hydrocarbon chemistry can be formulated, discusses past and current efforts for developing models, and suggests future experimental and analytical needs for improving approaches which

approximate the true hydrocarbon combustion chemistry. Quantitative detailed chemistry of the $H_2/CO/O_2$ mechanism will also be discussed in relation to hydrocarbon combustion. Another paper² in this workshop considers aromatics. Because of a lack of high temperature data on other hydrocarbons and for expediency, this discussion will be limited primarily to the normal alkanes, although some limited analysis of branched chain structures will be presented.

General Modelling Considerations

Let us first consider the general oxidation characteristics of the normal alkanes. We shall exclude discussion of methane oxidation because it has received considerable attention in terms of detailed modelling (e.g., References 3 and 4) and because its oxidation is dominated by (the difficulty of) methyl radical oxidation. This trait is not characteristic of any of the higher alkane oxidation systems and is the reason methane should not be used in experimental programs to represent a general hydrocarbon oxidation process. In these discussions, it should be kept in mind that any empirical model must be quantitatively valid over a variety of fuel/air ratios and relatively wide ranges of pressure, temperature and residence times if it is to be useful in practical combustion modelling. Some recent experimental work at Princeton⁵ adequately demonstrates many of the qualitative features of the hydrocarbon oxidation process and will be used later in the paper to quantitatively assess empirical modelling formulations.

Much of the conceptual approach given throughout this paper stems from our work with the Princeton turbulent flow reactor extensively described in several earlier publications.⁵⁻⁹

By restricting experiments to highly diluted mixtures of reactants, and extending the reactions over large distances, concentration gradients in this reactor are such that diffusion is negligible relative to the convective component; thus, the measured specie profiles are a direct result of chemical reaction alone. This fact has recently been corroborated in the modelling of methane/oxygen and moist

carbon monoxide/oxygen experiments.

It is important to reemphasize that in this flow reactor, uniform turbulence results not only in rapid mixing of the initial reactants, but also in radially uniform, 1-dimensional flow characteristics. Thus, real "time" is related to distance through the simple plug flow relations. However, the relation of a specific axial coordinate to real time is not well defined since the initial time coordinate occurs at some unknown location within the mixing region. One would suspect that the initial mixing history could therefore alter reaction phenomena occurring downstream. However, the existence of very fast elementary kinetics, which initiate chemical reaction before mixing is complete, permits rapid adjustment of the chemistry to local conditions as the flow approaches radial uniformity. Furthermore, the large dilution of the reactants and rapidity of the kinetics reduce the coupling of turbulence and chemistry to the point that local kinetics are closely predicted by local mean flow properties.¹⁰ This conclusion is also verified experimentally by excellent agreement of the derived elementary chemical kinetic data with that obtained from shock tubes and static reactor systems at other temperatures^{8,9} as well as by the initial analytical modelling efforts. These calculations also substantiate that the reactor surfaces do not significantly affect the gas phase kinetics of the large reactor core where measurements are made. Comparison of flow reactor data from reactor tubes of significantly different surface to volume ratio also corroborates this conclusion. Finally, and most importantly, the turbulent flow reactor approach permits kinetics measurements over a range of temperatures, 800 - 1400 K (reaction

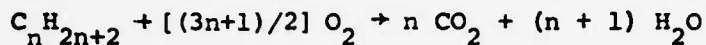
times 10-200 msec) which are generally inaccessible to low temperature methods (fast flow electron spin resonance, kinetic spectroscopy techniques, static reactors, etc.) and high temperature techniques (shock tubes, low pressure post flame experiments, stirred reactors), but which are important to combustion processes.

Figures 1 through 4 present data from the flow reactor for very fuel-lean oxidation of several alkane hydrocarbons above methane. The observed reaction profiles correspond to the "post-induction" phase of the oxidation. The induction period, i.e., the reaction period dominated by initial thermal or chemical attack on a CH bond of the fuel and other secondary chemical kinetic initiation processes typically occurs in the mixing region of the flow reactor and is extremely short. (There are some exceptions to this general statement which will be discussed later.) The induction phase of the chemical kinetics process can be significantly modified or even eliminated in practical systems by backmixing or diffusion of partially oxidized species and radicals produced in the post induction zone and thus initiation chemistry is generally not of great importance in most combustion systems.

Figures 1-4 clearly show that even in very lean oxidation there appears to be an initial isoenergetic region in which the decomposition of the alkane takes place. The conversion of the alkane appears to be primarily to alkenes and is clearly an endothermic process. However, the hydrogen formed during this pseudo-pyrolysis step simultaneously reacts to form water. This reaction essentially compensates the endothermicity of the initial "pyrolysis" step.

Subsequently, and with some energy release, the unsaturated hydrocarbons are converted to carbon monoxide and hydrogen while the

hydrogen present and being formed continues to oxidize. Finally, the large amount of carbon monoxide formed is oxidized to carbon dioxide, and most of the heat of reaction of the overall step



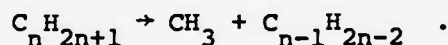
is released during this final reaction segment.

Earlier experimental investigations substantiate these qualitative observations for temperatures above 1000 K. As early as 1963, Orr,¹¹ presented shock tube results at 1 atm for n-heptane and iso-octane, and suggested similar behavior for these higher chain hydrocarbons. Levinson¹² later repeated, confirmed and extended these earlier studies on n-heptane. Initial decomposition of alkanes through olefin formation in shock tube studies of "ignition delay" has also been noted by several other authors.¹³⁻¹⁵ It should be noted that the induction period as defined earlier and ignition delay measurements only correspond closely for methane. For the higher hydrocarbons, shock tube ignition delay (especially when determined by pressure rise) corresponds more closely to the characteristic time required for carbon monoxide oxidation to begin. Major reaction of the initial fuel (and even the olefins formed) should logically occur more to the oxidation of carbon monoxide since the reaction rates constants of the reactions are one to two orders of magnitude faster than that for carbon monoxide.¹⁶ The shock tube observations of Hawthorne and Nixon¹⁷ qualitatively confirm these arguments by the fact that ignition delay for propane and its decomposition products (mixtures of propene and hydrogen) were found to be very similar.

It is well known that if a tertiary carbon exists in a hydrocarbon the hydrogen attached to it will be abstracted first, and if

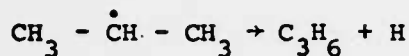
no tertiary-carbon atom is available, a hydrogen atom will be abstracted from the secondary carbon in the chain. There is no doubt that the initial attack on alkanes is a hydrogen abstraction by OH, H, and O radicals, and in fact, the elementary rate data¹⁶ show that the position of attack is a question of relative rates. Multiple tertiary carbon atoms are normally not encountered in a given hydrocarbon compound whereas one must realize that there are at least six CH bonds on terminal carbon atoms in every alkane structure. Thus, for example, if the difference in bond energy and the number of various bonds available, is taken into account at 1000 K, radicals formed from attack on a secondary compared to an primary carbon for propane and n-butane will be approximately 1 and 2.

In their review Fristrom and Westenberg¹⁸ state that the hydrocarbon radicals thus formed decompose into a methyl radical and an olefin with one less carbon number

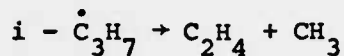


However, this general statement is not supported by flow reactor data for oxidation of the hexane isomers as shown in Figures 6 and 7.

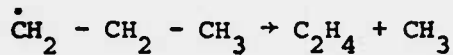
There should be a great preponderance of pentenes compared to other olefins early in the reaction if Fristrom and Westenberg's general statement were correct. However, experiments on deuterated compounds¹⁹⁻²² show that when a radical decomposes, a bond once removed from the site is broken — since in this case both a proton and hydrogen atom shift are not required. In addition, when there is a choice between a CH bond and a CC bond in these radicals, the CC bond is usually broken due to the lower bond strength. Thus, one finds



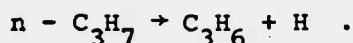
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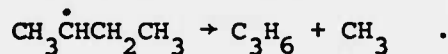
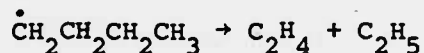
but



instead of



In the case of butyl radicals one finds:



There has been some unresolved controversy over whether any decomposition through the unfavored routes can occur. Some investigators have claimed that no direct decomposition via these reactions can take place, but that an internal rearrangement must occur before decomposition can occur by an unfavored route. Others claim that reactions such as



are fast and lead to the alternate routes. However, McNesby, et al.'s experiments¹⁹⁻²² show that though these alternate modes might occur, they are negligible below 800 K, but could make some contribution above 900 K.

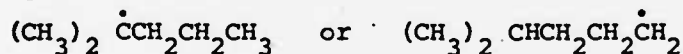
The results presented in Figures 5 and 6 tend to confirm the one bond removed rule and indicate that there is little or no decomposition by unfavored paths. In the case of propane, the rate constants for hydrogen abstraction indicate that iso- and normal-propyl radicals should be formed in nearly equal amounts, and therefore, one should find equal amounts of ethene and propene. In fact, one finds that the

ethene formed is 1.5 times the propene. This result could lead one to argue for isomerization reactions, but it is more likely that the extrapolation of the rate constants of radical attack on the primary fuel leads to the discrepancy. For butane, one predicts twice as much sec-butyl as n-butyl, but each n-butyl decomposes to an ethene and an ethyl radical and the ethyl will usually decompose to another ethene. Thus, again one expects nearly equal amounts of ethene and propene and again one finds 50% more ethene than propene.

The real confirmation of the rule come from the isohexane experiments presented in Figures 5 and 6. In the 2-methylpentane experiments the favored radicals are

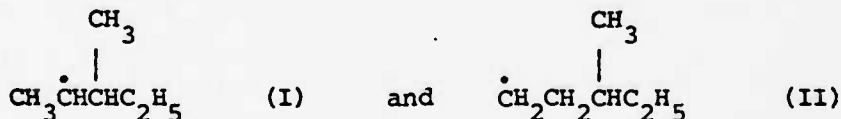


The former radical decomposes to $\text{C}_3\text{H}_6 + i - \text{C}_3\text{H}_7$ and therefore ultimately to two propenes while the latter form $\text{C}_3\text{H}_6 + n - \text{C}_3\text{H}_7$ (or 1-pentene + CH_3). Thus, C_3H_6 should greatly dominate C_2H_4 , which is explicitly what is observed experimentally. Furthermore, only isobutene will form from



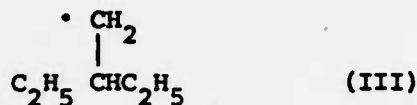
Since only one butene is observed, this result also seems to fit well with the one bond removed concept.

3-methylpentane, on the other hand, will react mainly to the radicals

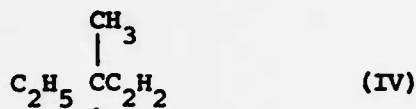


The first decomposes to $2 - \text{C}_4\text{H}_8 + \text{C}_2\text{H}_5$ (ultimately $2 - \text{C}_4\text{H}_8 + \text{C}_2\text{H}_4$) and the second forms $\text{C}_2\text{H}_4 + \text{sec} - \text{C}_4\text{H}_9$ (ultimately $\text{C}_2\text{H}_4 + \text{C}_3\text{H}_6$). Of

the other radicals



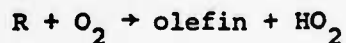
decomposes to $1 - \text{C}_4\text{H}_8 + \text{C}_2\text{H}_5\cdot$, while

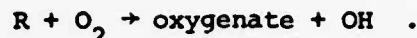


forms a pentene (2-methyl-1-butene) and a methyl radical. These predictions are also consistent with the observed results, in which $[\text{C}_2\text{H}_4] > [\text{C}_3\text{H}_6]$. The ethene is larger than butene because of the decomposition of radical (II) and because butene reacts faster than ethene. Furthermore, three butenes are observed: 1-butene, cis-2-butene, and trans-2-butene.

All these results appear to confirm the "one bond away from the radical site" theory of decomposition. Furthermore, the finding of only one butene product in the 2-methylpentane oxidation indicates that the isobutyl radical does not isomerize or break down in a non-standard fashion at 1000 K, unless it is in very small amounts. Thus, by estimating the probability of hydrogen abstraction based on the number of hydrogens available on each carbon atom, ease of removal in each case, and considering the cleavage rule discussed above, the concentration trends of olefin and lower alkanes derived from Figures 1-6 are quite predictable. These data are presented in Table I.

In addition to the decomposition reactions already discussed, the more complex radicals can also react directly with oxygen





It is important to note here that the competitive rates of the first of the above reactions and the ethyl radical decomposition reaction may be particularly critical in describing oxidation of ethane and perhaps that of the higher order alkanes. As pointed out by Walker,¹⁶ the latter of the above two reactions probably occurs in two or more steps. At temperatures below 800 K, the nature of the oxygenate depends on which radical is attacked. Many other routes are also available for formation of oxygenated species.

Figures 7 and 8 present results for the oxidation of ethane at equivalence ratios near one and one and one half.

Although on these more fuel rich studies, the same overall qualitative features of the oxidation reaction hold, the relative concentrations of intermediate species vary. The comparative characteristic times of alkane and alkene conversions are different (both from concentration and temperature effects) and the CO oxidation becomes almost non-existent as the oxygen concentration is lowered. In these richer systems hydrogen is no longer oxidized at a rapid rate to water and itself becomes an important intermediate species. Finally, it is worth noting the appearances of acetylene as an intermediate oxidation species under rich conditions. The point (time) of appearance indicates that it is an intermediate in the oxidation of the olefin, possibly produced by vinyl radical decomposition.²³ Since the production of soot precursor species is most likely related to the polymerization of acetylenic intermediates, the relation of acetylene production and oxidation to the olefin oxidation will be of value to understanding soot formation.

Summarizing the general characteristics of high temperature alkane oxidation:

1) As a result of the relatively difficult oxidation of methyl radicals, methane exhibits a very long induction period and its oxidation is not characteristic of the higher paraffins.

2) The induction period for higher hydrocarbons is very short relative to the total fuel lifetime and can be neglected under most practical combustion modelling situations.

3) The oxidation of the higher paraffins qualitatively proceeds through three distinct but overlapping phases.

- a. conversion of the alkanes to alkenes with the available hydrogen simultaneously converted to water
- b. conversion of the alkenes formed to carbon monoxide with the available hydrogen simultaneously converted to water
- c. conversion of carbon monoxide to carbon dioxide.

The simultaneous conversion of hydrogen is dependent on the amount of oxygen available and is potentially modified by the presence of hydrocarbons. Almost all of the energy release occurs from the conversion of carbon monoxide to carbon dioxide.

4) The relative quantities of olefins produced can be qualitatively estimated by considering site reactivity, the number of hydrogen abstraction sites and a "one bond away from the radical site" rule for decomposition.

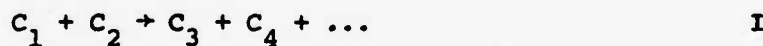
5) In fuel-rich alkyl oxidation systems, acetylene will form probably as a result of olefin oxidation and may be linked to the production of soot precursor species.

The above qualitative characteristics appear to apply over a relatively wide temperature range, at least for the case of ethane,⁵ and provide a reasonable behavioral model to which empirical formulations should be compared.

Empirical Modelling Concepts

The larger number and poor definition of the elementary reaction mechanisms necessary to detail the chemistry and the lack of evaluated rate constants for many of the included elementary steps has led both the fundamental kineticist and those who model to conclude that detailed approaches are presently intractable for realistic fuels. Yet, it is well recognized that detailed modelling may be required to properly account for the significant coupling of hydrocarbon, carbon monoxide, and NO_x kinetics, particularly in fuel-rich combustion. Thus far, only approximations of detailed chemistry have been employed to estimate rate of energy production and/or production of partially oxidized species from higher paraffin fuels. These schemes are in the form of "global" or "quasi-global" kinetic mechanisms.

The concept of overall (global) reaction kinetics and its use is a direct result of the complexity of most chemical reactions and the complicated fluid mechanical situation in which some knowledge of heat release and chemical rates is necessary.²⁴ The assumption invoked is that the course of chemical kinetic events may be described in terms of a few of the principal reactants and products (C_i) in a functional relation with much the same form as an elementary reaction process. Typically, the equation is of the form:



The rate for this process is defined by

$$-d[C_1]/dt = k_{\text{ov}} \sum_{i=1}^m [C_i]^{n_i} \quad \text{II}$$

k_{ov} , the overall specific rate constant, is expressed in the Arrhenius

form where

$$k_{ov} = f(T)A e^{-E/RT}$$

The n_i 's are defined as the orders of reaction with respect to C_i but are not necessarily equal to the stoichiometric coefficients of the overall reaction. $\sum n_i$ is termed the overall reaction order. The product of $f(T)$ and A is termed the overall frequency factor and, E is referred to as the overall activation energy.

These relations imply nothing about the actual kinetic mechanism (in terms of elementary reactions), although the parameters in the strictly empirical rate relation are sometimes governed by a single elementary step (or a number of steps) which basically controls the rate of the chemical process. Under what circumstances such an overall correlation is usable is largely dependent on both the detailed kinetic behavior of the reaction and the physical environment in which the expression is derived. For example, Levy and Weinberg²⁵ concluded that such an approach is not generally applicable to chemical measurements taken in flames; however, this fact may not arise from the chemistry itself, but from the physical structure and diffusive character of the flame studies.

Where a particular rate-determining step or sequence in the true chemical reaction mechanism occurs and the physical circumstances of the application are similar to those from which the expression was derived, the overall approximation is a valid and vastly simplifying idea. However, extension of such a correlation to experimental conditions outside the range of parameters for which it is derived should never be performed without experimental and/or analytical verification and only then with some reservation. Unfortunately, there is currently

little hope of avoiding this problem in the case of modelling hydrocarbon combustion.

Single step global reaction schemes commonly have been used in many combustion modelling exercises (e.g., References 26 and 27). Yet the only actual oxidation reactions for which parameters have been derived experimentally are those of methane and moist carbon monoxide.

Considerable global modelling studies have been performed on carbon monoxide and these have been reviewed by Dryer⁶ and Howard et al.²⁸ Methane ignition and oxidation kinetics have also been expressed in this manner, often in conjunction with developing detailed mechanisms, and many of these studies have also been reviewed.⁶

The post induction reaction of methane-oxygen mixtures was studied by Dryer and Glassman^{6,7} and their results lent encouragement to the belief that the rate of hydrocarbon consumption could be expressed by a simple global expression of the form of Equation II.

The rate of reaction in the post induction phase of the lean methane oxidation experimentally was found to be described well by the overall expression

$$-d[\text{CH}_4]/dt = 10^{13.2+0.2} e^{-(48400+1200)/RT} [\text{CH}_4]^{0.7} [\text{O}_2]^{0.8}$$

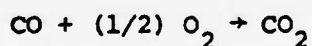
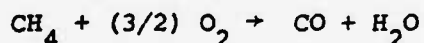
It should be noted that the parameters of this equation are significantly different than those found by investigators who have studied the induction (ignition delay) phase of this reaction in shock tubes and flow reactors. A review of available data through 1973²⁹ predicts the rate of reaction to be inhibited by the concentration of methane. Seery and Bowman³⁰ empirically correlated the ignition delay time as

$$(1/\text{Reaction Rate}) \sim \tau = 7.65 \times 10^{-18} e^{+51400/RT} [\text{CH}_4]^{0.4} [\text{O}_2]^{-1.6}$$

and developed a detailed elementary mechanism which reasonably predicted the relation. Figure 9 shows a comparison of the overall rate constant derived by Dryer⁶ and the results calculated from parameters predicted by detailed analytical studies of Bowman.³¹ The analytical overall rate constant was calculated from

$$k_{\text{ov}} = - \text{d}[\text{CH}_4]/\text{d}t / ([\text{CH}_4]^{0.7} [\text{O}_2]^{0.8})$$

Clearly there are two phases of this reaction which are not modelled by the same global parameters. Indeed, the experimental flow reactor data of Dryer show similar behavior (Figure 10). As described earlier, it is the post-induction reaction which is most important to practical combustion, and it is evident from Figure 9 that the relation which gives the overall general disappearance readily predicts the same qualitative behavior as the detailed methane oxidation mechanism over a wider temperature range and equivalence ratio than the experiments from which it was derived. Dryer⁶ completed the modelling of methane oxidation using a two step global representation:



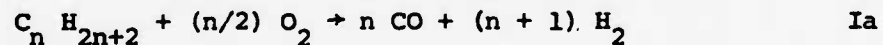
with the reaction rates described by

$$\begin{aligned} - \text{d}[\text{CH}_4]/\text{d}t &= 10^{13.2+0.2} e^{-(48400+1200)/RT} [\text{CH}_4]^{0.7} [\text{O}_2]^{0.8} \\ + \text{d}[\text{CO}_2]/\text{d}t &= 10^{14.6+0.25} e^{-(40000+1200)/RT} [\text{CO}] [\text{H}_2\text{O}]^{0.5} [\text{O}_2]^{0.25} \end{aligned}$$

It should be noted that both the overall rate constants and the reaction orders were experimentally derived, i.e., no parameters were assumed. Westbrook and Chang³² have recently compared calculated flame propagation through premixed and stratified mixtures using both

the detailed methane oxidation mechanism derived by Westbrook et al.³ and a global model for methane disappearance only (i.e., the overall heat of reaction was proportionally released with respect to methane disappearance). Results showed reasonable predictions could be globally achieved over a wide range of pressures and temperatures for propagation through premixed gases, but flame propagation through stratified mixtures was not well simulated by the single step global model. Only Appleby et al.³³ have attempted global modelling of higher paraffin oxidation (butane); however, those studies correlated only the maximum reaction rate of the initial fuel, are outside the temperature range of present interest ($T \approx 800$ K) and involved modelling only of the disappearance of the initial fuel. Global reaction modelling might have some potential for describing spatial energy release and reactant/final product distribution for higher hydrocarbons only if more than one global step is used.

Edelman and Fortune³⁴ have extended the multistep concept by developing a "quasi-global model" which combines the use of both global expressions and elementary reactions. Edelman and Fortune chose to approximate the higher paraffin oxidation to carbon monoxide and hydrogen as a unidirectional global reaction



with the rate given by

$$- d[C_n H_{2n+2}]/dt = [C_n H_{2n+2}]^a [O_2]^b k_{ov} \quad \text{IIa}$$

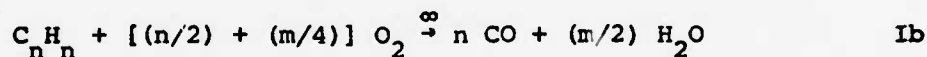
and combined these equations with a number of elementary reactions from the hydrogen/oxygen and carbon monoxide/oxygen reaction mechanisms (Table II). Values of $a = 1/2$ and $b = 1$ were assigned and

$$k_{ov} = 1.8 \times 10^9 \bar{w}^{-0.5} [T/1111 - 0.5] T^{0.5} p^{-0.2} e^{-13740/RT}$$

was initially determined from results of an analytical study of propane ignition kinetics.³⁴ \bar{w} is the average gram molecular weight of the reacting system, and dimensions in this equation are cal, K, moles-cm⁻³, atm, sec. Edelman and Fortune suggested 800 - 3000 K as the applicable temperature range. An attempt to validate the assumption that a quasi-global model based on propane characteristics also applied to higher paraffins was made by comparing the magnitudes of the ignition delay determined in the shock tube experiments of Nixon et al.³⁵ These experiments identified some similarity in the functional behavior and the order of magnitude of the ignition delay times for propane/and n-octane/oxygen mixtures. The quasi-global model using various global reaction rates (Table III) and in some cases an extended set of CHO reactions (Table IV) has been employed extensively by its developers in combustion ignition³⁶ and combustion-emission modelling,^{37,38} and notable successes have been reviewed on several occasions.^{39,40} The variation in the overall rate constant expression used for paraffin oxidation was a result of accumulating new experimental data from which the rate constant was derived.⁴¹ While the variation at one atmosphere has been over a factor of 30 at times (Figure 11), the first and the most recently quoted values are very similar (within a factor of 4 over 1000 to 2000 K). However, the pressure dependence of the relations are different, and as pressure increases, the more recent expression will predict a slower reaction rate. It should be noted that only in Reference 34 (Expression 1, Table IV) are the dimensions of the reported expression explicitly defined. In all other

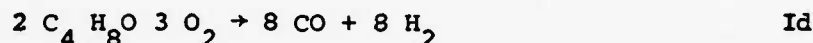
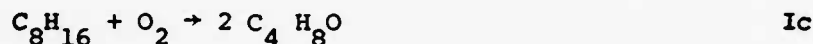
publications,³⁶⁻⁴⁰ the dimensions of the expressions are implicitly defined by listing the rate constant expression in tables of elementary reaction rate constants reported in cm, gm-mole, sec, K, atm units. Mellor⁴² has also noted dimensions of the later correlations as a footnote in Table 8 of his publication. However, the correlation itself has slightly different pressure and temperature dependence than those reported here. Nevertheless, Figure 11 appears to indicate that the expressions so interpreted are consistent with the initially reported correlation.³⁴ It will become apparent later that there is some unsolved difficulty with the correlations as published in all of the references mentioned.

Modified mechanisms based on the quasi-global concept³⁴ have also appeared in the literature. In attempting to predict gas turbine combustion NO_x emissions, Mellor^{42,43} has replaced Equation Ia with



and defined the rate constant of Equation IIa as infinite. This modification was based upon the results of Marteney.⁴⁴ However, Bowman in comments to Edelman et al.³⁷ showed that "infinite" quasi-global kinetics do not offer any significant advantages over the partial equilibrium approach for prediction of NO_x emissions. It should be noted that these calculations also show that quasi-global finite, and quasi global infinite, kinetics are equally capable of estimating NO_x emissions for residence times which are long in comparison to the time necessary to complete hydrocarbon combustion to its equilibrium product distribution. Thus, it should be remembered that in many cases and particularly for lean oxidation, prediction of NO_x emissions may not

be a sensitive enough test to judge the qualities of a proposed hydrocarbon oxidation model. Roberts et al.⁴⁵ have also derived a combustion mechanism based upon the results of Edelman.³⁴ Equation Ia was initially replaced with a set of two reactions



and finally modified to include a third reaction⁴⁶⁻⁴⁸



to describe the initial fuel disappearance. The model also significantly modified and extended the set of elementary reactions included by Edelman and Fortune³⁴ and added a number of intermediates (non-elementary) reactions of species such as HCO, H₂CO, CH₃, C₂H₄, C₂H₂, etc. (the complete mechanism appears in Reference 46). It is unclear in these publications how the rate expressions for Reactions Ic, Id, and Ie were derived. However, it appears that the reaction orders in the associated rate correlations are equal to the stoichiometric coefficients of Reactions Ic, d, e, and the rate constants themselves were obtained by matching the first correlation appearing in Table III.^{42,45-47} The mechanism derived in this manner has been used in numerical calculations for gas turbine combustors to predict the formation of nitric oxide,^{45,46,48} the effects of water addition on NO_x emissions,⁴⁹ carbon monoxide production in the primary zone⁵⁰ (including droplet effects⁵¹) and emissions produced by methanol and jet fuels.⁵²

These efforts cannot be reviewed comprehensively here, but it is of importance to note that the initial publication on quasi-global modelling³⁴ forms the conceptual and quantitative basis for the

desired model. In light of this and the precise quantitative kinetic data on higher hydrocarbon oxidation, just reported, it is interesting to investigate the predictive nature of the Edelman model for fuel disappearance and CO oxidation at temperatures near 1000 - 1200 K. This comparison should not overextend the model since Edelman et al. earlier have predicted with considerable success³⁶ continuous flow ignition delay experiments at flow reactor conditions. Figure 12 schematically represents the Esso continuous flow ignition delay experiment which was modelled. Pre-vaporized fuel is injected in a concentric configuration into a steady, pre-heated, high Reynolds number flow of air, and a stationary flame front is produced some distance, d_i , downstream from the injector. The ignition delay was defined as the distance d_i divided by the air flow velocity. This technique was used to investigate the effects of various additives on the ignition delay of both alkyl and cyclic structured hydrocarbons. Edelman et al. modelled the experiment by assuming instantaneous pre-mixing at the injector location and a, one-dimensional, adiabatic, constant pressure, reacting flow. The quasi-global kinetics model and rate constants reported in Tables II and III were used to describe the flow chemistry. Longitudinal diffusion was permitted and wall effects were neglected. Figure 13 presents a comparison of the calculated and measured ignition delays of various pure hydrocarbon fuels.

One would assume from the remarkable agreement that the combustion chemistry is well described. With the exception of the constant pressure assumption, an identical approach was used in the recent modelling of the Princeton flow reactor.³ However, a technique was derived to circumvent the requirement of comparing absolute overall

reaction times since initial mixing was found experimentally to significantly perturb the induction phases of the methane oxidation. One should be aware of similar quantitative difficulties with the Esso experimental data and that a mixing analysis is required to justify that such simple assumptions of the reaction flow do not produce fortuitous agreement. Unfortunately, no such analysis appears in the original publication. Furthermore, it is not evident in References 37 and 39 that significantly different overall rate parameters were required to reproduce ignition delay measurements for paraffin and cycloparaffin hydrocarbon fuels (see Table III).

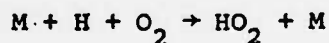
Figure 14 presents a summary of fuel disappearance predicted by the sub-global reaction step of the quasi-global model for the oxidation of the pure fuel under the initial conditions corresponding to Figures 2, 3, 5, and 6 appearing earlier. As a first approximation, constant (initial) reaction temperature and oxygen concentration were assumed, and the global reaction expression employed by Engleman et al.³⁸ was employed.

Complete fuel disappearance was predicted in all cases within reaction times less than 10^{-2} milliseconds, i.e., less than about 10^{-2} cm of the flow reactor duct. Relaxing the constraints used for this first approximation will result in even more rapid fuel disappearance. Predicted fuel disappearance could be brought into approximate agreement with experiment by multiplying the reported overall frequency factor by a number the order of 10^{-3} to 10^{-4} .

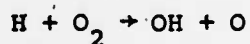
Comparisons using the complete quasi-global model (Expression 4, Table II and the reaction set of Table III) show similar disagreement.⁵³ It would appear that the global rate expressions reported in all the articles^{34,36-40} are either incorrectly stated, or that the agreement

between experimental and numerical comparisons used to establish and corroborate the models were fortuitous. In either case, other quasi-global models⁴⁵⁻⁴⁸ developed from this literature are in error. This problem has been referred to the originators for further clarification.

Furthermore, there appears to be some potentially serious inadequacies in the mechanism shown in Table III for predicting carbon monoxide oxidation over wide ranges of temperature and pressure. Westbrook et al.³ have recently shown that without the inclusion of the hydroperoxyl radical and hydrogen peroxide (Table IV) reactions, carbon monoxide oxidation in the flow reactor cannot be modelled satisfactorily. Without these additional reactions the carbon monoxide oxidation time under flow reactor conditions is significantly too short (factor of 4 to 5). The role of the HO₂ in the mechanism is not one of direct reaction with carbon monoxide but as a moderator of the concentration of O and OH radicals through competition of



with



This competition slows the rate of chain branching and decreases the superequilibrium concentrations of the radicals OH and O. The fact is that these reactions often are overlooked and remain of equal importance at higher temperatures as the reaction pressure is increased. For example, with $M = N_2$, the rates of conversion are approximately of equal value at 1 atm, 1000 K; 10 atm, 1500 K; 60 atm, 2000 K. Indeed, additional calculations using the mechanism shown in Table V confirm that at 1500 K, the same relative importance of HO₂ and H₂O₂ chemistry

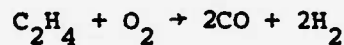
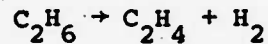
shown above is apparent at 10 atmospheres pressure.⁵³ Thus the use of a limited CO-H₂ mechanism in practical combustion modelling significantly may overpredict the rates of CO and H₂ conversion and the maximum (non-equilibrium) concentrations of OH and O radicals produced, and underpredict the characteristic time at which maximum radical overshoot is achieved. Indeed, the latter errors may cause difficulty in predicting Zeldovich NO_x production in real combustion systems.

Summary and Future Needs

While the Edelman and Fortune model for hydrocarbon oxidation appears to have several serious deficiencies, the concept upon which it is developed is quite appropriate for combustion modelling. Correct modelling of carbon monoxide/hydrogen oxidation in detail can estimate both the major energy release step of alkyl-hydrocarbon oxidation, and the radical intermediates (OH, O, H) necessary to predict the Zeldovich NO_x production and quenching of carbon monoxide. By adding elementary SO_2/SO_3 chemistry, the mechanism could also define the SO_2/SO_3 conversion which occurs during dilution or cooling of combustion gases. However, a global model for CO oxidation coupled with partial equilibrium might be sufficient for calculation of the Zeldovich NO_x production when one is only concerned with long residence times at high temperature. But, the more difficult problem is how to predict empirically the ignition delay period for the carbon monoxide conversion. From the qualitative hydrocarbon oxidation description assembled earlier, it is apparent that the initiation of CO_2 formation and the formation of soot precursor species coincides with the oxidation of olefins formed from the initial hydrocarbon and not with that of the initial hydrocarbon itself. These two conversion steps may indeed have different temperature and concentration dependences and thus we have suggested⁵³ that accurate modelling of hydrocarbon oxidation over the required temperature range will necessitate empirical prediction of each of these hydrocarbon conversion processes; the conversion of primary fuel to olefins, the conversion of olefins to CO. Flow reactor experiments can provide the necessary data for construction

of the models at temperatures in the vicinity of 1000 - 1200 K, however, other experimental techniques at higher temperatures and other pressures will be required to extend the models over the required ranges of parameters. The introduction of dye laser instrumentation to shock tubes should permit development of information somewhat similar to that currently available from the flow reactor.

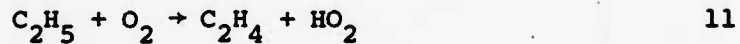
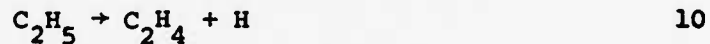
Global rate expressions of ethane recently have been determined⁵ and provide some further support for this proposed modelling approach. In the case of ethane oxidation the sub-global expressions of the quasi-global model would be



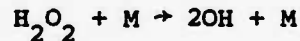
It was found that two distinct regimes requiring different global rate expressions exists; a fuel lean regime for which $\alpha \leq 2.2$, and a stoichiometric and fuel-rich regime for which $\alpha \geq 5.5$. The parameter α is defined by

$$k_{10}/k_{11} [\text{O}_2]_0$$

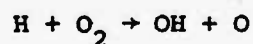
where Reactions 10 and 11 are



The fact that two regimes exist is believed to be a result of a shift in the primary branching reaction from



in the lean regime to



in the stoichiometric and fuel-rich regime. This shift is produced by

the relative ratio of the two primary sources of H and HO₂ (which lead to H₂O₂), Reactions 10 and 11.

The existence of two different sets of global reaction rate expressions for paraffin and olefin conversion which apply over different ranges of α would at first sight appear to be a complicating factor. However, if one uses available values³ of rates constants for Reactions 10 and 11 and further assumes that Reaction 10 is indeed at its high pressure limit, it is found that under most practical conditions, the ethane oxidation proceeds primarily in the stoichiometric and rich regime (see Table VI). For that regime, the global rate expressions derived from flow reactor data at atmospheric pressure, over the temperature range 976 - 1155 K and over the equivalence ratio range of 0.38 to 1.6 are

$$-d[\text{C}_2\text{H}_6]/dt = 10^{13.41 \pm 0.45} e^{-(39210 \pm 2500)/RT} [\text{C}_2\text{H}_6]^{0.8} [\text{O}_2]^{0.75} \quad \text{III}$$

and

$$-d[\text{C}_2\text{H}_4]/dt = 10^{11.92 \pm 0.37} e^{-(50970 \pm 1770)/RT} [\text{C}_2\text{H}_4]^{0.25} [\text{O}_2]^{0.85} \quad \text{IV}$$

All parameters in these equations were experimentally derived.

The development of a quasi-global model using these rate expressions is currently under investigation and results are too incomplete at this time to report. Yet it is possible to infer that the rate expressions found apply over wider parameter ranges than those studied in the flow reactor. We have recently compared the initial fuel disappearance predicted by these equations at 1500 - 1800 K with the shock tube ignition delay data of Cooke and Williams.¹⁵ These investigators measured shock tube ignition delay using various

techniques for three ethane/oxygen mixtures which should be characteristic of the stoichiometric and fuel-rich regime. Cooke and Williams suggested that a majority of the initial fuel had disappeared by the time CO_2 emission was initiated and called this ignition delay τ_{CO_2} . Table VII lists the initial conditions for the three ethane/oxygen/argon mixtures investigated and the values of τ_{CO_2} calculated from experimental correlation which they derived. Figure 15 shows the ethane disappearance calculated using Equation III and the initial conditions defined in Table VII for $\phi = 1.0$. The pressure was assumed to be at one atmosphere, and the temperature was assumed to be constant at 1500 or 1800 K. The global rate expression derived in the flow reactor successfully predicts a fuel disappearance time within a factor of two of the CO_2 emission ignition delay. The reaction times are nearly 10^3 shorter at the shock tube temperatures and the agreement is probably as good as can be expected without experimental shock tube chemical profile information. Agreement may actually be better than indicated since the temperature should rise slightly during the fuel decay and some fuel may remain when CO_2 emission begins. It is worth noting from Table VII that the total disappearance time for ethane is so short that in most conventional combustion systems, the fuel would have disappeared long before gas temperatures approaching 1800 K could be reached. Thus, knowledge of hydrocarbon disappearance correlations extending to near 1800 K may be adequate for most practical combustion modelling. Additional data will also be required to establish any pressure dependence not already appearing in the concentration terms of rate equations.

In comparison to the combustion chemistry of aromatics, the oxidation and pyrolysis kinetics of alkyl hydrocarbons are relatively well understood. However, the qualitative understanding we have gained has not yet been fully exploited in developing semi-empirical mechanisms which successfully predict both qualitative and quantitative behavior except in weakly coupled gross quantities. The currently available "quasi-global" models have been shown to have several limitations, particularly the published values for the overall global rate expressions, poorly defined rate parameters, and limited detailed mechanisms for H_2 and CO oxidation. It is suggested that more strongly coupled parameters than ignition delay and NO_x emissions should be used in the future to corroborate model validity. It appears that we must begin to employ our new technology to add to our qualitative and quantitative knowledge of high temperature oxidation through the use of resonant dye laser techniques in instrumentation capable of data acquisition over the necessary ranges of pressure, temperature, and equivalence ratio (shock tubes and flow reactors). Finally, we should be aware of the effects of turbulence and how it might be incorporated in generated semi-empirical models for comparison with more simple reacting turbulent systems (stirred reactors, etc.).

Acknowledgments

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Table I

RELATIVE HYDROCARBON INTERMEDIATE CONCENTRATIONS PRODUCED

DURING OXIDATION OF SEVERAL PURE ALKYL-HYDROCARBONS

<u>Fuel</u>	<u>Relative Hydrocarbon Intermediate Concentrations</u>
ethane	ethene >> methane
propane	ethene > propene >> methane > ethane
butane	ethene > propene >> methane > ethane
hexane	ethene > propene > butene > methane >> pentene > ethane
2-methyl pentane	propene > ethene > butene > methane >> pentene > ethane
3-methyl pentane	ethane > butane > propene > methane >> pentene > ethane

Table II

C-H-O CHEMICAL KINETIC REACTION MECHANISM

FOR THE EDELMAN QUASI-GLOBAL MODEL (REFERENCE 35)

$$k_f = AT^b \exp(-E/RT)$$

REACTION	Forward		
	A	b	E/R
2. CO+OH = H+CO ₂	5.6 x 10 ¹¹	0	543
3. OH+H ₂ = H ₂ O+H	2.19 x 10 ¹³	0	2590
4. OH+OH = O + H ₂ O	5.75 x 10 ¹²	0	393
5. O+H ₂ = H+OH	1.74 x 10 ¹³	0	4750
6. H+O ₂ = O+OH	2.24 x 10 ¹⁴	0	8450
7. M+O+H = OH+M	1 x 10 ¹⁶	0	0
8. M+O+O = O ₂ +M	9.38 x 10 ¹⁴	0	0
9. M+H+H = H ₂ +M	5 x 10 ¹⁵	0	0
10. M+H+OH = H ₂ O+M	1 x 10 ¹⁷	0	0

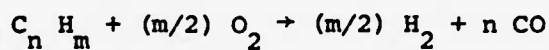
dimensions are cal, K, moles-cm⁻³, atm, sec.

reverse rate constants, k_r , are obtained from k_f and the equilibrium constant k_c .

Table III

GLOBAL RATE CONSTANTS USED BY EDELMAN AND OTHERS

FOR THE EDELMAN QUASI-GLOBAL MODEL



$$-d[C_n H_m]/dt = k_{ov} [C_n H_m]^{0.5} [O_2]^{1.0^*}$$

Rate Constant, k_{ov}	References
1) $\frac{1.8 \times 10^9}{(\bar{w})^{0.5}} [T(^{\circ}K)/1111 - 0.5] T^{0.5} P^{-0.2} e^{-13700/RT^+}$	34
2) $5.52 \times 10^8 T^{1.0} P^{-0.825} e^{-24400/RT}$	37
3) $6.9 \times 10^9 T^{1.0} P^{-0.825} A e^{-EQR/RT}$	36
a) $A = 1.0$, $EQR = 24400$, paraffin oxidation	
b) $A = 347$, $EQR = 39300$, cyclic oxidation	
4) $5.52 \times 10^8 T^{1.0} P^{-0.825} e^{-24800/RT}$	38-40

+ \bar{w} = average molecular weight

* dimensions are cal, K, moles-cm⁻³, atm, sec.

Table IV

EXTENDED C-H-O CHEMICAL KINETIC REACTION MECHANISM USED IN THE

EDELMAN QUASI-GLOBAL MODEL (REFERENCE 39)

$$k_f = AT^b \exp(-E/RT)$$

Reaction	A	Forward b	E/R
$\text{CO} + \text{OH} = \text{H} + \text{CO}_2$	5.6×10^{11}	0	543
$\text{CO} + \text{O}_2 = \text{CO}_2 + \text{O}$	3×10^{12}	0	25000
$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$	1.8×10^{19}	-1	2000
$\text{H}_2 + \text{O}_2 = \text{OH} + \text{OH}$	1.7×10^{13}	0	24700
$\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$	2.19×10^{13}	0	2590
$\text{OH} + \text{OH} = \text{O} + \text{H}_2\text{O}$	5.75×10^{12}	0	393
$\text{O} + \text{H}_2 = \text{H} + \text{OH}$	1.74×10^{13}	0	4750
$\text{H} + \text{O}_2 = \text{O} + \text{OH}$	2.24×10^{14}	0	8450
$\text{M} + \text{O} + \text{H} = \text{OH} + \text{M}$	1.0×10^{16}	0	0
$\text{M} + \text{O} + \text{O} = \text{O}_2 + \text{M}$	9.38×10^{14}	0	0
$\text{M} + \text{H} + \text{H} = \text{H}_2 + \text{M}$	5.0×10^{15}	0	0
$\text{M} + \text{H} + \text{OH} = \text{H}_2\text{O} + \text{M}$	1.0×10^{17}	0	0
$\text{O} + \text{N}_2 = \text{N} + \text{NO}$	1.36×10^{14}	0	37750
$\text{N}_2 + \text{O}_2 = \text{N} + \text{NO}_2$	2.7×10^{14}	-1.0	60600
$\text{N}_2 + \text{O}_2 = \text{NO} + \text{NO}$	9.1×10^{24}	-2.5	64600
$\text{NO} + \text{NO} = \text{N} + \text{NO}_2$	1.0×10^{10}	0	44300
$\text{NO} + \text{O} = \text{O}_2 + \text{N}$	1.55×10^9	1.0	19450
$\text{M} + \text{NO} = \text{O} + \text{N} + \text{M}$	2.27×10^{17}	-0.5	74900
$\text{M} + \text{NO}_2 = \text{O} + \text{NO} + \text{M}$	1.1×10^{16}	0	33000
$\text{M} + \text{NO}_2 = \text{O}_2 + \text{N} + \text{M}$	6.0×10^{14}	-1.5	52600
$\text{NO} + \text{O}_2 = \text{NO}_2 + \text{O}$	1.0×10^{12}	0	22900
$\text{N} + \text{OH} = \text{NO} + \text{H}$	4.0×10^{13}	0	0
$\text{H} + \text{NO}_2 = \text{NO} + \text{OH}$	3.0×10^{13}	0	0
$\text{CO}_2 + \text{N} = \text{CO} + \text{NO}$	2.0×10^{11}	-1/2	4000
$\text{CO} + \text{NO}_2 = \text{CO}_2 + \text{NO}$	2.0×10^{11}	-1/2	2500

dimensions are cal, K, moles-cm⁻³, atm, sec.

Reverse rate constants, k_r , are obtained from k_f and the equilibrium constant, k_c

Table V
CARBON MONOXIDE OXIDATION MECHANISM INCLUDING
HO₂ AND H₂O₂ CHEMISTRY (REFERENCE 3)

Rate constants [$k_f = AT^n \exp(-E/RT)$]

<u>Reaction</u>	<u>A</u>	<u>n</u>	<u>E</u>
1. OH + CO = CO ₂ + H	1.5 x 10 ⁷	1.3	-0.765
2. H + O ₂ = OH + O	2.19 x 10 ¹⁴	0	16.79
3. H ₂ + O = OH + H	1.82 x 10 ¹⁰	1	8.9
4. O + H ₂ O = OH + OH	6.76 x 10 ¹³	0	18.36
5. H + H ₂ O = OH + H ₂	9.33 x 10 ¹³	0	20.37
6. O + H + M = OH + M	1.0 x 10 ¹⁶	0	0
7. O + O + M = O ₂ + M	5.01 x 10 ¹⁵	-0.25	0
8. H ₂ + M = H + H + M	2.19 x 10 ¹⁴	0	96.0
9. O ₂ + H ₂ = OH + OH	7.94 x 10 ¹⁴	0	44.7
10. H ₂ O + M = H + OH + M	2.19 x 10 ¹⁶	0	105.1
11. CO + O + M = CO ₂ + M	5.89 x 10 ¹⁵		4.10
12. CO + O ₂ = CO ₂ + O	3.16 x 10 ¹¹	0	37.6
13. H + O ₂ + M = HO ₂ + M	1.51 x 10 ¹⁵	0	-1.00
14. O + OH + M = HO ₂ + M	1.0 x 10 ¹⁷	0	0
15. HO ₂ + O = O ₂ + OH	5.0 x 10 ¹³	0	1.0
16. H + HO ₂ = OH + OH	2.51 x 10 ¹⁴	0	1.90
17. H + HO ₂ = H ₂ + O ₂	2.51 x 10 ¹³	0	0.70
18. OH + HO ₂ = H ₂ O + O ₂	5.01 x 10 ¹³	0	1.00
19. HO ₂ + HO ₂ = H ₂ O ₂ + O ₂	1.0 x 10 ¹³	0	1.00
20. H ₂ O ₂ + M = OH + OH + M	1.2 x 10 ¹⁷	0	45.50
21. H + H ₂ O ₂ = HO ₂ + H ₂	1.7 x 10 ¹²	0	3.78
22. CO + HO ₂ = CO ₂ + OH	1.0 x 10 ¹⁴	0	23.00
23. H ₂ O ₂ + OH = H ₂ O + HO ₂	1.0 x 10 ¹³	0	1.80

dimensions are Kcal, K, moles-cm⁻³, atm, sec.

Reverse rate constants, k_r are obtained from k_f and the equilibrium constant k_c

Table VICALCULATIONS OF THE ETHANE OXIDATION REGIMESAS FUNCTIONS OF TEMPERATURE AND MOLE FRACTION OF OXYGEN

$$\alpha \equiv k_{10}/k_{11} [O_2]$$

<u>Temperature K</u>	<u>1000</u>	<u>1200</u>
Lean regime; $\alpha \leq 2.2$, $x_{O_2}^{\circ}$	≥ 0.05	≥ 0.95
Stoichiometric and fuel- rich regime $\alpha \geq 5.5$, $x_{O_2}^{\circ}$	≤ 0.02	≤ 0.38

Table VII

COMPARISON OF IGNITION DELAYS BASED ON CO₂ EMISSION (REFERENCE 15)

ETHANE DISAPPEARANCE CALCULATED USING EQUATION III

Mixture	ϕ	$x_{C_2H_6}^{\circ}$	$x_{O_2}^{\circ}$	x_{Ar}°	τ_{CO_2} (μ sec)		$\tau_{C_2H_6}$ (μ sec)	
					1500 K	1800 K	1500 K	1800 K
1	0.5	0.00625	0.4375	0.95	61.4	18.7	145	26
2	1.0	0.0111	0.0389	0.95	90.6		180	
3	2.0	0.0182	0.0318	0.95	147		225	

Figures

- Figure 1. Chemical Composition of Spread Ethane-Air Reaction.
- Figure 2. Chemical Composition of Spread Propane-Air Reaction.
- Figure 3. Chemical Composition of Spread n-Butane-Air Reaction.
- Figure 4. Chemical Composition of Spread n-Hexane/Air Reaction.
- Figure 5. Chemical Composition of Spread 2-Methylpentane-Air-
Reaction.
- Figure 6. Chemical Composition of Spread 3-Methylpentane-Air-
Reaction.
- Figure 7. Chemical Composition of Spread Ethane-Oxygen Reaction.
- Figure 8. Chemical Composition of Spread Ethane-O₂ Reaction.
- Figure 9. Comparison of Analytical and Experimental Overall
Disappearance Rate of Methane.
- Figure 10. Determination of E for the Post Induction Phase
Oxidation of Methane.
- Figure 11. Overall Rate Constants for Paraffin Oxidation of
Table IV at One Atmospheric Pressure.
- Figure 12. Schematic of Esso Research Continuous Flow Autoignition
Test System (Reference 36).
- Figure 13. Continuous Flow Ignition Delay Time Results for Pure
Fuel/Air Mixtures; Comparison of Esso Data with Quasi-Global Pre-
diction of Edelman et al. (Reference 36).
- Figure 14. Fuel Disappearance vs. Time Predicted by Edelman
Global Reactions for Conditions Shown in Figures 1-6.
- Figure 15. Ethane Disappearance vs. Time, Comparison of Global
Prediction (Reference 5) and Experiment (Reference 15).

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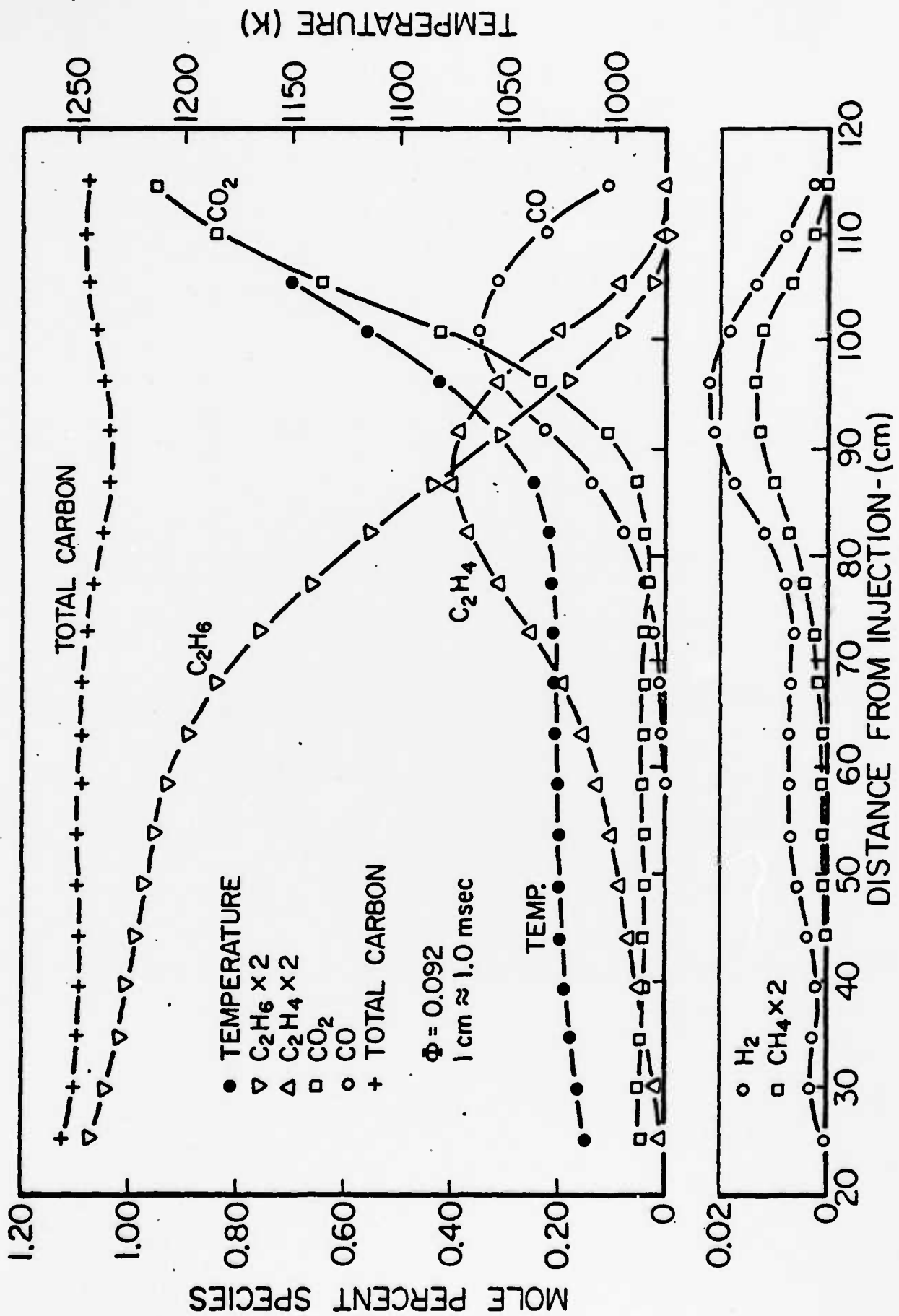


FIGURE 1

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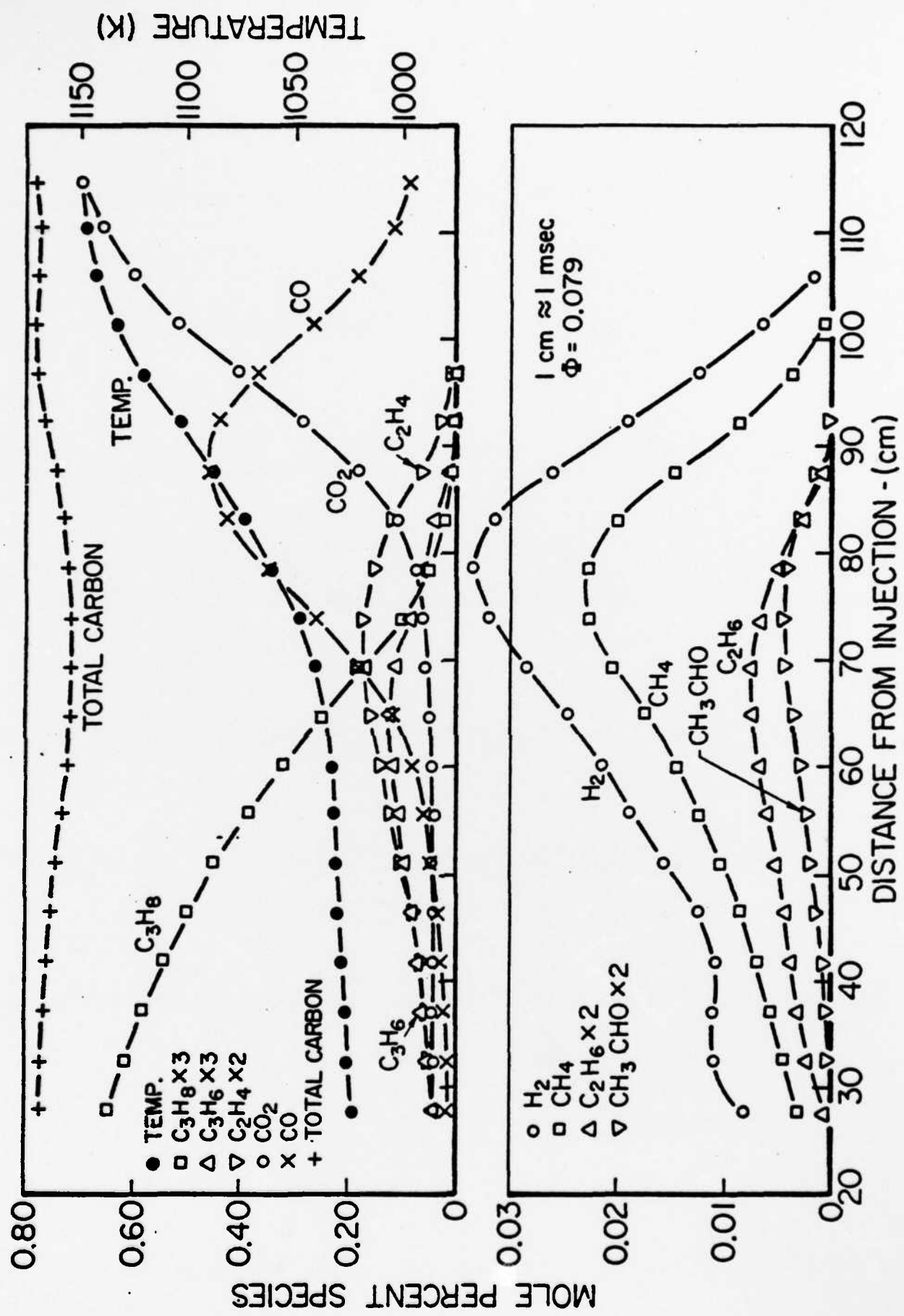


FIGURE 2

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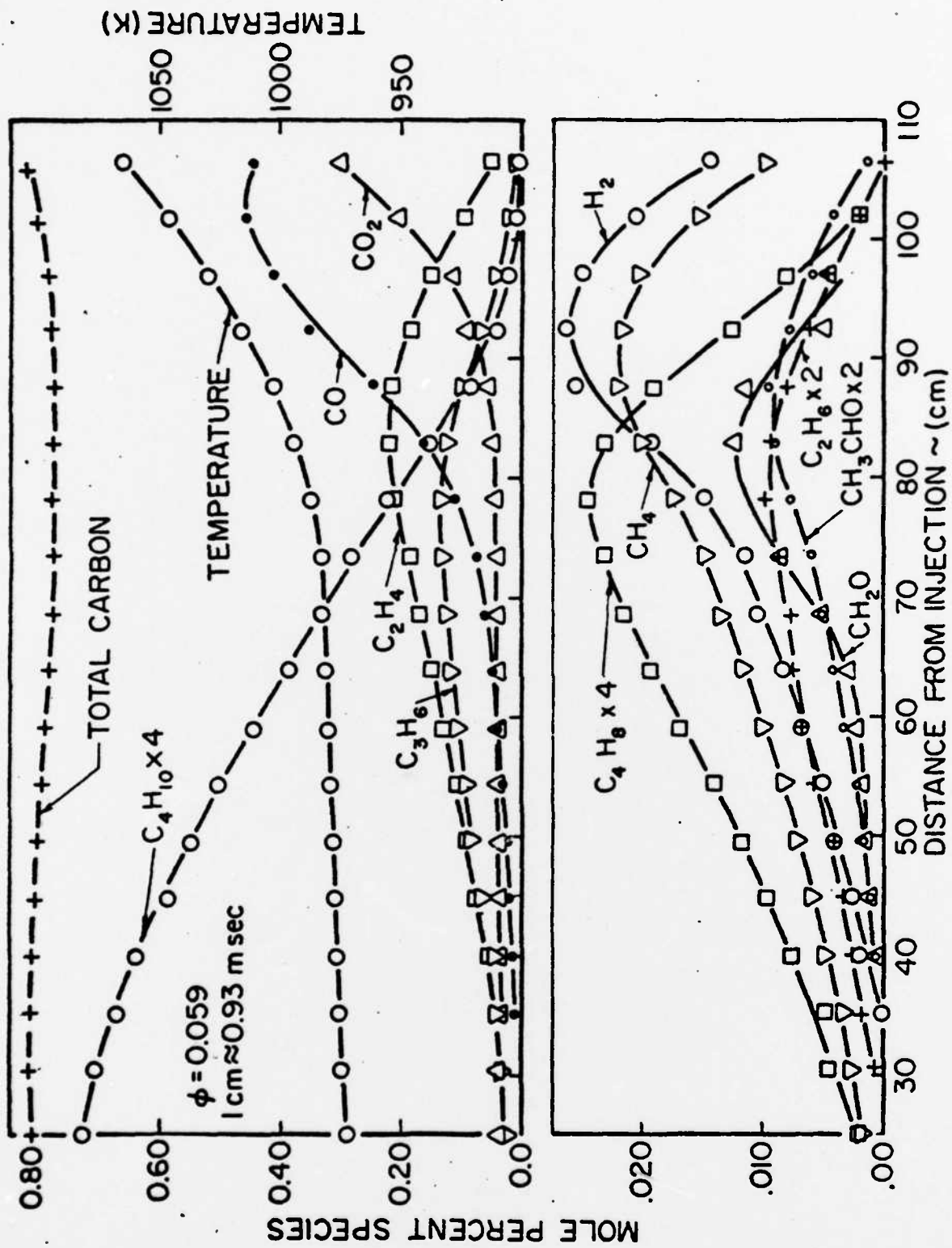


FIGURE 3

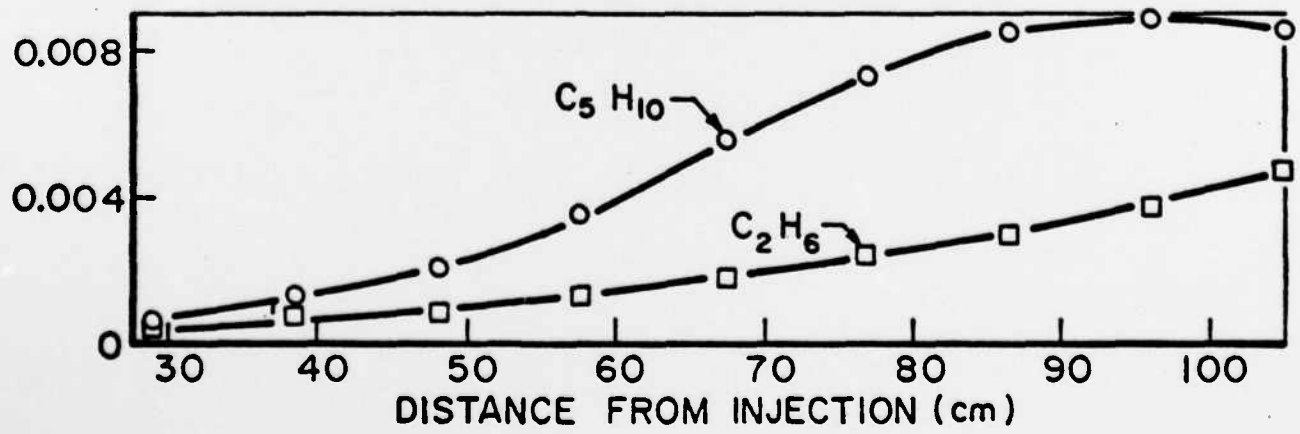
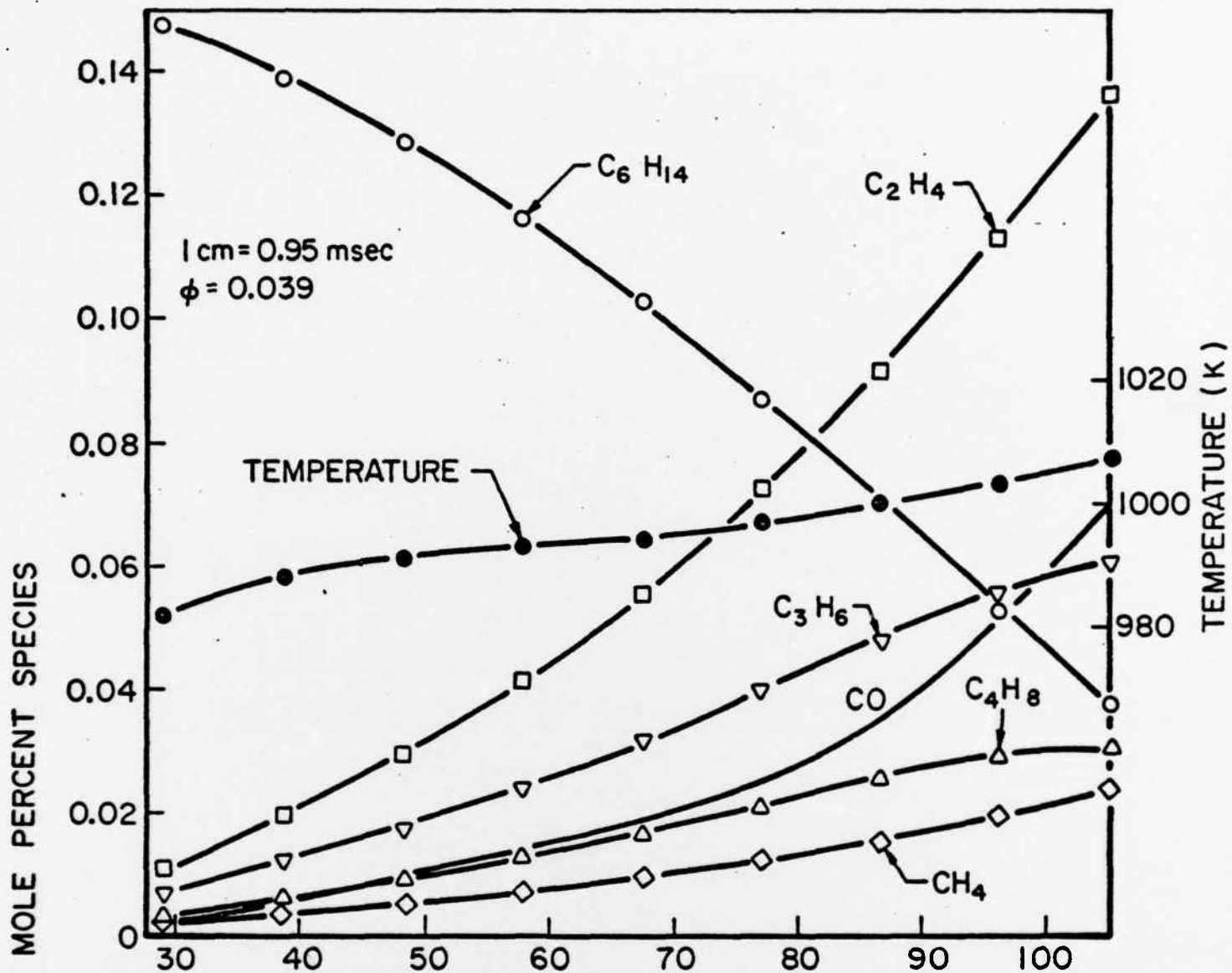


FIGURE 4

J. D. Bryan & L. Elmerman
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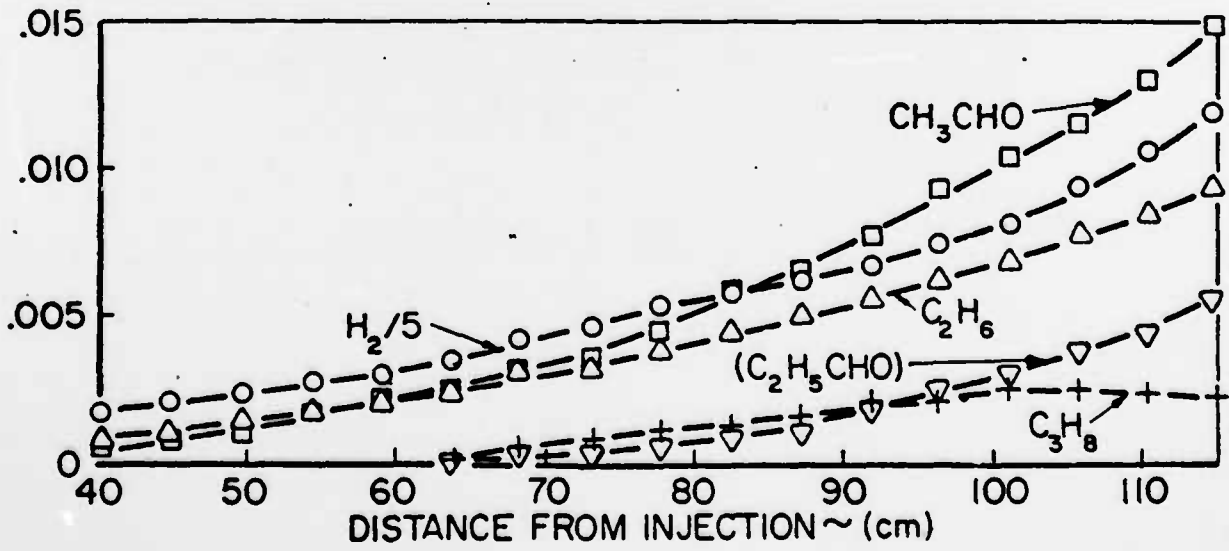
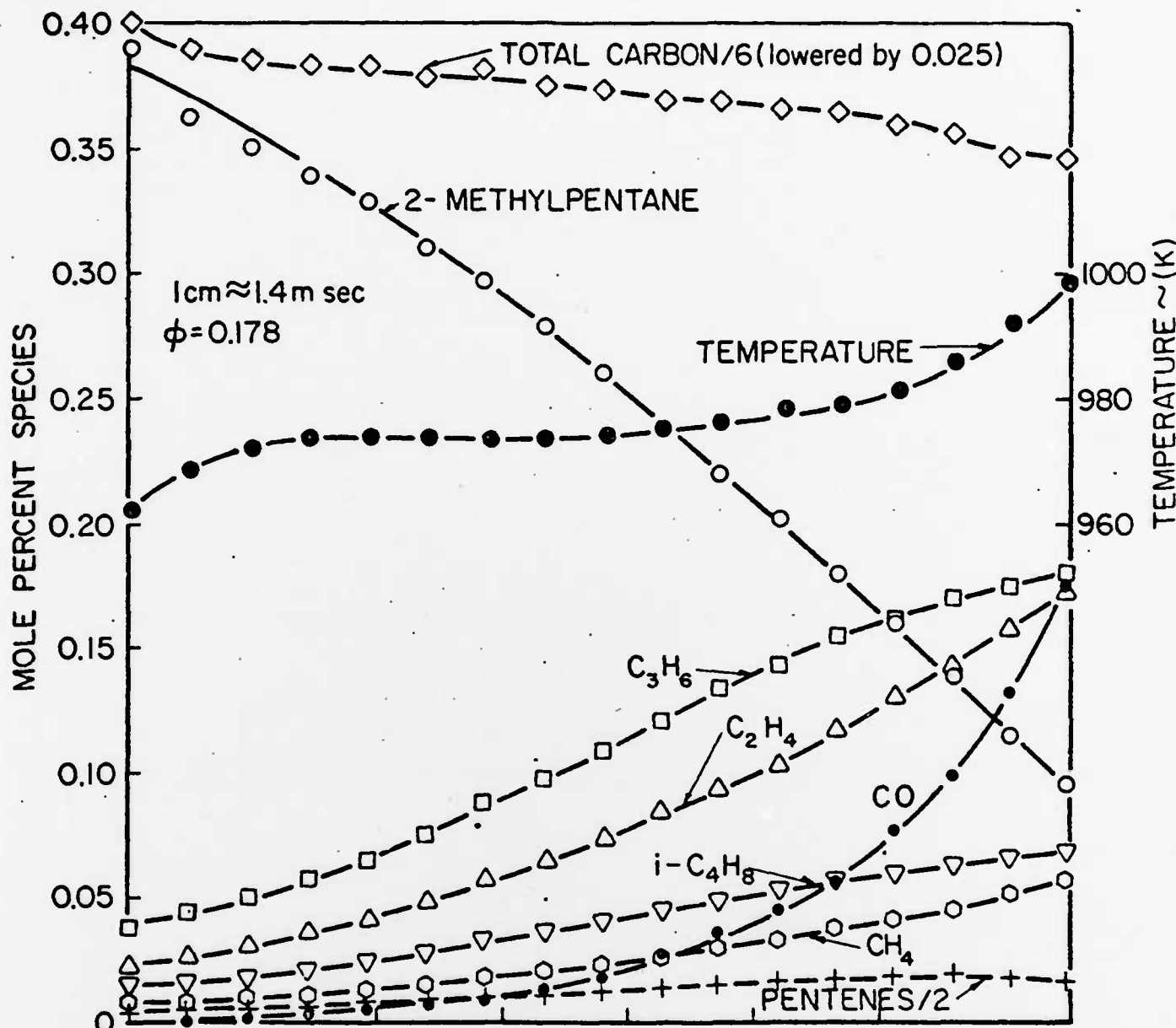


FIGURE 5

F. S. Dwyer & J. E. Elmerman
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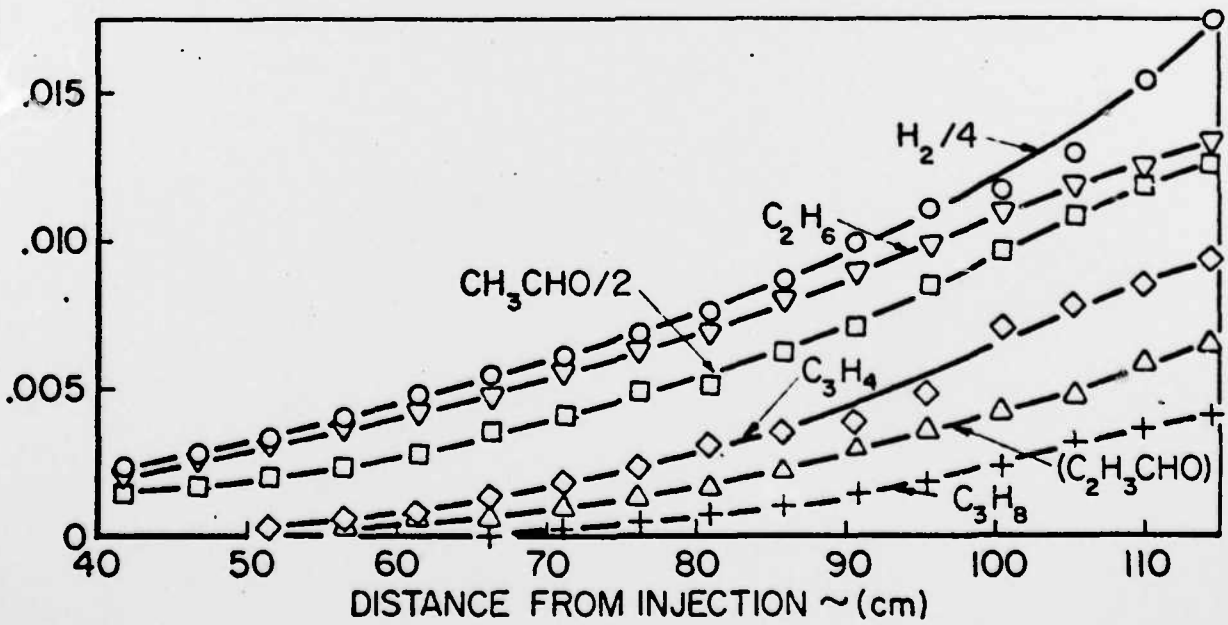
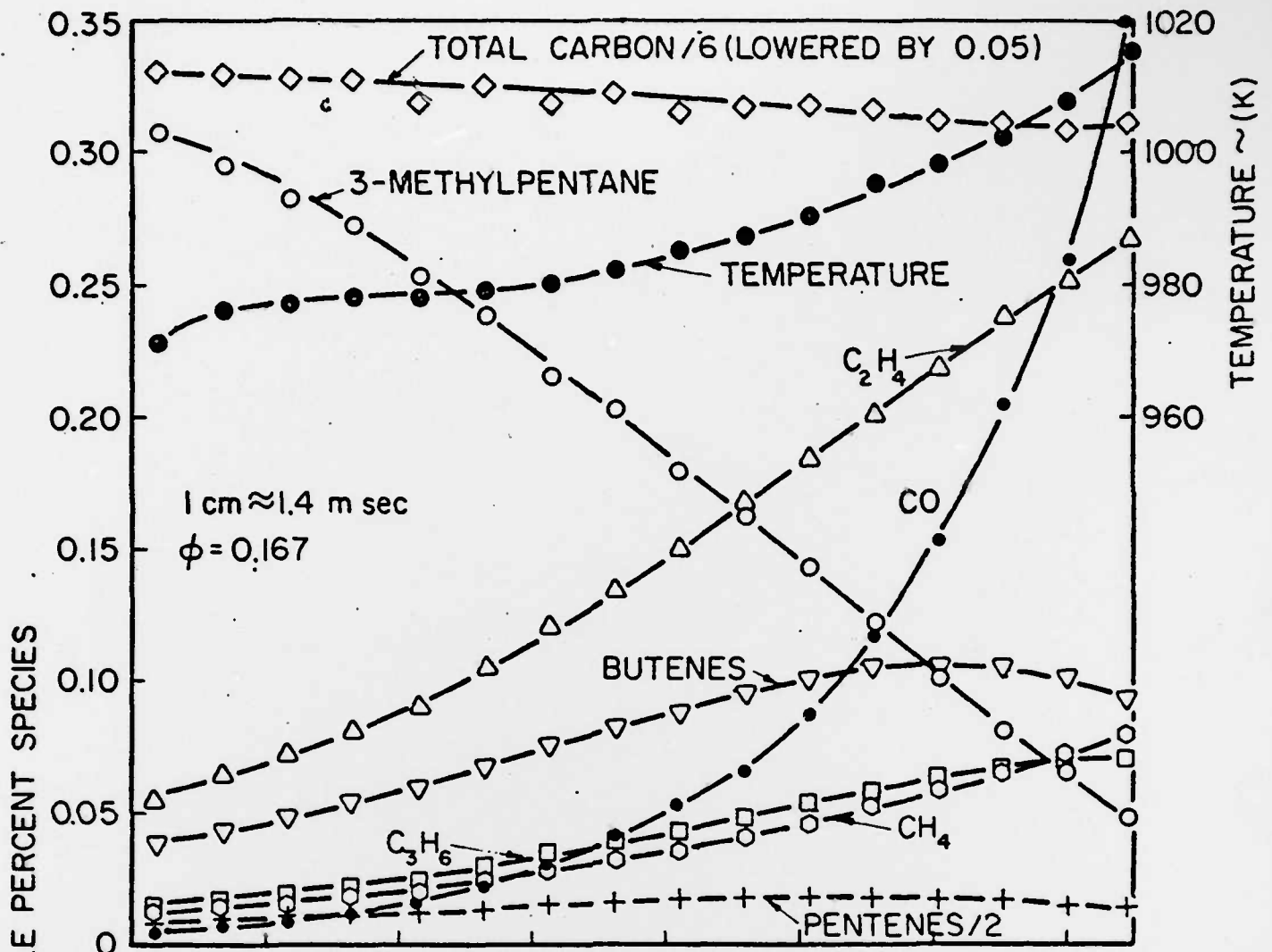


FIGURE 6

AP 13 2 4354 77
 F. X. Dryer & S. Glassman

W. D. Clayton & J. S. Blodgett

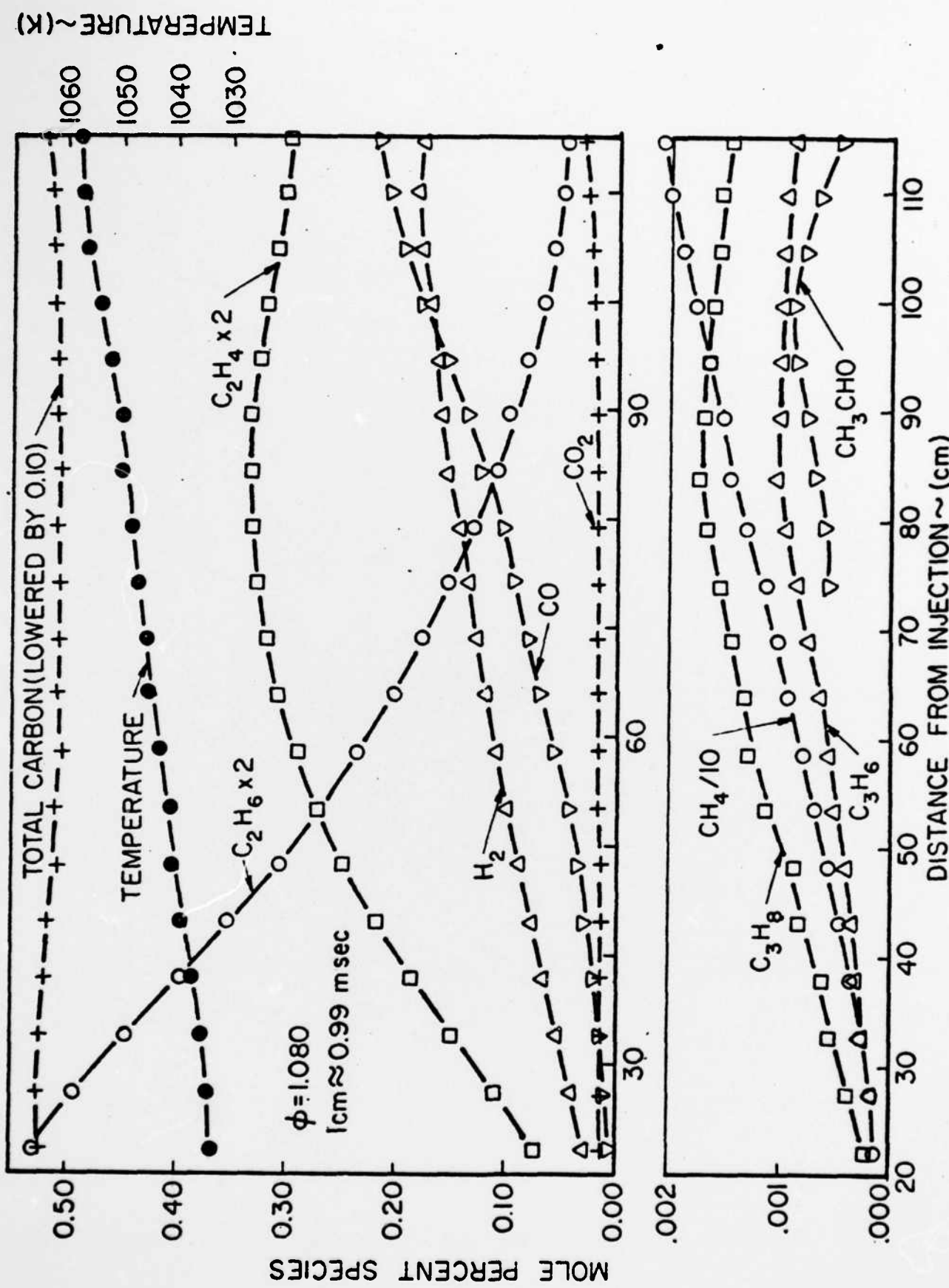


FIGURE 7

A. L. Hyman & L. E. Glusker
6100 R 0710 73

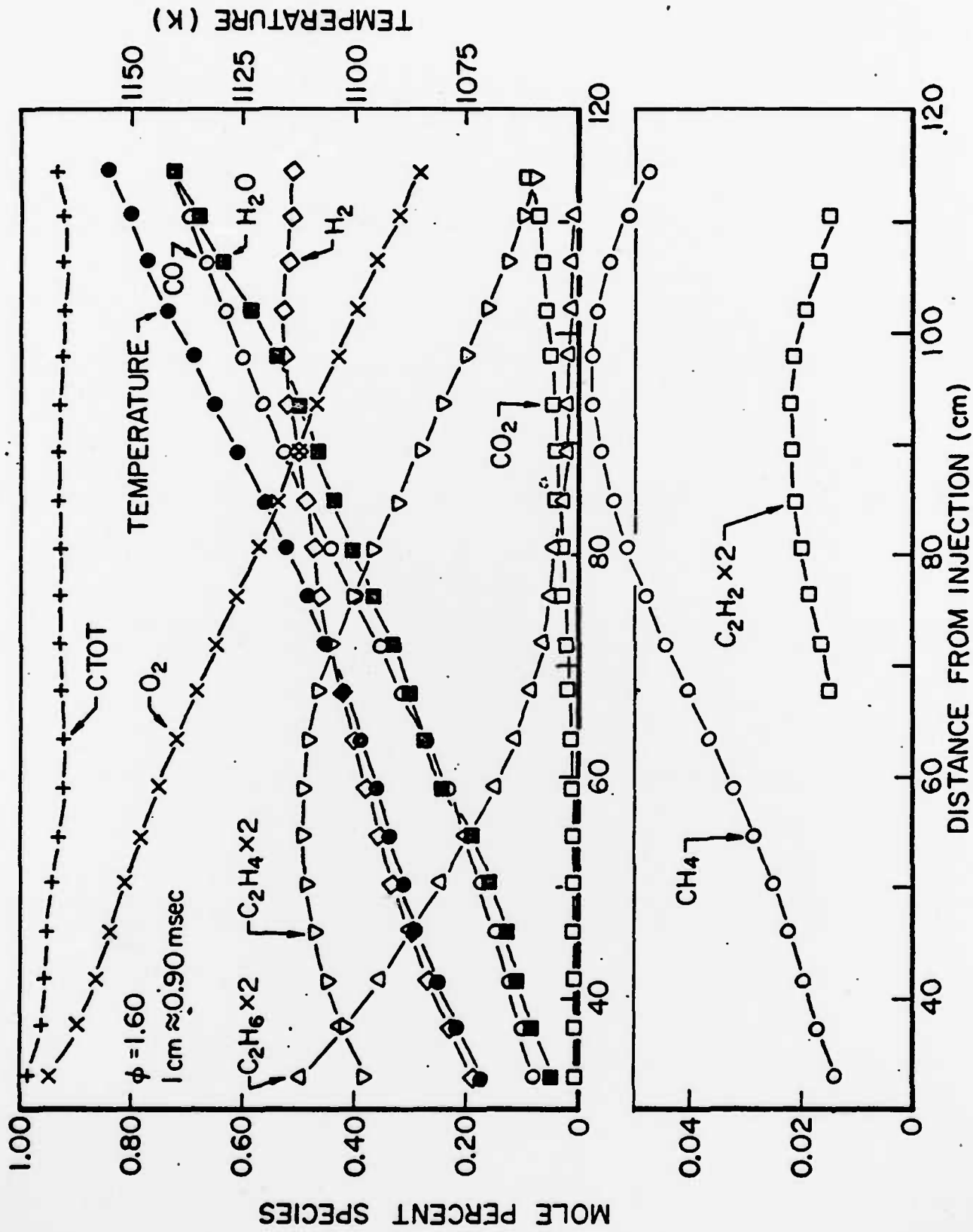


FIGURE 8

L. D. Dryer & S. S. Shuman
 6100 079 73

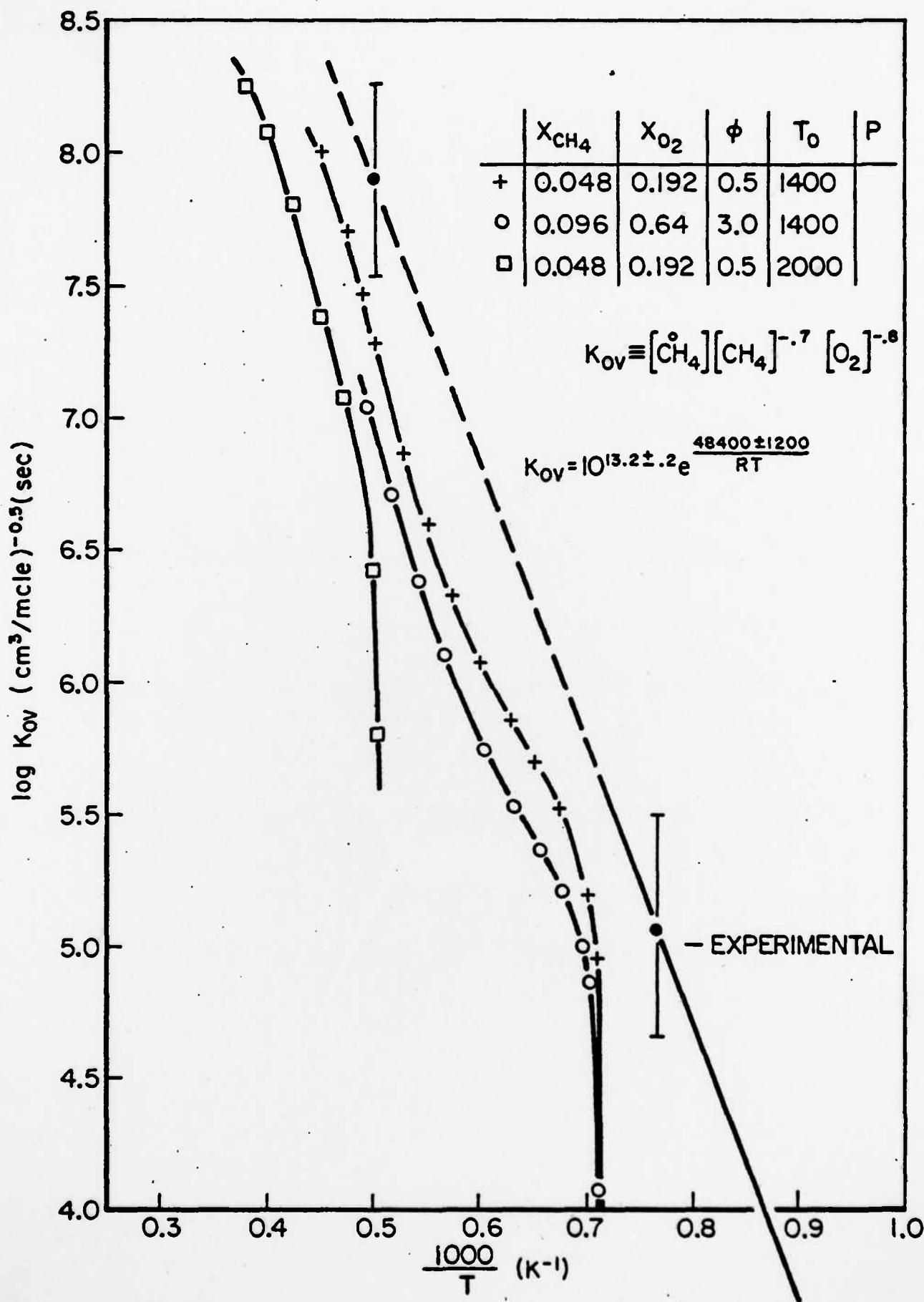


FIGURE 3

F.L. Dryer & S. Glasman

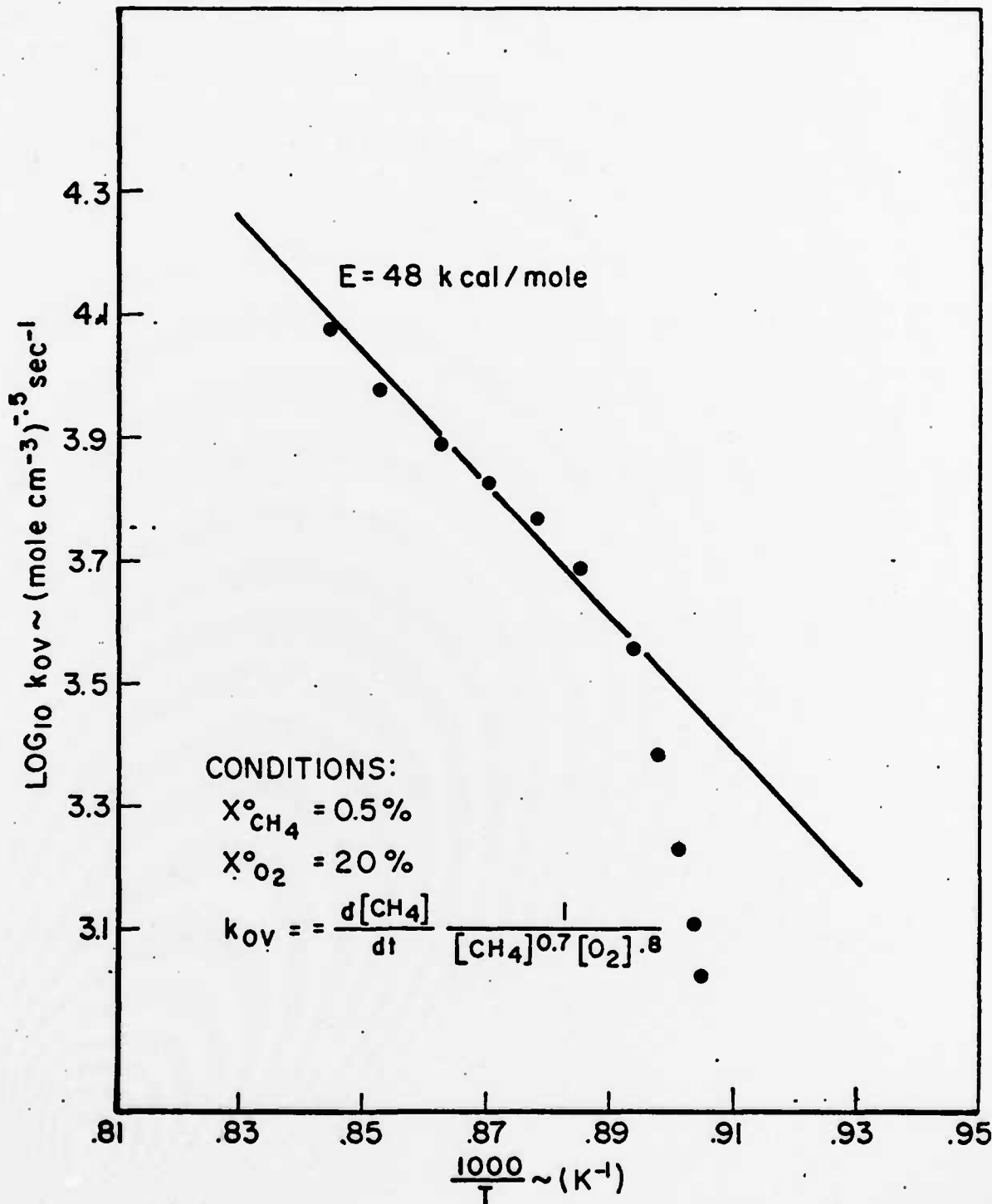


FIGURE 10

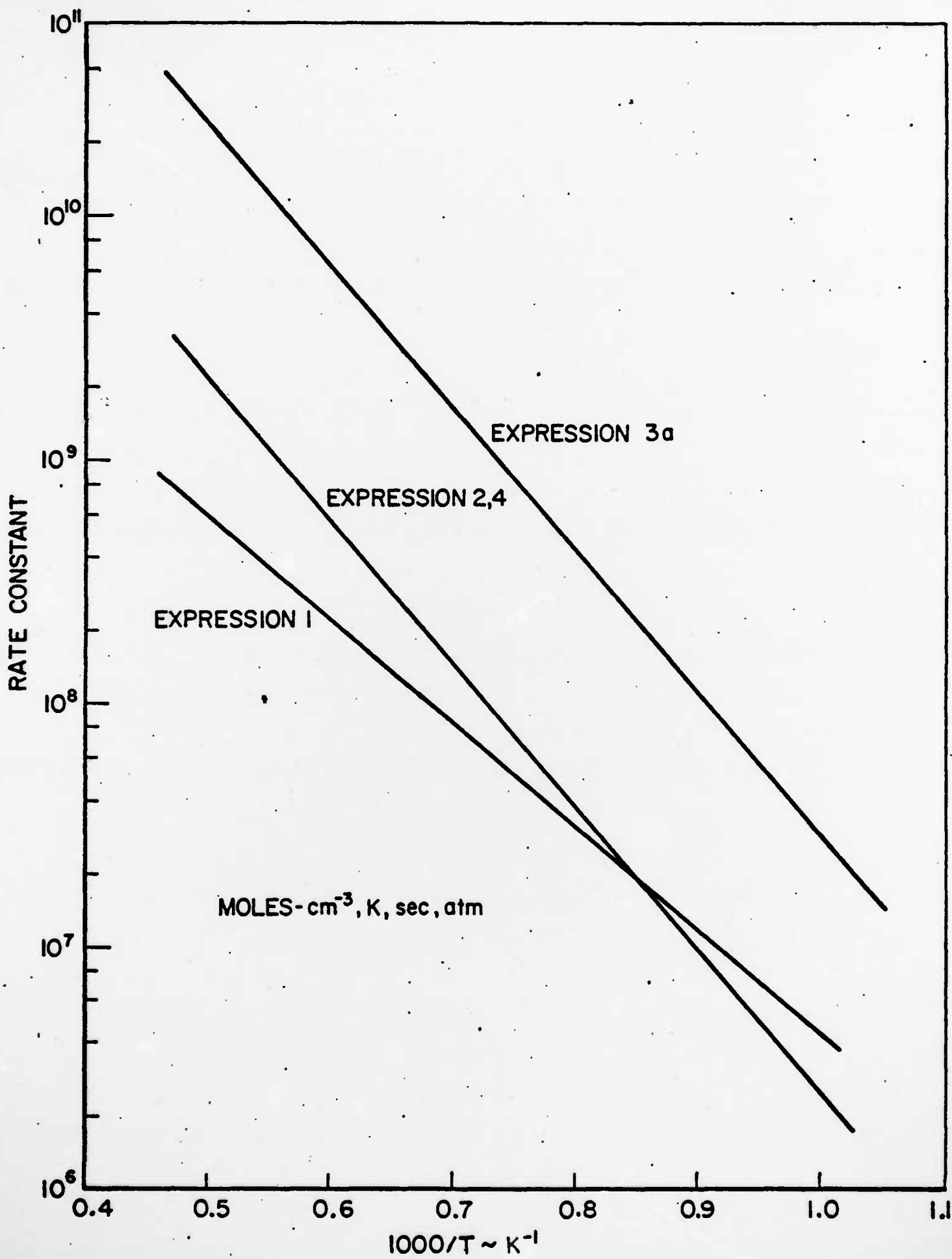


Figure 11

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H. L. Dryden and S. Standen

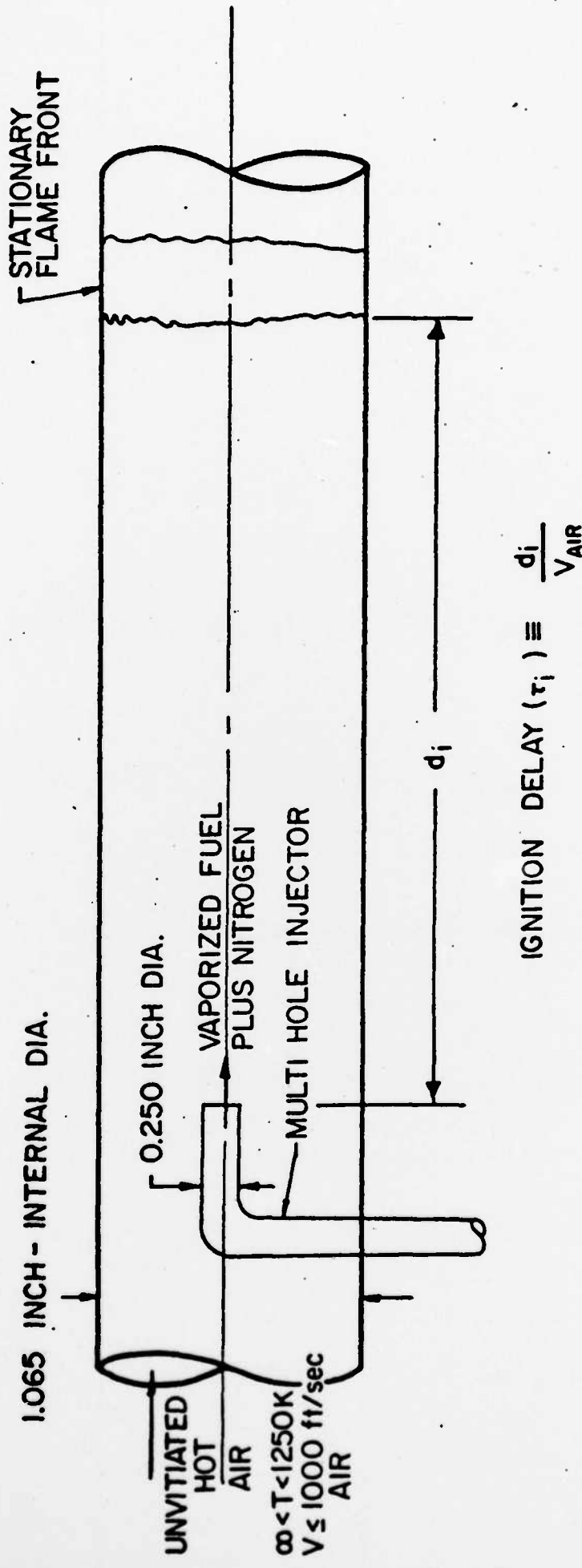


FIGURE 12

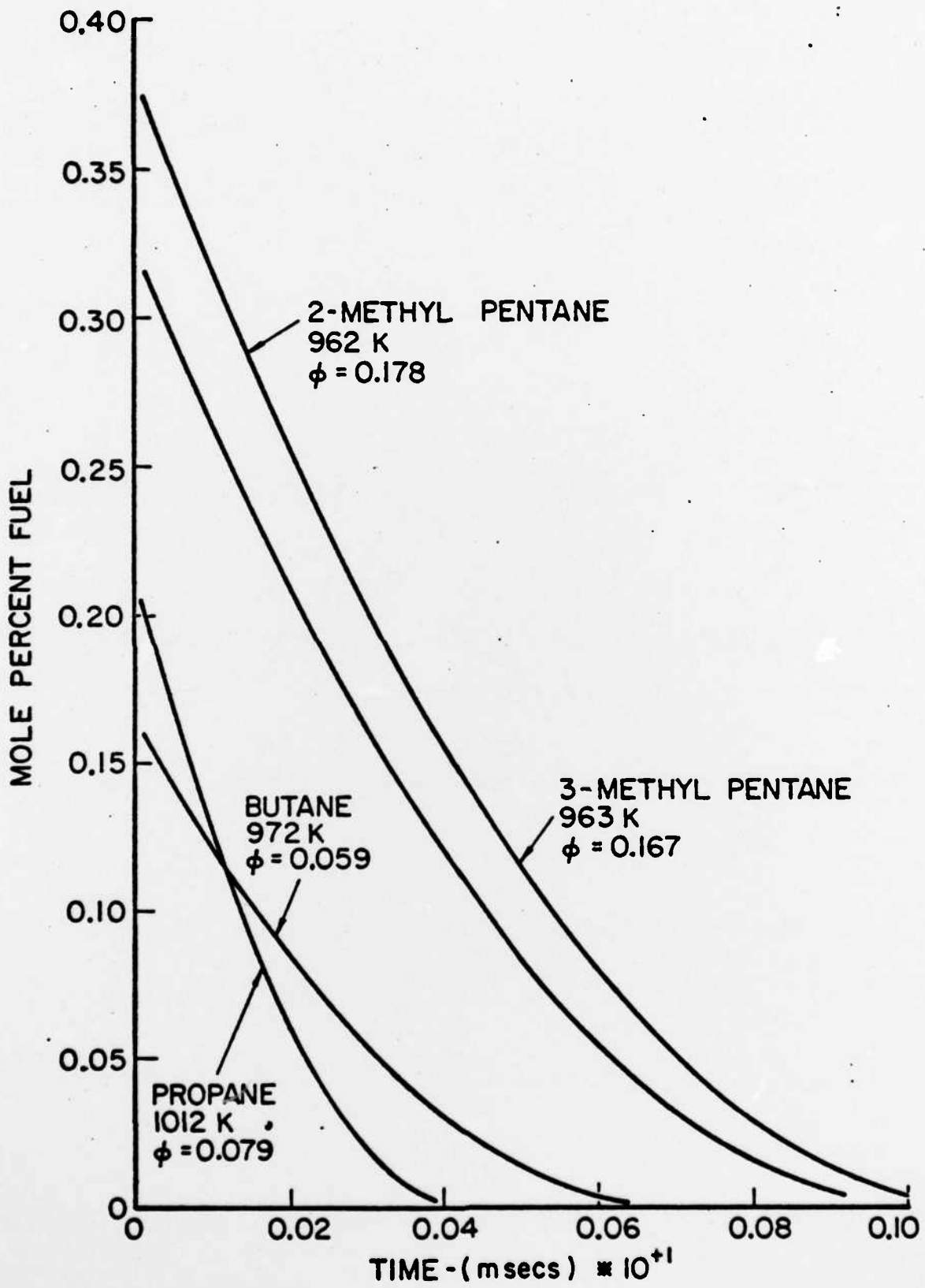
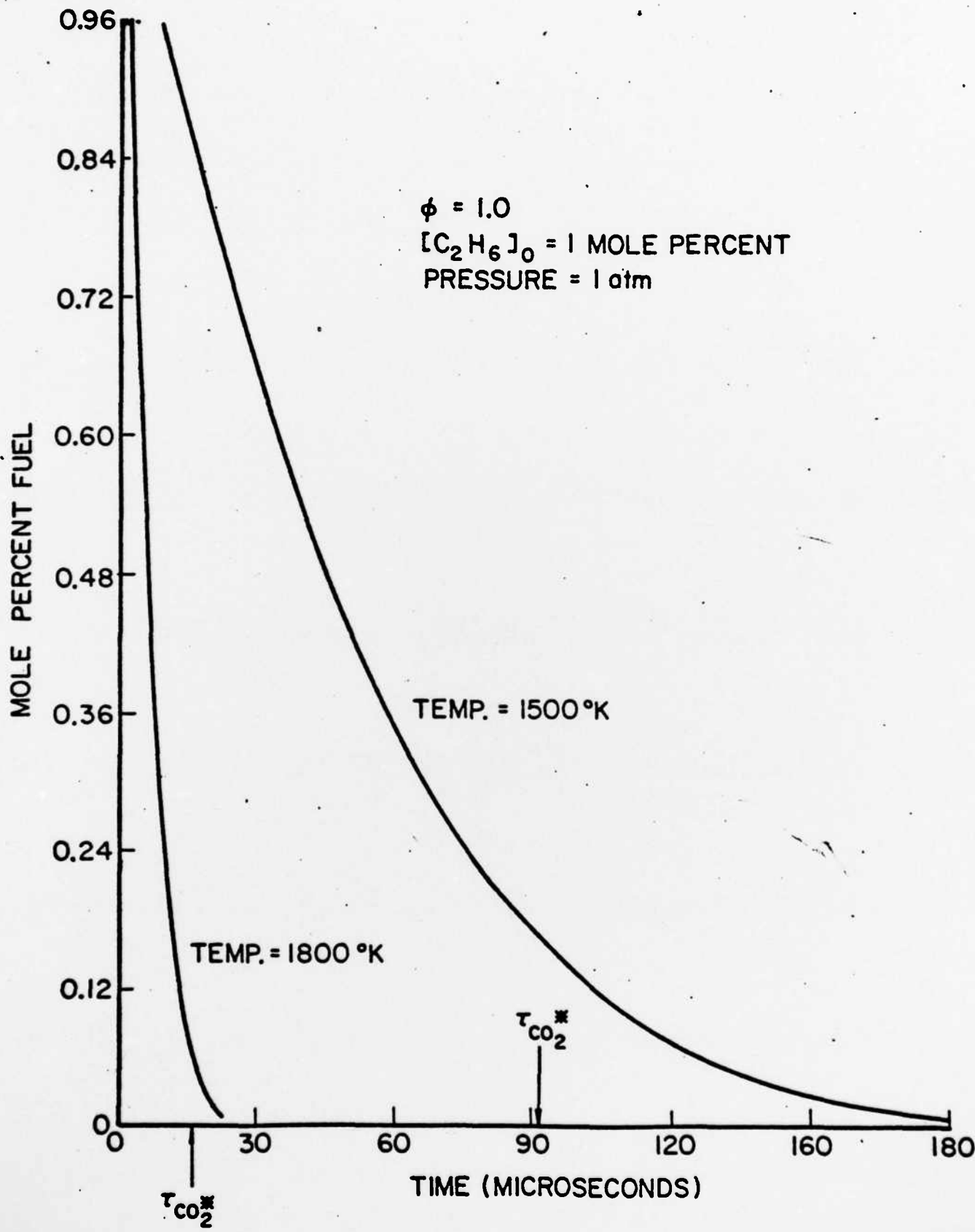


Figure 14.

J. P. Heywood & S. H. Kang



L. A. Meyer & Blazynski

Figure 15