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THEORETICAL KINETIC COMPUTATIONS IN COMPLEX REACTING SYSTEMS

David A. Bittker
NASA Lewis Research Center
Cleveland, Ohio

This paper describes NASA Lewis' studies of complex reacting systems at high temperature. The changes which occur are the result of many different chemical reactions occurring at the same time. Both an experimental and a theoretical approach are needed to fully understand what happens in these systems. The latter approach is discussed herein. We present the differential equations which describe the chemical and thermodynamic changes, and we describe their solution by numerical techniques using a detailed chemical mechanism. Several different comparisons of computed results with experimental measurements are also given. These include the computation of (1) species concentration profiles in batch and flow reactions, (2) rocket performance in nozzle expansions, and (3) pressure versus time profiles in hydrocarbon ignition processes. The examples illustrate the use of detailed kinetic computations to elucidate a chemical mechanism and to compute practical quantities such as rocket performance, ignition delay times, and ignition lengths in flow processes.

INTRODUCTION

For many years Lewis has been studying complex, reacting gas-phase systems at high temperature. The changes that occur in such systems are the result of many individual chemical reactions occurring at the same time. We use a two-step approach to understand what happens in such a system: (1) experimental measurement of the temporal changes in temperature, pressure, or composition of the system, and (2) theoretical computation of these changes in an attempt to match the experimental results. This report describes our work in the computation of complex-system chemical kinetics as focused on combustion systems. Brabbs describes our experimental efforts in his paper for this symposium. Early attempts to compute the progress of complex reactions involved various simplifications. These were of two types: (1) one or two global reactions were substituted for the actual set of many individual, simultaneous reactions which occur in a gaseous system with several species present, and (2) reactions involving some of the very reactive atoms and radicals were assumed to be very fast and, therefore, always in chemical equilibrium. Differential equations for the rates of change of a few key species were solved analytically. Although both of these approaches have had limited success, they only explain some of the general features of a complex reaction. They are, at best, simplified approximations of the actual process, which are only valid under a limited set of conditions. The most fruitful approach to complex kinetics computations is to numerically integrate a system of differential equations derived from the laws of conservation of mass, energy, and (if flow is involved) momentum. These differential equations involve the rates of change of species concentrations σ_i (moles per unit mass of mixture) and temperature T, and they may also involve density ρ and velocity V for a flow process. When these differential equations are solved, a set of individual reactions is assumed to occur simultaneously among all the species, and these reactions are usually assumed to be reversible (with the ratio of the forward to reverse rate constant being equal to the equilibrium constant for any reaction).

There are two ways to use these detailed kinetic computations. First, they may be used to elucidate a reaction mechanism or to determine a single unknown rate constant in conjunction with experimental data. On the other hand, they may be used with a known mechanism to compute practical combustion quantities such as

(1) Kinetic rocket or jet engine performance
(2) Composition of engine exhaust gases
(3) Ignition delays in combustible mixtures
(4) Ignition lengths and nozzle performance in supersonic combustion

Examples of some of these computations performed at NASA Lewis are given later in this paper.

GENERAL THEORY

A reacting system containing NS species is assumed to have NR independent chemical reactions proceeding simultaneously. The general set of reactions is written

$$\sum_{i=1}^{NS} \nu_{ij} S_i \underset{k_{-j}}{\overset{k_j}{\rightleftharpoons}} \sum_{i=1}^{NS} \nu'_{ij} S_i \qquad j=1,2,\ldots, NR$$

Using the law of mass action, we can write the forward and reverse rate of each reaction as

$$R_j = k_j \prod_{i=1}^{NS} (\rho\sigma_i)^{\nu_{ij}} \tag{1}$$

$$R_{-j} = k_{-j} \prod_{i=1}^{NS} (\rho\sigma_i)^{\nu'_{ij}} \tag{2}$$

where ρ is the mass density of the mixture and σ_i the concentration of species S_i, (moles per unit mass of mixture). The rate constant for the forward reaction k_j is written in the modified Arrhenius form

$$k_j = A_j T^{n_j} e^{-E_j/RT} \tag{3}$$

The reverse rate constant k_{-j} is obtained from the law of microscopic reversibility:

$$\frac{k_j}{k_{-j}} = (K_{eq})_j \tag{4}$$

In these last equations,

E_j = activation energy for the j^{th} reaction, energy/mol

T = temperature, K

R = universal gas constant

$(K_{eq})_j$ = equilibrium constant for reaction j

For any reacting system, batch or flow, the appropriate continuity equations are differentiated to give a set of differential equations for the variation of the concentrations and temperature with time. For a flow reaction, differential equations for density and velocity will also be obtained. The resulting system of equations is solved numerically in combination with the ideal gas equation of state:

$$\rho = \frac{p}{RT \sum_{i=1}^{NS} \sigma_i} \tag{5}$$

where p is the pressure of the mixture.

For the case of constant pressure and adiabatic batch reaction, the equations are as follows:

$$\frac{d\sigma_i}{dt} = \frac{W_i}{\rho} \qquad i=1,2,\ldots, NS \tag{6}$$

where W_i, the molar rate of formation of species S_i, is given by

$$W_i = \sum_{j=1}^{NR} (\nu'_{ij} - \nu_{ij})(R_j - R_{-j}) \tag{7}$$

and

$$\frac{dT}{dt} = - \frac{\sum_{i=1}^{NS} W_i h_i}{\sum_{i=1}^{NS} \sigma_i c_{p,i}} \tag{8}$$

where

h_i = molar enthalpy of species S_i

$c_{p,i}$ = molar heat capacity of species S_i

The standard Runge-Kutta or other explicit numerical techniques cannot be used to solve these equations. Although the differential equations are inherently stable, they have widely different time constants for relaxation to their final equilibrium solution. Therefore, the step sizes required for solution stability are prohibitively small. These systems of equations are called stiff, and the problem of solving them accurately has been studied for many years. Several new implicit integration methods have been developed for solving these stiff equations. Although they have been quite successful in improving the accuracy and efficiency of the solutions, there is still a need for additional development of better methods. Problems of accuracy and of efficient step-size selection can still arise. Methods need to be developed for automatic selection of the optimum integration parameters. Therefore, research is actively proceeding at many institutions to develop more efficient integration methods (refs. 1 to 4).

There is another kinetic combustion model of interest to practical engine designers - namely, highly backmixed reacting flow in what is usually called the well-stirred reactor. We assume the limiting condition of zero-dimensional flow or instantaneous backmixing of the reacted gases with the cold, unreacted gases. Although this model is an oversimplification of highly turbulent reacting flow, it is a very useful first-order approximation for some practical reacting-flow systems.

The process is a constant pressure combustion with mass flow rate $\dot{m}$ through a reactor of constant volume v. The average residence time in the reactor is

$$t_r = \frac{\rho v}{\dot{m}} \tag{9}$$

For each species we can write a continuity relation which says the following: The difference between the species molar flow rate into and out of the reactor is equal to its rate of formation (or destruction) by chemical reaction in the reactor. These continuity equations are

$$\frac{\dot{m}}{v}(\sigma_i^* - \sigma_i) + \sum_{j=1}^{NR} (\nu'_{ij} - \nu_{ij})(R_j - R_{-j}) \qquad i=1,2,\ldots, NS \tag{10}$$

The following energy conservation equation can also be written (if we assume that the process is adiabatic):

$$\sum_{i=1}^{NS} (\sigma_i h_i - \sigma_i^* h_i^*) = 0 \tag{11}$$

In these equations * indicates the unreacted gas mixture. Equations (10) and (11) are a set of nonlinear, algebraic equations for σ_i and the reactor temperature. They are solved by the Newton-Raphson iterative procedure. Logarithmic increments of the variables are used to avoid numerical problems (ref. 5).

NASA GENERAL CHEMICAL-KINETICS CODE

Many computer codes have been published which perform different kinds of chemical-kinetic computations. At NASA Lewis we published a general chemical-kinetics code, GCKP84 (ref. 6). It performs a wide variety of chemical-kinetics computations with convenience and efficiency.

It is designed to perform chemical-kinetics computations for several reaction models, including the following:

(1) General reaction in either a batch system or a one-dimensional, frictionless plug flow
(2) Combustion reaction in a well-stirred reactor (highly backmixed flow)
(3) Reaction behind a shockwave with boundary layer corrections
(4) Ignition processes in either a batch or flow system
(5) Nozzle expansion reactions

For each of these models the following general features of the code apply:

(1) Any chemical system may be used for which reaction rate constant data and species thermodynamic data are known.

(2) The process may be adiabatic, or the heat transfer between the reaction and its environment may be considered.

(3) A new efficient integration technique is employed (ref. 7).

(4) Any chemical reaction of the form $aA + bB \rightleftharpoons dD + eE$ may be used, including photochemical and ionic reactions.

(5) Simplified input for combustion reactions may be used.

The code contains an option to compute rocket performance parameters for nozzle flow and can be conveniently used to compute ignition lengths in supersonic flow. An option is also provided to perform a well-stirred reactor computation and, then, immediately expand the products through an assigned nozzle profile.

EXAMPLES OF CHEMICAL KINETIC COMPUTATIONS WITH GCKP84

Hydrogen-Oxygen Batch Reaction at Constant Temperature

Measurements of hydrogen peroxide formation in the constant-volume, isothermal reaction of hydrogen and oxygen at 500 °C were reported many years ago by Baldwin (ref. 8). The important reactions in the hydrogen-oxygen mechanism are as follows:

$$H_2 + O_2 = OH + OH$$

$H_2 + OH = H_2O + H$

$H + O_2 = OH + O$

$O + H_2 = OH + H$

$*H + O_2 + M = HO_2 + M$

$H + HO_2 = OH + OH$

$*H_2O_2 + M = OH + OH + M$

$*HO_2 + HO_2 = H_2O_2 + O_2$

$*H_2 + HO_2 = H_2O_2 + H$

The rate constants for many of these reactions have been measured fairly accurately, but some of the reactions involving H_2O_2 and HO_2 still have a significant uncertainty. The reactions important in determining H_2O_2 concentration are indicated by an asterisk. GCKP84 was used to compute the H_2O_2 versus time profile. After making several variations of the rate constants for the two most uncertain and important reactions ($H_2 + HO_2 \rightleftharpoons H_2O_2 + H$ and $HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$), we obtained the agreement between the experimental and computed results shown in figure 1. This example illustrates the use of kinetics computations in obtaining better rate-constant values for one or two key reactions when all other reactions in a mechanism are fairly well known. Of course, we cannot say that we have uniquely determined both reaction rate constants since we have two adjustable parameters. But we have put limits on their uncertainty. Of course, this type of exercise can only be done when the experimental variable being matched by computation is sensitive to small variations in the uncertain rate constants. This brings up the following general question: For a given change in any rate constant of the reaction mechanism, how much does each computed variable change? This is the relatively new field of study in chemical kinetics called sensitivity analysis.

In practice, even through a chemical mechanism may contain more than 100 reactions, only the rate constants of 15 or 20 may significantly affect the computed results when their values are changed. Recently, methods have been developed to systematically compute these effects in the form of sensitivity coefficients (refs. 9 to 11). This computation is performed along with the chemical-kinetics computation. The results of the latter computation are used as input to solve a second set of differential equations whose unknowns are sensitivity coefficients of the form

$$S_{i\ell} = \frac{k_\ell}{c_i} \frac{\partial c_i}{\partial k_\ell} \tag{12}$$

$$T_{i\ell m} = \frac{k_\ell k_m}{c_i} \frac{\partial^2 c_i}{\partial k_\ell \partial k_m} \tag{13}$$

The first-order coefficient $S_{i\ell}$ effectively gives the percentage change in c_i (i^{th} concentration variable) for a given percentage change in the rate constant of reaction ℓ. The second-order coefficient $T_{i\ell m}$ gives the effect on c_i of changes in both k_ℓ and k_m. It is now recognized that a sensitivity analysis must be performed for any complex reaction in order to pinpoint the important reaction paths and obtain a good understanding of the reaction mechanism.

Computation of Rocket Performance

One of the first uses of chemical kinetic computations was in the computation of rocket performance using a one-dimensional flow model. This performance is measured by the velocity of the hot gas at the nozzle exit point. As the gas expands and cools, its velocity (i.e., kinetic energy) is kept as high as possible by chemical recombination reactions which occur in the nozzle. These reactions convert high-potential-energy atoms and radicals into low-energy stable molecules. Maximum performance is obtained if these reactions maintain equilibrium conditions in the very short nozzle-residence time. But this is often not the case since the finite rates of the reactions are not fast enough. By knowing the rate constants for the important recombination processes one can compute kinetic performance that more accurately and realistically reflects the experimentally measured performance. An example of this is shown in figure 2 for the oxygen difluoride - diborane system (ref. 12). The three curves of performance as a function of oxidant/fuel ratio (fig. 2(b)) show the maximum and minimum theoretical performance (assuming equilibrium and frozen conditions) as well as the kinetically limited performance. The latter agrees rather well with actual measurements corrected for various losses. The reaction mechanism used is shown in table I. This system is interesting because only one reaction rate constant has to be accurately known in order to compute the kinetic curve. This is the recombination of hydrogen atoms to give molecular hydrogen. This fact was determined by a simple sensitivity analysis. Computed performance is unchanged for wide variations of the other rate constants. The reason for this situation can be seen from the heat release data in table I. The hydrogen atom recombination accounts for well over 50 percent of the heat release in the process, and this, of course, controls performance.

Two-Stage Well-Stirred Reactor

The practical use of the well-stirred reactor model of GCKP84 is illustrated by its simulation of a two-stage turbulent combustor. A theoretical and experimental study of two-stage, rich-lean combustion as a method of controlling nitrogen oxide emissions was performed at Lewis. This technique was suggested as a way of reducing the conversion of the organic nitrogen compounds in hydrocarbons (fuel-bound nitrogen) to nitric oxide during combustion. The objective of the work was to study the effect of operating conditions on emissions of both nitrogen oxides (NO_x) and carbon monoxide (CO) (ref. 13). Both the nitrogen and the hydrogen content of the fuel were changed to simulate coal-derived syncrude fuels. These fuels contain high percentages of aromatic hydrocarbons and therefore have a lower hydrogen-to-carbon ratio than today's petroleum-based fuels. Experiments were performed in the two-stage flame-tube apparatus shown in figure 3. The fuels were mixtures of propane, toluene, and pyridine blended to give a range of hydrogen and nitrogen contents. The primary-zone equivalence ratio was varied from 0.7 to about 1.8. The products of first-stage combustion were rapidly diluted with air injection and burned at a final equivalence ratio of 0.5. The final NO_x and CO concentrations were measured. The two-stage flame tube was modeled analytically by a two-stage stirred-reactor computation closely simulating the experimental fuels. Instantaneous mixing of the secondary dilution air was assumed. A detailed chemical mechanism was used for propane and toluene oxidation and for NO_x formation. The fuel-bound nitrogen was input as nitrogen atoms and all mixing and heat-transfer effects were neglected. This very simplified model of a quite complex process was able to predict most of the observed trends of NO_x and CO formation with variation of nitrogen and hydrogen concentrations in the fuel. The model's prediction of other trends, which were not measured experimentally, gave additional information about the advantages and disadvantages of using this rich-lean combustion for emissions control. A comparison of some experimental and computed results for NO_x and CO concentration as a function of primary equivalence ratio is given in figures 4 and 5. The simple model qualitatively predicts the observed trends. It can be seen that using a rich primary equivalence ratio does reduce NO_x formation very significantly. However, at the same time, this technique increases the formation of CO, which is also undesirable. Thus, one set of conditions cannot minimize both pollutants, and tradeoffs will have to be made to obtain desired emissions levels for any practical situation. This work has shown that a simple kinetic model can sometimes be used to qualitatively explain the observed trends in a highly complicated combustion system.

Ignition Delays in Benzene-Oxygen-Argon Mixtures

Our current work involves the study of the mechanism of hydrocarbon oxidation. We are studying the aliphatic hydrocarbons by measuring ignition delays and concentration profiles during the shock-heated oxidation of hydrocarbon-oxygen-argon mixtures. Then a detailed chemical mechanism is formulated and used in detailed kinetics computations to match the observed experimental data over a wide range of initial composition, temperature, and pressure. We are also studying the simplest aromatic, benzene. A partial mechanism for benzene oxidation is as follows:

$$C_6H_6 + O_2 = C_6H_5 + HO_2$$

$$C_6H_6 = C_6H_5 + H$$

$$C_6H_6 = C_4H_4 + C_2H_2$$

$$H + O_2 = OH + O$$

$$H + O_2 + M = HO_2 + M$$

$$O + C_6H_6 = C_6H_5 + OH$$

$$OH + C_6H_6 = C_6H_5 + H_2O$$

$$C_6H_5 + O_2 = C_6H_5O + O$$

$$C_6H_5O + M = C_5H_5 + CO + M$$

$$CO + OH = CO_2 + H$$

The experimental program is described by T.A. Brabb's paper presented at this symposium. I attempted to match experimental ignition delay data for benzene-oxygen-argon mixtures that were taken by another investigator at Lewis. The reaction zone behind the experimental reflected shock is approximated by a constant volume batch reaction. The theoretically computed temperature and pressure (for nonreacting conditions) behind the shock are used as starting conditions. A typical, computed profile of pressure as a function of time is shown in figure 6. The ignition delay τ is determined from the first significant pressure rise; this is similar to determining the experimental τ value from the measured pressure trace. The mechanism we used includes over 100 reactions involving benzene and its degradation products, acetylene, phenol, phenylacetylene, ethylene, and methane. It includes all the reactions of the hydrogen-oxygen system as well. Values from the literature were used for all reaction rate constants except the quite uncertain ones of the benzene, phenol, and phenylacetylene reactions. These were varied within reasonable limits to get the best overall agreement between computed and experimental τ values. Starting mixture equivalence ratios ranged from 0.5 to 2, temperatures ranged from about 1200 to 1700 K, and initial pressures ranged from 2 to 6 atm. A simple sensitivity study made by changing rate constants one at a time has shown that the τ values are most sensitive to the rate constant for the $C_6H_5 + O_2$ reaction, which is quite uncertain. Other rate constants which are uncertain and have a significant effect are those for $C_6H_6 \rightleftharpoons C_4H_4 + C_2H_2$ and $C_6H_5 \rightleftharpoons C_4H_3 + C_2H_2$. In figure 7 we show some comparisons between computed and experimental ignition delays. We have used only the experimental data points which are considered the most accurate for the mechanism matching. These are the data with τ values of 100 msec or greater. Shorter ignition delays may have significant error due to the nonuniformity of the reaction mixture and the heating effects. The computed line for log τ versus 1/T comes within ±50 percent for all but one point which differs by about a factor of two. While this mechanism does fairly well, it is certainly not complete and has two significant problems. First, it tends to predict delays longer than the experimental ignition delays for the lean mixtures and shorter than the experimental delays for the rich mixture. Second, it does not predict the experimentally observed effect of dilution with argon at a constant equivalence ratio of 1.0. Therefore, more work needs to be done on this oxidation mechanism. A full understanding of the oxidation will probably not be achieved until further experimental data are obtained on concentration profiles of a key species, such as the phenyl radical or carbon dioxide. Work along these lines is proceeding at Lewis and other laboratories.

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TABLE I. - OF_2-B_2H_6 MECHANISM

[Equivalence ratio = 1.63.]

Reaction	Net reaction rate, percent	Heat of reaction, ΔH, kcal/mole	Energy release rate, percent
$H + H + M \rightleftharpoons H_2 + M$	32.3	-104	53.1
$BO + HF \rightleftharpoons BOF + H$	26.8	-33	13.9
$H + F + M \rightleftharpoons HF + M$	5.1	-136	11.1
$H + OH + M \rightleftharpoons H_2O + M$	5.2	-119	9.8
$BF + OH \rightleftharpoons BOF + H$	3.9	-58	3.5
$F + H_2 \rightleftharpoons HF + H$	4.5	-32	2.3
$H_2 + OH \rightleftharpoons H_2O + H$	9.7	-15	2.3
$BF + O \rightleftharpoons BO + F$	9.3	8	1.2
$H + BF_2 \rightleftharpoons HF + BF$	2.4	-25	1.0
$BO + F + M \rightleftharpoons BOF + M$	.3	-169	.7
$BF + O + M \rightleftharpoons BOF + M$	.2	-160	.6
$O + H + M \rightleftharpoons OH + M$	.3	-102	.5
Total	100.0		100.0

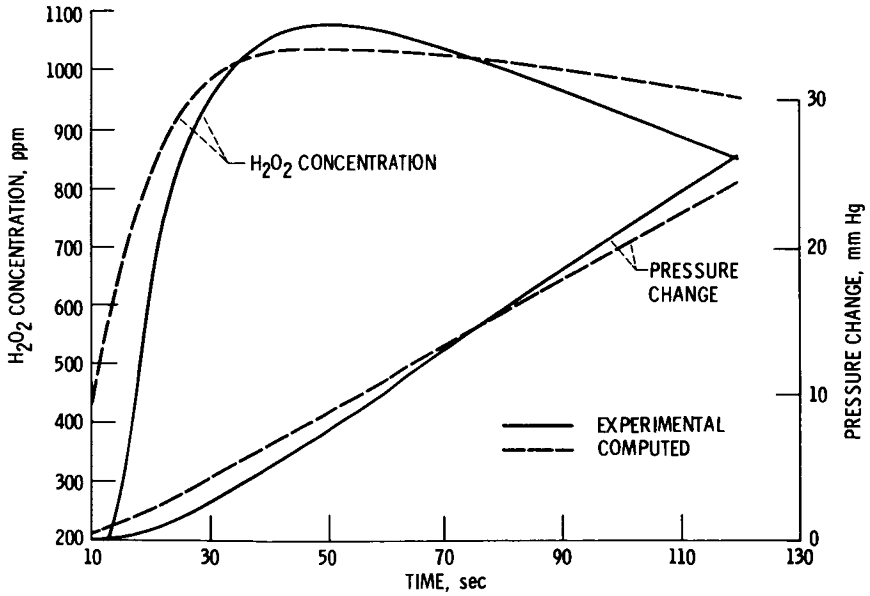

Figure 1. - Computed and experimental results for hydrogen-oxygen reaction. Temperature, T, 500 °C.

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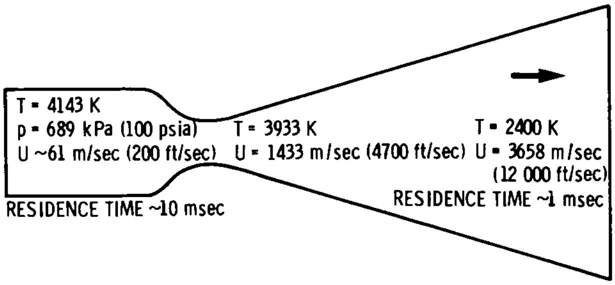
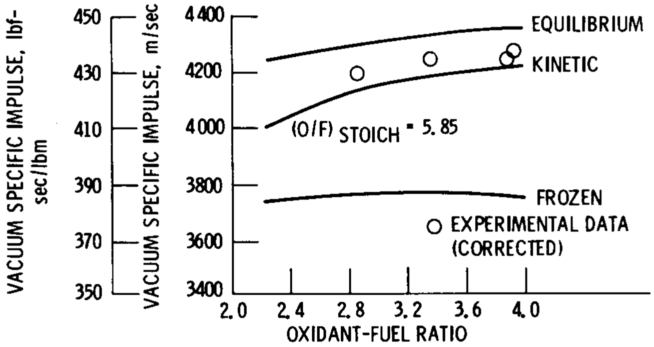


(a) Rocket engine conditions for OF_2-B_2H_6 propellant. Equivalence ratio, 1.63.



(b) Performance of OF_2-B_2H_6 rocket propellant. Chamber pressure, 689 kPa (100 psia).

Figure 2. - Oxygen difluoride-diborane (OF_2-B_2H_6) rocket combustion.

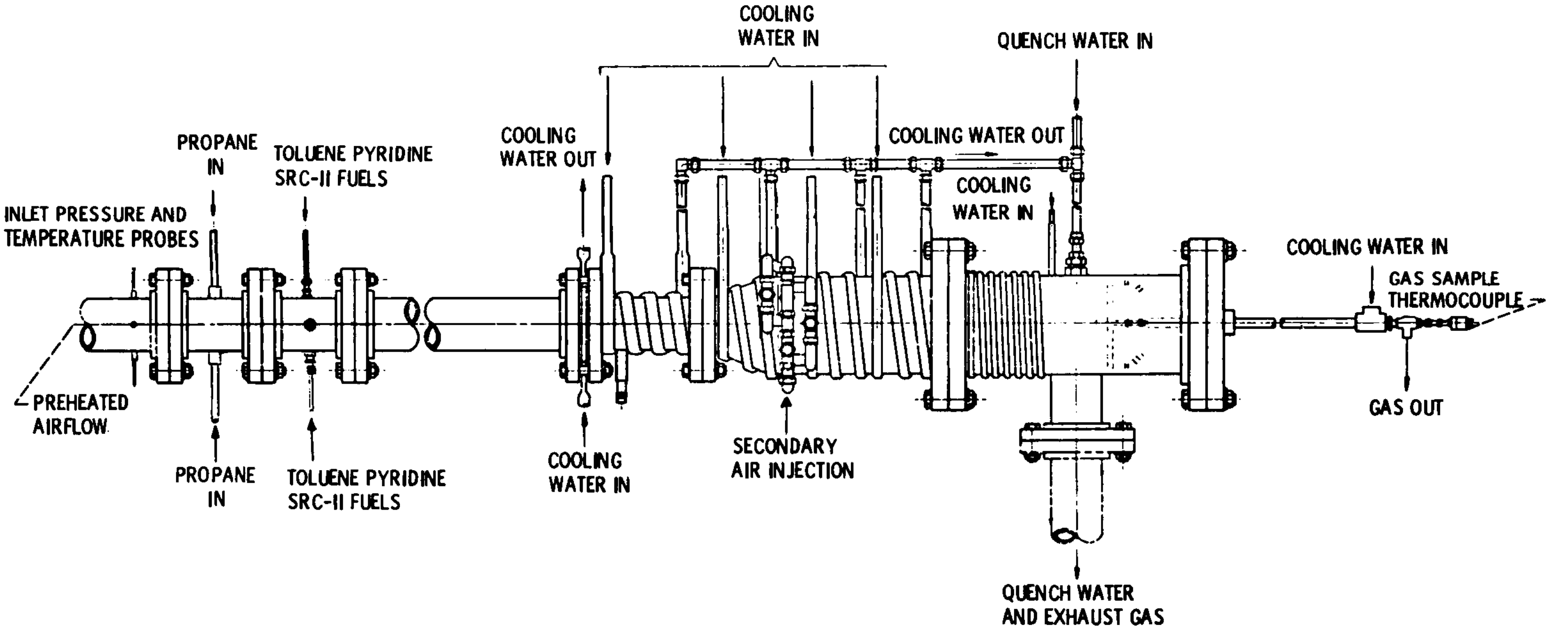


Figure 3. - Flame-tube apparatus.

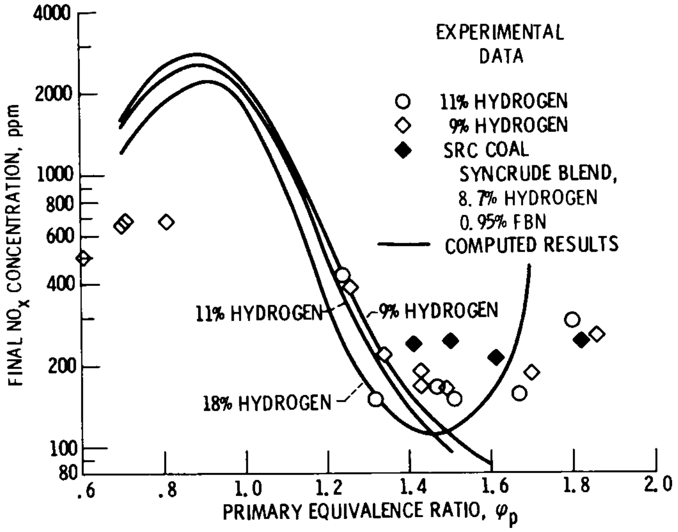


Figure 4. - Effect of hydrogen content on NO$_x$ emissions. Fuel-bound nitrogen, 1.0 percent; secondary equivalence ratio, 0.5; secondary residence time, ≅ 2 msec.

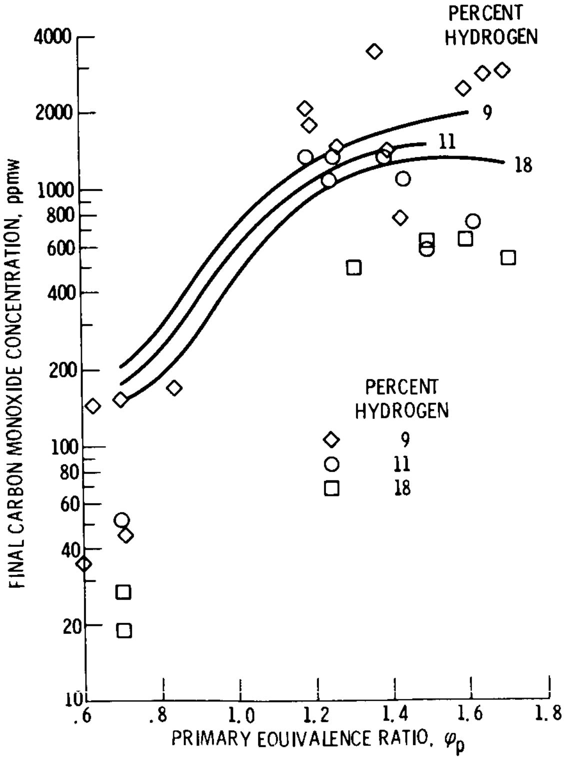


Figure 5. - Effect of percent hydrogen on carbon monoxide emissions for hydrocarbon combustion. Fuel-bound nitrogen, 0 percent; secondary equivalence ratio, 0.5; secondary residence time, ≅ 2 msec.

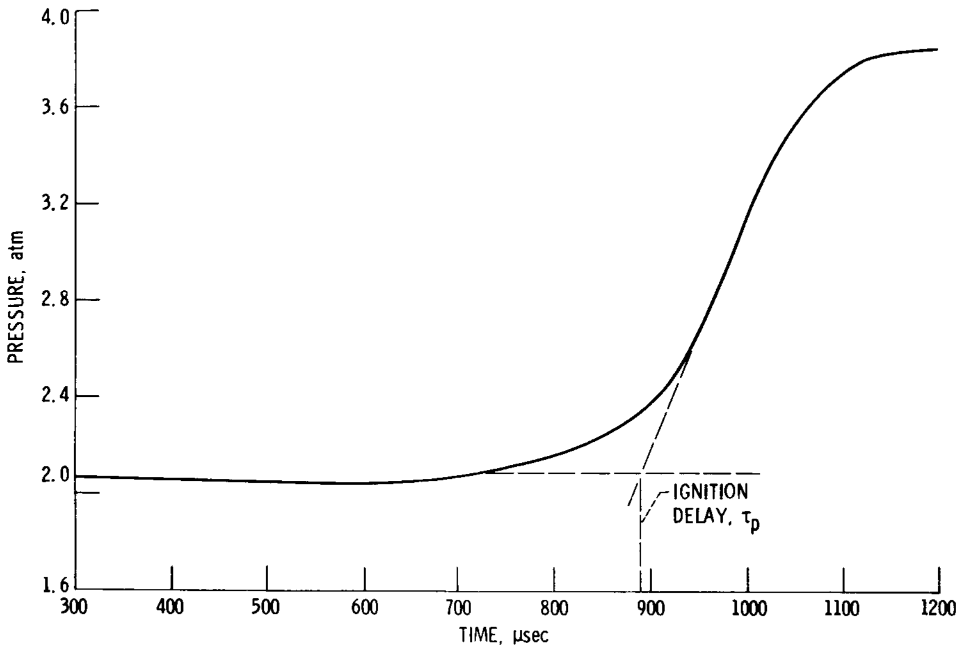


Figure 6. - Computed pressure as function of time for benzene-oxygen-argon shock ignition. Initial temperature, 1366 K; equivalence ratio, φ, 2.0.

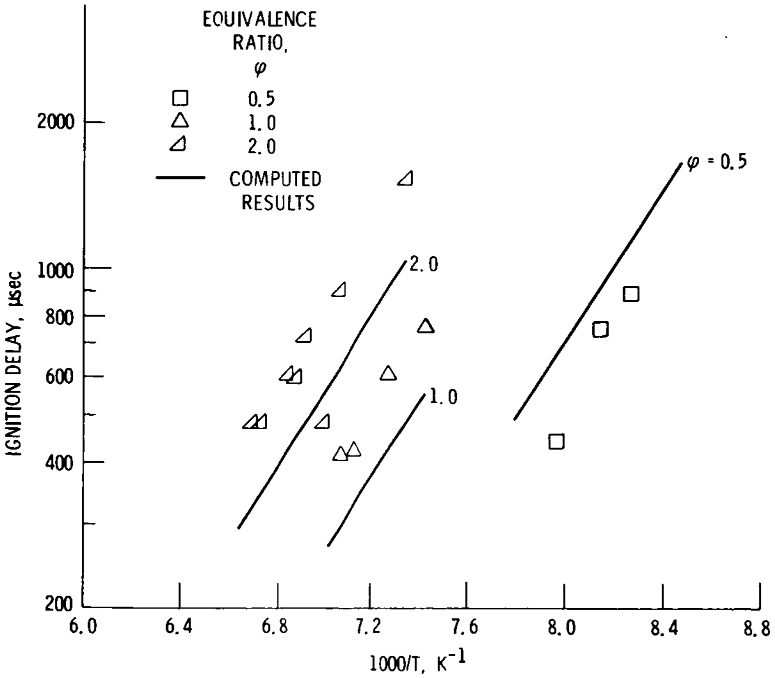


Figure 7. - Ignition delay data for benzene-oxygen-argon mixtures.