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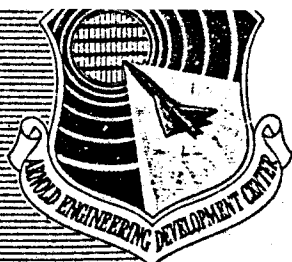
*Dr. Roy J. Schulz*

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**THE EFFECT OF  
NON-EQUILIBRIUM FREE-RADICAL CONCENTRATION  
ON IGNITION DELAY IN THE HYDROGEN-AIR SYSTEM**

**By**

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a subsidiary of Sverdrup and Parcel, Inc.

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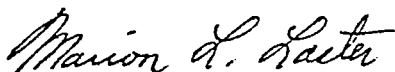
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## ABSTRACT

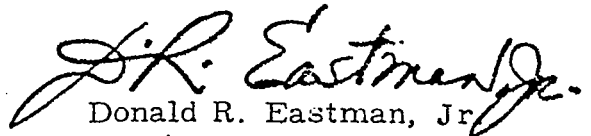
This report presents a theoretical discussion of the effect of non-equilibrium quantities of free radicals on the ignition delay in the hydrogen-air system. A correlation was found between the ignition delay computed from complete reaction kinetics and the initial rate of the reaction  $O_2 + H = OH + O$ . A rate equation is derived in which a modified expression for the total free radical content is substituted for the H concentration. The implications of non-equilibrium amounts of free radicals on the testing and operation of high velocity combustion systems are discussed.

PUBLICATION REVIEW

This report has been reviewed and publication is approved.



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## NOMENCLATURE

|         |                                                                   |
|---------|-------------------------------------------------------------------|
| $A_i$   | The reaction rate coefficient for the $i$ th reaction             |
| $E_i$   | Activation energy of the $i$ th reaction                          |
| $K$     | Equilibrium constant                                              |
| $k_i$   | Reaction rate constant of the $i$ th reaction = $A_i e^{-E_i/RT}$ |
| $P$     | Pressure                                                          |
| $R$     | Universal gas constant                                            |
| $r_i$   | Rate of the $i$ th reaction = $\left(\frac{dX_A}{dt}\right)_i$    |
| $T$     | Temperature                                                       |
| $(X_A)$ | Mole fraction of component A                                      |
| $\tau$  | Time                                                              |

## SUBSCRIPTS

|                 |                 |
|-----------------|-----------------|
| 1, 2, 3, 4, $i$ | Reaction number |
| 0               | At time = 0     |
| FR              | Free radical    |

## 1.0 INTRODUCTION

Currently, there is considerable interest in the ignition and combustion processes which occur in supersonic flow (Refs. 1-6). In most cases of interest, the ignition temperatures are relatively low, typically under 2000°K as opposed to greater than 2000°K for shock tube experiments. Two reasons for the interest in low temperature ignition phenomena are (1) very high initial temperature means a high combustion temperature with attendant dissociation losses and (2) even moderately high static temperatures are very difficult and expensive to obtain in steady flow facilities. With these relatively low temperatures, ignition delay can occupy a sizable fraction of the length of the combustion chamber, and therefore, the factors which affect ignition delay become important.

In a classical ignition reaction in which the reactants are relatively slowly heated, ignition will occur when the equilibrium free-radical concentration reaches a point where the rate of formation of free radicals by chain branching reactions exceeds their loss by recombination on the vessel walls. Except in the case of adiabatic compression, heat transfer rates prevent heating a gas fast enough so that the free-radical content is not in equilibrium with the parent species. In supersonic flow where rapid adiabatic compressions and expansions are the rule, it is almost impossible to perform these processes slowly enough so that equilibrium will be reached, and therefore, the reacting mixtures may depart radically from their equilibrium free-radical contents.

The purpose of this investigation is to present the effect of non-equilibrium free-radical content on ignition properties and to determine the difficulties or benefits which may result from these effects. This investigation was made in the Research Branch of the Rocket Test Facility (RTF), Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC).

## 2.0 DISCUSSION

In the hydrogen-air system, the length of the ignition delay is controlled by the rate of increase in free radicals through the four following reactions (Ref. 7):




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No reactions with nitrogen are considered in this work. The rate of formation of a particular radical (A) from reactants (B) and (C) through a particular reaction (i) is

$$\left( \frac{dX_A}{d\tau} \right)_i = \frac{P A_i e^{-E_i/RT}}{RT} (X_B)(X_C)$$

The rate of the reaction will depend on the temperature and reactant concentrations: its sensitivity to temperature will depend on the activation energy ( $E_i$ ).

In a supersonic test facility, it is possible to have the free-radical content of the gas stream much larger than the value at equilibrium at the local static temperature. This would occur when the gas had been heated and rapidly expanded through a nozzle. The free-radical concentrations could be nearly in equilibrium with conditions at the nozzle throat. It could also occur to an even greater degree in systems heated by an electrical discharge where greater than equilibrium amounts of dissociation products could occur in the arc and remain frozen during the expansion process.

If the concentration of free radicals is high enough to cause the initial rate of reaction to exceed some critical value, the reaction will proceed exponentially to a local equilibrium condition. Reactions (1) and (2) feed each other with free radicals and (3) and (4) produce more reactants for (1) and (2) from the OH produced by (1) and (2). The set of reactions will proceed until an equilibrium is reached between the reactions as shown and the reverse reactions or until the free-radical concentrations become so high that the recombination reactions become important. The critical value of the reaction rate depends on several factors which depend on the recombination rates of the radicals involved and on the time available for ignition. The time factor is important in flow systems since, at 10,000 ft/sec with an ignition delay of 0.01 sec, ignition would occur 100 ft from the point of initiation and for practical purposes might as well not occur at all.

The rates of the four principal reactions in the forward direction are:

$$\left. \begin{aligned} r_1 &= 4 \times 10^{14} \frac{P}{RT} e^{-\frac{18000}{RT}} (X_{O_2})(X_H) \\ r_2 &= 3 \times 10^{14} \frac{P}{RT} e^{-\frac{6000}{RT}} (X_{H_2})(X_O) \\ r_3 &= 3 \times 10^{14} \frac{P}{RT} e^{-\frac{2500}{RT}} (X_{OH})^2 \\ r_4 &= 3 \times 10^{14} \frac{P}{RT} e^{-\frac{2500}{RT}} (X_{OH})(X_{H_2}) \end{aligned} \right\} \text{Ref. 8}$$

In the low temperature range ( $< 2000^\circ\text{K}$ ) reaction (1) will be, by far, the slowest because of the large activation energy and will control the overall rate of the reactions since it provides the only mechanism by which  $\text{O}_2$  may react. For example, at  $1000^\circ\text{K}$  and equivalent reactant concentrations and pressure, reaction (2) will occur 300 times as fast as reaction (1).

The rate of formation of  $\text{O}$  by reaction (1) is proportional to  $X_{\text{H}}$ . However, when the temperature is low, it may be assumed that in the very early parts of the reaction, reactions (2) and (4) will proceed nearly to completion before (1) will start. Reaction (3) is neglected since it is normally several orders of magnitude slower than (4) by the ratio of  $X_{\text{OH}}$  to  $X_{\text{H}_2}$  since  $k_3 = k_4$ .

Since, in the very early part of the ignition delay period,  $X_{\text{H}_2}$  changes only slightly and may be assumed to be constant, an analytical solution for the rates of reactions (1) and (2) may be obtained from the following equations:

$$\frac{dX_{\text{H}}}{d\tau} = \frac{P}{RT} \left[ K_2 (X_{\text{H}_2}) (X_{\text{O}}) + K_4 (X_{\text{OH}}) (X_{\text{H}_2}) \right]$$

$$\frac{dX_{\text{OH}}}{d\tau} = \frac{P}{RT} \left[ K_2 (X_{\text{H}_2}) (X_{\text{O}}) - K_4 (X_{\text{OH}}) (X_{\text{H}_2}) \right]$$

and

$$(X_{\text{OH}}) + (X_{\text{H}}) = 2(X_{\text{O}})_0 - 2(X_{\text{O}}) + (X_{\text{OH}})_0 + (X_{\text{H}})_0$$

which is:

$$(X_{\text{O}}) = (X_{\text{O}})_0 e^{-\frac{K_2 P (X_{\text{H}_2}) \tau}{RT}}$$

$$(X_{\text{OH}}) = \frac{K_2 (X_{\text{O}})_0}{K_4 - K_2} \left[ e^{-\frac{K_2 P (X_{\text{H}_2}) \tau}{RT}} - e^{-\frac{K_4 P (X_{\text{H}_2}) \tau}{RT}} \right] + (X_{\text{OH}})_0 e^{-\frac{K_4 P (X_{\text{H}_2}) \tau}{RT}}$$

$$(X_{\text{H}}) = 2(X_{\text{O}})_0 - 2(X_{\text{O}}) + (X_{\text{OH}})_0 - (X_{\text{OH}}) + (X_{\text{H}})_0$$

The results of these equations for a stoichiometric mixture of  $H_2$  and  $O_2$  with O or OH at 500°R are shown in Figs. 1a and b, respectively. They show that under low temperature conditions, the O and OH will react to produce H in the very early part of the ignition delay period

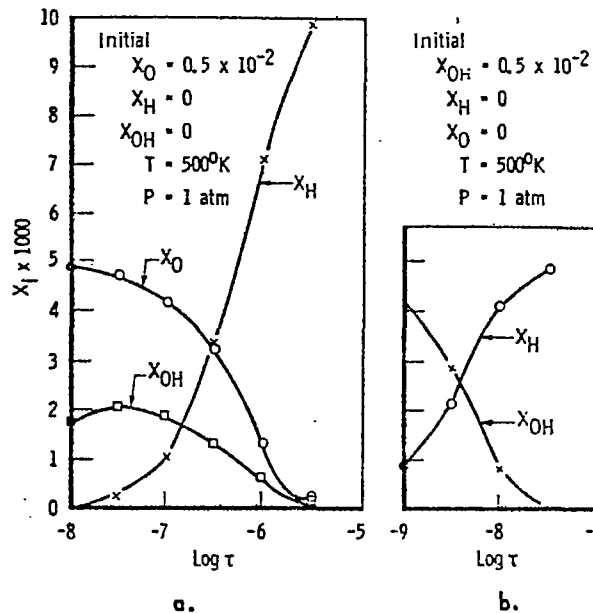


Fig. 1 Free-Radical Concentrations in the Very Early Part of the Ignition Delay Period

with each O resulting in two H atoms and each OH in one H atom. If the reverse reactions had not been neglected, the OH would tend toward the equilibrium value rather than zero, and the amount of H produced would be less. However, it may be shown by the equilibrium constants for the reactions that the reactions will essentially go to completion in the forward direction.

For the reaction  $OH + H_2O \rightarrow H$  (reaction 4), the equilibrium constant is

$$K = \frac{(X_{H_2O})(X_H)}{(X_{OH})(X_{H_2})} = \left. \begin{array}{l} 17000 \text{ at } 1000^\circ K \\ 2 \times 10^6 \text{ at } 500^\circ K \end{array} \right\} (\text{Ref. 9})$$

And for the sum effect of reactions (2) and (4)  $2H_2 + O \rightarrow H_2O + 2H$ , the equilibrium constant is

$$K = \frac{(X_{H_2O})(X_H)^2}{(X_{H_2})^2(X_O)} = \left. \begin{array}{l} 8500 \text{ at } 1000^\circ K \\ 2.2 \times 10^5 \text{ at } 500^\circ K \end{array} \right\} (\text{Ref. 9})$$

(Since the equilibrium constants are large, the reactions will go essentially to completion in the direction shown. Therefore, under conditions where reaction (1) is slow compared to the others, the O and OH will react to form H by reactions (2), (3), and (4), and  $(X_H)_0$  will be approximately equal to  $(X_H)_0 + 2(X_O)_0 + (X_{OH})_0$  very early in the ignition delay period.)

Under these conditions, the initial rate of reaction (1) will be:

$$(r_1)_0 = \frac{P K_1 (X_{O_2})_0 (X_{FR})_0}{RT} \quad \text{where } K_1 = 4 \times 10^{14} e^{-\frac{18000}{RT}}$$

(Ref. 8)

$$(X_{FR})_0 = (X_H)_0 + (X_{OH})_0 + 2(X_O)_0$$

The correlation between the ignition delay time (chosen as the time where  $(X_{H_2}) = 0.5 (X_{H_2})_0$ ), obtained from solutions to the General Applied Science Laboratory Computer program for the kinetics of the  $H_2O_2$  system (Ref. 7) and the initial rate of reaction (1),  $(r_1)_0$ , is shown in Fig. 2. If the initial conditions are known, the delay time can be predicted from the plot within a factor of 2.

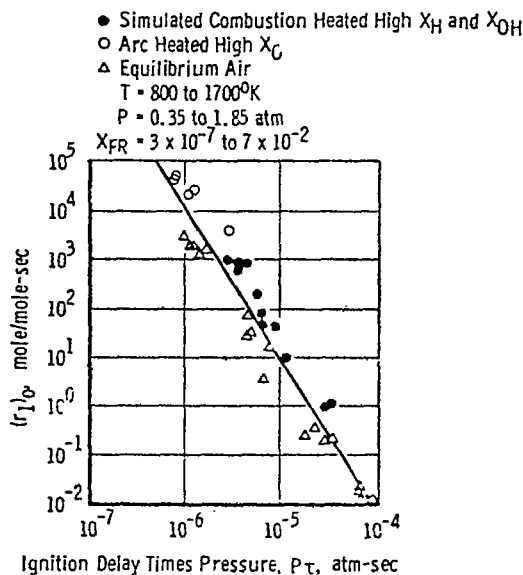


Fig. 2 Correlation between the Parameter  $(r_1)_0$  and Ignition Delay Time

If the wide range of starting conditions are considered, the correlation seems good. Mixtures with an excess of free radicals seem to have a somewhat larger delay time for the same  $(r_1)_0$  than equilibrium mixtures. Pressure seems to have large effect on delay, whereas the concentration terms seem to have a smaller effect.

If an ignition delay of  $50 \mu \text{ sec}$  is selected as a maximum which can be tolerated because of equipment size, a minimum  $(r_1)_0$  of 0.2 must be maintained at 1 atm. By using this as a criteria, a relationship may be obtained for a minimum ignition temperature for any free-radical concentration. This relationship is shown in Fig. 3 for a case where partially dissociated hydrogen is mixed stoichiometrically with air.

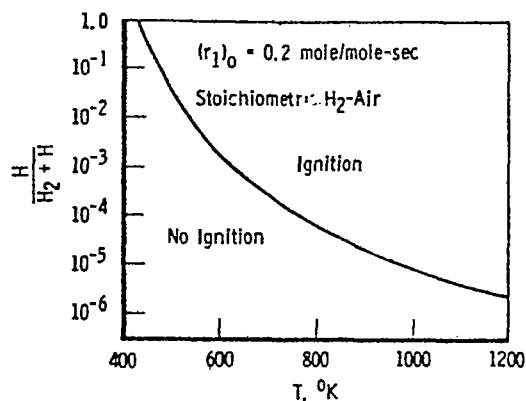


Fig. 3 Effect of Non-Equilibrium  $\text{H}_2$  Dissociation on Ignition Temperature

Another example of the effect of non-equilibrium free-radical concentrations on ignition is shown in Fig. 4. In this case, air was assumed

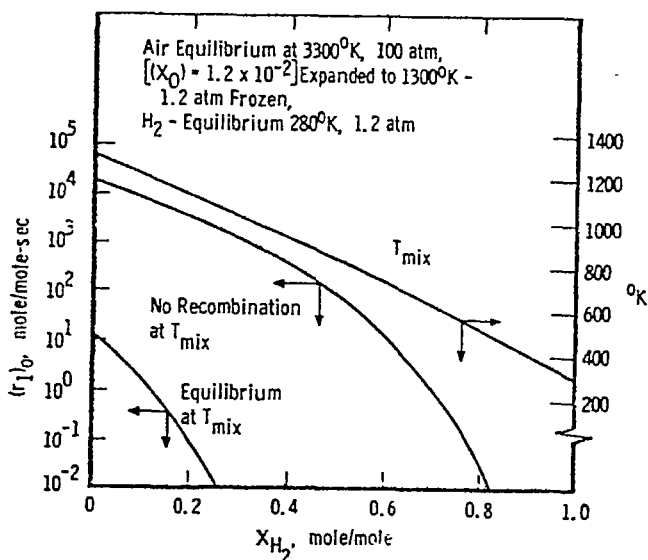


Fig. 4 Effect of Arc Heating Air on the Ignition of  $\text{H}_2$ -Air Mixtures

to have been arc heated and expanded through an isentropic nozzle with a frozen composition equal to the equilibrium composition at 100 atm and 3300°K. It was then mixed with  $H_2$  at 280°K in such a manner that the static enthalpy of the mixture was equal to the static enthalpy of each component times its respective mole fraction (no velocity change on mixing). With the non-equilibrium a.r., ignition would occur in all mixtures up to about 75 percent  $H_2$ , whereas with equilibrium air at the same static temperature, there would probably not be ignition above about 20 percent  $H_2$ . These results would be modified somewhat in a real mixing zone where the velocity and, therefore, the static enthalpy would change with the mixture ratio.

There are two factors which cause a large uncertainty in the conclusion obtained from the above results. First, there is no assurance that the ignition criteria of  $(\tau_1)_0$  is valid in as extreme a case as 500°K and hydrogen dissociation of 2 percent as shown in Fig. 3. Second, the rate constants and reaction mechanisms used are accepted as valid at normal combustion temperatures (Ref. 8), but there is no assurance that they apply at 1000°K and below. However, it is reasonable to assume that a large effect of non-equilibrium free radicals on ignition exists and that ignition can occur much below the normally accepted temperatures when the free-radical content is high.

### 3.0 CONCLUDING REMARKS

It has been shown that the presence of non-equilibrium quantities of free radicals in a mixture of  $H_2$  and air can greatly affect the rate of the reactions involving these species and, therefore, the time required for ignition. There are a number of implications which may be drawn from this conclusion with regard to the design and testing of propulsion systems operating with high velocity in the combustor.

1. In a ground test facility where the air must be heated to a high total temperature, the gas composition will freeze during the expansion at some temperature above the test static temperature, and the excess of free radicals will speed up the ignition delay reactions which occurs on mixing the air with fuel.
2. Conversely, in a free-flight system, the concentration of free radicals will lag the equilibrium value during the compression in the diffuser. This may result in a substantially reduced rate of chemical reaction when the mixing with  $H_2$  occurs.

3. In many research investigations where the objective is to investigate a process such as the effects of heat release on aerodynamics or mixing rates, it may not be important if the ignition chemistry is somewhat modified. Non-equilibrium amounts of free radicals could be provided by partial vitiation or seeding with arc heated gas and used to circumvent the very high total temperatures necessary to get sufficient static temperature to cause reaction in high velocity flow.
4. It might be feasible to use a device such as a high frequency, high voltage arc to partly dissociate either or both reactants without much heating so that experiments could be performed at much lower temperatures than would be possible with thermally heated systems.
5. Finally, one must very carefully specify departures from equilibrium when reporting temperatures at which ignition occurs in a supersonic flow system.

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