



## THERMAL EXPLOSION OF HYDROGEN-OXYGEN MIXTURE AT CONSTANT PRESSURE

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### ABSTRACT

The behavior of the chemical reaction of hydrogen-oxygen molecules has an essential importance in the study of the combustion in rocket engines. A numerical method for the prediction of the behavior of the constant pressure adiabatic explosion of hydrogen-oxygen mixtures using Gear operator technique is presented.

The analysis can solve for the chemical kinetics of the reaction (temperature & composition), activation energy of the reaction, effect of the free radical generation rate on the thermal explosion behavior, and for explosion limits (1st, 2nd, 3rd) at various pressures and initial temperatures of the mixture. The case of stoichiometric mixing ratio is computed and compared with published experimental data.

### INTRODUCTION

Having premixed gases of fuel and oxidizer molecules contained in a vessel, these molecules will collide with the walls of the vessel. According to the pressure and temperature of the mixture and to the material of the walls or the coating material, the molecular bond will be broken to generate certain amount of free radicals. This reaction is called the chain-initiation step. These radicals are responsible for starting a chain of chemical reactions as a result of their collision with the reactant molecules. If a product and a free radical are created, this reaction is called chain-propagation step. If two free radicals are created, this reaction is called chain-branching step (this reaction is responsible for accelerating the rate of the chain reactions). Finally, if two products are created, this reaction is called chain-breaking step (this reaction is responsible for the termination of the chain reactions). Any combustion process should contain all these steps taking place in parallel. In the transient period, when the temperature is sharply increasing and the chemical composition is rapidly varying, the chain-branching should be the dominant reaction. By the end of the transient period, the chain-breaking should become the dominant reaction.

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At steady state, when the temperature and the chemical composition reach their equilibrium state, the ratio of the forward-to-backward rates of each reaction is equal to the equilibrium constant of that reaction at the steady state explosion temperature.

The present work is a theoretical investigation into the thermal explosion of Hydrogen-Oxygen molecules at constant pressure in a thermally isolated vessel. The chemical kinetics technique is adapted to study the behavior of the reaction including the composition and temperature time dependent, the steady state temperature and composition, the time of the thermal explosion, and the activation energy of that reaction. Also, it is an attempt to explore the effect of the vessel wall material on the reaction rate, and to determine the pressure explosion limits.

## THEORETICAL

### Chemical Kinetics

When premixed Hydrogen and Oxygen molecules are contained in a vessel, the chemical reaction can be expressed by the chain reaction steps, presented in Table 1.

**Table 1** Chain chemical kinetics and its related constants\*

No	Reaction	$k_f$			$k_b$		
		log A	n	$E_a$	log A	n	$E_a$
1	$H_2 + OH \rightleftharpoons H_2O + H$	13.34	0	5.15	13.98	0	20.30
2	$H + O_2 \rightleftharpoons OH + O$	14.27	0	16.79	13.17	0	0.68
3	$O + H_2 \rightleftharpoons OH + H$	10.26	1	8.90	9.92	1	6.95
4	$H + O_2 + M \rightleftharpoons HO_2 + M$	15.22	0	-1.00	15.36	0	45.90
5	$H + H + M \rightleftharpoons H_2 + M$	15.48	0	0.00	14.34	0	96.00
6	$O + O + M \rightleftharpoons O_2 + M$	15.67	-0.28	0.00	15.71	0	115.00
7	$H + OH + M \rightleftharpoons H_2O + M$	23.15	-2.0	0.00	16.34	0	105.00
8	$H + O + M \rightleftharpoons OH + M$	16.00	0	0.00	19.90	-1	103.72
9	$HO_2 + H \rightleftharpoons H_2 + O_2$	13.40	0	0.70	13.74	0	57.80

\*  $k_f$  and  $k_b$  are written as  $AT^n \exp(-E_a/RT)$  and have units of  $cm^3/g\text{-mol}\cdot s$ , except for trimolecular reaction.  $E_a$  has units kcal/g-mol, [1].

The rate of appearance of each species can be expressed using Arrhenius rate of reaction equation, [2] as follows:

$$\frac{d[H_2O]}{dt} = [k_{f1}[H_2][OH] - k_{b1}[H_2O][H]] + [k_{f7}[H][OH][M] - k_{b7}[H_2O][M]] \quad (1)$$

$$\begin{aligned} \frac{d[H_2]}{dt} = & [-k_{f1}[H_2][OH] + k_{b1}[H_2O][H]] + [-k_{f3}[O][H_2] + k_{b3}[OH][H]] \\ & + [k_{f5}[H][H][M] - k_{b5}[H_2][M]] \end{aligned} \quad (2)$$

$$\begin{aligned} \frac{d[O_2]}{dt} = & [-k_{f2}[H][O_2] + k_{b2}[OH][O]] + [-k_{f4}[H][O_2][M] + k_{b4}[HO_2][M]] \\ & + [k_{f6}[O][O][M] - k_{b6}[O_2][M]] + [k_{f9}[HO_2][H] - k_{b9}[H_2][O_2]] \end{aligned} \quad (3)$$

$$\begin{aligned} \frac{d[H]}{dt} = G + & [k_{f1}[H_2][OH] - k_{b1}[H_2O][H]] + [-k_{f2}[H][O_2] + k_{b2}[OH][O]] \\ & + [k_{f3}[O][H_2] - k_{b3}[OH][H]] + [-k_{f4}[H][O_2][M] + k_{b4}[HO_2][M]] \\ & + [-k_{f5}[H][H][M] - k_{b5}[H_2][M]] + [-k_{f7}[H][OH][M] - k_{b7}[H_2O][M]] \\ & + [-k_{f8}[H][O][M] + k_{b8}[OH][M]] + [-k_{f9}[HO_2][H] + k_{b9}[H_2][O_2]] \end{aligned} \quad (4)$$

$$\begin{aligned} \frac{d[O]}{dt} = & [k_{f2}[H][O_2] - k_{b2}[OH][O]] + [-k_{f3}[O][H_2] + k_{b3}[OH][H]] \\ & + [-k_{f6}[O][O][M] + k_{b6}[O_2][M]] + [-k_{f8}[H][O][M] + k_{b8}[OH][M]] \end{aligned} \quad (5)$$

$$\frac{d[HO_2]}{dt} = [k_{f4}[H][O_2][M] - k_{b4}[HO_2][M]] + [-k_{f9}[HO_2][H] + k_{b9}[H_2][O_2]] \quad (6)$$

where the symbol  $[\ ]$  indicates the molar concentration of the species contained between these square brackets, and  $T$ ,  $R$ ,  $E_a$ ,  $k_f$ ,  $k_b$  are temperature, universal gas constant, activation energy and forward and backward rates of reaction respectively.

The temperature time dependence is given by the energy equation at constant pressure, [3] as

$$\frac{dT}{dt} = - \frac{1}{e} \frac{\sum_i w_i h_i}{\sum_i C_{pi} x_i} \quad (7)$$

where

$w_i$  = rate of molar production of the species  $i$  per unit volume,  
 $h_i$  = molar enthalpy,  
 $C_{pi}$  = specific heat at constant pressure of species  $i$ ,  
 $x_i = c_i / \sum_i c_i$  mole fraction of the species  $i$ ,  
 $e = p/RT$

The solution of this system of Ordinary Differential Equations ODE's gives the molar concentration of each species and the temperature of the reaction as a function of time.

### Activation Energy

According to the kinetic theory, not every collision between two molecules leads to a sure reaction, but there must be a minimum energy level for each collision to ensure the reaction. That energy is called the activation energy  $E_a$  and its value depends on the nature of the colliding molecules. Therefore there is a certain value of  $E_a$  for each of the chain reaction steps. By the same principle, The overall reaction between  $H_2$  and  $O_2$  (as an example for the exothermic reactions) has an overall activation energy level. That energy level is expressed by the Arrhenius rate of reaction  $k$  equation [1], as

$$k = A T^n \exp(- E_a/RT) \quad (8)$$

Or, in logarithmic form

$$\ln(k) = \ln(A T^n) - (E_a/RT) \quad (8')$$

Taking into consideration that  $A$  is very large, and  $n$  is small,  $\ln(A T^n)$  can be considered as a constant. Plotting  $\ln(k)$  against  $1/T$ , the slope of the curve is equal to  $E_a/R$ .

### Effect of Vessel Material on the Time of Explosion

The collisions of the  $H_2$ -molecules with the walls of the vessel generate a certain amount of H-radicals. The rate of that generation depends on the material of the wall or its coating material and on the vessel volume-to-wall surface ratio. Although this phenomenon was experimentally detected, an accurate correlation of this dependence has not been yet obtained. In the present work a generation factor  $G$ , expressing the rate of generation of free radicals due to the presence of the walls, is introduced to study the effect of the wall on the behavior of the thermal explosion. Also, it is worth to be mentioned that the values of both forward and backward rates of reactions of chain reaction equations 4-8 in table 1 depend on the vessel material and its volume-to-surface area ratio, [4]. Investigation of this phenomenon is beyond the scope of this paper. For more details, refer to reference [5].

### Explosion Limits

In general, the nature of the  $H_2-O_2$  reaction is strongly affected by the concentration and temperature of the reacting molecules. At very low pressure, the frequency of molecular collision is very low to sustain reaction at that energy level. By increasing the pressure, the rate of the collision increases so that explosion starts to occur. That pressure is called the first limit of explosion. Above that limit, the chain-branching steps are dominating the reaction. By further increase of the pressure, the rate of the reaction increases until the second limit appears and explosion can no further be attained, and a region of no explosion appears. In this region the chain-branching steps become the dominant reaction. By further pressure increase, the third limit is reached and the explosion appears again due to the domination of the chain-branching steps.

### COMPUTER CODE

Due to the stiff nature of the system of ODE's, DGEAR (ODE's solver in IMSL library) method is used for the numerical solution of the system. The thermodynamic data are obtained from JANAF tables included in a computer file.

The computer code, Fig.1 is designed so that the fuel to oxidizer ratio  $\Phi$  in molar basis, the initial temperature of the reaction  $T_i$ , the pressure of the reaction  $p$ , and the generation function  $G$  are the input parameters. The value of each parameter can be chosen before running the code.

The induction period is defined by having 25 °C increase above the initial temperature. The steady state condition is defined by having a temperature increase per unit time  $dT/dt < 5000.0$  °K/S.

## RESULTS

The computer code can be used to study the following:

- The kinetics of the thermal explosion.
- The effect of the vessel material on the time of the explosion.
- Determination of the activation energy of the reaction.
- Determination of the explosion limits.

## Chemical Kinetics of Explosion

The computer code is devised mainly to determine the chemical composition and temperature of the reaction as function of time. Two computer runs were executed for the values of  $\Phi = 2.0$  and 4.0 while the pressure, initial temperature and generation factor were chosen to be fixed for both runs. Their values were 5 torr, 1000 °K and  $10^{-10}$  moles/cm<sup>3</sup> s of H-atoms respectively.

The constant G indicates the same vessel volume and material for each run. Obtained data for  $\Phi = 2.0$  are presented in Fig.2. The concentration-time dependence of the Hydroperxyl HO<sub>2</sub>, due to its very low concentration compared to the other molecules, is presented in Fig.3. The steady state explosion temperature, induction period, time of explosion and composition for  $\Phi = 2.0$  and 4.0 are summarized in table 2.

Table 2. Steady state parameters

H <sub>2</sub> /O <sub>2</sub> in molar basis $\Phi$		2.0	4.0
Explosion temperature T <sub>exp</sub> , K		2710	2670
Induction period t <sub>ind</sub> , ms		6.0	9.0
Explosion period t <sub>exp</sub> , ms		24.5	36.0
Molar fraction	H <sub>2</sub>	0.17403	0.3772
	O <sub>2</sub>	0.06867	0.006428
	H	0.17938	0.20323
	O	0.072155	0.01673
	HO	0.106827	0.04702
	H <sub>2</sub> O	0.398	0.34934
	HO <sub>2</sub>	0.36x10 <sup>-5</sup>	0.0537x10 <sup>-5</sup>

## Effect of The Vessel on The Time of Explosion

Vessels with different materials or different volume-to-surface area ratio generate free radicals with different rates. This generation factor affects the time of explosion. The computer code is implemented to solve for the time of explosion for

different values of  $G$  but fixed values of  $\bar{\alpha}$ ,  $p$ ,  $T_I$  being 2.0, 5 torr and 1000 °K respectively. Obtained data are represented in Fig.4. which shows that the time of explosion decreases as  $G$  increases. It shows also that there is no explosion for  $G < 10^{-15}$  moles/cm<sup>3</sup> of H-atoms, which means that H<sub>2</sub> and O<sub>2</sub> molecules can not react together in the absence of the walls of the vessel or any catalyst material.

#### Determination of the Activation Energy of the Reaction

Several runs were executed to compute the time of the induction period for different initial temperature but fixed values of  $\bar{\alpha}$ ,  $p$ ,  $G$  being 2, 5 torr,  $10^{-10}$  moles/cm<sup>3</sup> of H-atoms respectively. Obtained data are arranged in table.3

Table 3. Induction Period vs Initial Temperature

Initial temperature $T_I$ (k)	Induction period $T_{ind}$ (ms)	$\ln(1/t_{ind})$ ( $\ln s^{-1}$ )
500	no explosion	---
750	32.6	3.42344
1000	3.4	5.683979
1500	0.4	7.824046

where  $k = 1 / t_{ind}$

The value of  $\ln(1/t_{ind})$  is plotted versus  $T_I^{-1}$  as shown in Fig.5. The trace is a straight line the slope of which equals 6603.77, which gives  $E_a = 54.9$  [KJ] for  $\bar{\alpha} = 2.0$ .

#### Determination of the Explosion Limits

Several runs were executed with fixed values of  $\bar{\alpha} = 2.0$  and  $G = 10^{-10}$  mole/cm<sup>3</sup> of H-atoms and different values of  $T_I$  from 600 K up to 1100 K with increment of 50 K. For each value of  $T_I$ , the explosion was detected for different values of  $p$  starting from  $p = 2$  Torr up to  $p = 10000$  Torr. Explosion was detected if the time of explosion  $t_{exp} < 100$  ms. If  $t_{exp} > 100$  ms, the program stops execution and gives a message "No Explosion". Obtained data are plotted in semi-logarithmic scale and presented in Fig.6 which shows the three limits of explosion.

Comparison of the calculated diagram with published experimental data of the mixture in a spherical KCL-coated vessel of 7.4 cm diameter shows good agreement of the general trend. The two curves might have been identical if the generation factor of tested vessel were equal to  $10^{-10}$  moles/cm<sup>3</sup> of H-atoms.

To determine the generation factor of the vessel material with specified diameter, the program can be used to plot the curve of explosion limits with different values of  $G$ . The value of  $G$  which gives an identical curve compared with the experimental one is equal the generation factor of that vessel.

### CONCLUSION

A computer program is coded to study the behavior of the  $H_2-O_2$  thermal explosion. Calculated data using that code shows good agreement with published experimental data.

### NOMENCLATURE

A	Constant of the rate of reaction.
$[C_i]$	Concentration of the species i.
$C_{p,i}$	Molar specific heat at constant pressure of species i.
$E_a$	Activation energy.
G	Generation factor of H-atom due to the walls of vessel.
$h_i$	Molar enthalpy of the species i.
$k_b$	Backward rate of reaction.
$k_f$	Forward rate of reaction.
M	Material.
n	Temperature index of the rate of reaction equation.
p	Pressure.
R	Universal gas constant.
T	Temperature.
T <sub>i</sub>	Initial temperature.
$t_{ind}$	Induction period.
$t_{exp}$	Explosion period.
$x_i$	Molar fraction of the species i.
$w_i$	Rate of molar production of species i per unit volume.
$\Phi$	Molar fuel to oxidizer ratio.
$\rho$	Density.

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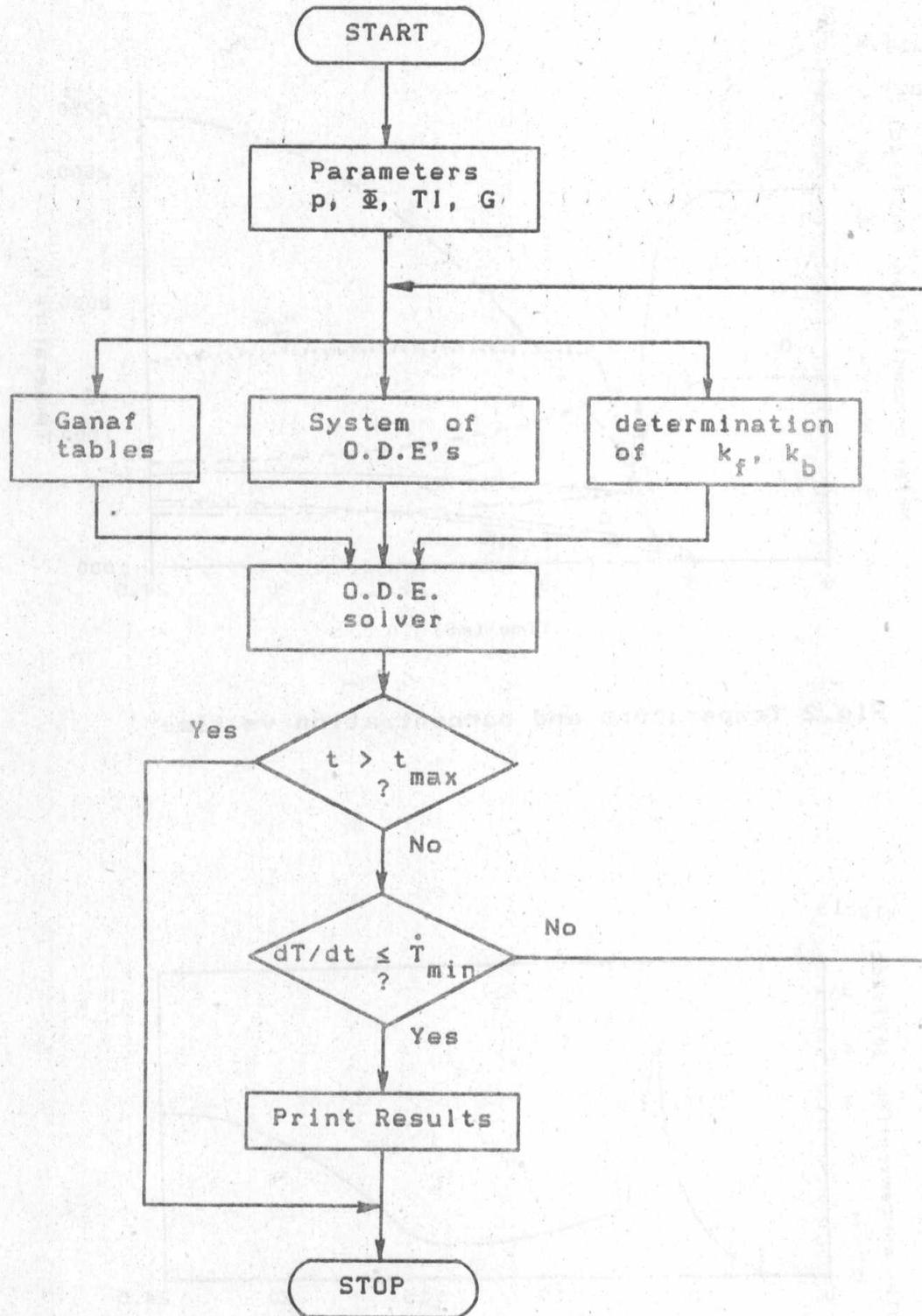


Fig.1 Flow chart of the Computer Code

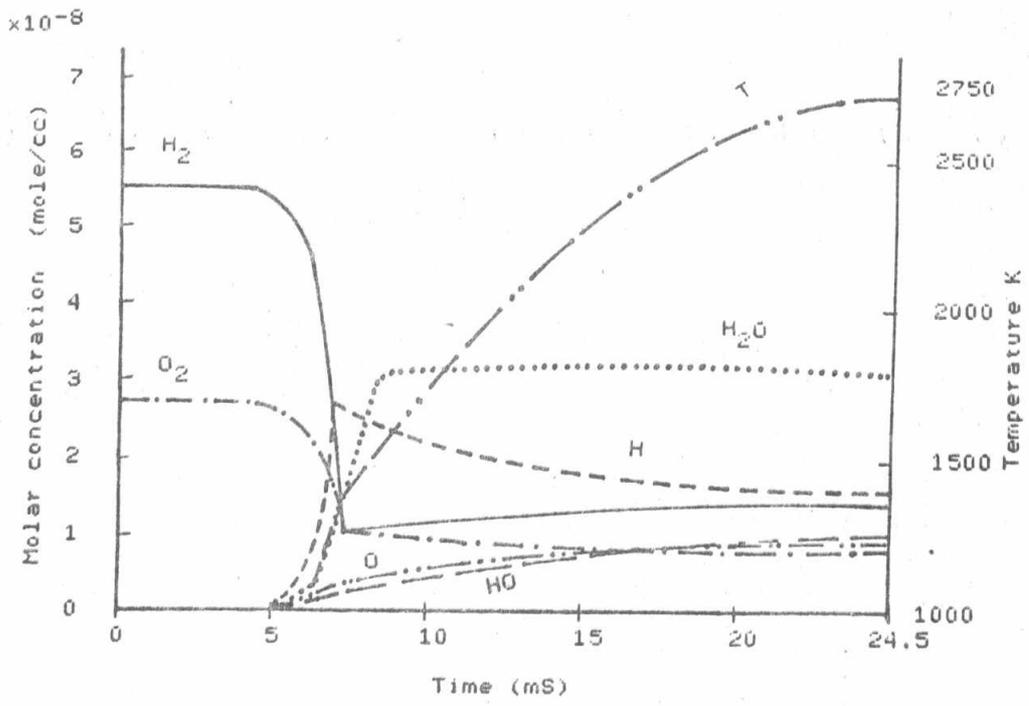


Fig.2 Temperature and concentration vs time

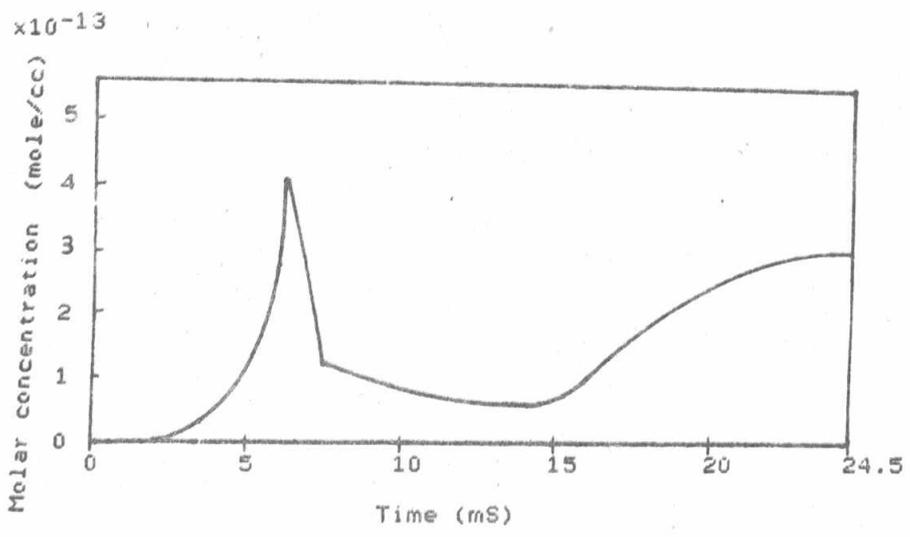


Fig.3 Hydroperoxyl concentration vs time

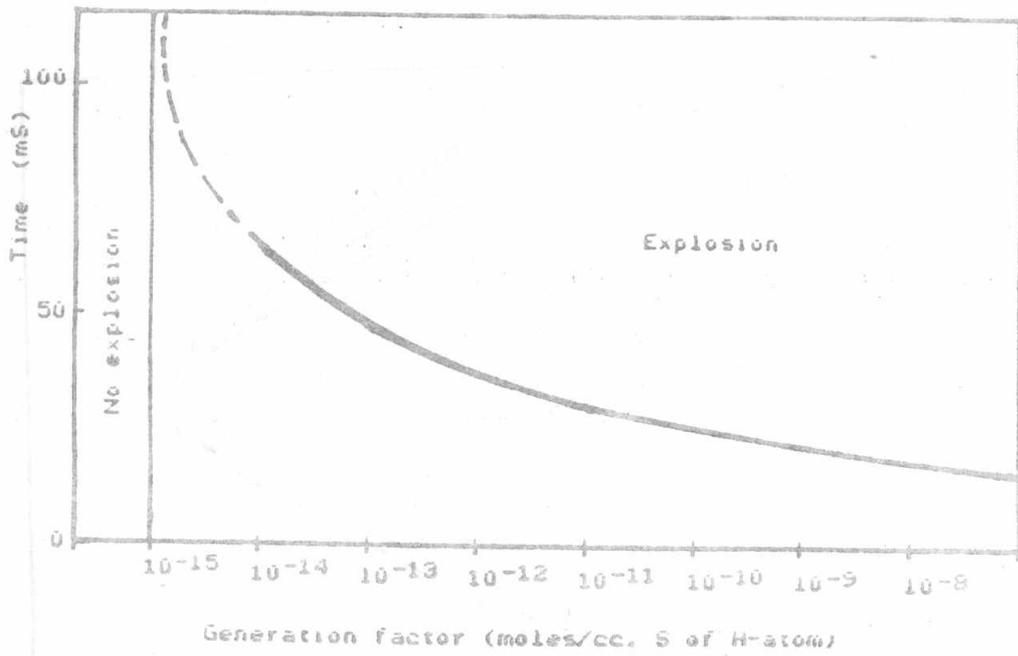


Fig.4 Time of explosion vs generation factor

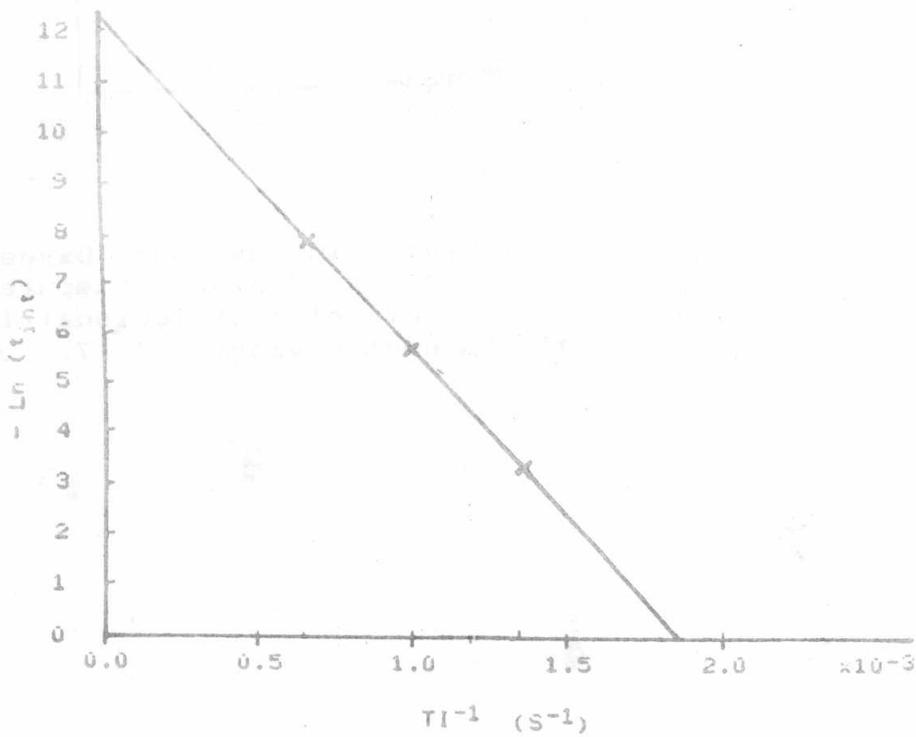


Fig.5 Reaction rate vs inverse of the initial temperature

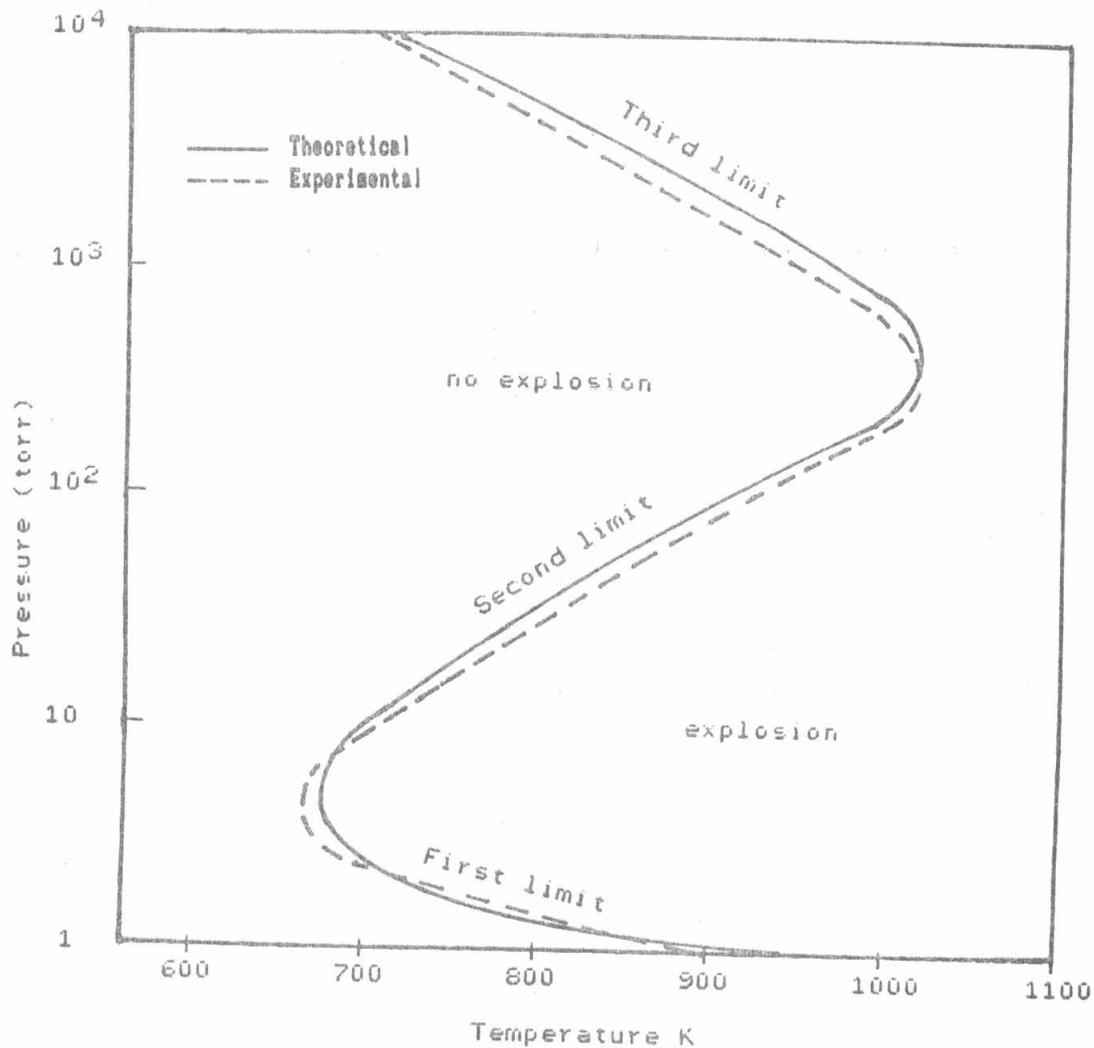


Fig.6 Explosion limit of a stoichiometric Hydrogen-Oxygen mixture for  $G = 10^{-10}$  moles/cm<sup>3</sup> of H-atoms, compared with published experimental data of a stoichiometric mixture in a spherical KCL-coated vessel of 7.4 cm diameter.