

# 5 Cinética Química

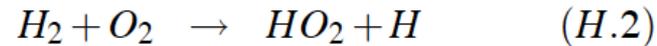
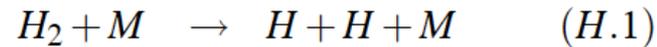
5a. Aula

# Sistema H<sub>2</sub>-O<sub>2</sub>

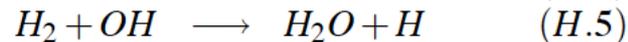
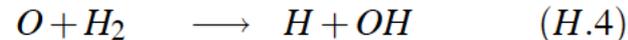
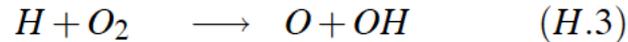
- Propulsão de foguetes
- Submecanismo presente em quaisquer hidrocarbonetos

# Mecanismo

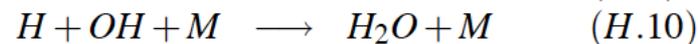
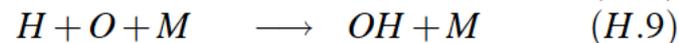
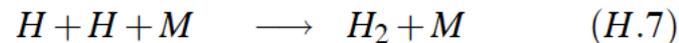
- Reações INICIADORAS



- Reações PROPAGADORAS H, OH, O

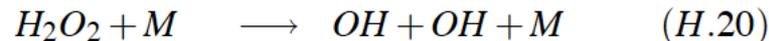
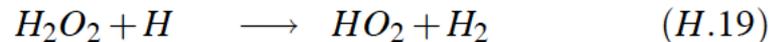
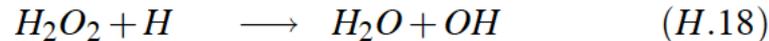
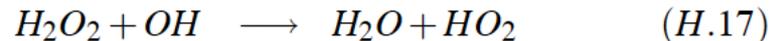
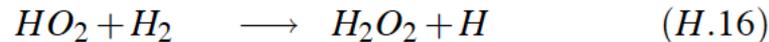
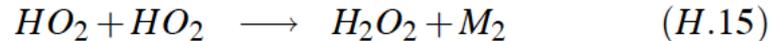
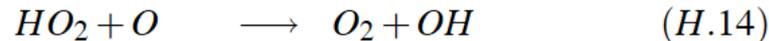
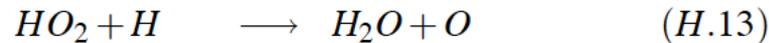
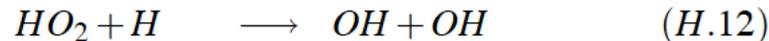
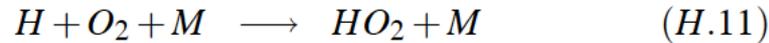


- Terminais



# Mecanismo

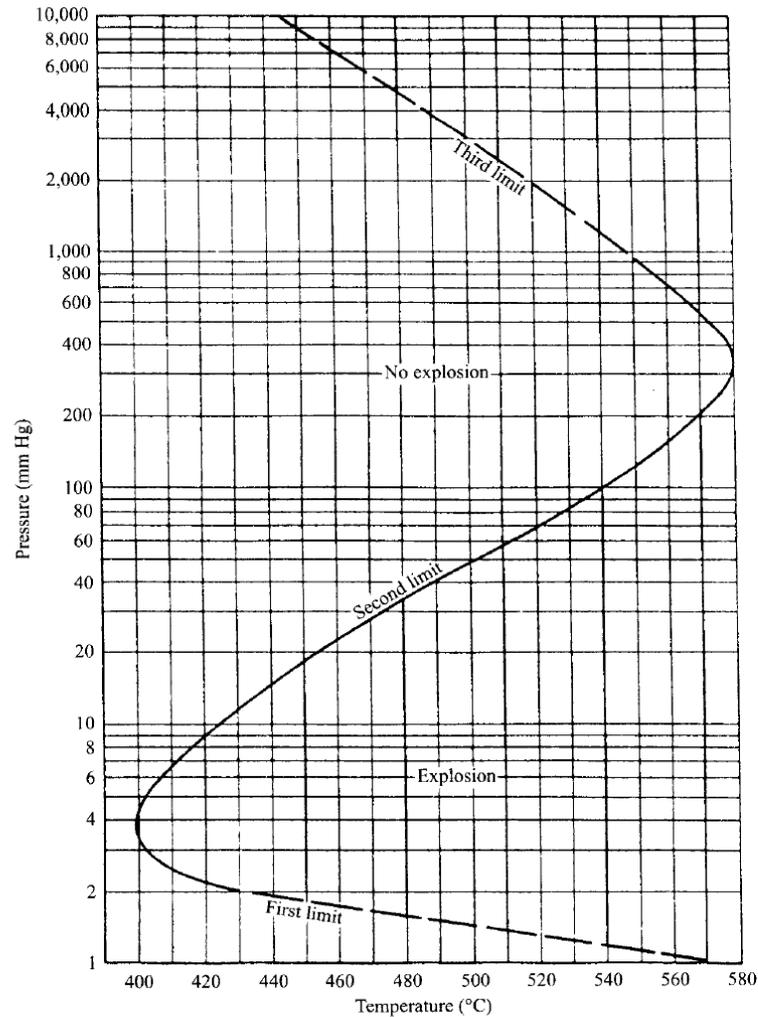
- Reações PROPAGADORAS  $HO_2$ ,  $H_2O_2$



Dependendo de P e T as reações reversas são também importantes.

→ 40 reações; ESPÉCIES:  $H_2$ ,  $O_2$ ,  $H_2O$ ,  $OH$ ,  $O$ ,  $H$ ,  $HO_2$ ,  $H_2O_2$ .

# Mecanismo – Limites de Explosão



**Figure 5.1** Explosion limits for a stoichiometric hydrogen–oxygen mixture in a spherical vessel.

| SOURCE: From Ref. [2]. Reprinted by permission of Academic Press.

# Mecanismo – Limites de Explosão

- LIMITES DE EXPLOSÃO  
para  $T = 500^\circ$ , por exemplo,

até  $P \approx 1.5\text{mmHg}$

NÃO EXPLODE { Predominam reações de parede:  
 $radical \xrightarrow{k_{wall}}$  Absorção

$1.5 < P < 50\text{mmHg}$

EXPLODE { H.3-H.4 prevalecem em relação à reação de parede  
(Tab 4.4) $P \uparrow$ ,  $[radical] \uparrow$  linear,  $\frac{d[A_2]}{dt} \uparrow$  geométrica

$p > 50\text{mmHg}$

NÃO EXPLODE { competição entre  
RAMIFICAÇÃO H.3 e TERMINAL H.11  
 $HO_2$  é "estável" → destruição na parede

$P > 3000\text{mmHg}$

{ H.16 abre a cadeia de  $H_2O_2$

# Mecanismo – Limites de Explosão/ Atraso de Ignição

*COMBUSTION AND FLAME* 74: 53–69 (1988)

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## **Ignition Processes in Hydrogen–Oxygen Mixtures**

**U. MAAS and J. WARNATZ**

*Physikalisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 253,  
6900 Heidelberg, West Germany*

Ignition processes in the hydrogen–oxygen system were simulated by solving the corresponding conservation equations (i.e., conservation of mass, energy, momentum, and species mass) for one-dimensional geometries using a detailed reaction mechanism and a multispecies transport model. An additional source term in the energy conservation allowed the treatment of induced ignition, and a realistic model for the destruction of reactive species at the vessel surface was used to treat auto-ignitions in static reactors. Spatial discretization using finite differences and an adaptive grid point system led to a differential–algebraic equation system, which was solved numerically by extrapolation or by backward differencing codes. Comparisons with experimental works show that one common reaction mechanism is able to simulate shock-tube-induced ignitions (modeled by treating the reaction system as a homogeneous mixture heated up by the shock wave) as well as the three explosion limits of the hydrogen–oxygen system. Minimum ignition energies are calculated for various mixture compositions, pressures, radii of the external energy source, and ignition times, and it is shown that for long ignition times the "uniform pressure assumption" is a quite good approximation for computing minimum ignition energies.

# Mecanismo – Atraso de Ignição

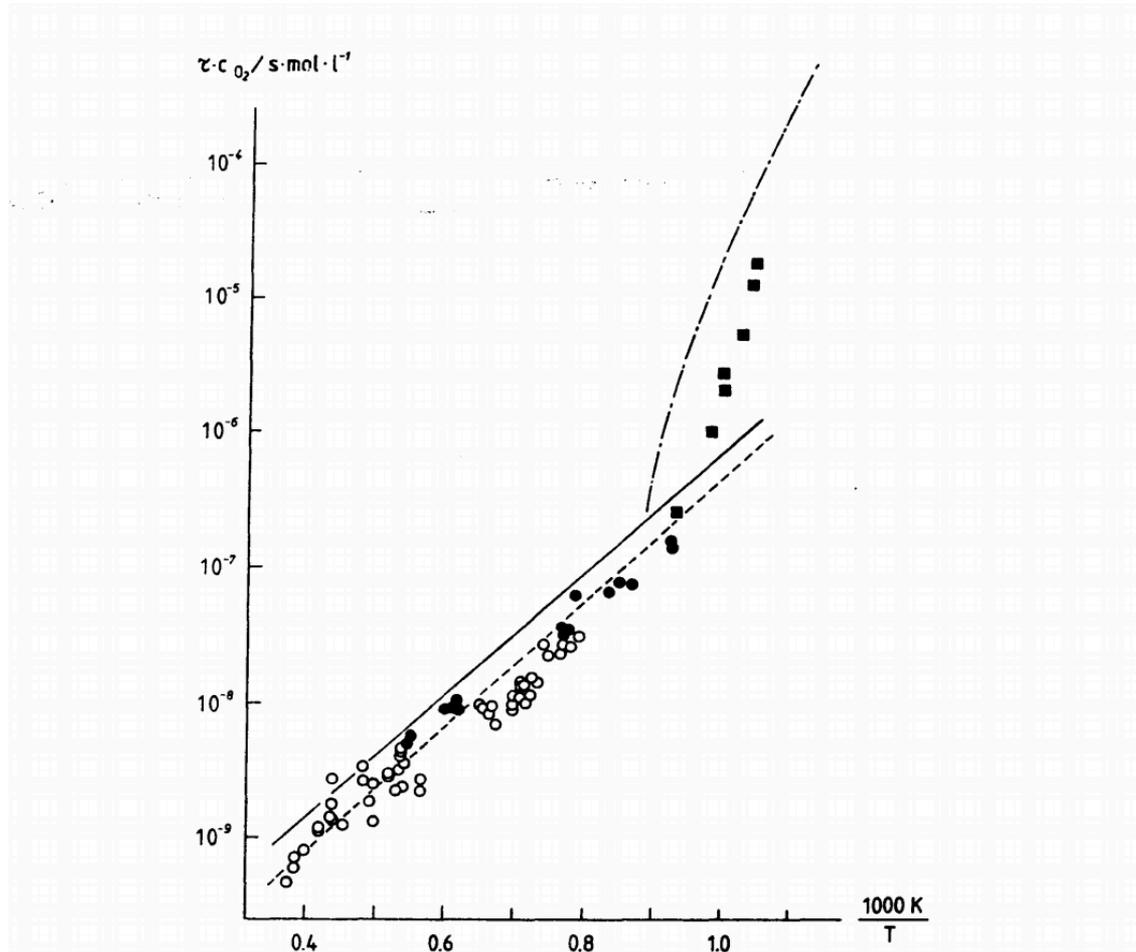


Fig. 1. Ignition delay times for hydrogen–oxygen–argon mixtures: (a) 8 % H<sub>2</sub>, 2% O<sub>2</sub> and 90% Ar,  $P = 5$  atm: -·- calculated, ■ experimental values [26]; criterion: maximum OH concentration (both in experiment and calculation); (b) 4% H<sub>2</sub>, 2% O<sub>2</sub> and 94% Ar,  $P = 1$  atm: -- calculated, ° experimental values [27]; criterion: maximum change of OH concentration; (c) 1% H<sub>2</sub>, 2% O<sub>2</sub> and 97% Ar,  $P = 1$  atm: — calculated, • experimental values [27]; criterion: maximum change of OH concentration.

# Mecanismo – Atraso de Ignição

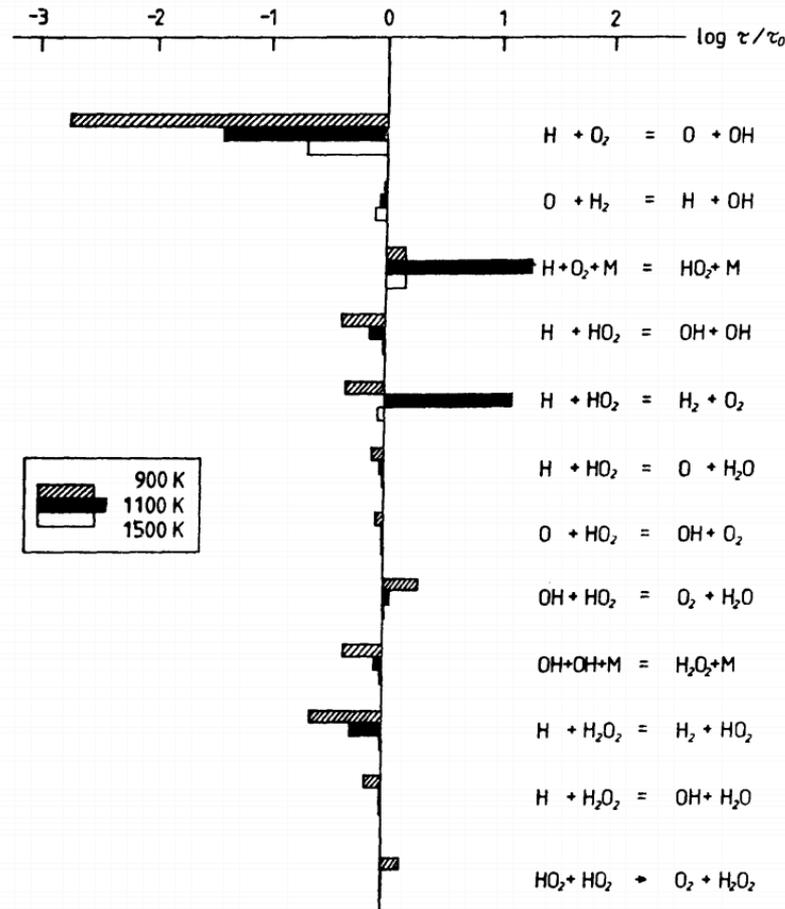


Fig. 2. Sensitivity test for ignition delay times in a hydrogen-oxygen-argon mixture (8% H<sub>2</sub>, 2% O<sub>2</sub> and 90% Ar) at 1 bar;  $\tau_0$  refers to unchanged rate coefficients and  $\tau$  refers to a tenfold increase of the rate coefficient of the reaction considered and its reverse reaction.

# Mecanismo – Limites de Explosão

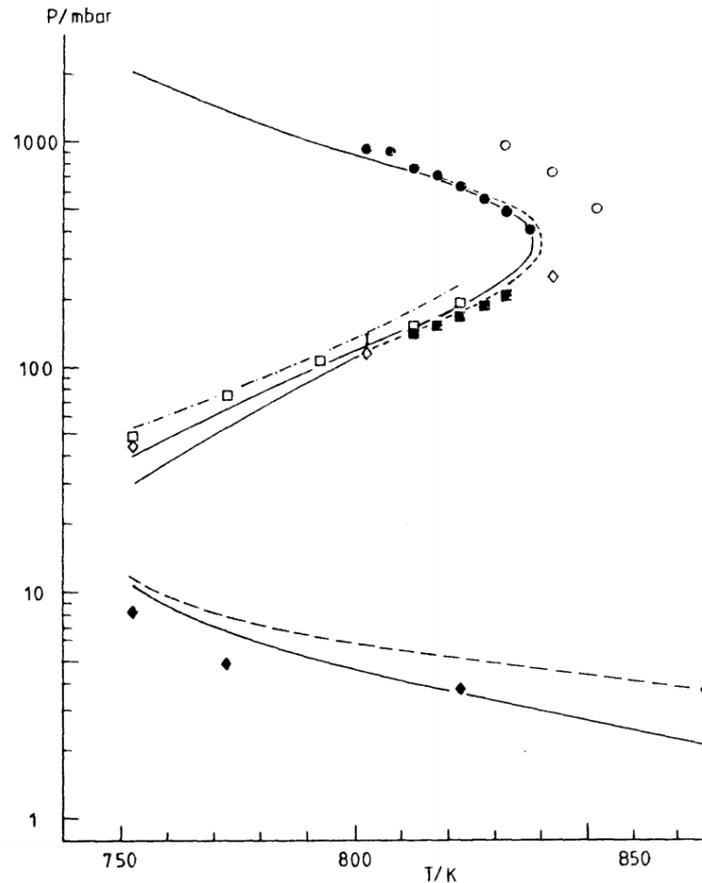


Fig. 11. Calculated and experimental ignition limits for 2:1 hydrogen-oxygen mixtures in a spherical reaction vessel 7.4 cm in diameter: -- calculated,  $\gamma = 10^{-2}$ ; — calculated,  $\gamma = 10^{-3}$ ; -·- calculated,  $\gamma = 10^{-4}$ . Experimental results: ■ thinly KCl-coated vessel [29], ○ heavily KCl-coated vessel [29], ● KCl-coated vessel [29], ◇ KCl-coated vessel [30], I clean Pyrex vessel [30], □ B<sub>2</sub>O<sub>3</sub>-coated vessel [31]. Calculated and experimental first explosion limit in a cylindrical silica reaction vessel 1.8 cm diameter: ◆ experimental [32]; -- calculated,  $\gamma = 10^{-3}$ ; -·- calculated,  $\gamma$  see text.

# Mecanismos de Formação de NOx

- "Minor Specie" problemática → poluição

*ROTAS(PATHS)* :

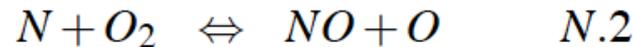
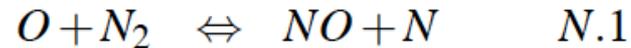
- Mecanismo térmico ou Zeldovich
- Mecanismo Prompt ou Fenimore
- Mecanismo  $N_2O$ -Intermediário
- Mecanismo Fuel

# Mecanismos de Formação de NOx

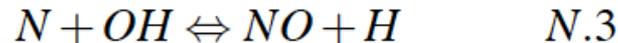
- *NO*-Térmico (Zeldovich)
  - dominante a altas  $T$  e larga faixa  $\Phi$
- *NO*-Fenimore (prompt)
  - combustão rica  $\Phi > 1.0$
- $N_2O$ -Mecanismo
  - Mistura extremamente pobre e baixa  $T$
- Fuel *NO*
  - Quando o combustível contém  $N$

# Mecanismos de Formação de NOx

## Mecanismo de Zeldovich (Térmico)



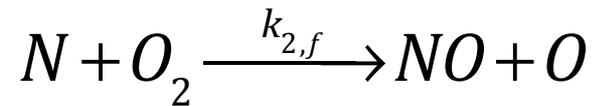
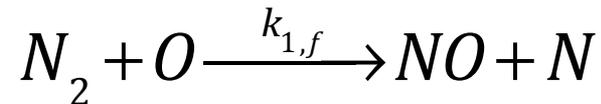
extended:



- $k_f$ 's, ( $k_b$ 's) tabelados.
- $O$ ,  $O_2$ , e  $OH$  aparecem também no mecanismo de oxidação do combustível.
- Normalmente, as escalas de tempo das reações de oxidação do combustível são mais rápidas que as de  $NO$ . Assim, os mecanismos podem ser des-acoplados e  $O_2$ ,  $O$ ,  $OH$  e  $N_2$  são assumidos em EQUILÍBRIO.

# Mecanismo Global de Formação de NO<sub>x</sub>

- Mecanismo de Zeldovich



- Em altas Temperaturas, as reações de Nox são muito mais lentas que as reações de combustão que envolvem oxigênio. Assume-se Equilíbrio para oxigênio:

# Mecanismos de Formação de NOx

- Hipóteses:

- $N$  está em REG. PERMANENTE

- $[NO] \ll [NO]_{eq}$ . Reação reversa de  $N.1, N.2, N.3$  são desprezadas.

Assim:

$$\frac{d[NO]}{dt} = 2k_{N.1,f}[O]_{eq}[N_2]_{eq} \quad (124)$$

- Problemas e Conclusões:

- Hipótese Equilíbrio  $O, OH$  (Superequilíbrio  $O$  e  $OH$ )

- Alta  $E_a$  de  $N.1$  ( $319.050 \text{ kJ/kmol}$ ) (dependência de  $T$ )

- Baixa  $T$  ( $< 1800 \text{ K}$ )  $\rightarrow$  insignificante

- $NO \rightarrow$  post-flame calculation (mais lento que o combustível)

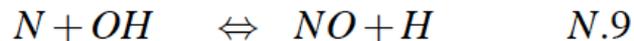
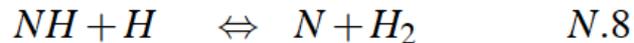
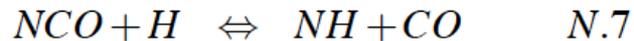
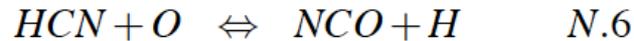
# Mecanismos de Formação de NOx

## Mecanismo Fenimore (Prompt)

- *NO* formado rapidamente na região da frente de chama (pré-misturada)
- Associado à combustão de hidrocarbonetos
- Radicais *HC* atacam  $N_2$ :



para  $\Phi \leq 1.2$  segue:

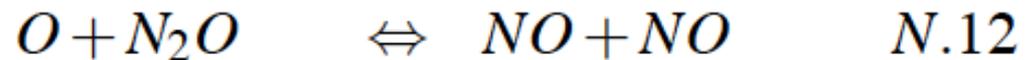
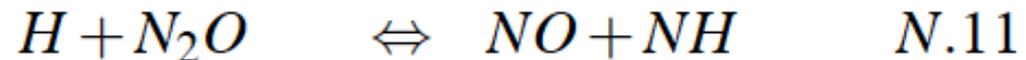
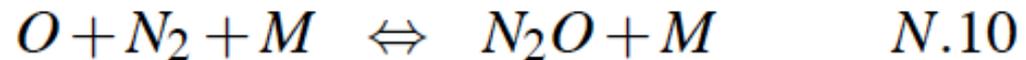


para  $\Phi > 1.2 \Leftrightarrow$  seqüências mais complexas

# Mecanismos de Formação de NOx

## Mecanismo $N_2O$ -intermediário

$\Phi < 0.8$ , baixa  $T$



Importante em GT, pré-misturada e pobre

# Mecanismos de Formação de NOx

## Fuel NO

- $N$  vem do combustível (carvão 2%)
- $N \rightarrow HCN$  em  $NH_3 \rightarrow$  prompt