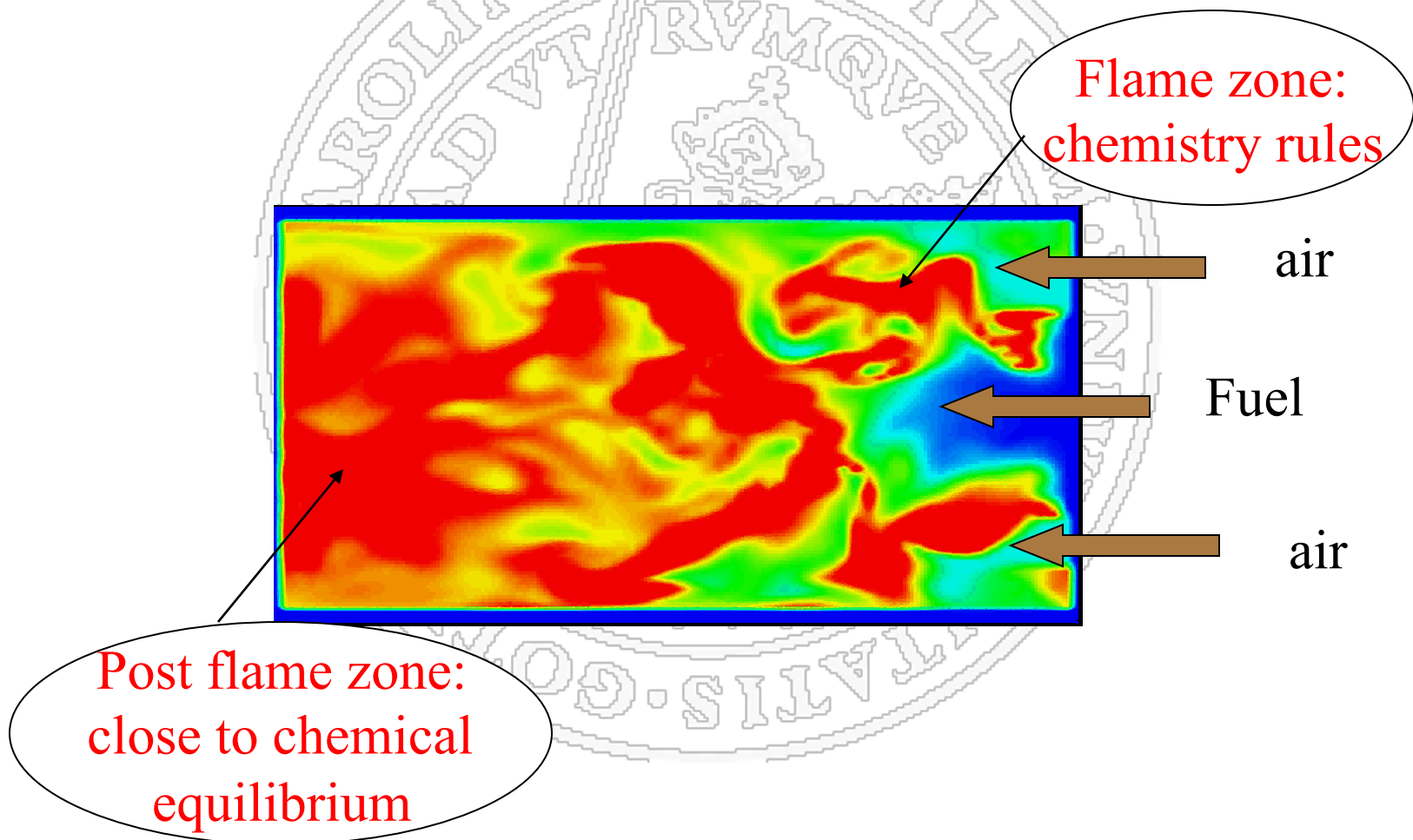


## Lecture 3

# Chemical Kinetics

# Chemical kinetics plays important role in flame zone

- A swirling stabilized flame



# What does **chemical kinetics** do?

- **Chemical kinetics** deals with
  - how fast chemical reactions proceed, i.e. **reaction rates**
  - what chemical reactions occurs in a chemical process, i.e. **reaction mechanisms**
- Chemical kinetics is the **key** to understand
  - how does a flame propagate
  - why a flame can be quenched ...

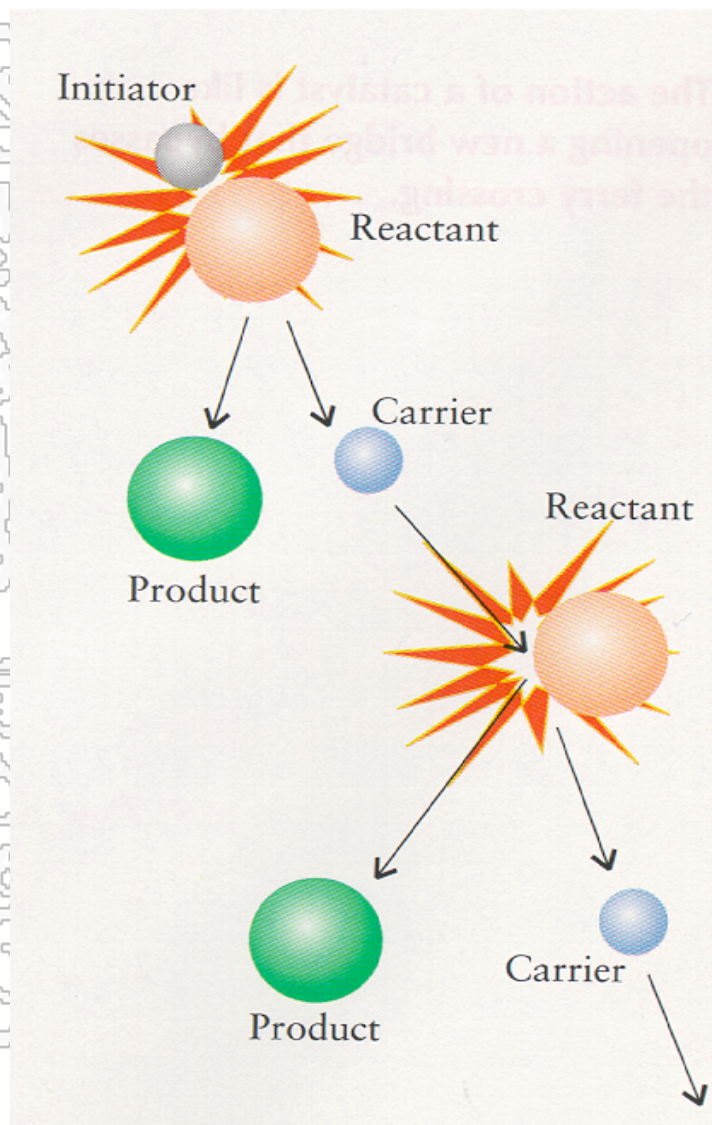
# Outline

- Elementary reactions
  - law of mass action
  - Arrhenius expression
- Reaction mechanisms
  - detailed mechanism
  - reduced mechanism
  - global mechanism
- $\text{H}_2\text{-O}_2$  explosion,  $\text{NO}_x$  formation

# Elementary reactions



# Detailed reaction mechanisms (1)

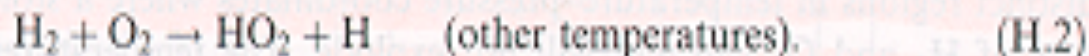
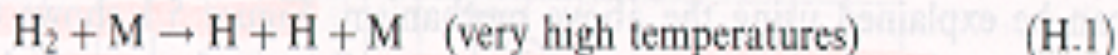




## Detailed reaction mechanisms (2) $\text{H}_2 + \text{O}_2$ mechanism

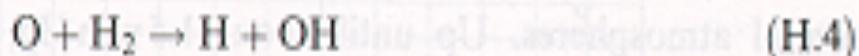
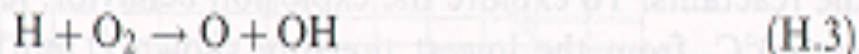
### Chain initiating

The initiation reactions are:



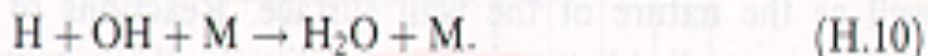
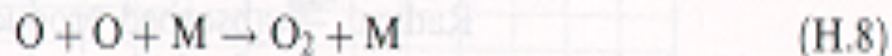
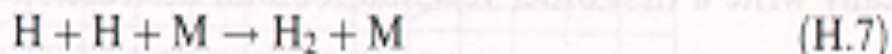
### Chain branching

Chain-reaction steps involving O, H, and OH radicals are:



### Chain propagating

Chain-terminating steps involving O, H, and OH radicals are the three-body recombination reactions,



### Chain terminating

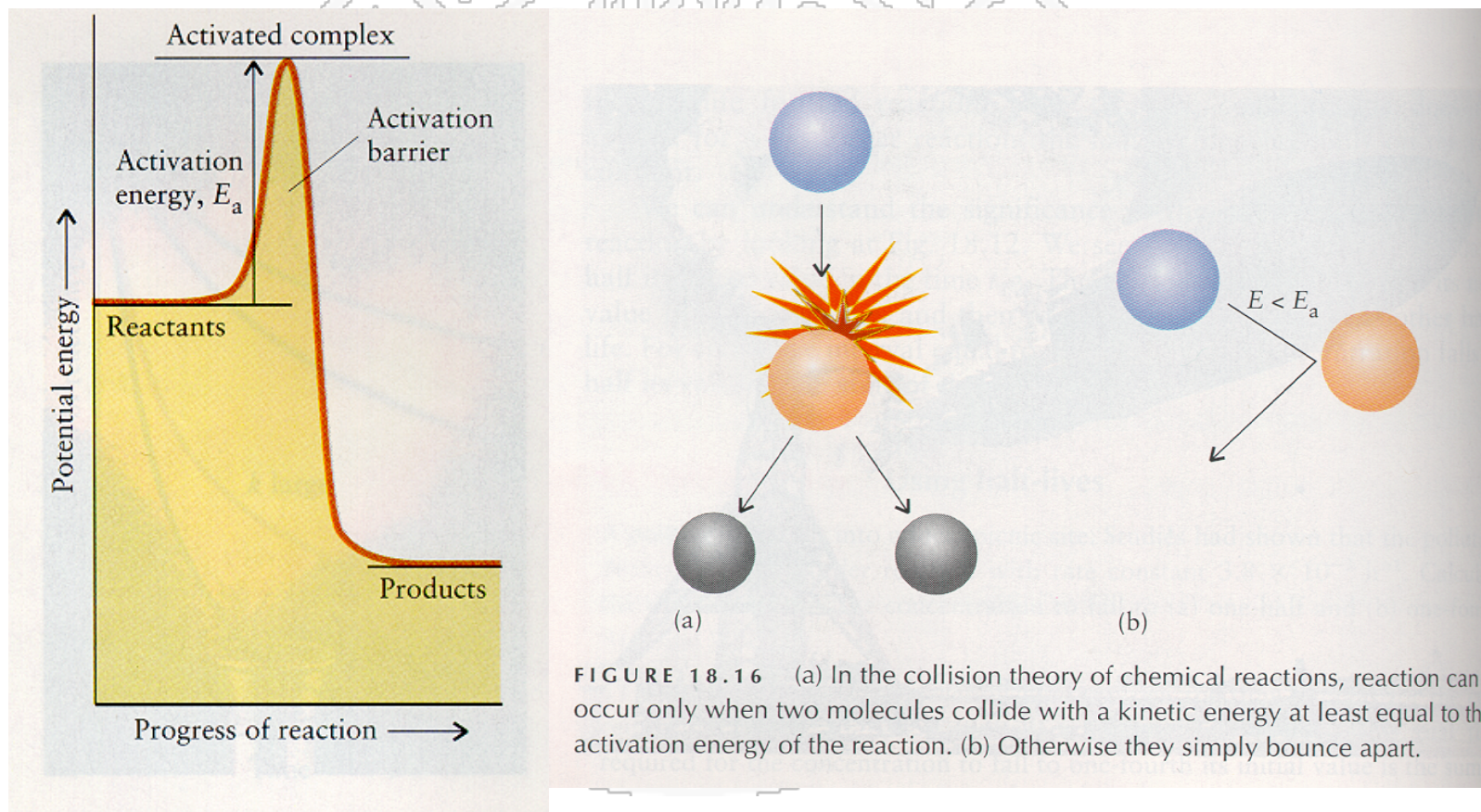
# Elementary reaction (1)

- Definition
  - the actual reaction among individual atoms and/or molecules
- Types of elementary reactions
  - uni-molecular reaction (thermal dissociation)
  - bi-molecular reaction (most of reactions of this type)
  - ter-molecular reaction (recombination reactions)
- Physical interpretation of elementary reaction
  - Collision theory
  - Activated complex theory
  - ...



# Elementary reaction (2)

Physical interpretation of **bimolecular and termolecular reactions** (collision theory)



## Elementary reaction (3)

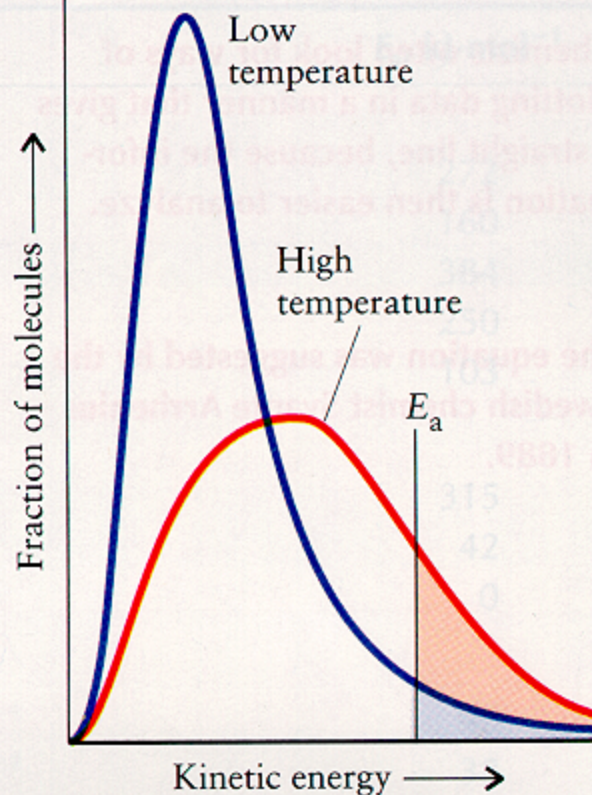
- Physical interpretation of **unimolecular reaction** (activated complex theory)



M = third body  
= any molecules

## Elementary reaction (4)

- Physical interpretation of effect of temperature on elementary reactions (collision theory)

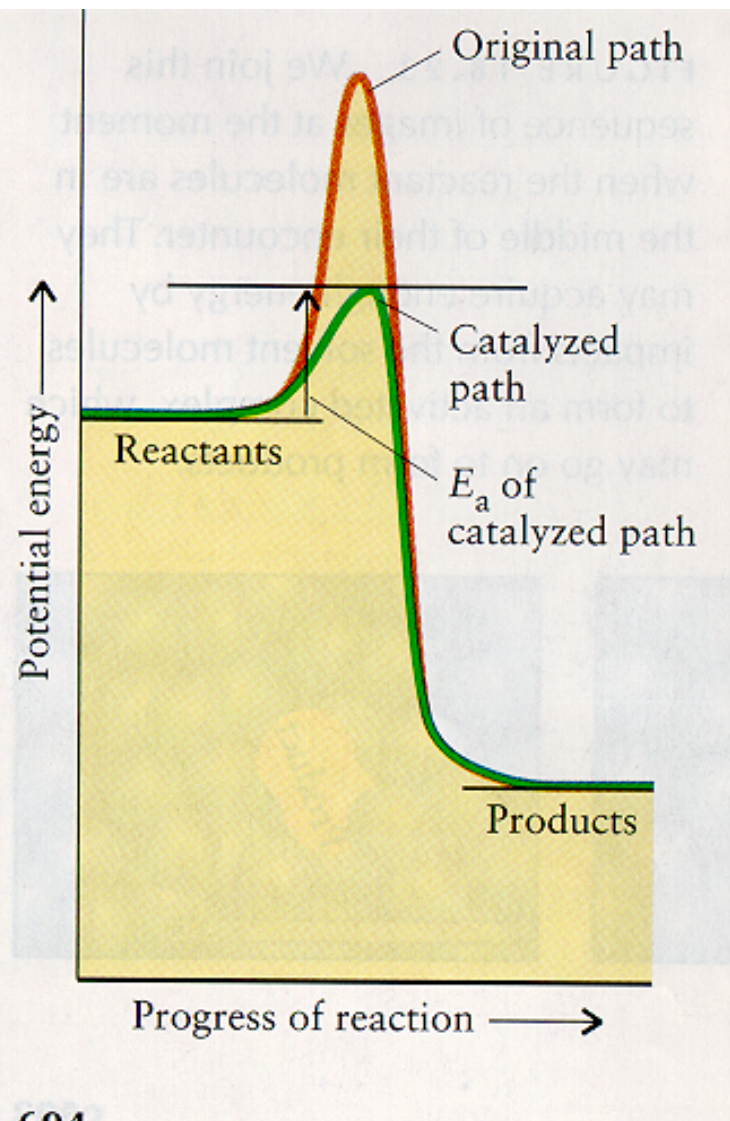


**FIGURE 18.18** The fraction of molecules that collide with a kinetic energy that is at least equal to the activation energy,  $E_a$ , is denoted by the shaded areas under each curve. The fraction increases rapidly as the temperature is raised.



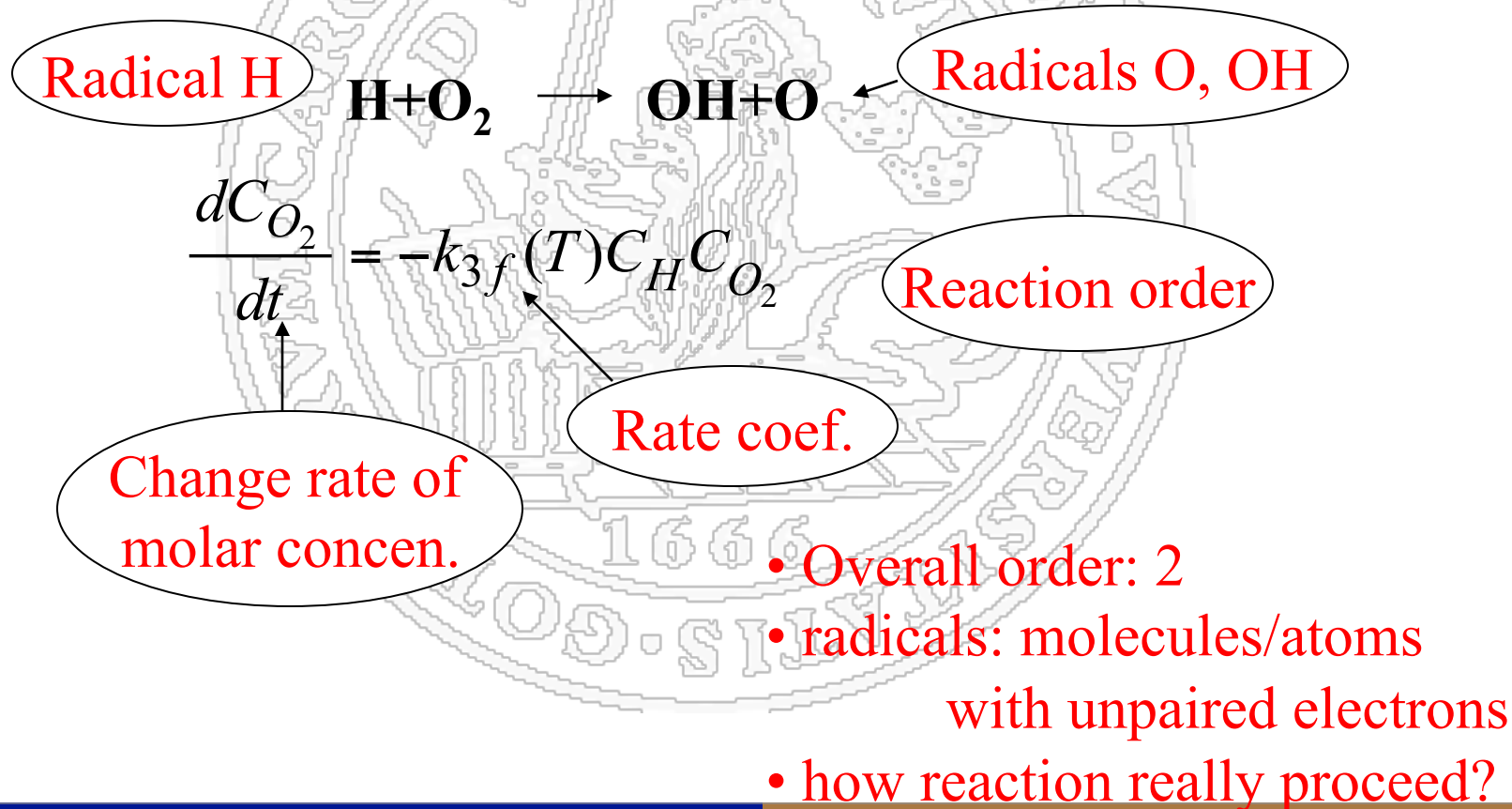
## Elementary reaction (5)

- Physical interpretation of effect of catalysis on elementary reactions (collision theory)



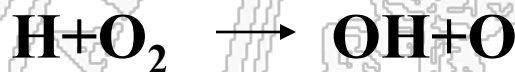
# Reaction rate for Elementary reactions (1)

- Law of mass action



## Reaction rate for Elementary reaction (2)

- Bimolecular reaction



$$\frac{dC_{\text{O}_2}}{dt} = -k_{3f}(T)C_{\text{H}}C_{\text{O}_2}, \quad k_{3f}(T) = \underbrace{AT^b}_{\text{Frequency factor}} \underbrace{\exp(-E_A/R_uT)}_{\text{Arrhenius expression}}$$

- Arrhenius form often used; experimental data is used to find model constants  $A$ ,  $E_A$ ,  $b$
- collision theory for rate coef.
- Second overall order

Frequency factor

Arrhenius expression

Activation energy



## Reaction rate for Elementary reaction (3)

- Unimolecular reaction



Oxygen  
dissociation  
at high p

$$\frac{dC_{\text{O}_2}}{dt} = -k_{\text{uni}}(T)C_{\text{O}_2}$$

- Termolecular reaction



Recombination  
of radical H

$$\frac{dC_{\text{H}}}{dt} = -k_{\text{ter}}(T)C_{\text{M}}C_{\text{H}}^2$$

Third  
body

- third body M carry away energy formed

## Reaction rate for Elementary reaction (5)

- Effect of pressure on reactions rate

$$\frac{dC}{dt} \propto kC^n \propto kY^n \rho^n \propto kY^n p^n \propto p^n$$

- at high pressures termolecular reactions become more important than bimolecular reactions and unimolecular reactions

## Reaction rate for Elementary reaction (6)

- How to obtain rate coefficients?
  - Theoretical calculations (difficult)
  - experiments (mostly used approach)
  - if the forward reaction rate is known, one can use equilibrium constants to calculate the backward reaction, and vice versa.

# Reaction rate for Elementary reaction (7)

- Units used in reaction rate calculation

Kinetic data are often given in engineering unit - cm, mole, s, etc. (Turns book Table 5.3). If you change C to SI unit, do not forget to change k to SI unit as well. Remember k's unit is different for different reactions. Recommendation: use cm, mole, s ... unit first to calculate the rate, then translate to SI unit

$$\frac{dC}{dt} \propto kC^n$$

Diagram illustrating the units of the reaction rate equation  $\frac{dC}{dt} \propto kC^n$ :

- The unit of  $\frac{dC}{dt}$  is  $\frac{\text{mole}}{\text{cm}^3 \text{ s}}$ .
- The unit of  $C^n$  is  $\left(\frac{\text{mole}}{\text{cm}^3}\right)^n$ .
- The unit of  $k$  is  $\left(\frac{\text{mole}}{\text{cm}^3}\right)^{1-n} \frac{1}{\text{s}}$ .

A question mark (?) is placed between the units of  $\frac{dC}{dt}$  and  $k$ , indicating the relationship between them.

# Reaction Mechanisms



# Reaction mechanisms

- Global reaction mechanism models
  - a combustion process using **one**, **two** or a **few steps**, for example one step reaction



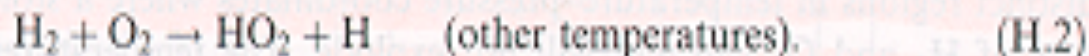
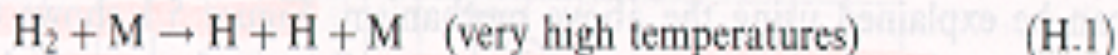
- Detailed reaction mechanism consists of
  - hundreds **elementary reactions**, for example methane oxidation mechanism listed in Turns book
- Reduced mechanism simplifies detailed reaction mechanism by reducing the number of elementary reactions



## Detailed reaction mechanisms (2) $\text{H}_2 + \text{O}_2$ mechanism

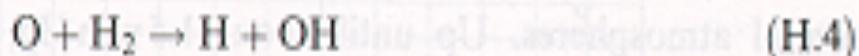
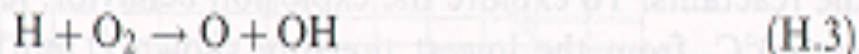
### Chain initiating

The initiation reactions are:



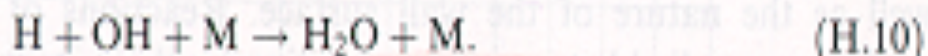
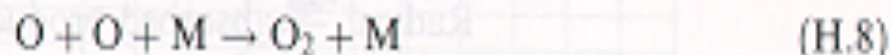
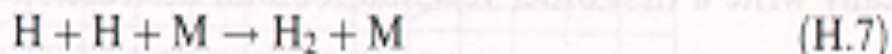
### Chain branching

Chain-reaction steps involving O, H, and OH radicals are:



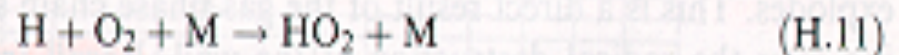
### Chain propagating

Chain-terminating steps involving O, H, and OH radicals are the three-body recombination reactions,

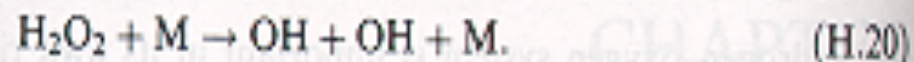
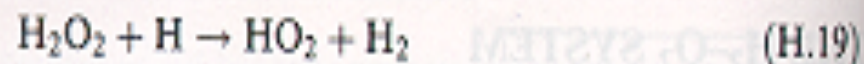
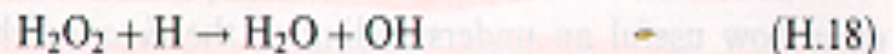
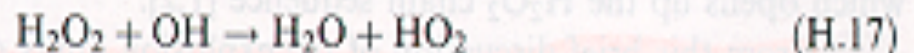
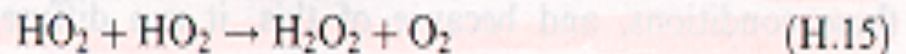
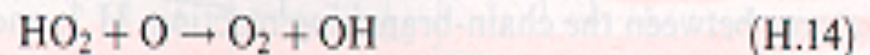
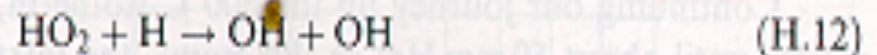


### Chain terminating

To complete the mechanism, we need to include reactions involving  $\text{HO}_2$ , the hydroperoxy radical, and  $\text{H}_2\text{O}_2$ , hydrogen peroxide. When



becomes active, then the following reactions, and the reverse of H.2 come into play:

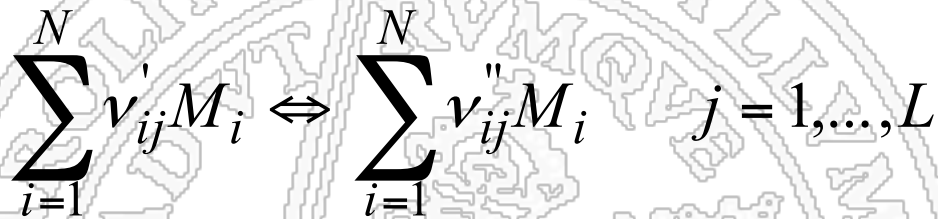


Detailed  
reaction  
mechanism  
(3)

-  
 $\text{H}_2 + \text{O}_2$

# Reaction rate for Elementary reaction (4)

- For a detailed reaction mechanism



- reaction rates for species  $i$

$$\omega_i \equiv \frac{dC_i}{dt} = \sum_{j=1}^L \left( \nu''_{ij} - \nu'_{ij} \right) q_j$$

forward rate

Backward rate

$$q_j = k_{jf} \prod_{i=1}^N C_i^{\nu'_{ij}} - k_{jb} \prod_{i=1}^N C_i^{\nu''_{ij}}$$

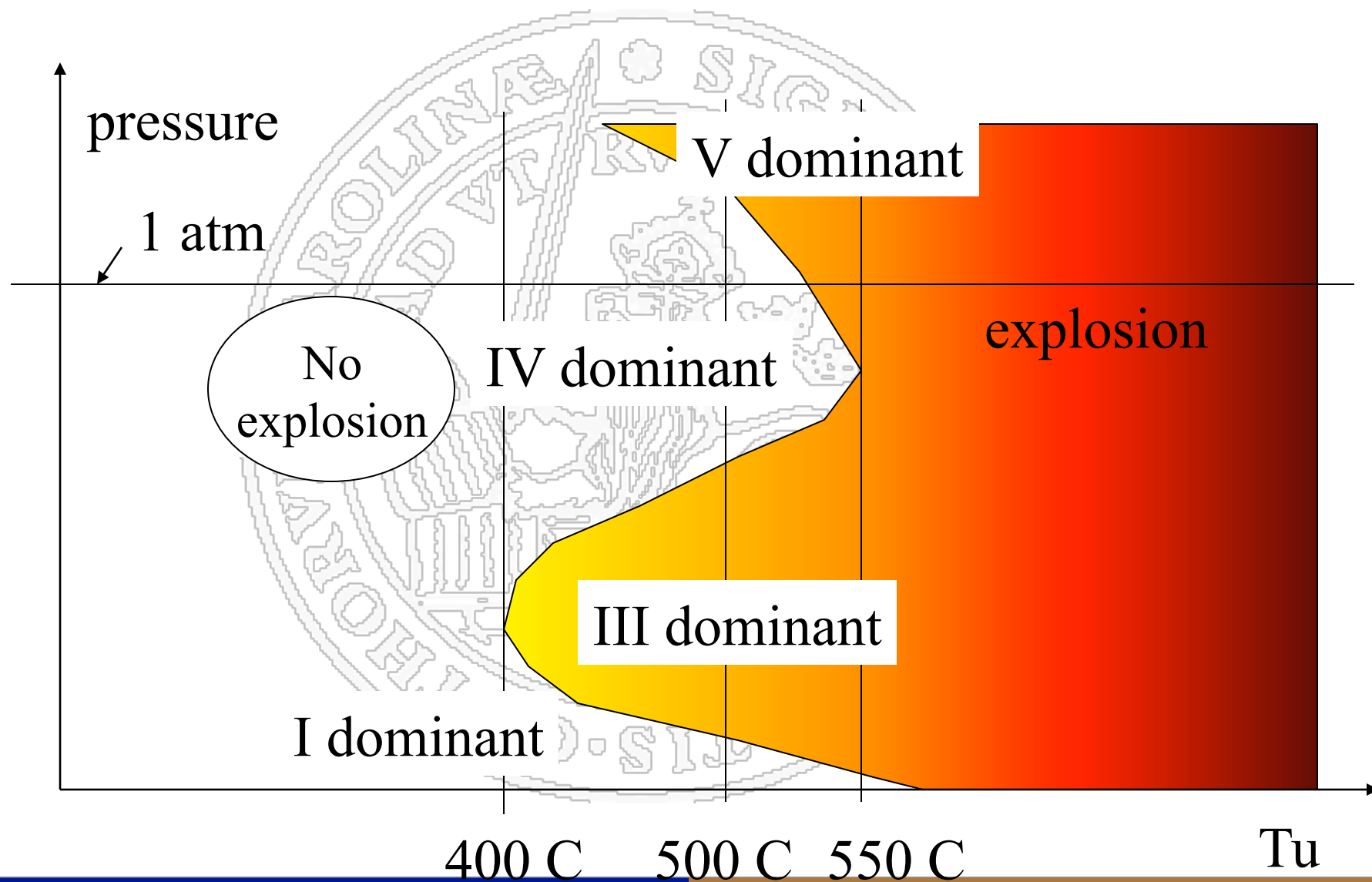
# An example: H<sub>2</sub>-O<sub>2</sub> explosion

## a chemical explanation

- heterogeneous reaction:
  - **Radicals + Wall  $\rightarrow$  products** (I)
- chain initiating
  - **H<sub>2</sub> + M  $\rightarrow$  H+H+M** (II)
- chain branching and propagating
  - **H+O<sub>2</sub>  $\rightarrow$  O+OH** (III)
- chain terminating
  - **H+O<sub>2</sub>+M  $\rightarrow$  HO<sub>2</sub>+M** (IV)
- chain branching
  - **HO<sub>2</sub> + H  $\rightarrow$  OH+OH** (V)

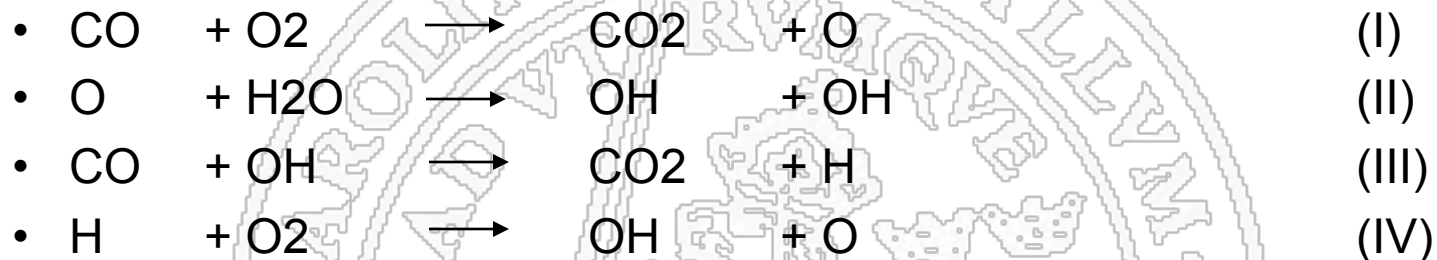


# H<sub>2</sub>-O<sub>2</sub> explosion diagram (a sketch)



## Example 2: CO-O<sub>2</sub> reaction

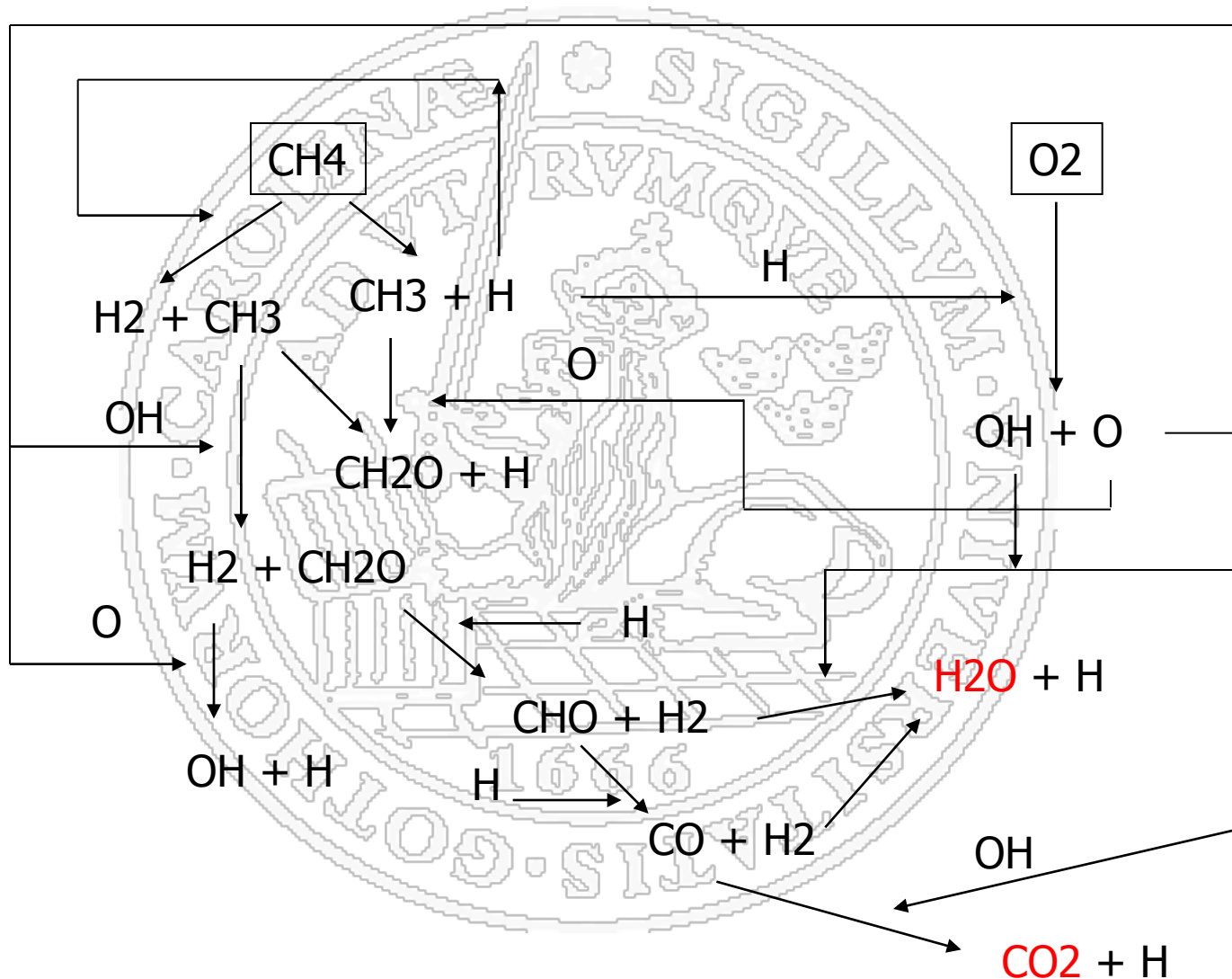
### effect of humidity



- (I) slow
- (III) much faster
- (IV) key reaction even for moisture CO combustion!!!



# CH<sub>4</sub>-O<sub>2</sub> reaction path

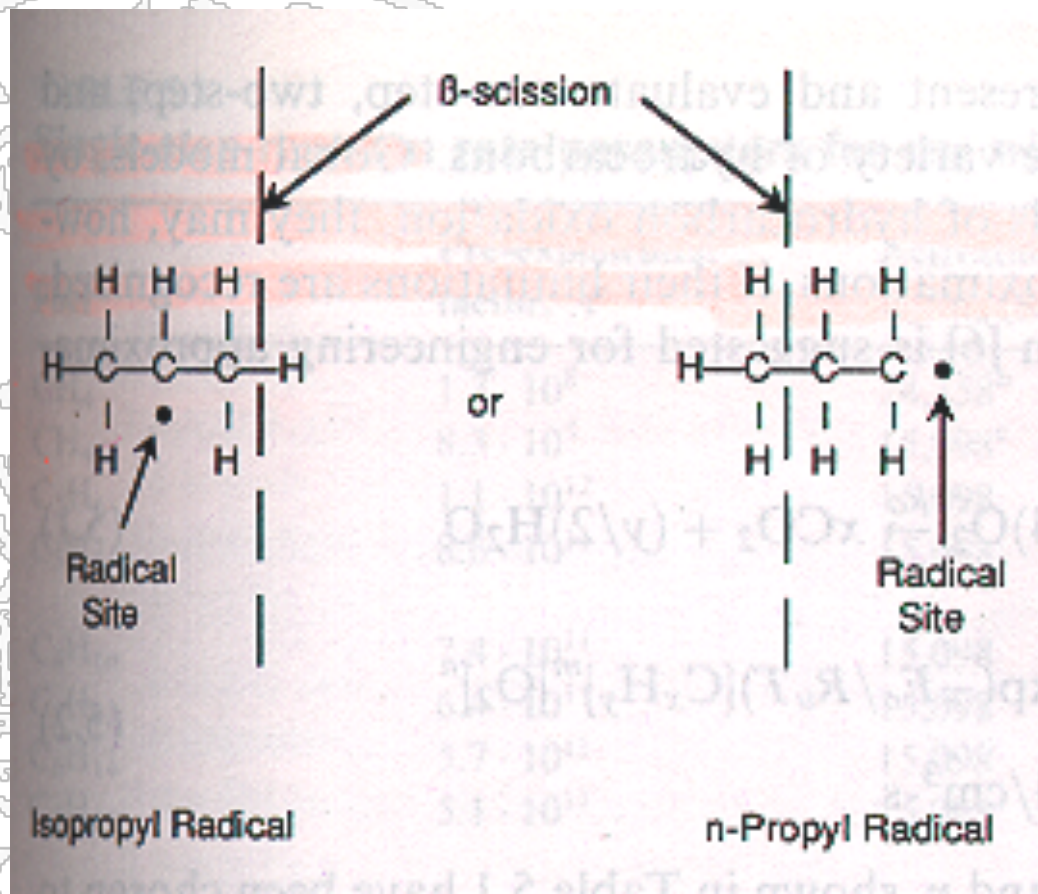


# CH<sub>4</sub>-O<sub>2</sub> reaction mechanism

- CH<sub>4</sub> + M  $\longrightarrow$  CH<sub>3</sub> + H + M
- CH<sub>4</sub> + H  $\longrightarrow$  CH<sub>3</sub> + H<sub>2</sub>
- CH<sub>3</sub> + O  $\longrightarrow$  CH<sub>2</sub>O + H
- CH<sub>3</sub> + OH  $\longrightarrow$  CH<sub>2</sub>O + H<sub>2</sub>
- CH<sub>2</sub>O + H  $\longrightarrow$  HCO + H<sub>2</sub>
- HCO + H  $\longrightarrow$  CO + H<sub>2</sub>
- CO + OH  $\longrightarrow$  CO<sub>2</sub> + H<sub>2</sub> (CO mechanism)
- H<sub>2</sub> mechanism

# $C_nH_{2n}-O_2$ reaction mechanism ( $n>1$ )

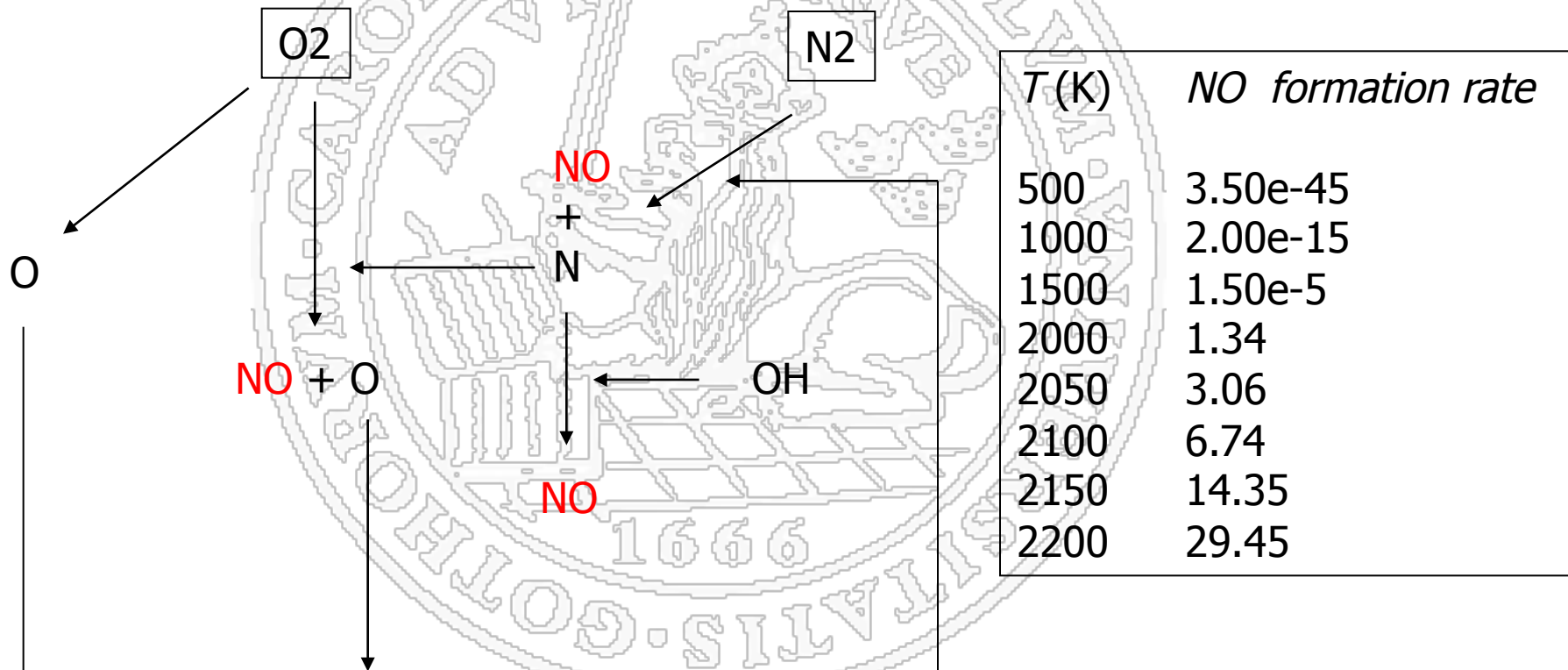
- H abstract
- beta-scission rule
- high C break down
- to HCO
- to CO
- to CO<sub>2</sub>



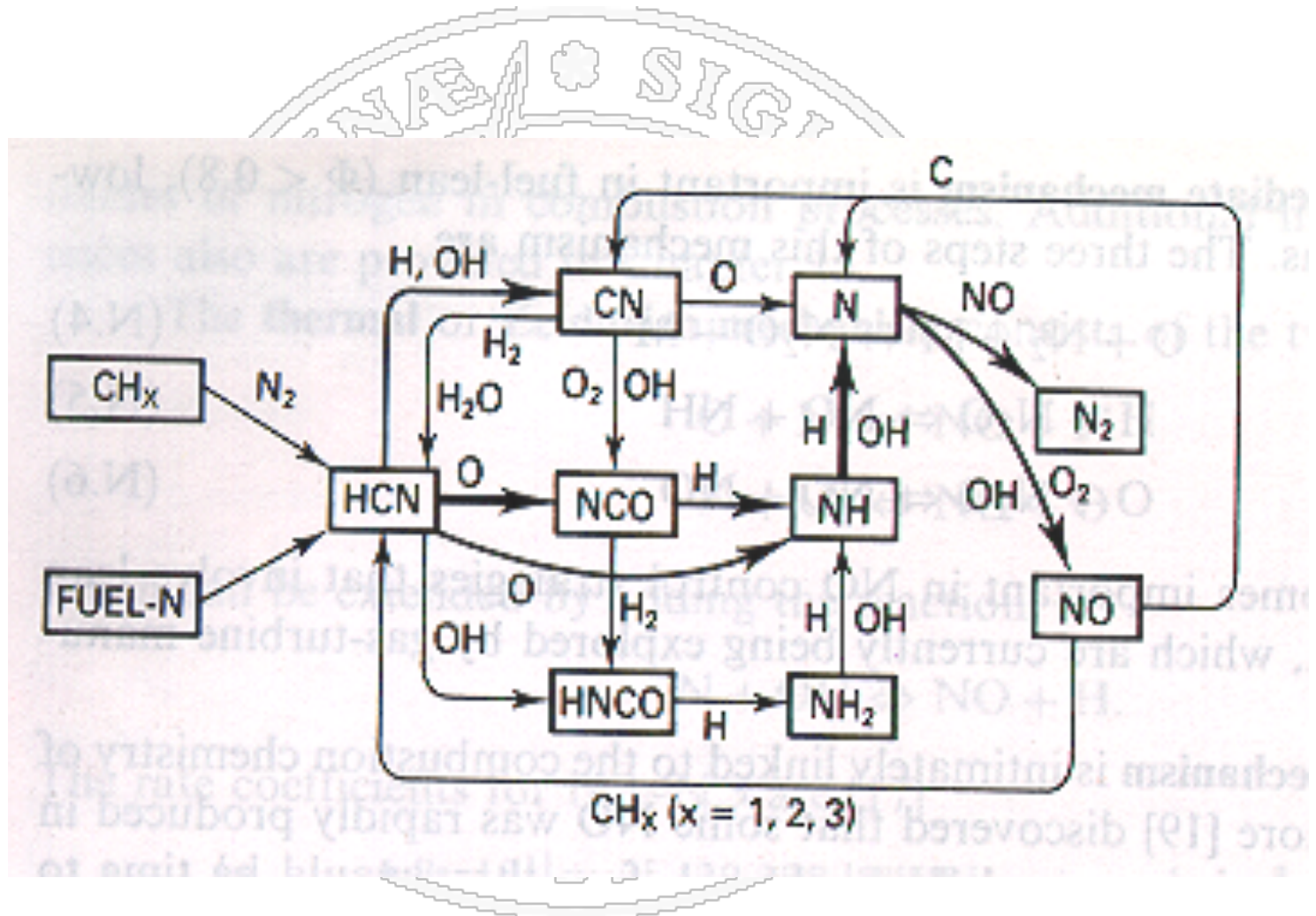
C-C bond weaker than C-H bond: C-C 85 kcal/bond; C-H 98 kcal/bond

# Thermal NO mechanism

$$k_{NO} \equiv 2k_{26}K_{28}^{1/2} = 6 \times 10^{16} T^{-1/2} \exp\left(-\frac{69090}{T}\right)$$



# Fuel NO<sub>x</sub> formation mechanism



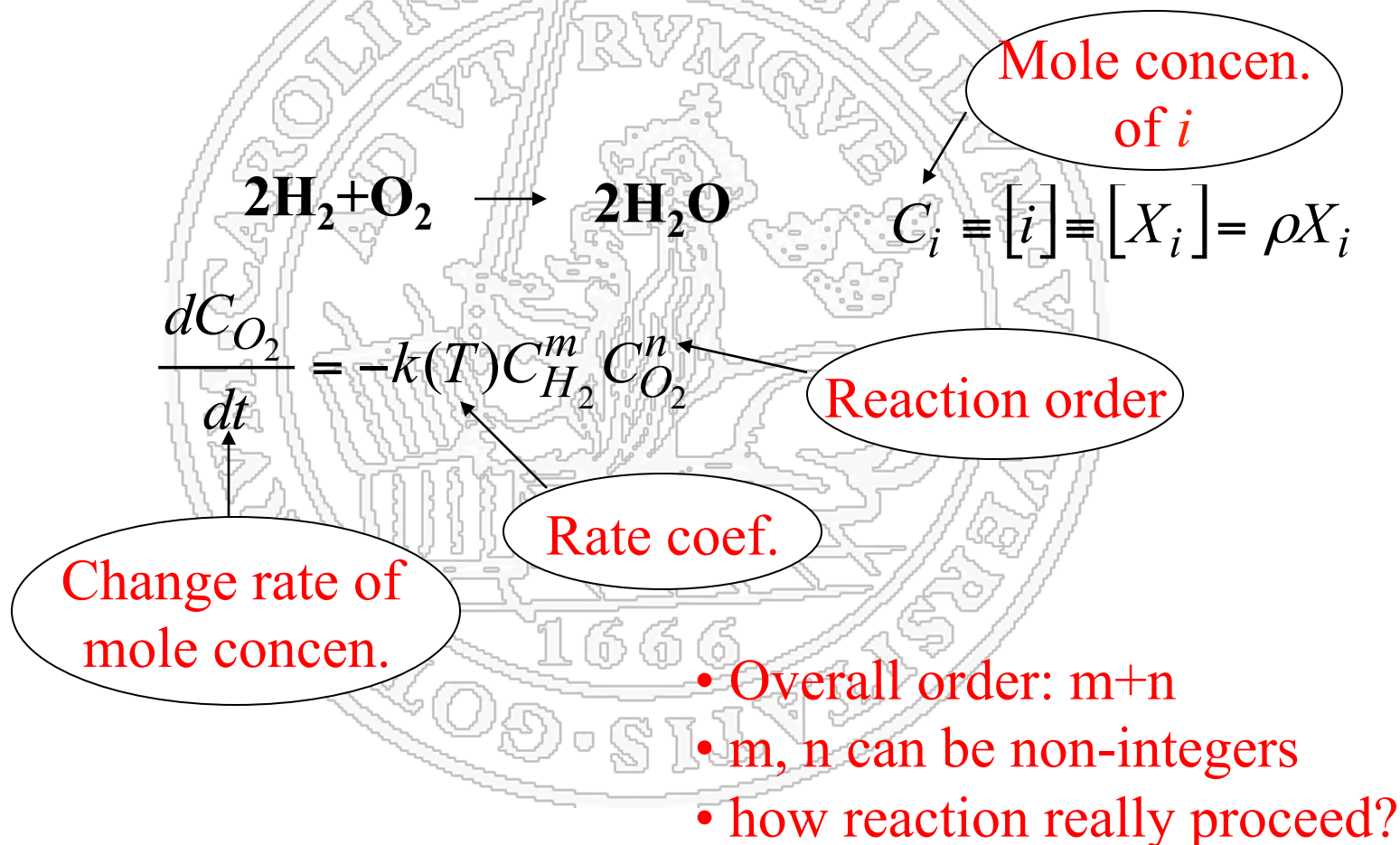


- How to simplify a detailed reaction mechanism?
  - Some reactions proceed faster than others. If both the forward and backward reactions are fast, one can assume this reaction is in **partial equilibrium**
  - Some species are in **lower concentrations** than others. If the net formation and destruction rate of this species are small, one may assume this species is in **steady states**.
  - ILDM (intrinsic low dimensional manifold)
  - Experimental approach



# Reaction rate for Global reaction mechanism (1)

- hydrogen and oxygen reaction



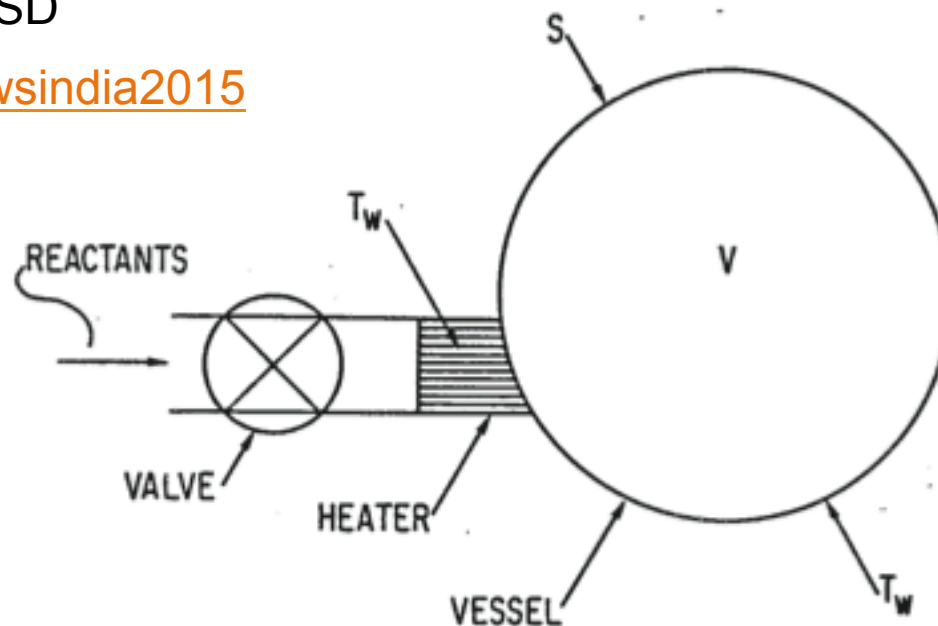
## Reaction rate for Global reaction mechanism (2)

- How to determine rate **coefficients** and  $m, n$ ?
  - rate **coefficients**,  $m, n$  are obtained from curve-fitting with experimental data
- Advantages
  - simple to use
- disadvantages
  - not directly related to the fundamental reaction process
  - rate **coefficients**,  $m, n$  only valid for short range of temperature and equivalence ratio

# Thermal explosion (thermal runaway)

K. Seshadri, UCSD

<http://nccrd.in/iciwsindia2015>



- ▶ Chemical Reaction: Reactants  $\rightarrow$  Products      One step global reaction
- ▶ Molar rate of consumption of fuel per unit volume

$$w = BC_{F,u}\phi \exp[-E/(RT)] \quad \text{First order reaction}$$

where  $\phi = C_F/C_{F,u}$ ,  $C_F$  the concentration of fuel,  $C_{F,u}$  the initial concentration of fuel. and  $T$  the temperature.

# Thermal explosion (thermal runaway)

- Balance equation for fuel

Change of fuel mass  $\rightarrow V \frac{d\phi}{dt} = -VB\phi \exp\left(-\frac{E}{RT}\right)$  Chemical reaction rate

where  $V$  is the volume of the vessel.

- Energy balance

Change of Sensible energy  $\rightarrow \rho c_v V \frac{dT}{dt} = VQ_F B C_{F,u} \phi \exp\left(-\frac{E}{RT}\right) - hS(T - T_w)$  Heat release rate Heat loss to wall

where  $Q_F$  is the heat release per mole of fuel consumed,  $h$  the heat transfer coefficient,  $S$  the surface area of the vessel, and  $T_w$  the wall temperature.

Initial conditions at  $t = 0$  are

$$\phi = 1, \quad T = T_w$$

# Thermal explosion (thermal runaway)

Define

$$\tau = \frac{t}{t_c}, \quad \theta = \frac{T - T_w}{\epsilon T_w}$$

where

$$\begin{aligned} t_c &= \frac{V \rho c_v}{Sh} = \text{time for cooling} \\ \epsilon &= \frac{RT_w}{E} = \frac{\text{thermal energy at wall temperature}}{\text{activation energy}} \end{aligned}$$

$\epsilon \ll 1$ . Define a quantity  $\gamma \ll 1$  as

$$\gamma = \frac{\rho c_v T_w}{Q_F C_{F,u}} = \frac{\text{thermal energy at wall temperature}}{\text{heat release}}.$$

The parameter  $\delta$  is given by

$$\delta = (\gamma \epsilon)^{-1} t_c B \exp \left( -\frac{E}{RT_w} \right) = \frac{\text{cooling time}}{\text{reaction time}}.$$

The quantity  $\delta$  is of the order of unity.

# Thermal explosion (thermal runaway)

The nondimensional describing equations are

- Balance equation for fuel

$$\frac{d\phi}{d\tau} = -\epsilon\gamma\delta\phi\exp\left(\frac{\theta}{1+\epsilon\theta}\right).$$

$\epsilon \ll 1$

- Energy balance

$$\frac{d\theta}{d\tau} = \delta\phi\exp\left(\frac{\theta}{1+\epsilon\theta}\right) - \theta$$

$\epsilon \ll 1$

Initial conditions at  $\tau = 0$  are

$$\phi = 1, \theta = \theta_0 = (T_u - T_w)/(T_w\epsilon).$$

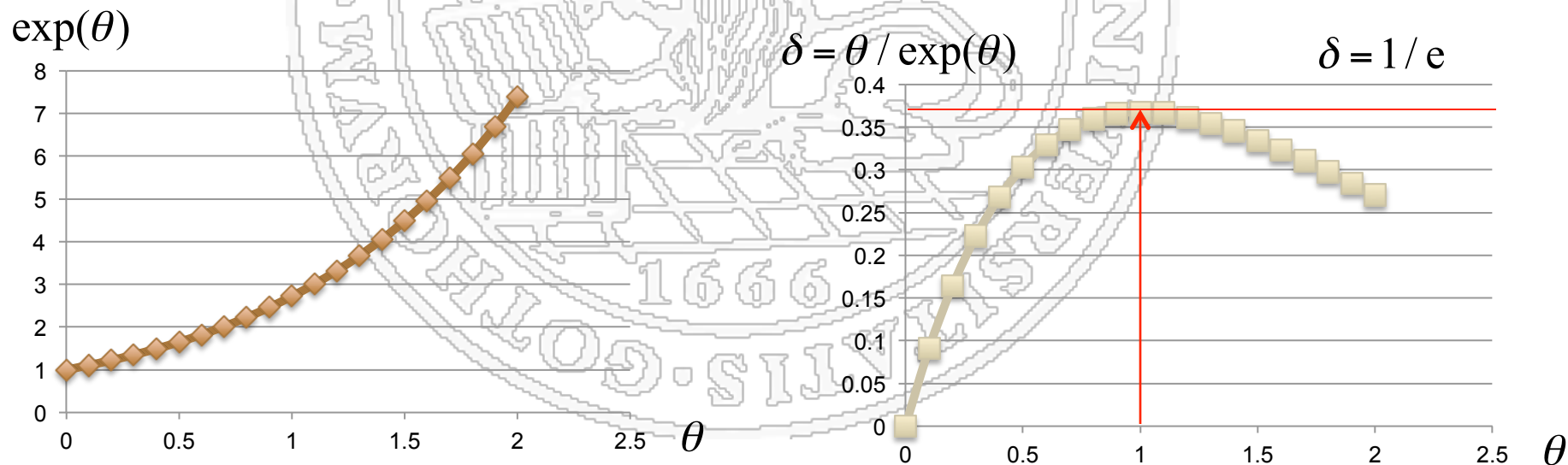


# Thermal explosion (thermal runaway)

- Critical condition for thermal runaway

$$\frac{d\theta}{d\tau} = \delta \exp\left(\frac{\theta}{1 + \epsilon\theta}\right) - \theta = 0 \longrightarrow \delta \exp(\theta) = \theta$$

$$\phi \approx 1 \quad \epsilon \approx 0$$



# Thermal explosion (thermal runaway)

If  $\delta \gg e^{-1}$ , heat loss term can be neglected because it is of the order of  $\delta^{-1}$ . With the definition  $\hat{\tau} = \delta\tau$ , the energy conservation equation is

$$\frac{d\theta}{d\hat{\tau}} = \exp(\theta)$$

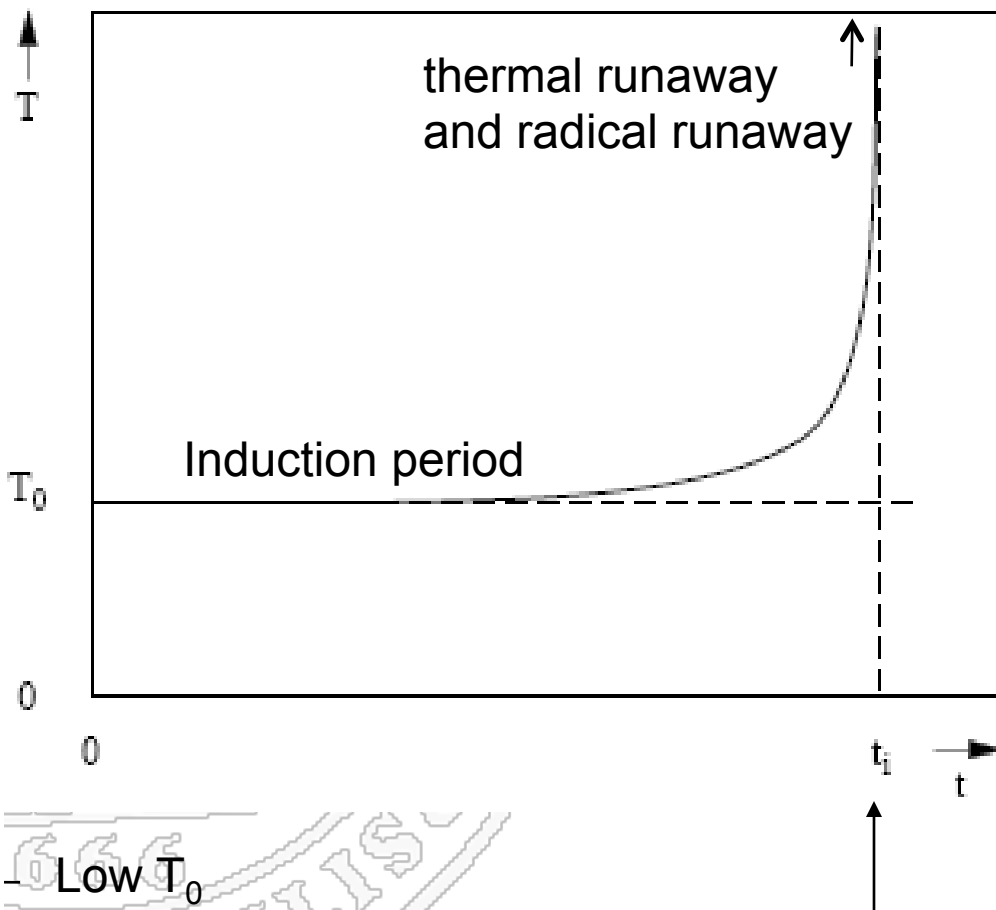
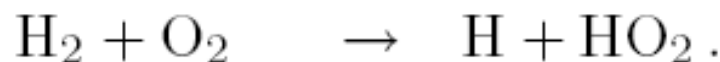
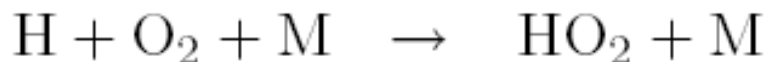
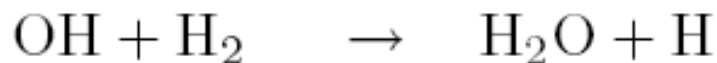
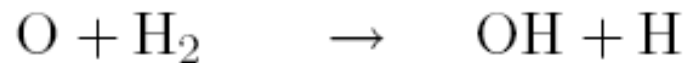
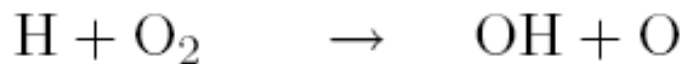
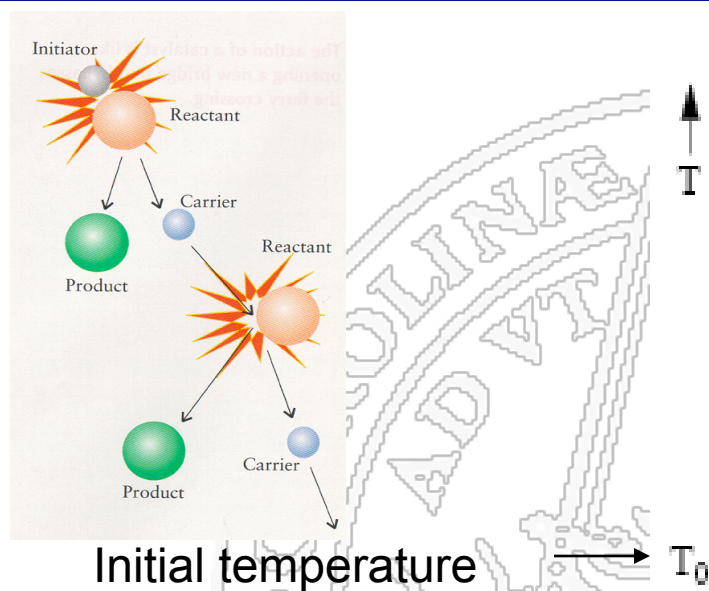
The initial condition at  $\hat{\tau} = 0$  is  $\theta = 0$ . Solution to the energy equation is

$$\theta = -\ln(1 - \hat{\tau}).$$

At  $\hat{\tau} = 1$ ,  $\theta \rightarrow \infty$ . Thus the ignition delay time  $t_e$  is given by

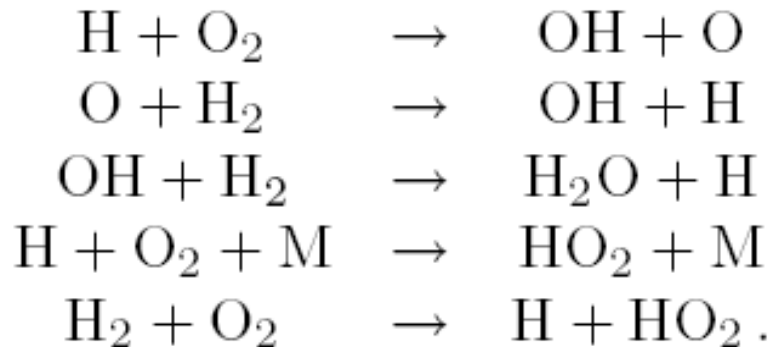
$$t_e = \frac{\rho c_v R T_w^2}{E Q_F B} \exp\left(\frac{E}{R T_w}\right)$$

# Hydrogen/air auto-ignition



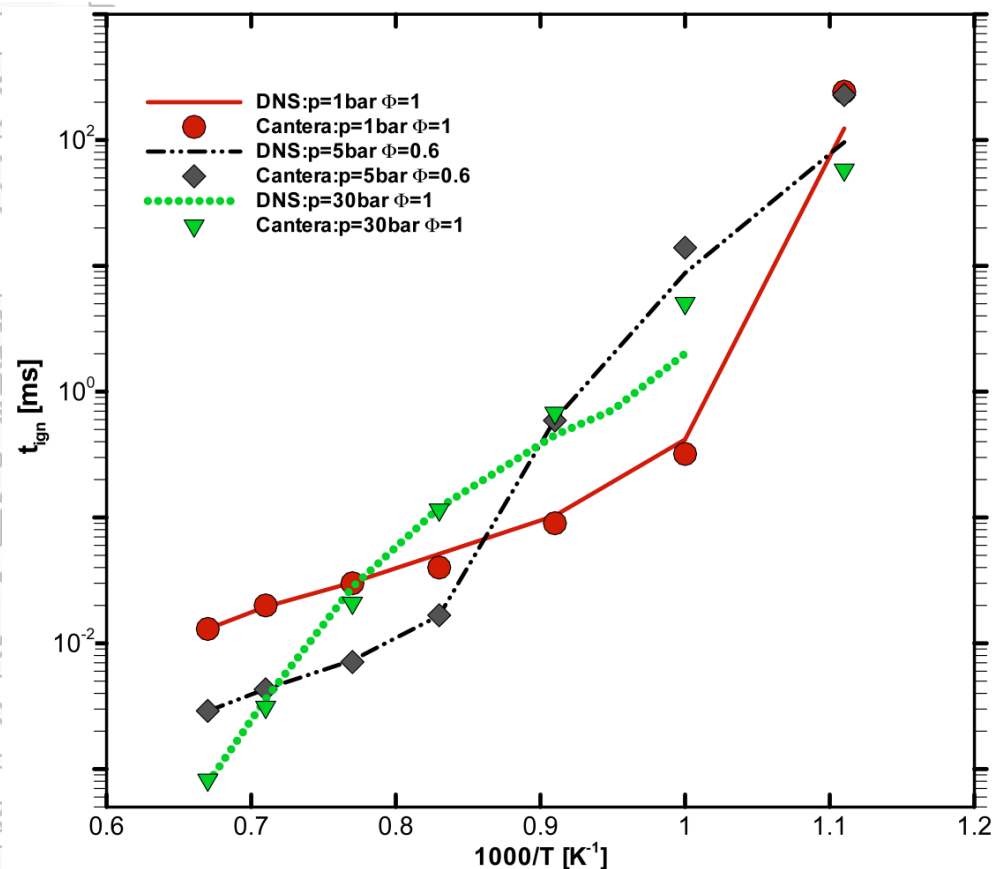
Ignition delay time

# Hydrogen/air auto-ignition



Combustion duration

| rpm  | CAD | time    |
|------|-----|---------|
| 1000 | 30  | 5 ms    |
| 2000 | 30  | 2.5 ms  |
| 3000 | 30  | 1.25 ms |



Ignition delay time of H<sub>2</sub>/air mixture

From Fan Zhang, Yajing Wu

# n-heptane-air auto-ignition

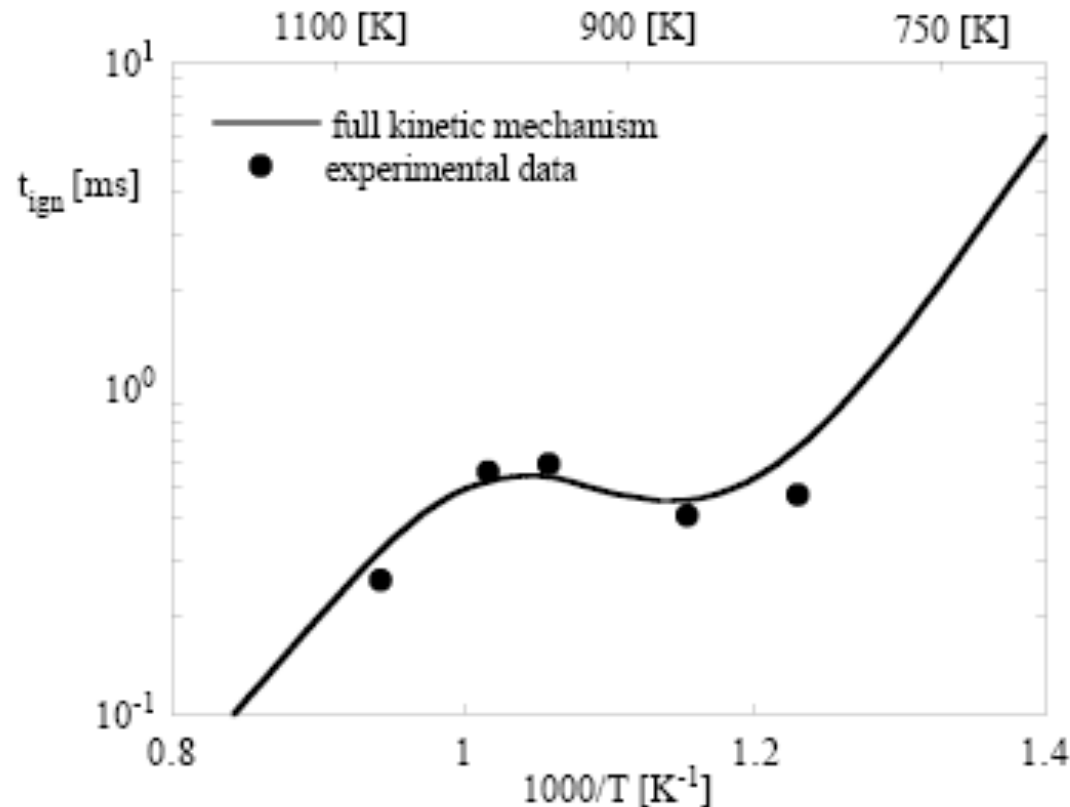


Fig. 4.6: Comparison of calculated ignition delay times for stoichiometric n-heptane-air mixtures by a full kinetic mechanism of 1011 elementary reactions with experimental data [4.4] at 40 atm.

From N. Peters, 15 lectures, 1992