Module 4: Chemistry of combustion

Lecture 21: Chain Branching Explosion

The Lecture Contains:

- Chain Branching Explosion
- Multistep Reaction Mechanism
- Quasi-Steady State Approximation
- Partial Equilibrium Approximation (PEA)
- Global Kinetics

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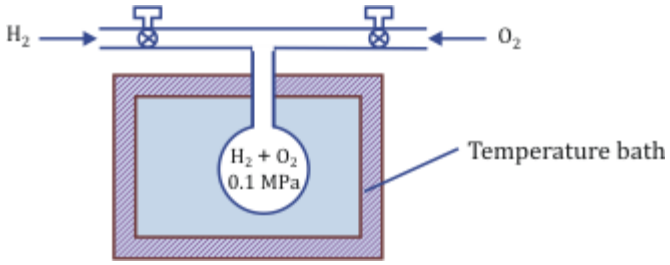
Chain Branching Explosion

Explosion:

Very rapid combustion of fuel and oxidizer, leading to violent release of energy.



(Figure 20.2)

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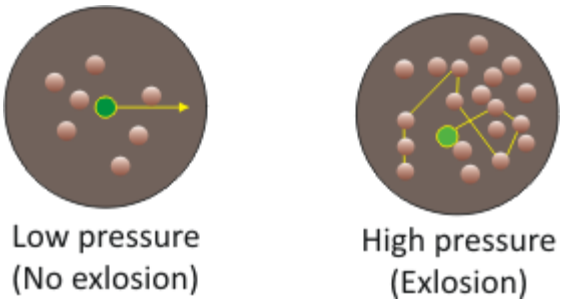
Chain Branching Explosion

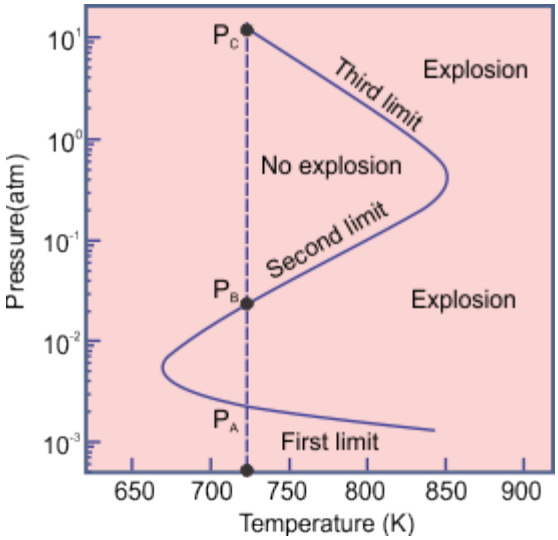
- To begin with, stoichiometric mixture of H_2 and O_2 is kept in a container.
- Temperature is increased beyond 773 K.
- **Result:** Very rapid chemical reaction with explosion.



(Figure 21.1)

Regimes in the explosion chart

1. First limit
2. Second limit
3. Third limit



(Figure 21.2)

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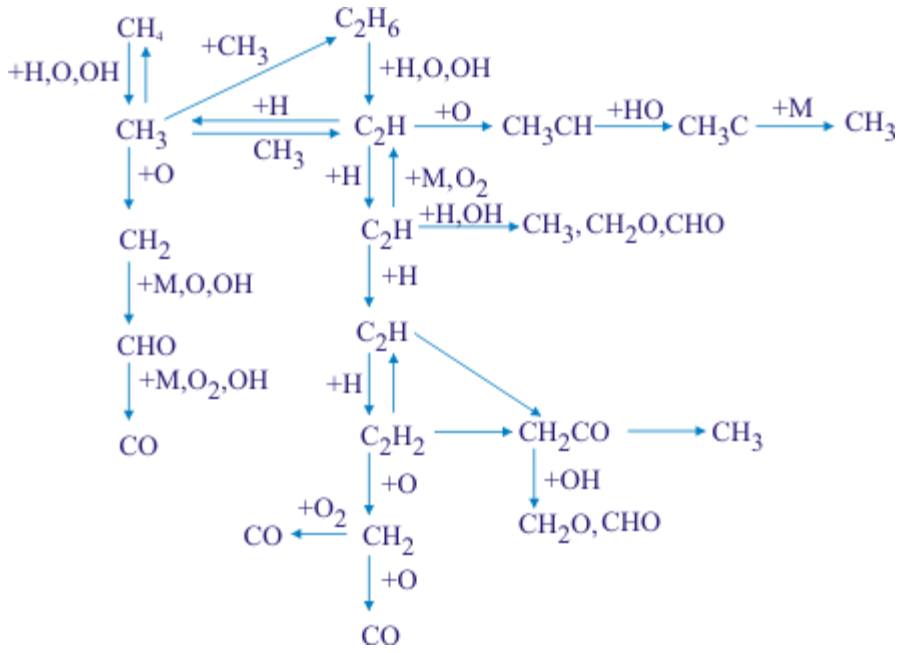
Multistep Reaction Mechanism



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Quasi-Steady State Approximation

- Radicals are formed during combustion
- Half life period of radicals - Very small
- Rate of formation = Rate of destruction

Relate radical concentration with
measurable concentration of other species

Consider the two step chain reaction,

$A_1 \xrightarrow{k_1} A_2$; $A_2 \xrightarrow{k_2} A_3$;

Reaction rate of the three species,

$$\frac{dC_{A_1}}{dt} = -k_1 C_{A_1} \qquad \frac{dC_{A_2}}{dt} = k_1 C_{A_1} - k_2 C_{A_2} \qquad \frac{dC_{A_3}}{dt} = k_2 C_{A_2}$$

Initial condition, $at\ t = 0;\ C_{A_1} = C_{A_1,in};\ C_{A_2} = 0;\ C_{A_3} = 0$

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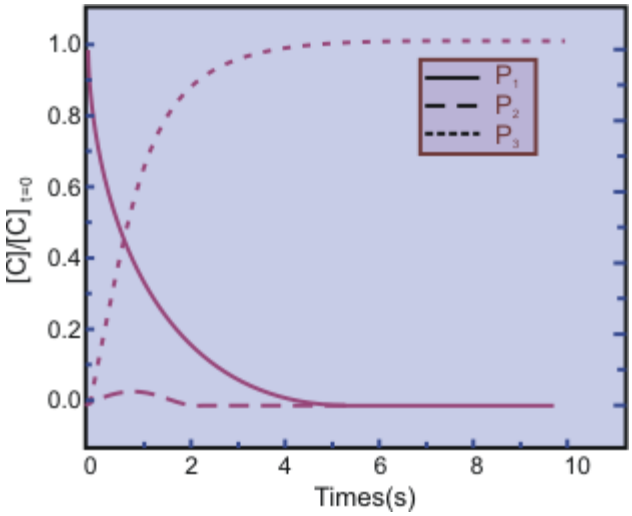
Applying initial condition,

$$C_{A_1} = C_{A_1,in}\, e^{(-k_1 t)}$$

$$C_{A_2} = C_{A_1,in}\, \frac{k_1}{k_1 - k_2}\left[e^{(-k_2 t)} - e^{(-k_1 t)}\right]$$

$$C_{A_3} = C_{A_1,0}\left[1 - \frac{k_1}{k_1 - k_2} e^{(-k_2 t)} + \frac{k_2}{k_1 - k_2} e^{(-k_1 t)}\right]$$



(Figure 21.3)

Applying QSSA method to A_2,

$$\frac{dC_{A_2}}{dt} = k_1 C_{A_1} - k_2 C_{A_2} \approx 0$$

$$k_1 C_{A_1} = k_2 C_{A_2}\,; \qquad \frac{dC_{A_3}}{dt} = k_1 C_{A_1,in} e^{(-k_1 t)}\,;$$

$$\frac{dC_{A_3}}{dt} = k_1 C_{A_1}\,; \qquad C_{A_3} = C_{A_1,in}\left[1 - e^{(-k_1 t)}\right];$$

QSSA method predicts the concentration of species especially when $k_2 \gg k_1$

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Partial Equilibrium Approximation (PEA)

PEA expresses concentration of unknown species in terms of known concentrations.

Consider NO formation mechanism,

$$O + N_2 \Leftrightarrow NO + N \qquad k_f = 2 \times 10^{14}\, e^{(-315/RT)}$$

Reaction Rate (RR) for NO species:

$$\frac{dC_{NO}}{dt} = k_f C_O C_{N_2}$$

Note 1: O and N_2 concentration are required to determine RR

Note 2: Rate of formation and destruction of O is very high

Difficult to measure the concentration of O!!!

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Step 1:

Assume partial equilibrium for O_2 molecule

PEA	QSSA
Reaction attains steady state	Species attains steady state

Step 2:

Relate O_2 molecule to O by

$O_2 \Leftrightarrow 2O$

Equilibrium constant

$$K_C = \frac{C_o^2}{C_{O_2}}$$

Note !

- Thermal NO – Less dependent on CO_2
- Thermal NO – Temperature dependent
- NO reduction – By reducing combustion temperature

Reaction Rate (RR) for NO species:

$$\frac{dC_{NO}}{dt} = k_f \left(K_C \, C_{O_2} \right)^{0.5} C_{N_2}$$

Caution !

- In real situation, particular reaction may not attained equilibrium
- PEA provides satisfactory results only at high temperature !

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Global Kinetics

Single step methane combustion:

$$CH_4 + 2O_2 \xrightarrow{k_f} CO_2 + 2H_2O$$

Overall reaction rate (CH_4)

$$\frac{dC_{CH_4}}{dt} = Ae^{(-E/R_uT)} C_{CH_4}^m C_{O_2}^n$$

Global kinetic scheme for an arbitrary hydrocarbon (C_xH_y):

$$C_xH_y + (x + y/4)O_2 \xrightarrow{k_f} xCO_2 + (y/2)\,H_2O$$

Overall reaction rate (C_xH_y)

$$\frac{dC_xH_y}{dt} = -A_f e^{(-E/R_uT)} C_{C_xH_y}^m C_{O_2}^n$$

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