# H_2 Mechanism

1 Branched Chain Mechanism

1.1 Radical

A radical is a molecule, atom, or ion that has unpaired valence electrons. Because of this, radicals are often highly reactive and play crucial roles in combustion reactions.

1.2 Branched Chain Mechanism

A branched chain mechanism in combustion refers to a reaction mechanism where the chain reaction (the sequence of reactions that sustains the combustion process) branches out or multiplies due to certain reactions that produce more than one free radical species as products. It includes 5 kinds of reactions.

Initiation: Create radicals from zero.

$$mA \xrightarrow{k_i} R + ? \qquad \Delta R = +1 \tag{1}$$
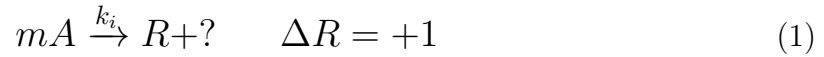
Chain Branching: Create radicals from non-zero.

$$A + R \xrightarrow{k_b} P + nR \qquad \Delta R = n - 1 \tag{2}$$
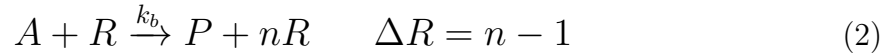
Chain Propagating: No change of the number of radicals.
Wall Termination: Decrease radicals due to wall.

$$R \xrightarrow{k_w t} P \qquad \Delta R = -1 \tag{3}$$

Gas Termination: Decrease radicals due to gas reaction.

$$R + M + M \xrightarrow{k_{gt}} P + M \qquad \Delta R = -1 \tag{4}$$

2 Explosion

2.1 Definition

An explosion, from the perspective of radical reactions, can be understood as a highly exothermic reaction that results in the rapid release of energy in the form of heat and light, often with the generation of a shock wave. It involves a very fast, self-propagating reaction process in which a reaction leads to the creation of radicals that spur on further reactions.

2.2 Explosion Limit

The explosion limit is related to the net production rate of radicals, which can be expressed as:

$$\frac{d[R]}{dt} = k_i[A]^m + (n-1)k_b[R][A] - k_{gt}[R][M]^2 - k_{wt}[R] \tag{5}$$

Assume steady state for [R], then:

$$[R]_{ss} = \frac{k_i[A]^m}{(1-n)k_b[A] + k_{gt}[M]^2 - k_{wt}} \tag{6}$$

Explosion requires "unbounded" growth of radicals, which means:

$$[R]_{ss} \to \infty \tag{7}$$

$$(1-n)k_b[A] + k_{gt}[M]^2 - k_{wt} = 0 \tag{8}$$

Then the explosion limit could be defined as:

$$n \geq n_{expl} = 1 + \frac{[M]^2 + k_{wt}/k_{gt}}{k_b[A]/k_{gt}} \tag{9}$$
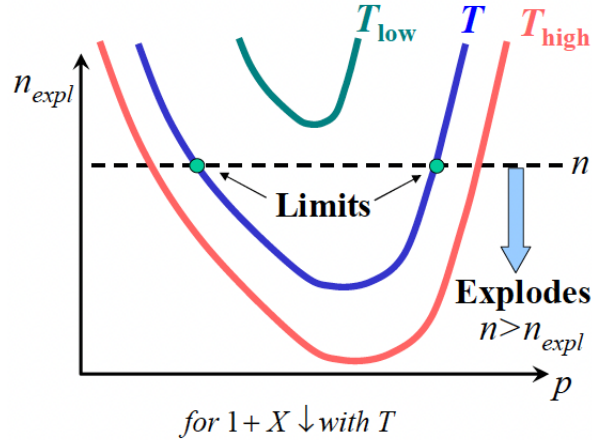
2.3 Pressure Dependence

Figure 1: Explosion Limit.

Replace the concentration by pressure, we get:

$$n_{expl} = 1 + \frac{C_1 p^2 + k_{wt}/k_{gt}}{C_2 p k_b[A]/k_{gt}} \tag{10}$$

When $p \to 0$:
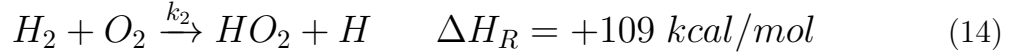
$$n_{expl} = 1 + \frac{k_{wt}/k_b}{C_2 p} \tag{11}$$

When $p \to \infty$:

$$n_{expl} = 1 + \frac{C_1}{C_2}\frac{k_{gt}}{k_b}p \tag{12}$$

3 $H_2 - O_2$ Explosion

3.1 Mechanism

Initiation:

$$H_2 + M \xrightarrow{k_1} H + H + M \qquad \Delta H_R = +106 \; kcal/mol \tag{13}$$

$$H_2 + O_2 \xrightarrow{k_2} HO_2 + H \qquad \Delta H_R = +109 \; kcal/mol \tag{14}$$

Chain Branching:

$$H + O_2 \xrightarrow{k_3} OH + O \qquad \Delta H_R = +16 \; kcal/mol \tag{15}$$

$$O + H_2 \xrightarrow{k_4} OH + H \qquad \Delta H_R = +2 \; kcal/mol \tag{16}$$

Chain Propagating:

$$OH + H_2 \xrightarrow{k_5} H_2O + H \qquad \Delta H_R = -15 \; kcal/mol \tag{17}$$

$$H + O_2 + M \xrightarrow{k_6} HO_2 + M \qquad \Delta H_R = -24 \; kcal/mol \tag{18}$$

Termination:

$$O + O + M \xrightarrow{k_7} O_2 + M \qquad \Delta H_R = -59 \; kcal/mol \tag{19}$$

$$OH + H + M \xrightarrow{k_8} H_2O + M \qquad \Delta H_R = -58 \; kcal/mol \tag{20}$$

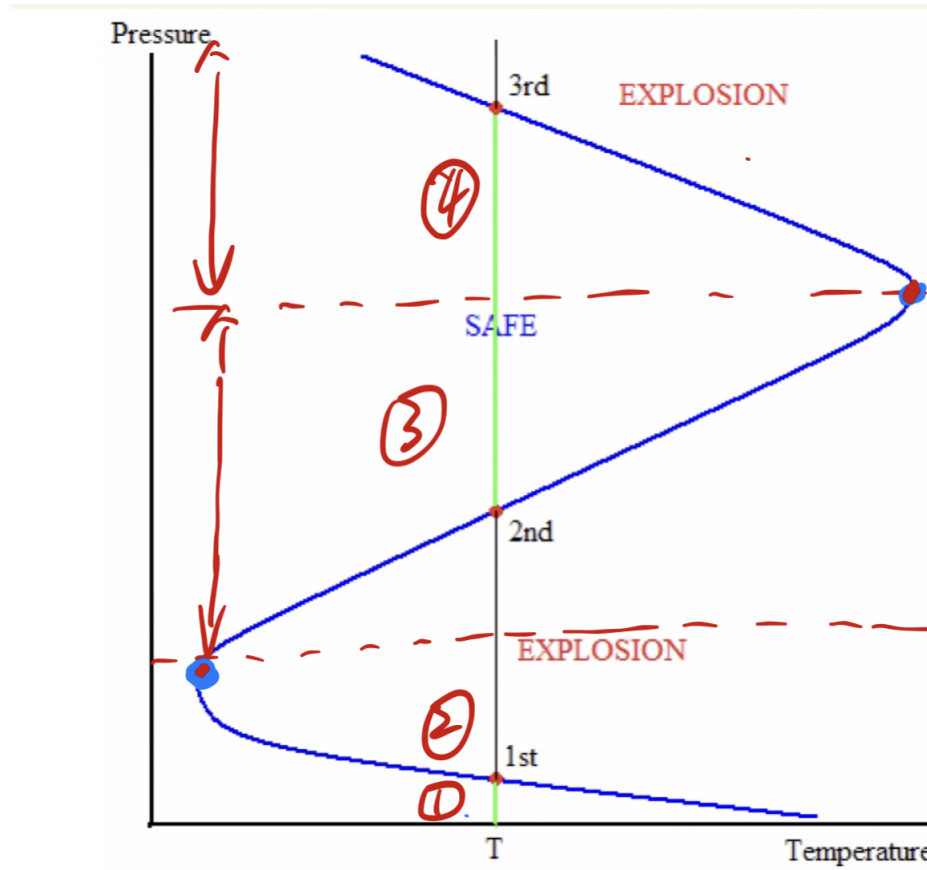$$H, O, OH, HO_2 \to wall \tag{21}$$
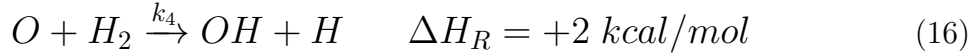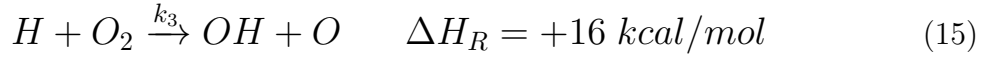
3.2 Explosion Limit
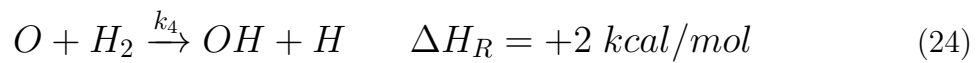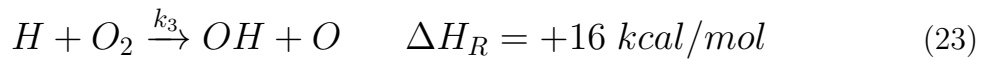

Figure 2: $H_2 - O_2$ Explosion Limit.

3.2.1 Region 1

In this region, pressure is low, net loss of $[H]$ due to wall termination.

$$\frac{d[H]^-}{dt} = k_{wall}[H] \tag{22}$$

3.2.2 Region 1 to Region 2 (Pass First Limit)

During this process, the reactions include:

$$H + O_2 \xrightarrow{k_3} OH + O \qquad \Delta H_R = +16 \; kcal/mol \tag{23}$$

$$O + H_2 \xrightarrow{k_4} OH + H \qquad \Delta H_R = +2 \; kcal/mol \tag{24}$$

$$OH + H_2 \xrightarrow{k_5} H_2O + H \qquad \Delta H_R = -15 \; kcal/mol \tag{25}$$

$$OH + H_2 \xrightarrow{k_5} H_2O + H \qquad \Delta H_R = -15 \; kcal/mol \tag{26}$$

Notice that there is $[H]$ in, $3[H]$ out. Also, (H.3) reaction is the slowest, so it is the limited reaction. Therefore, the consumption rate is $k_3[H][O_2]$, and the production rate is $3k_3[H][O_2]$, and:

$$\frac{d[H]^+}{dt} = 2k_3[H][O_2] \tag{27}$$

In this region, wall termination still dominates the termination process, therefore:

$$\frac{d[H]^+/dt}{d[H]^-/dt} = \frac{2k_3[H][O_2]}{k_{wt}[H]} = 2\frac{k_3[O_2]}{k_{wt}} \propto P \tag{28}$$

Here, we define:

$$\frac{d[H]^+/dt}{d[H]^-/dt} = \frac{1}{n_{expl}} \tag{29}$$

When the pressure increases, n_{expl} decreases,n becomes easier to be greater than n_{expl}, which will cause the explosion. This is the **first explosion limit**. In summary, when the pressure is very low, net production of $[H]$ is too slow to overcome the wall termination, so it will not explode. When the pressure is high, branching/propagating for [H] dominate, so it will explode.

3.2.3   Region 3 (Pass Second Limit)

In this region, the $[H]$ production mechanism is the same, which is:

$$\frac{d[H]^+}{dt} = 2k_3[H][O_2] \tag{30}$$

However, the main termination is dominated by:

$$H + O_2 + M \xrightarrow{k_6} HO_2 + M \qquad \Delta H_R = -24 \ kcal/mol \tag{31}$$

Even though this reaction is a propagation reaction, but in this condition, it removes $[H]$ and transfer to $[HO_2]$. $[HO_2]$ is relatively unreactive at this pressure and temperature condition, can diffuse and destroyed at walls.
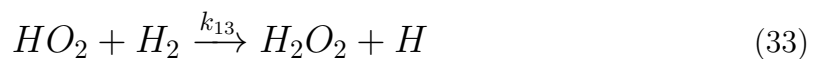
Therefore:

$$\frac{d[H]^+/dt}{d[H]^-/dt} = \frac{2k_3[H][O_2]}{k_6[H][O_2][M]} \propto \frac{k_3}{k_6}\frac{1}{[M]} \propto \frac{1}{P} \tag{32}$$

As pressure increases, n_{expl} also increases, n will be harder to be greater than n_{expl}, so it will be harder to explode.

3.2.4   Region 4 (Pass Third Limit)

In this region, the [H] production is dominated by a chain branching reaction:

$$HO_2 + H_2 \xrightarrow{k_{13}} H_2O_2 + H \tag{33}$$

And the consumption of [H] is dominated by wall termination of $[HO_2]$. Therefore:

$$\frac{d[H]^+/dt}{d[H]^-/dt} = \frac{k_{13}[HO_2][H]}{k_{wt}[HO_2]} \propto P \tag{34}$$

When the pressure increases, n_{expl} decreases,n becomes easier to be greater than n_{expl}, which will cause the explosion.

4 Induction Time

The induction time in combustion refers to the period from the beginning of the reaction (or the time when the reactants are mixed and ignition energy is provided) to the moment when a rapid, self-sustained combustion reaction begins. During this time, energy is being absorbed from the surroundings and the concentration of free radicals and other reactive intermediates is building up.
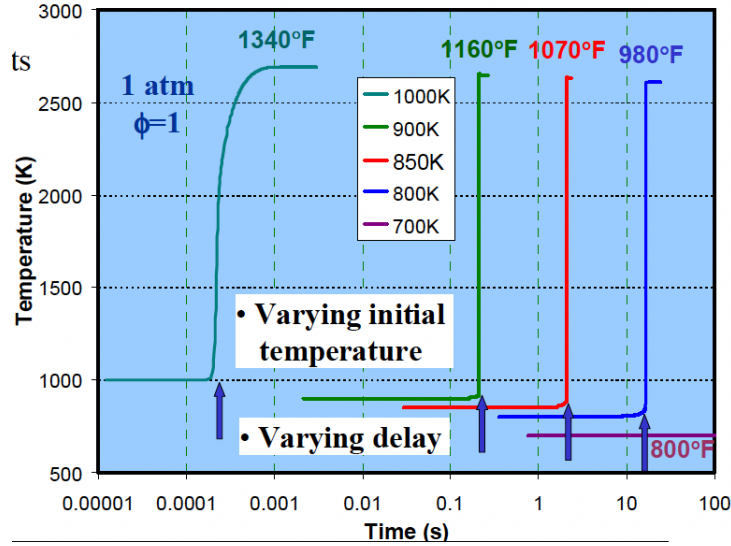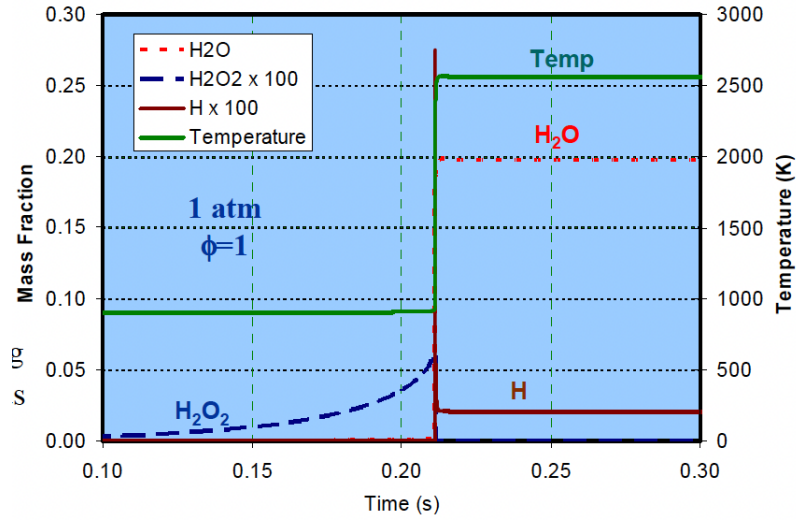

Figure 3: Overall Reaction Process.

Figure 4: Induction Period.

As shown in the graph, the induction period is dominated by radical buildup. The temperature rise is small, and the chain branching is slow.
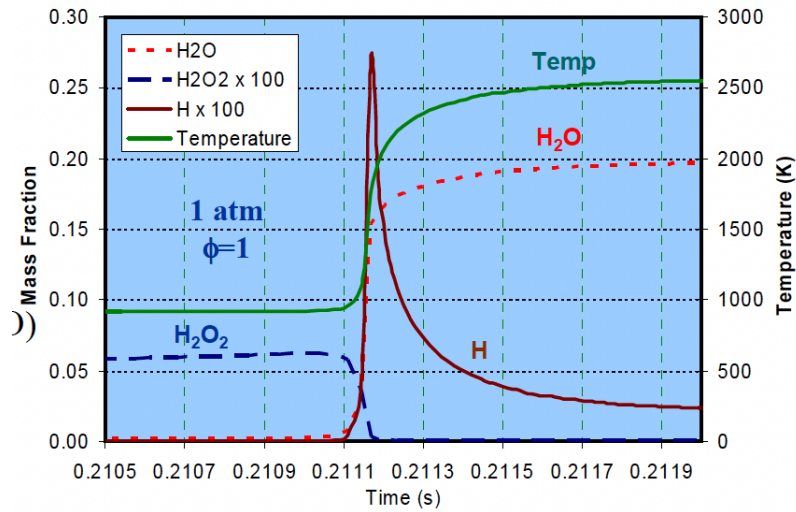

Figure 5: Fast Reaction.

When there is enough H_2O_2, there will be sudden rise of radicals and temperature.