

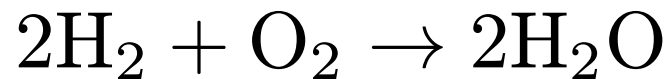
3. Combustion Chemistry

- For many kinetically controlled systems, the number of elementary reaction steps is so large that simple analytical solutions are not possible.
- Most of the time, a large number of chemical species are involved.
- Even in combustion of simple hydrocarbons, number of species involved is quite high.
- To illustrate how the fundamental principles of chemical kinetics apply to real-world problems, we will consider some examples.

Hydrogen-Oxygen Reaction

The reaction between hydrogen and oxygen is a good example of a multicomponent kinetic system. To describe the system properly, we should consider eight major species and at least 16 reactions.

- The overall reaction is:



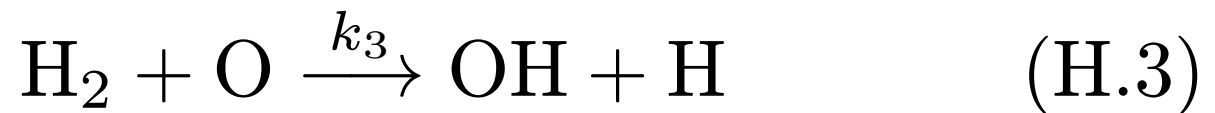
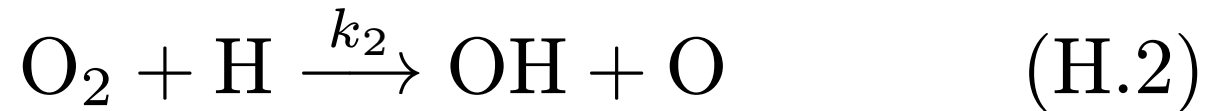
This reaction is exothermic; but mixtures of gaseous hydrogen and oxygen are quite stable at atmospheric conditions. Any conceivable direct reaction between the two gases is zero.

- The reaction half-time at atmospheric conditions has been estimated to be much larger than the age of the universe.
- If the reaction is initiated by some free-radical species, then the reaction proceeds very rapidly and violently.
- The radicals are typically H and O atoms produced from the dissociation of H₂ and O₂, respectively.
- We will consider a simplified mechanism that represents the gross features of H₂ + O₂ at low *P*.

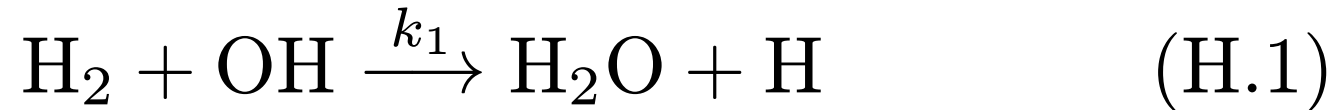
- Initiation



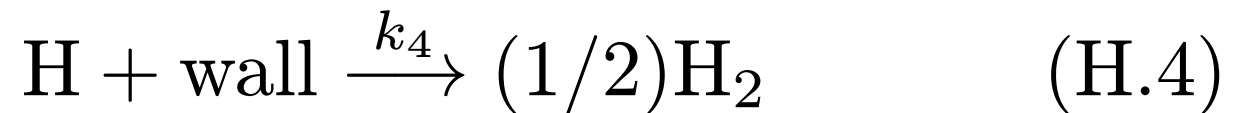
- Chain branching



- Chain propagation

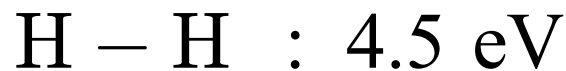


- Chain termination



- Initiation step is the dissociation of some amount of molecular species by a spark, flame, electric discharge, or some other means.

- Bond energies:



- Reaction (2) is endothermic by 0.7 eV (about 70 kJ/mol) and progresses slowly.

- Reactions (3) and (1) are endothermic by 0.1 eV, and these reactions are relatively fast.

- The OH and O radicals are therefore rapidly consumed, and the principal chain carrier is H atoms.

- We will find the rate equation for the free-radical density n^* , which is taken to be the same as that for [H] atoms:

$$\begin{aligned} \frac{dn^*}{dt} &= \frac{d[\text{H}]}{dt} \\ &= k_o[\text{H}_2] - k_2[\text{H}][\text{O}_2] + k_3[\text{O}][\text{H}_2] + k_1[\text{OH}][\text{H}_2] \\ &\quad - k_4[\text{H}] - k_5[\text{H}][\text{O}_2][\text{M}] \end{aligned} \quad (3.1)$$

- For other free-radical species:

$$\frac{d[\text{OH}]}{dt} = k_2[\text{H}][\text{O}_2] + k_3[\text{O}][\text{H}_2] - k_1[\text{OH}][\text{H}_2] \quad (3.2)$$

$$\frac{d[\text{O}]}{dt} = k_o[\text{O}_2] + k_2[\text{H}][\text{O}_2] - k_3[\text{O}][\text{H}_2] \quad (3.3)$$

- Since $[\text{O}]$ and $[\text{OH}]$ are both much lower than $[\text{H}]$, we can assume that both of these species are at steady-state:

$$\frac{d[\text{OH}]}{dt} = \frac{d[\text{O}]}{dt} = 0 \quad (3.4)$$

that yields

$$[\text{O}]_{\text{ss}} = \frac{k_o[\text{O}_2] + k_2[\text{H}][\text{O}_2]}{k_3[\text{H}_2]} \quad (3.5)$$

and for [OH],

$$[\text{OH}]_{\text{ss}} = \frac{k_2 [\text{H}][\text{O}_2] + k_3 [\text{O}][\text{H}_2]}{k_1 [\text{H}_2]} \quad (3.6)$$

Substituting for [O]_{ss}

$$[\text{OH}]_{\text{ss}} = \frac{2k_2 [\text{H}][\text{O}_2] + k_o [\text{O}_2]}{k_1 [\text{H}_2]} \quad (3.7)$$

- We substitute the steady-state values of [OH] and [O] radicals in the rate equation for free-radical density

$$\begin{aligned}
\frac{dn^*}{dt} &= k_o[\text{H}_2] - k_2[\text{H}][\text{O}_2] + k_3 \frac{k_2[\text{H}][\text{O}_2] + k_o[\text{O}_2]}{k_3[\text{H}_2]} [\text{H}_2] \\
&+ k_1[\text{H}_2] \frac{2k_2[\text{H}][\text{O}_2] + k_o[\text{O}_2]}{k_1[\text{H}_2]} - k_4[\text{H}] - k_5[\text{H}][\text{O}_2][\text{M}] \\
&= \underbrace{k_o([\text{H}_2] + 2[\text{O}_2])}_{w_o} + \underbrace{(2k_2[\text{O}_2])}_f - \underbrace{(k_4 - k_5[\text{O}_2][\text{M}])}_g n^*
\end{aligned}
\tag{3.8}$$

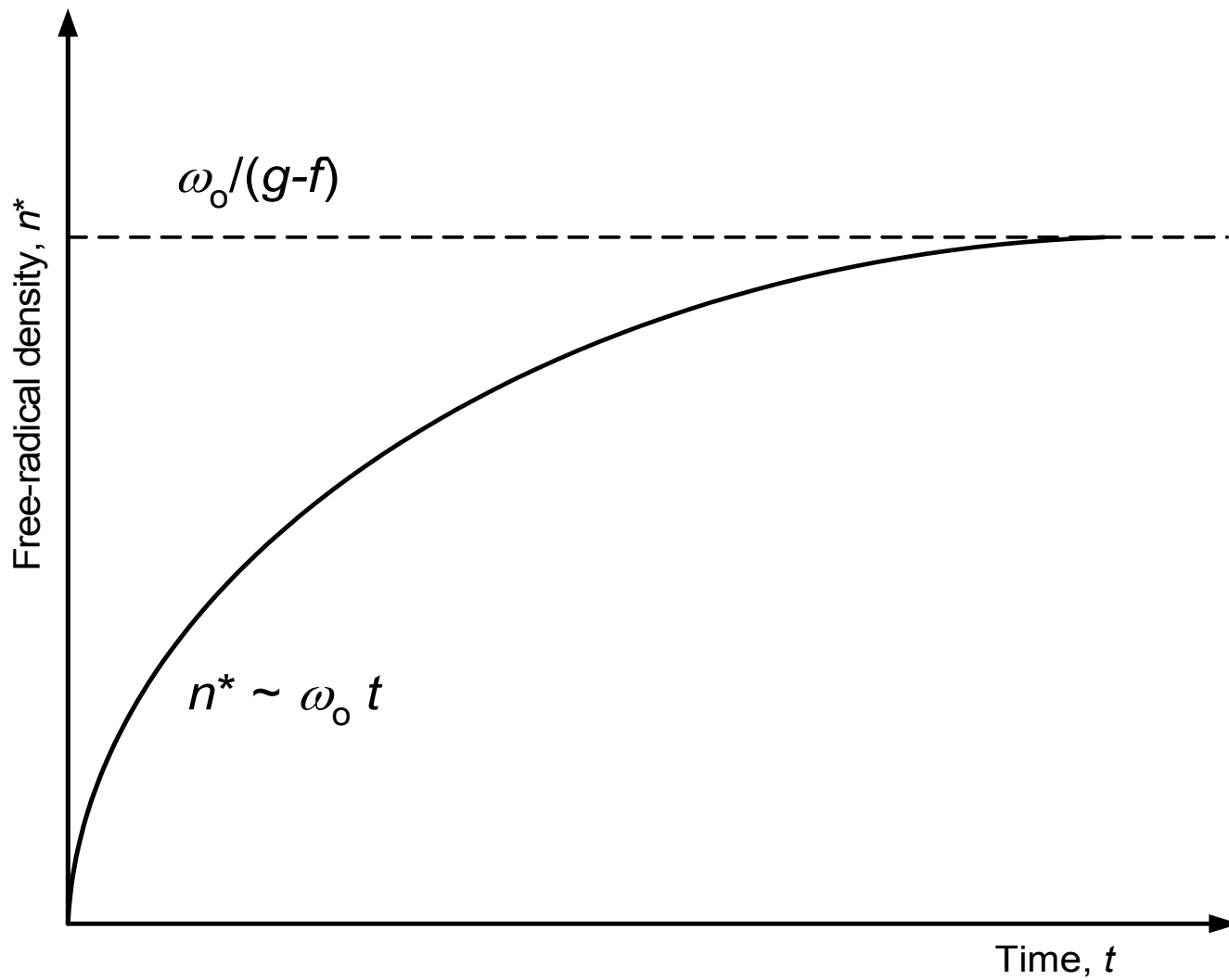
so that

$$\frac{dn^*}{dt} = w_o + (f - g)n^*
\tag{3.9}$$

- f : chain branching
- g : chain termination
- Two classes of solutions are possible:
 1. $g > f$: termination exceeds branching
 2. $g < f$: branching exceeds termination
- Solution 1 implies that

$$k_4 > (2k_2 - k_5[M])[O_2] \quad (3.10)$$

so that $g > f$ is assured at sufficiently low O_2 pressures.



- The solution is then

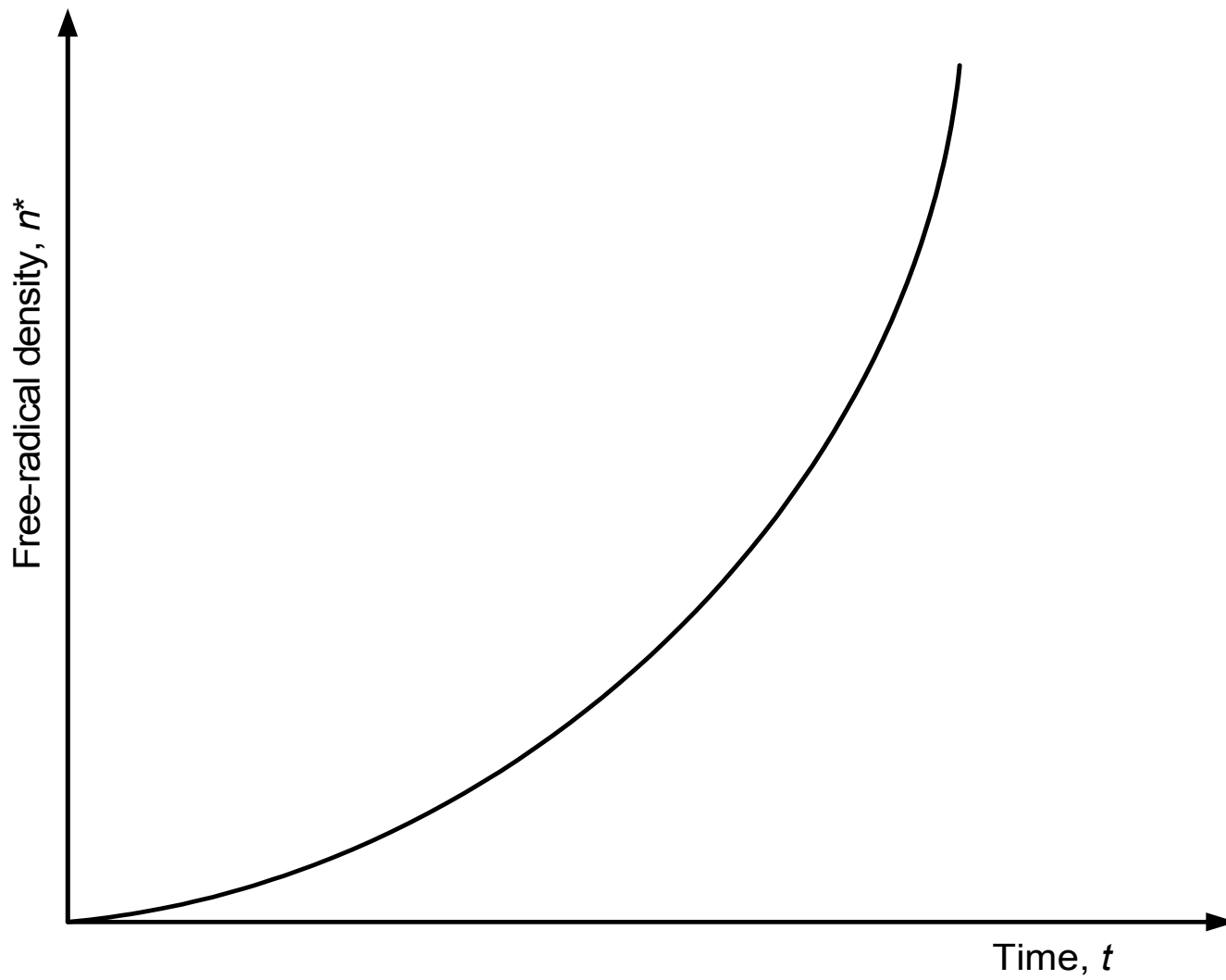
$$n^* = \frac{w_o}{g - f} \{1 - e^{-(g-f)t}\} \quad (3.11)$$

- At short times, n^* increases almost linearly with slope $\sim w_o t$ and reaches a steady-state value of

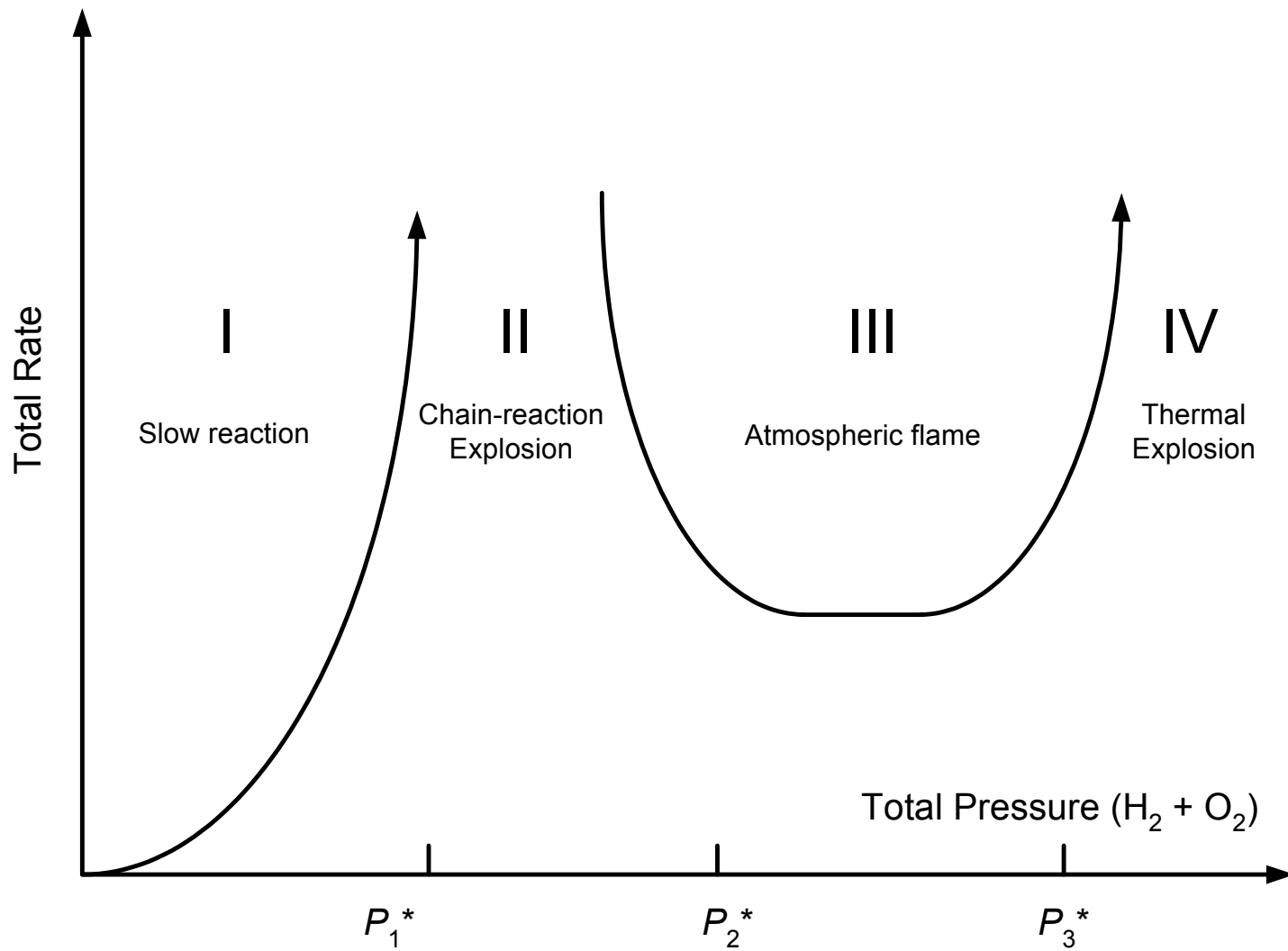
$$n_{ss}^* = w_o / (g - f) \quad (3.12)$$

- At higher O₂ pressures $g < f$, then

$$n^* = \frac{w_o}{f - g} \{e^{(f-g)t} - 1\} \quad (3.13)$$

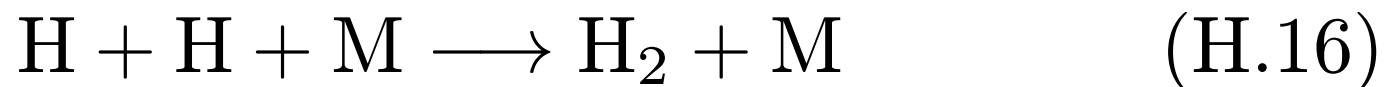
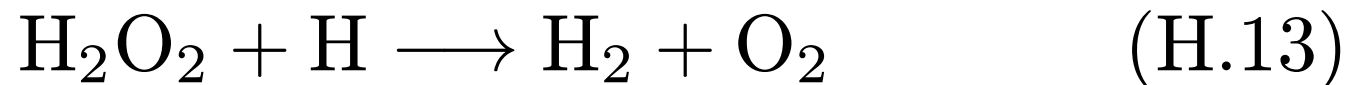
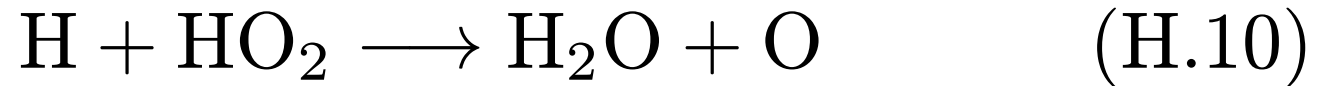
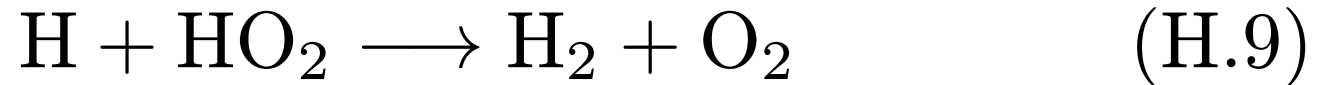
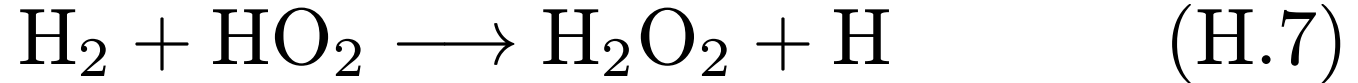
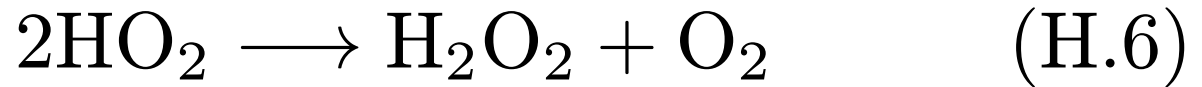


- In this case, the free-radical concentration increases exponentially, and, since the overall rate depends on the radical concentration, the reaction velocity increases rapidly. This is usually termed as an explosion.
- The hydrogen-oxygen reaction behaves quite differently in different pressure regimes.
- It is possible to construct an explosion boundary for the hydrogen-oxygen reaction as a function of temperature and pressure.

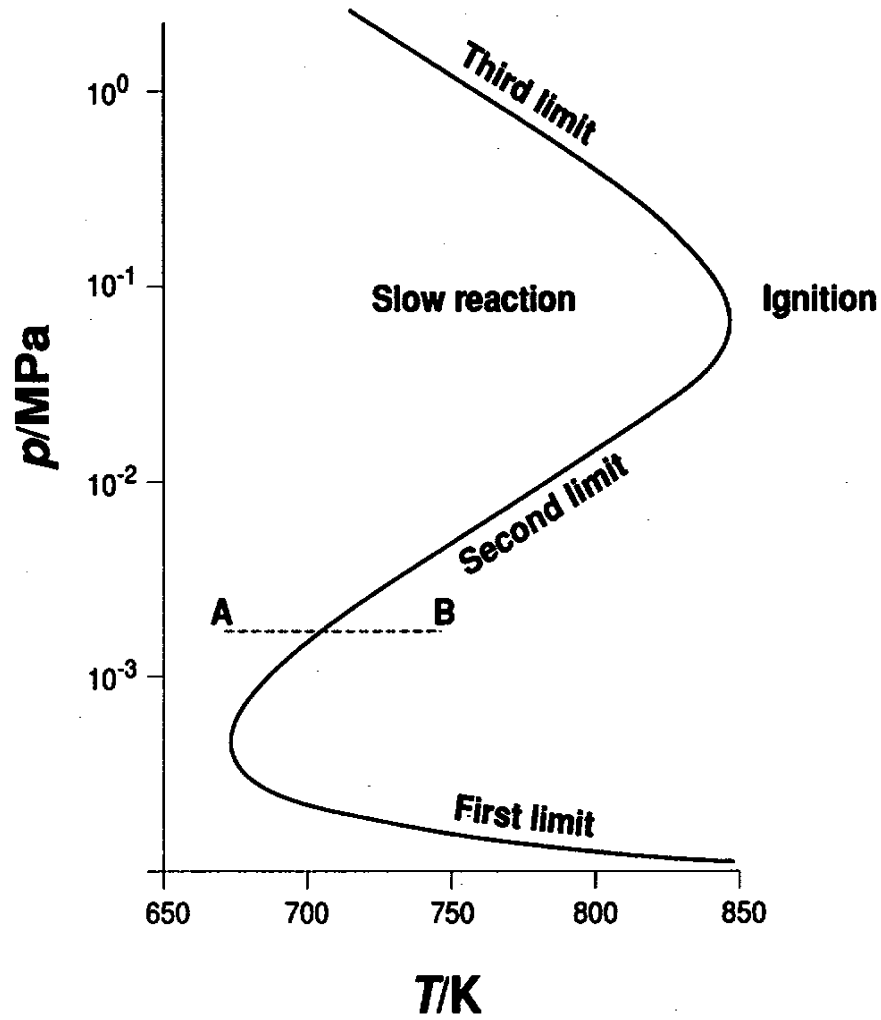


- *Region I*: The reaction is wall-recombination limited, and proceeds to a steady-state.
- *Region II*: f begins to exceed g , the branched-chain reaction takes over and explosion ensues.
- *Region III*: As the pressure is further increased, the explosion is quenched and another regime of steady-state is encountered.

In III, kinetics are dominated by relatively unreactive HO_2 (hydroperoxyl) radicals. Other reactions, in addition to those we considered above, are important and include the following:



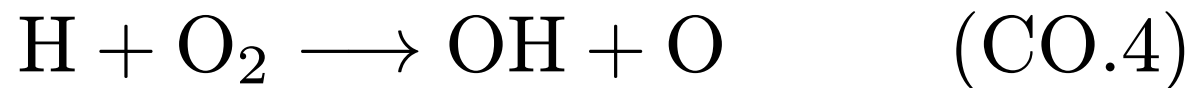
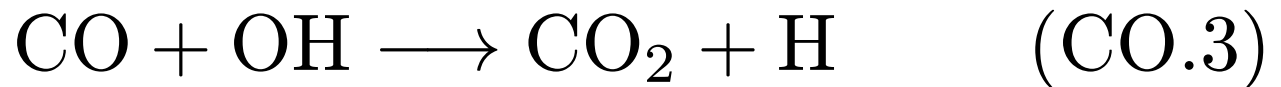
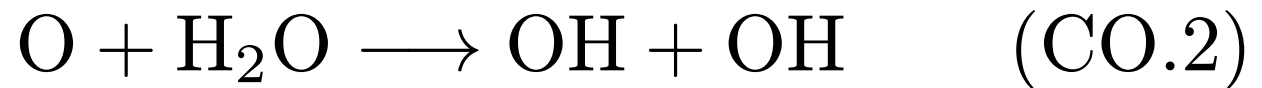
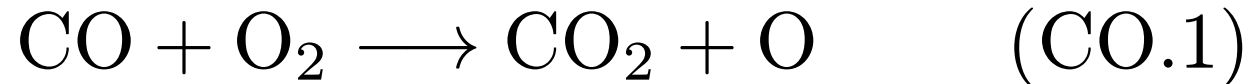
- *Region IV*: At a still high pressure, the amount of heat liberated in the exothermic steps of the mechanism becomes larger than can be dissipated by conduction and other thermal transport processes, and the temperature rises. This, in turn increases the rates of initiation and provides heat for endothermic chain-branching reactions leading to more heat release, resulting in a thermal explosion.
- Experimentally observed ($P - T$) boundaries of the $\text{H}_2\text{-O}_2$ reaction in a closed vessel is shown below.



Carbon Monoxide Oxidation

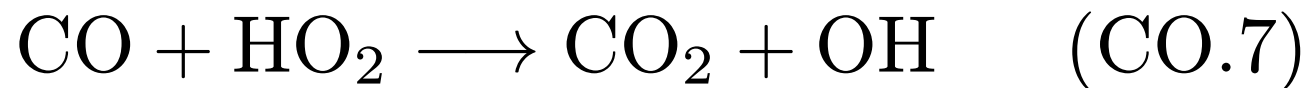
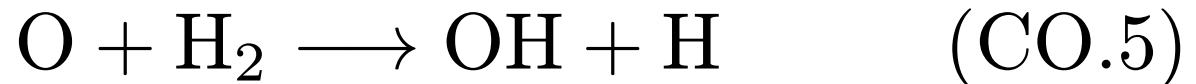
- Oxidation of CO is important in hydrocarbon combustion.
- From a *very simplistic* point-of-view, hydrocarbon combustion (related to C content) can be characterized as a two-step process:
 - breakdown of fuel to CO.
 - oxidation of CO to CO₂.
- CO oxidation is extremely slow in the absence of small amounts of H₂ or H₂O.

- If the H₂O is the primary hydrogen-containing species, the CO oxidation can be described by:



- (CO.1) is slow; not much contribution to CO₂ formation, but chain initiation reaction.
- (CO.3) is the actual CO oxidation step; also chain-propagation step producing H atoms.

- (CO.2) and (CO.4) are chain-branching reactions producing OH, and OH and H, respectively.
- (CO.3) reaction is the key step in CO oxidation.
- If H₂ is present, then following steps are involved:



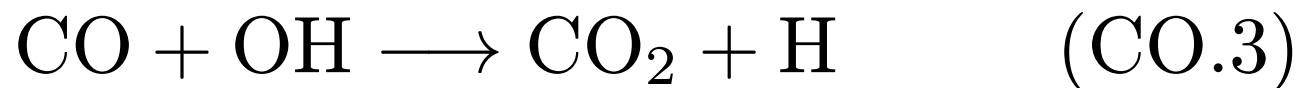
- In the presence of H₂, the entire H₂-O₂ reaction system should be included to describe CO oxidation.

Oxidation of Higher Paraffins

General Scheme:

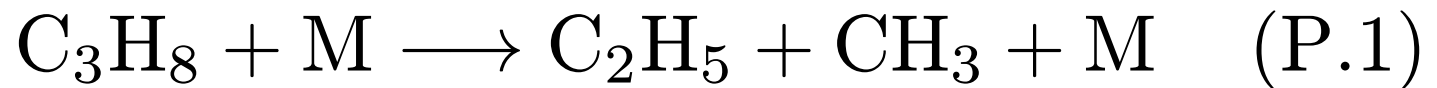
- Alkanes=Paraffins: saturated, straight chain or branched-chain, single-bonded hydrocarbons.
- General formula: C_nH_{2n+2} .
- Generic oxidation discussion will be for $n > 2$.
- Methane (and ethane) display some unique characteristics not common with higher alkanes.
- Overview of the key points of alkane oxidation.

- Three sequential processes:
 - I. Fuel is attacked by O and H; breaks down to H₂ and olefins (double-bonded straight hydrocarbons). H₂ oxidizes to H₂O.
 - II. Unsaturated olefins form CO and H₂. Almost all H₂ converts to water.
 - III. CO burns to CO₂ releasing almost all of the heat associated with combustion:

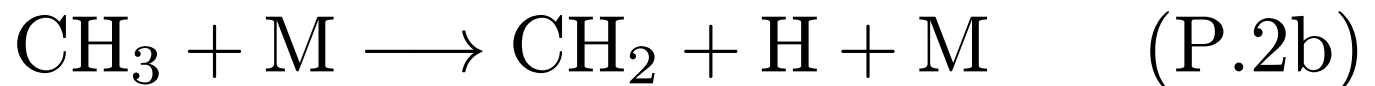


- These three processes can be further detailed as (with the example of propane, C₃H₈):

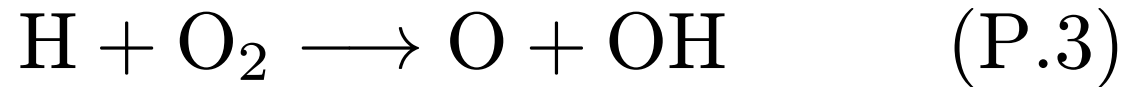
Step#1. A C-C bond is broken in the original fuel molecule. A C-C bond is weaker than an H-C bond.



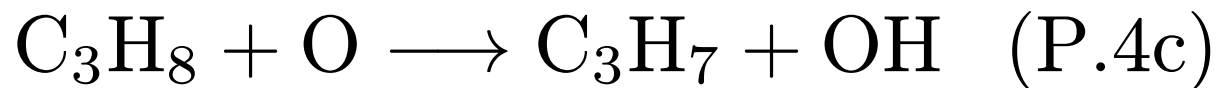
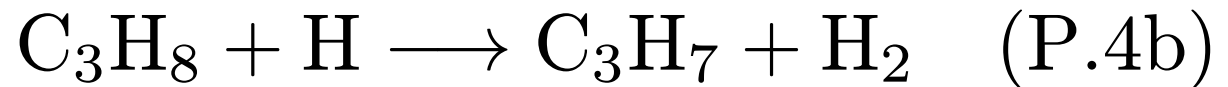
Step#2. Two resulting hydrocarbon radicals break down further to olefins: *H-atom abstraction*.



Step#3. H atoms from Step#2 starts a radical pool:



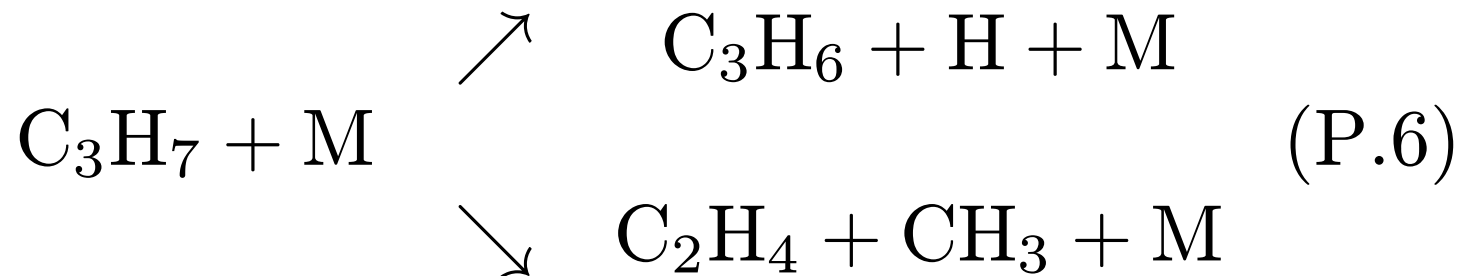
Step#4. With the development of a radical pool, attack on the fuel molecule intensifies.

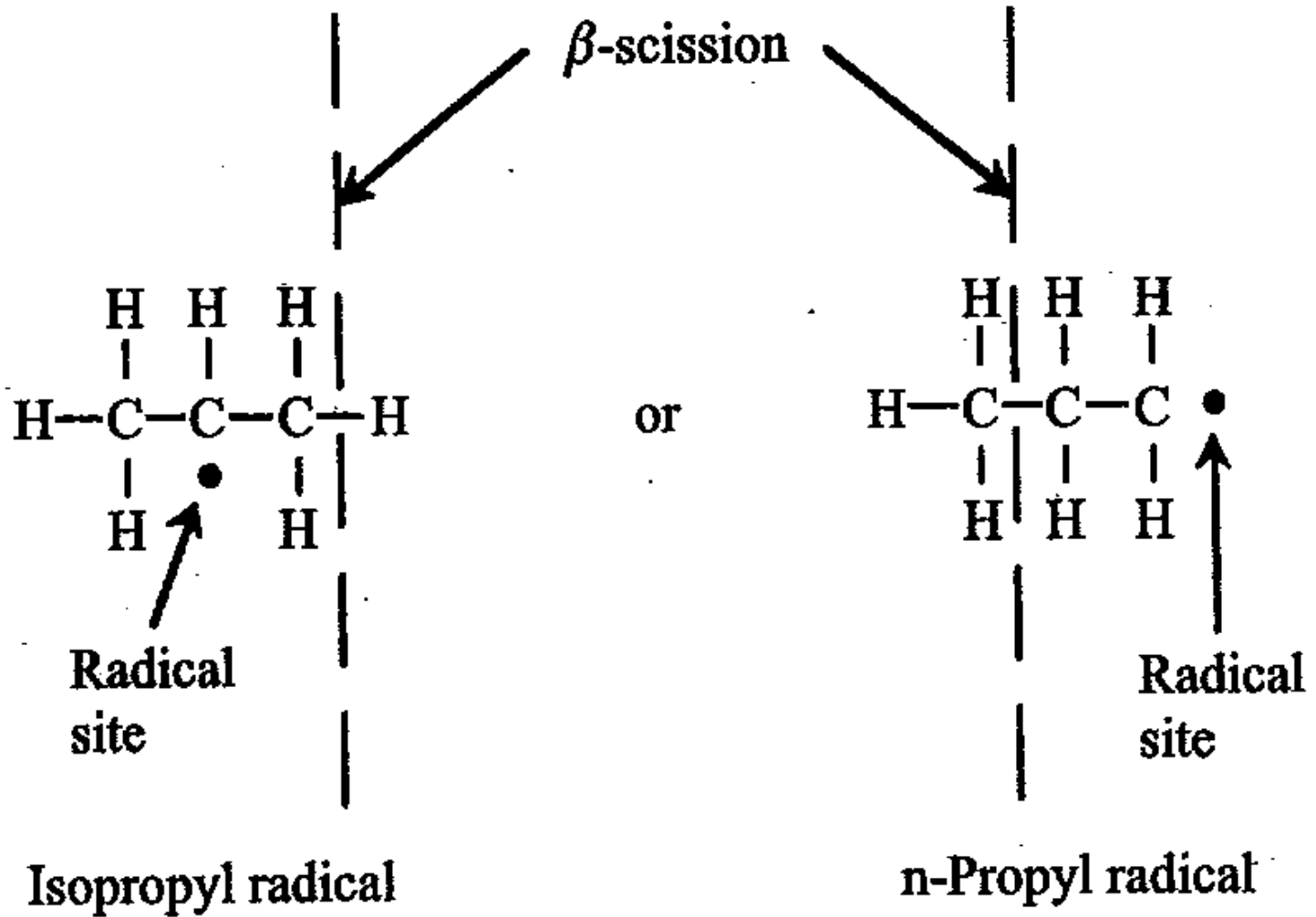


Step#5. Hydrocarbon radicals decay to olefins and H atoms via H-atom abstraction.

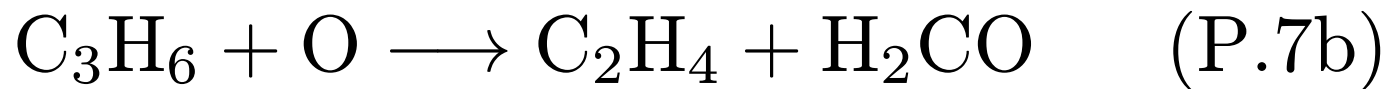


This process obeys the *β -scission rule*, which states that C-C or C-H bond broken will be the one that is one place removed from the radical site.



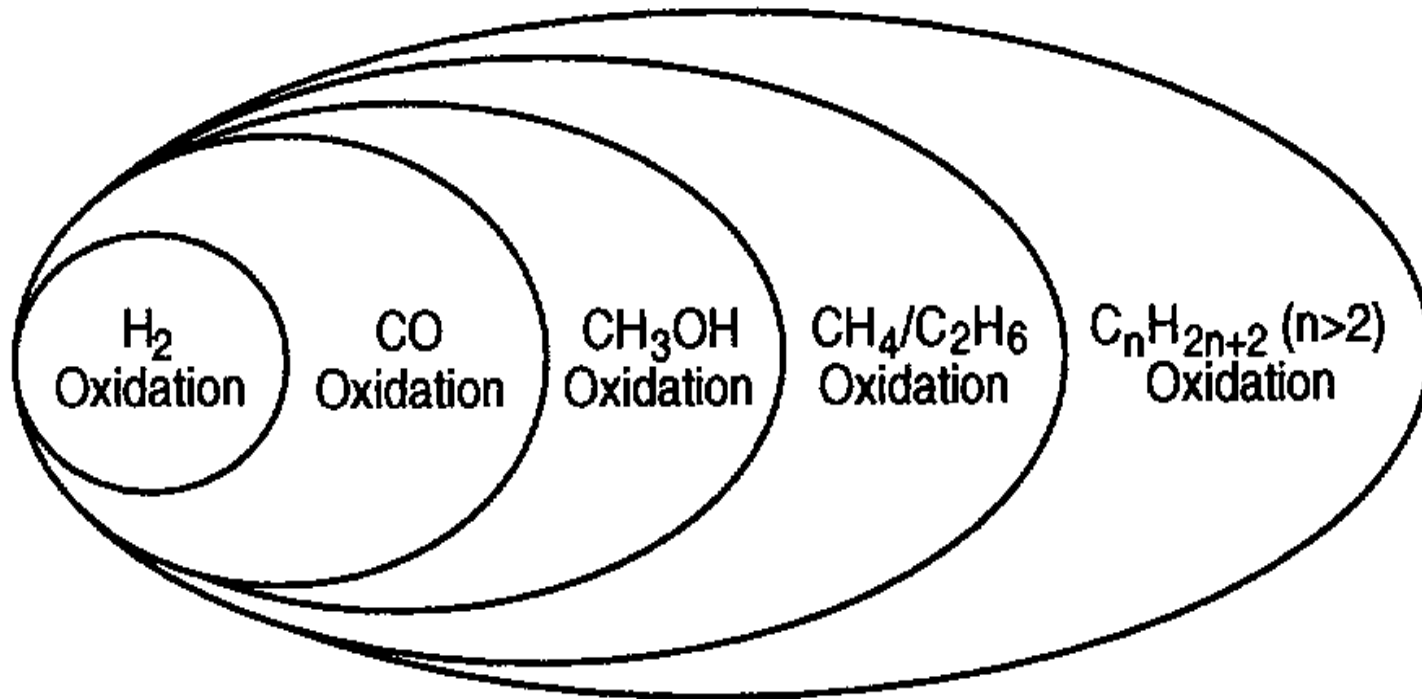


Step#6. Oxidation of olefins created in Steps#2 and 5 by O that produces formyl radicals (HCO) and formaldehyde (H₂CO).



Step#7. Methyl radicals (CH₃), formaldehyde (H₂CO), and methylene (CH₂) oxidize.

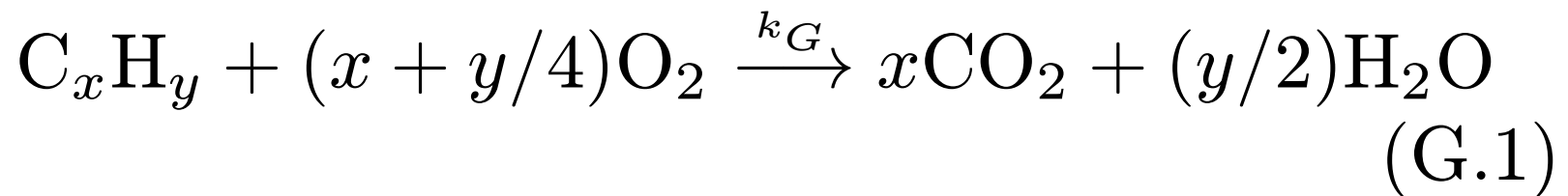
Step#8. Carbon monoxide oxidizes following the CO mechanism discussed previously.



Hierarchy in the reaction mechanism
describing alkane combustion.

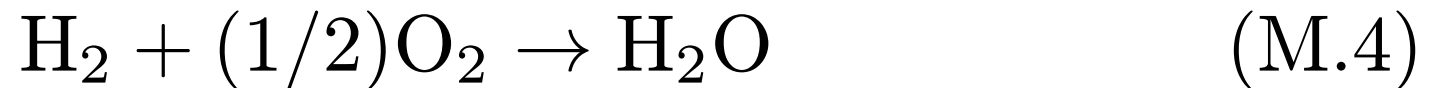
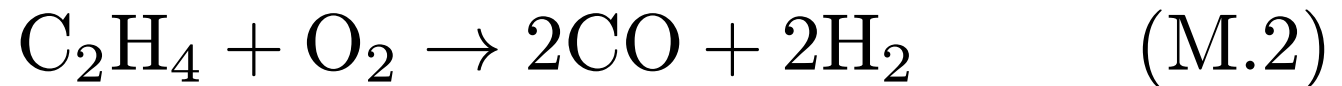
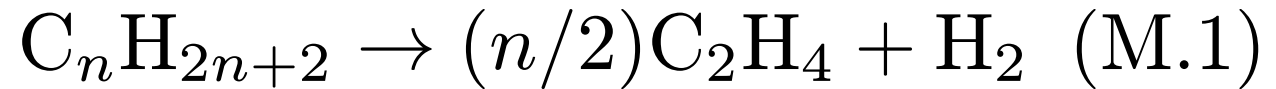
Global Mechanisms:

- Global models do not capture all the features of hydrocarbon combustion, but they may be useful in simple engineering approximations as long as their limitations are recognized.
- A single-step expression:

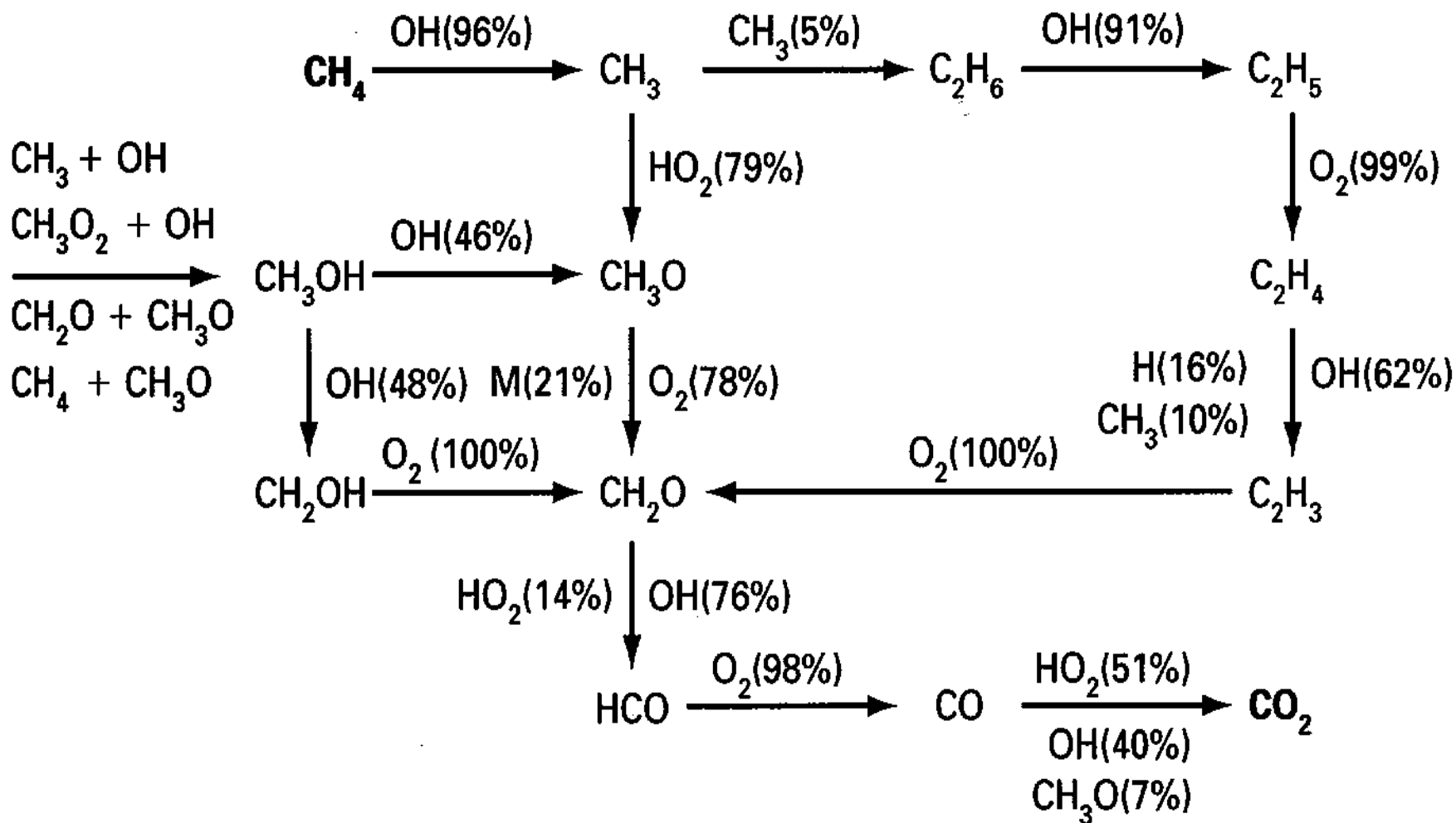


$$\frac{d[\text{C}_x\text{H}_y]}{dt} = -A \exp[-E_a/(R_u T)] [\text{C}_x\text{H}_y]^m [\text{O}_2]^n \quad (\text{G.2})$$

- A multi-step global mechanism:



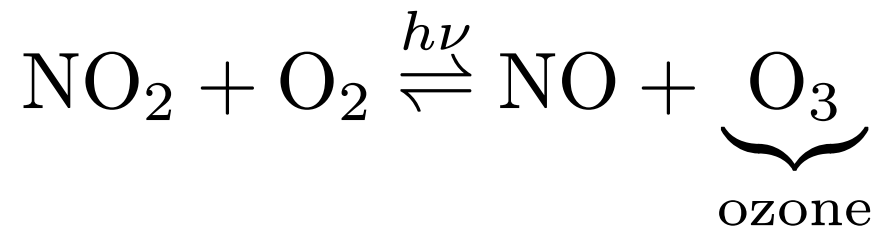
which assumes that the intermediate hydrocarbon is ethylene (C_2H_4).



Methane oxidation mechanism

Nitrogen Oxide Kinetics

- Combustion products contain NO at levels of several hundred to several thousand parts per million (ppm) and NO₂ levels in tens of ppm.
- In the atmosphere, in the presence of ultraviolet sunlight, an equilibrium is established:



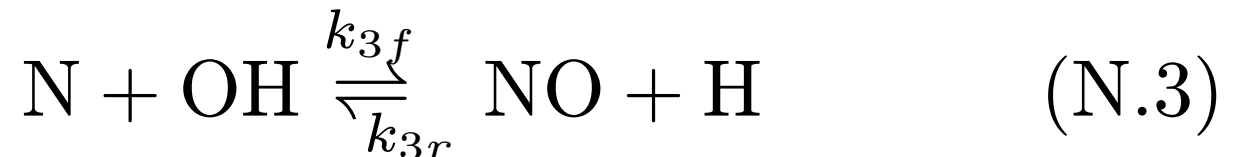
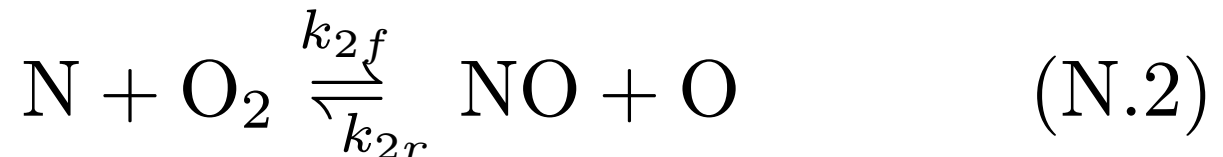
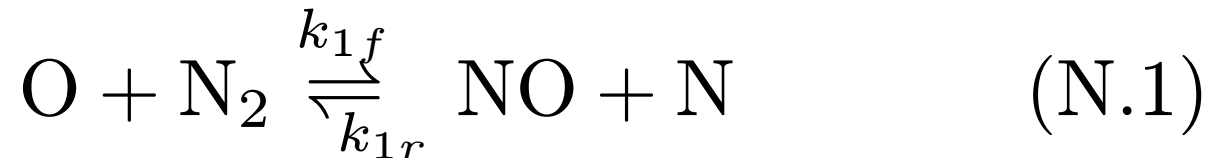
- Presence of certain hydrocarbons (e.g., unburned hydrocarbons from combustion, methane from various sources) slowly unbalances the above reaction.
- NO contributes to destruction of ozone in stratosphere.
- NO contributes to production of ground level ozone.
- NO is involved in photochemical smog and haze.

The main sources of nitrogen oxide, NO_x , emissions from combustion are:

- *Thermal* NO: oxidation of molecular nitrogen in the postflame zone.
- *Prompt* NO: formation of NO in the flame zone (*Fenimore* mechanism).
- N_2O -*intermediate* mechanism.
- *Fuel* NO: oxidation of nitrogen-containing compounds in the fuel.

Relative importance of these three are dependent on the operating conditions and fuel. In most practical combustion devices the thermal NO is the main source.

- The basic mechanism for thermal NO production is given by six reactions known as *extended Zeldovich mechanism*:



- The contribution of reaction 3 is small for lean mixtures, but for rich mixtures it should be considered. Forward reaction 1 controls the system, but it is slow at low temperatures (high activation energy). Thus it is effective in post-flame zone where temperature is high and the time is available.
- Concentrations of 1000 to 4000 ppm are typically observed in uncontrolled combustion systems.
- From reactions 1-3, the rate of formation of thermal NO can be calculated:

$$\frac{d[\text{NO}]}{dt} = k_{1f}[\text{O}][\text{N}_2] - k_{1r}[\text{NO}][\text{N}] + k_{2f}[\text{N}][\text{O}_2] - k_{2r}[\text{NO}][\text{O}] + k_{3f}[\text{N}][\text{OH}] - k_{3r}[\text{NO}][\text{H}] \quad (3.14)$$

- To calculate the NO formation rate, we need the concentrations of O, N, OH, and H.
- In detailed calculations, these are computed using detailed kinetic mechanisms for the fuel used.
- For very approximate calculations, these may be assumed to be in chemical equilibrium.

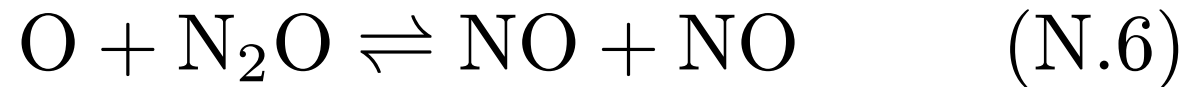
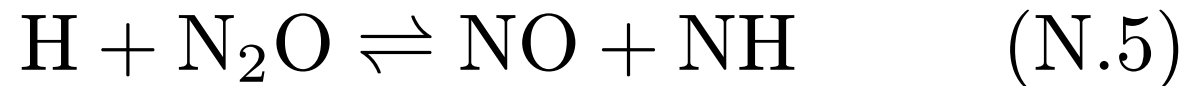
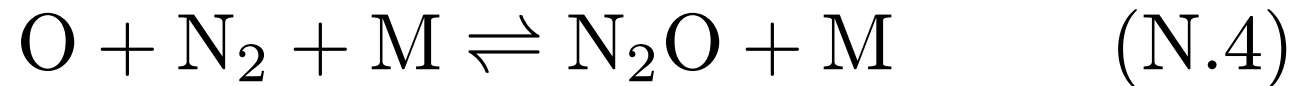
- At moderately high temperatures N does not stay at thermodynamic equilibrium. A better approximation could be to assume N to be at steady-state.
- From reactions 1-3, we have

$$\begin{aligned}
 \frac{d[\text{N}]}{dt} &= k_{1f}[\text{O}][\text{N}_2] - k_{1r}[\text{NO}][\text{N}] - k_{2f}[\text{N}][\text{O}_2] \\
 &+ k_{2r}[\text{NO}][\text{O}] - k_{3f}[\text{N}][\text{OH}] + k_{3r}[\text{NO}][\text{H}] = 0 \\
 [\text{N}]_{\text{ss}} &= \frac{k_{1f}[\text{O}][\text{N}_2] + k_{2r}[\text{NO}][\text{O}] + k_{3r}[\text{NO}][\text{H}]}{k_{1r}[\text{NO}] + k_{2f}[\text{O}_2] + k_{3f}[\text{OH}]} \quad (3.15)
 \end{aligned}$$

- The reaction rate constants, in $[\text{m}^3/\text{kmol s}]$, for 1-3 are as follows:

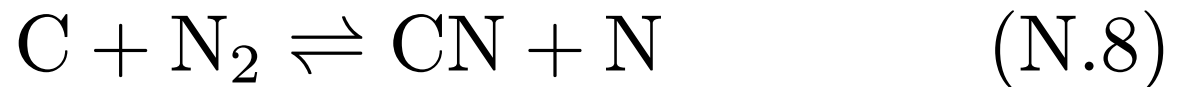
$$\begin{aligned}k_{1f} &= 1.8 \cdot 10^{11} \exp(-38,370/T) \\k_{1r} &= 3.8 \cdot 10^{10} \exp(-425/T) \\k_{2f} &= 1.8 \cdot 10^7 T \exp(-4680/T) \\k_{2r} &= 3.8 \cdot 10^6 T \exp(-20,820/T) \\k_{3f} &= 7.1 \cdot 10^{10} \exp(-450/T) \\k_{3r} &= 1.7 \cdot 10^{11} \exp(-24,560/T)\end{aligned}\tag{5.16}$$

- N_2O -*intermediate mechanism* is important in very-lean combustion ($\Phi < 0.8$). This mechanism can be represented by:

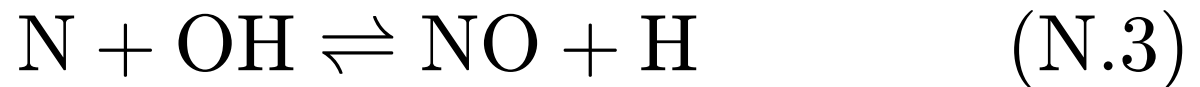
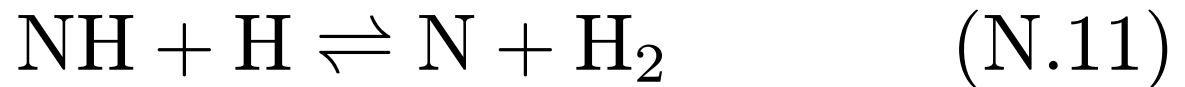
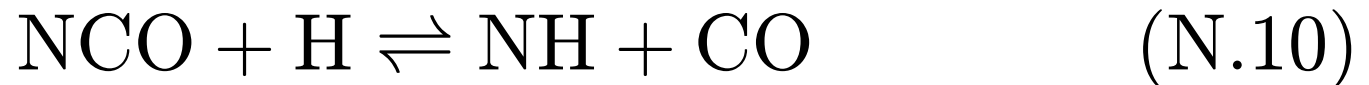


- This mechanism is important in NO control strategies in lean-premixed gas turbine combustion applications.

- It has been shown that some NO is rapidly produced in the flame zone long before there would be time to form NO by the thermal mechanism. This is also known as the *Fenimore mechanism*:
 - The general scheme is that hydrocarbon radicals form CN and HCN



- The conversion of hydrogen cyanide, HCN, to form NO is as follows



- For equivalence ratios higher than 1.2, chemistry becomes more complex and it couples with the thermal mechanism.