Aerospace Combustion

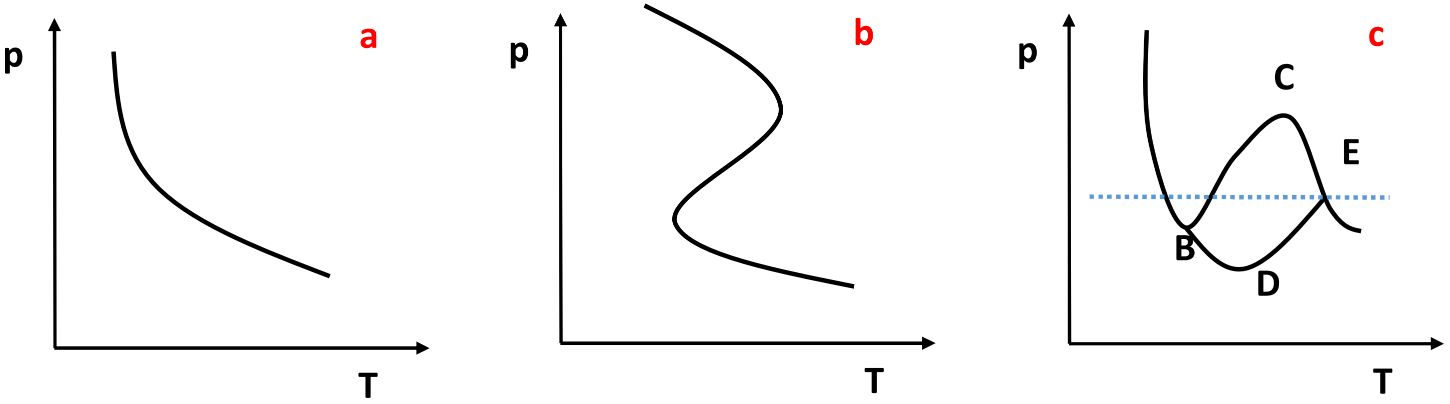
Lecture 6:

Short Introduction to Chemical Kinetics

Chemical Kinetics

How Does it Burn ?

Fuel + Oxidizer → Products + Energy



Pressure - temperature diagrams for different types of reactions:

a) Thermal feedback solely
b) Chain branching-thermal interaction typical for hydrogen oxidation
c) Chain branching-thermal interaction typical for alkane oxidation

The answer requires a detailed chemical kinetics mechanism.

Chemical Kinetics

Chemistry is Complex (even for simple molecular reactions)

Let’s look at the reaction of hydrogen and oxygen, a gas mixture which is highly explosive. It can be described with 1 global reaction.

Stoichiometric global reaction equation:

$$2\ H_2 + O_2 = 2\ H_2O$$

This chain-branching reaction is highly exothermic; but mixtures of gaseous hydrogen and oxygen are quite stable at atmospheric conditions. Any conceivable direct reaction between the two gases is zero. In fact, the reaction half time at atmospheric conditions is estimated to be larger than the age of the universe.

But, if the reaction is initiated by some free-radical species, the reaction proceeds extremely rapid and violent and in some cases even explosive.

Chemical Kinetics

Chemistry is Complex

Let’s stick to the reaction of hydrogen and oxygen $2\ H_2 + O_2 = 2\ H_2O$

Species

• Reactants	H_2, O_2
• Intermediates,	H_2O_2
• Radicals	H, O, OH, HO_2
• Products	H_2O, (Major species)

Chain Initiation Reactions (Generation of Radicals)

$$\begin{aligned} H_2 + M &\rightleftharpoons 2\,H^* + M \\ O_2 + M &\rightleftharpoons 2\,O^* + M \\ H_2 + O_2 &\rightleftharpoons 2\,OH^* \end{aligned}$$

M can either be a molecule which collides with the reactants to initiate the radical formation or an atom of a hot surface.

Chain Propagation Reactions (Generation of Radicals)

$$\left.\begin{aligned} H^* + O_2 &\rightleftharpoons OH^* + O^* \\ O^* + H_2 &\rightleftharpoons OH^* + H^* \end{aligned}\right\} \text{Branching reactions}$$

$$OH^* + H_2 \rightleftharpoons H_2O + H^* \quad \text{Extension reaction}$$

Chemical Kinetics

Chemistry is Complex

Chain Termination Reactions (Consumption of Radicals)

$2\,H^* + M \rightleftharpoons H_2 + M$
$2\,O^* + M \rightleftharpoons O_2 + M$
$H^* + OH^* + M \rightleftharpoons H_2O + M$

A well-developed mechanism describes correctly the balance between the chain extension rate and the chain termination rate.

That is provided with the complete reaction pool (particle zoo) (a generation and a consumption of components, heat release) and the correct rate constants of reactions.

H_2/O_2 Reactions

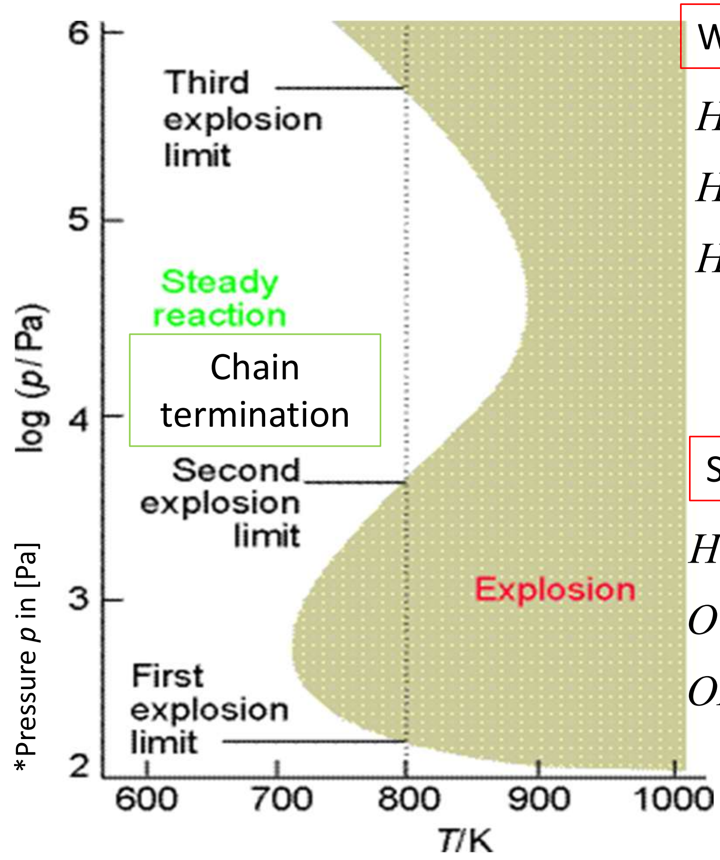
Chain Reactions
1) $H^* + O_2 \rightleftharpoons O^* + OH^*$
2) $O^* + H_2 \rightleftharpoons H^* + OH^*$
3) $OH^* + H_2 \rightleftharpoons H^* + H_2O$
4) $O^* + H_2O \rightleftharpoons OH^* + OH^*$

Dissociation/Recombination
5) $H_2 + M \rightleftharpoons 2\,H^* + M$
6) $O^* + O^* + M \rightleftharpoons O_2 + M$
7) $O^* + H^* + M \rightleftharpoons OH^* + M$
8) $H^* + OH^* + M \rightleftharpoons H_2O + M$

Formation and Consumption of HO_2^*
9) $H^* + O_2 + M \rightleftharpoons HO_2^* + M$
10) $HO_2^* + H^* \rightleftharpoons H_2 + O_2$
11) $HO_2^* + H^* \rightleftharpoons OH^* + OH^*$
12) $HO_2^* + O^* \rightleftharpoons OH^* + O_2$
13) $HO_2^* + OH^* \rightleftharpoons H_2O + O_2$

Formation and Consumption of H_2O_2
14) $HO_2^* + HO_2^* \rightleftharpoons H_2O_2 + O_2$
15) $H_2O_2 + M \rightleftharpoons OH^* + OH^* + M$
16) $H_2O_2 + H^* \rightleftharpoons H_2O + OH^*$
17) $H_2O_2 + H^* \rightleftharpoons H_2 + HO_2^*$
18) $H_2O_2 + O^* \rightleftharpoons OH^* + HO_2^*$
19) $H_2O_2 + OH^* \rightleftharpoons H_2O + HO_2^*$

H_2 – O_2 Chemistry (Homogeneous Ignition)



Weak chain branching

$$H + O_2 \xleftrightarrow{k_9} HO_2 + M$$

$$HO_2 + H_2 \xleftrightarrow{k_{17}} H_2O_2 + H$$

$$H_2O_2 + M \xleftrightarrow{k_{15}} OH + OH + M$$

Strong chain branching

$$H + O_2 \xleftrightarrow{k_1} HO_2 + M$$

$$O + H_2 \xleftrightarrow{k_2} H + OH$$

$$OH + H_2 \xleftrightarrow{k_3} H_2O + H$$

Species:
H_2, O_2, H_2O, (Major species);
H, O, OH, HO_2, H_2O_2 (Radicals)

Light Hydrocarbon Oxidation: General Scheme

In a very simplistic point-of-view, hydrocarbon combustion (related to number of C atom) can be seen as a two-step process:

a) breakdown of fuel into CO
b) oxidation of CO to CO_2.

$$RH + M \leftrightarrow X + CH_3$$

…….

$$CH_3 + O \leftrightarrow CH_2O + H$$
$$CH_2O + X \leftrightarrow CHO + XH$$
$$CHO + M \leftrightarrow H + CO + M$$
$$CHO + O_2 \leftrightarrow CO + HO_2$$
$$CHO + OH \leftrightarrow CO + H_2O$$
$$CHO + H \leftrightarrow CO + H_2$$
$$CO + OH \leftrightarrow CO_2 + H$$

Small chemistry

Chemical Kinetics

Light Hydrocarbon Oxidation: CO Oxidation

CO Oxidation is a very slow process in absence of even small amounts of H_2 or H_2O

In case of H_2O as the primary hydrogen-containing species, CO oxidation can be described by

1) $CO + O_2 \leftrightarrow CO_2 + O^*$
2) $O^* + H_2O \leftrightarrow OH^* + OH^*$
3) $\boxed{CO + OH^* \leftrightarrow CO_2 + H^*}$
4) $H^* + O_2 \leftrightarrow OH^* + O^*$

1) Is slow; not sufficient contribution to CO_2 formation, but chain initiation reaction
3) is the actual CO oxidation step; also chain propagation step producing H radicals
2) and 4) are chain-branching reactions producing OH and OH +O

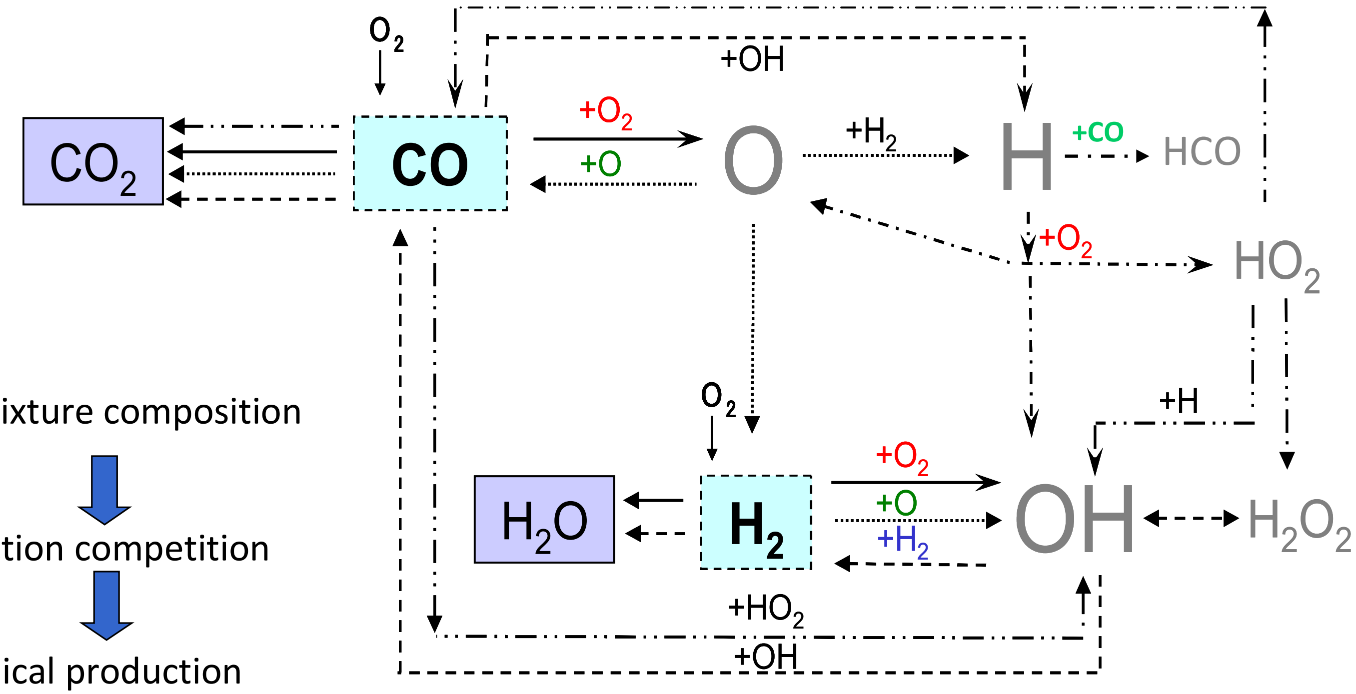
In the presence of H_2, the following reactions are involved:

5) $O^* + H_2 \leftrightarrow OH^* + H^*$
6) $OH^* + H_2 \leftrightarrow H_2O + H^*$
7) $CO + HO_2 \leftrightarrow CO_2 + OH^*$

If H_2 is present, the entire H_2-O_2 reaction system should be included to describe CO oxidation

Principle Scheme of Radical Production

H_2 + CO chemistry



P, T, ϕ, mixture composition

Reaction competition

Radical production
and distribution

Methane Combustion

Species

- Input species, reactants
- products
- intermediates
- radicals

CH_4, O_2

$CO_2, H_2O, C_2H_6, H_2,$

$CH_3O2, CH_2O, C_2H2, C_2H_4,$

$CH_3, O, H, OH, HO_2, C_2H_5,$
C_2H_3, CH_2, CH_3O

Chain-initiation

$$RH + M \leftrightarrow X + CH_3$$

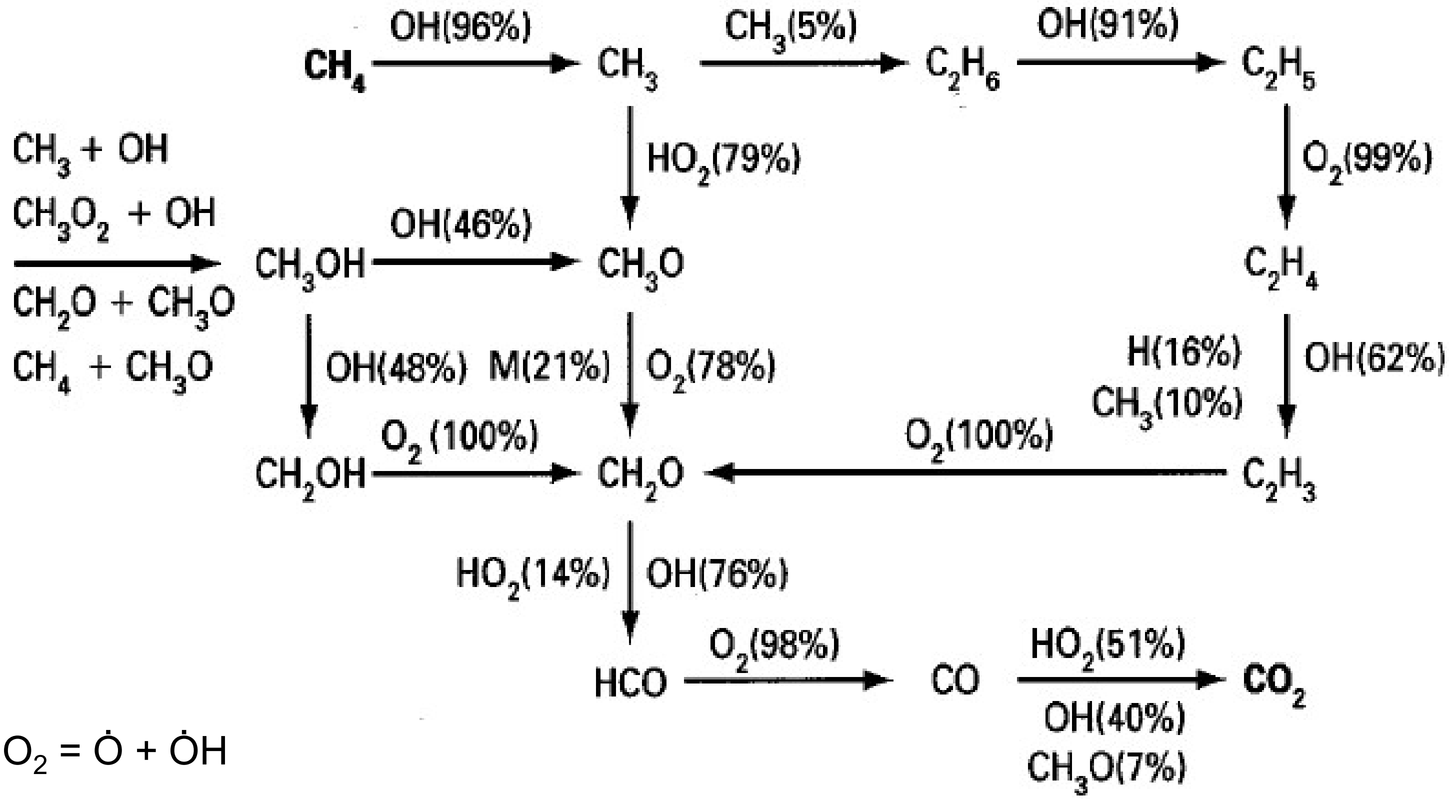
$$\ldots$$

$$
\begin{aligned}
CH_3 + O &\leftrightarrow CH_2O + \mathrm{H}\\
CH_2O + X &\leftrightarrow CHO + XH\\
CHO + M &\leftrightarrow H + CO + M\\
CHO + O_2 &\leftrightarrow CO + HO_2\\
CHO + OH &\leftrightarrow CO + H_2O\\
CHO + H &\leftrightarrow CO + H_2\\
CO + OH &\leftrightarrow CO_2 + H
\end{aligned}
$$

H_2 + CO chemistry

Chemical Kinetics

Methane Combustion

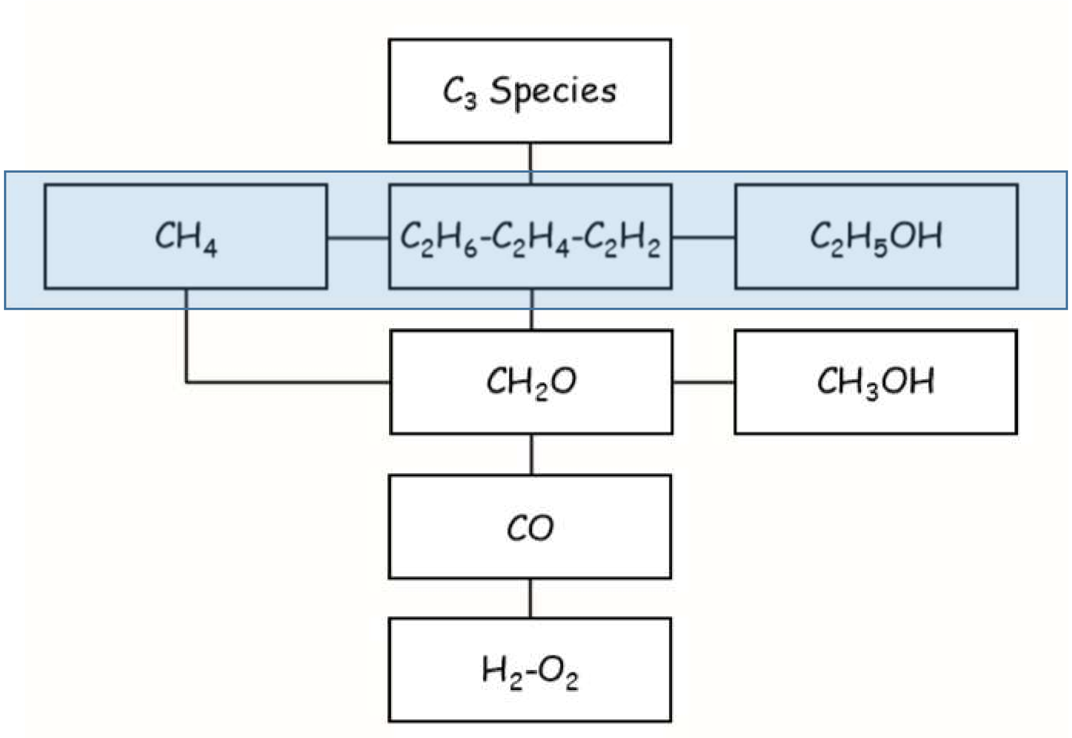


$\dot{H} + O_2 = \dot{O} + \dot{O}H$

k = 1.04×10e14 exp(–15286/RT) cm3 mol-1 s-1

Chemical Kinetics

Oxidation of Higher Alkanes

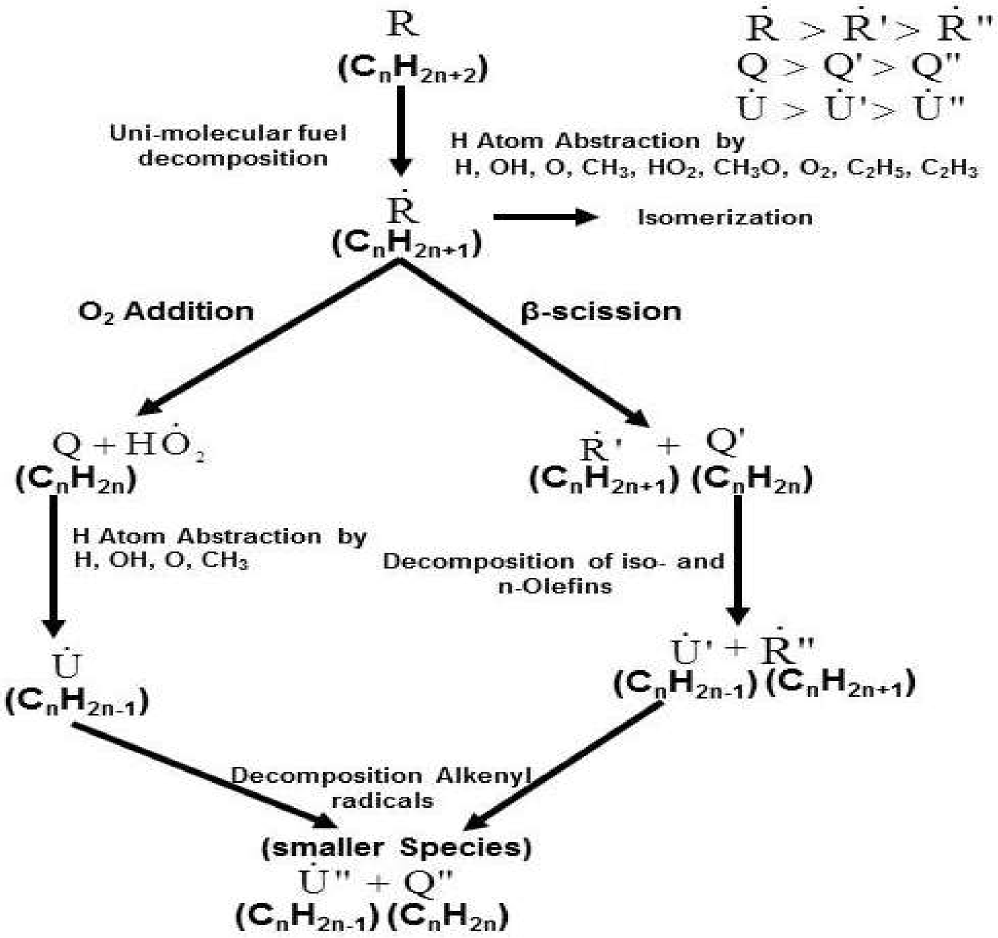


FUEL → CH_3, relatively unreactive, and C_2H_5, relatively reactive

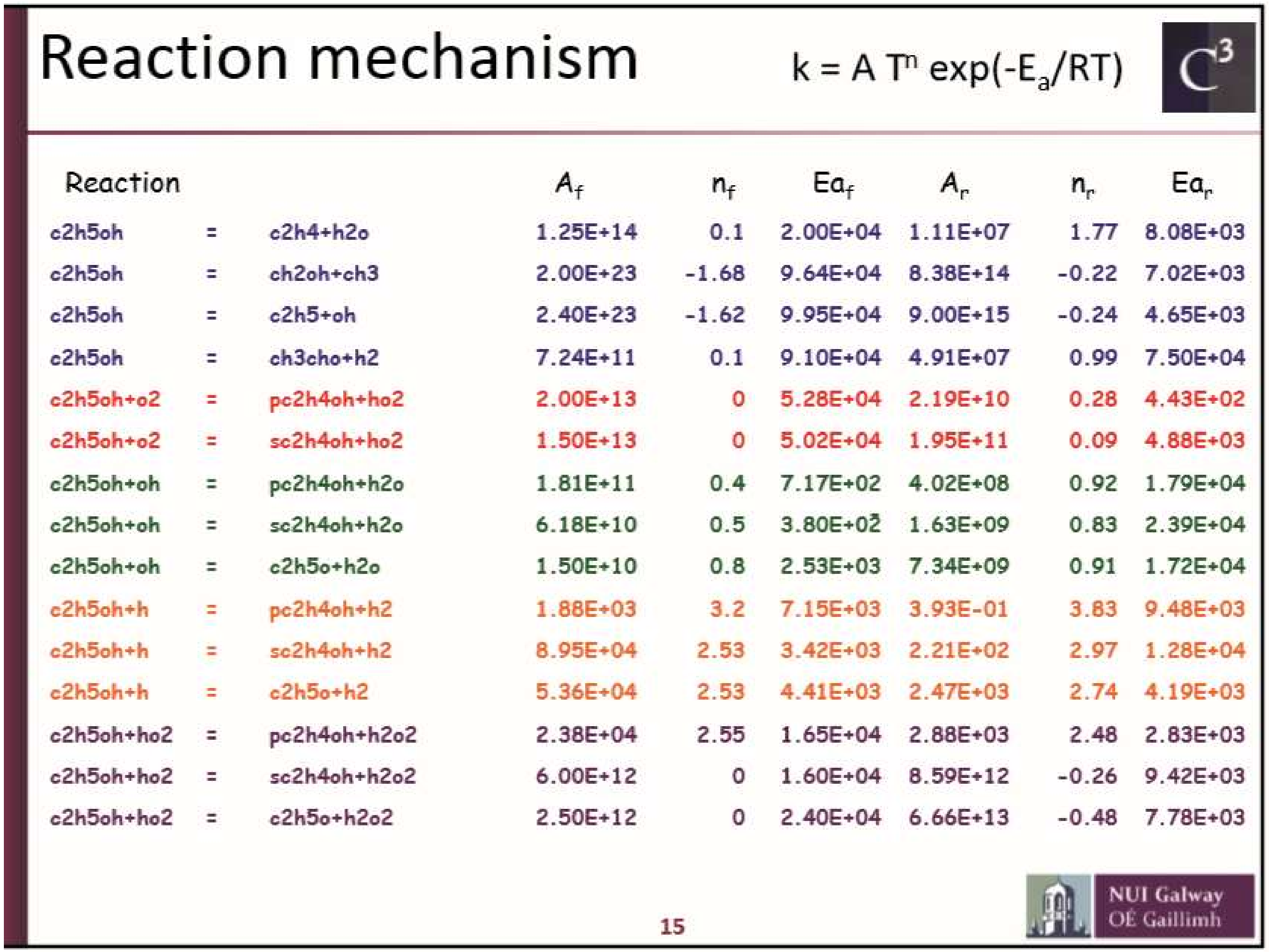
Long Alkanes Oxidation

High Temperature Route

Main Reaction Paths



Long Alkanes Oxidation



Reaction mechanism

$k = A\,T^{n} \exp(-E_a/RT)$

Reaction			A_f	n_f	Ea_f	A_r	n_r	Ea_r
c2h5oh	=	c2h4+h2o	1.25E+14	0.1	2.00E+04	1.11E+07	1.77	8.08E+03
c2h5oh	=	ch2oh+ch3	2.00E+23	-1.68	9.64E+04	8.38E+14	-0.22	7.02E+03
c2h5oh	=	c2h5+oh	2.40E+23	-1.62	9.95E+04	9.00E+15	-0.24	4.65E+03
c2h5oh	=	ch3cho+h2	7.24E+11	0.1	9.10E+04	4.91E+07	0.99	7.50E+04
c2h5oh+o2	=	pc2h4oh+ho2	2.00E+13	0	5.28E+04	2.19E+10	0.28	4.43E+02
c2h5oh+o2	=	sc2h4oh+ho2	1.50E+13	0	5.02E+04	1.95E+11	0.09	4.88E+03
c2h5oh+oh	=	pc2h4oh+h2o	1.81E+11	0.4	7.17E+02	4.02E+08	0.92	1.79E+04
c2h5oh+oh	=	sc2h4oh+h2o	6.18E+10	0.5	3.80E+02	1.63E+09	0.83	2.39E+04
c2h5oh+oh	=	c2h5o+h2o	1.50E+10	0.8	2.53E+03	7.34E+09	0.91	1.72E+04
c2h5oh+h	=	pc2h4oh+h2	1.88E+03	3.2	7.15E+03	3.93E-01	3.83	9.48E+03
c2h5oh+h	=	sc2h4oh+h2	8.95E+04	2.53	3.42E+03	2.21E+02	2.97	1.28E+04
c2h5oh+h	=	c2h5o+h2	5.36E+04	2.53	4.41E+03	2.47E+03	2.74	4.19E+03
c2h5oh+ho2	=	pc2h4oh+h2o2	2.38E+04	2.55	1.65E+04	2.88E+03	2.48	2.83E+03
c2h5oh+ho2	=	sc2h4oh+h2o2	6.00E+12	0	1.60E+04	8.59E+12	-0.26	9.42E+03
c2h5oh+ho2	=	c2h5o+h2o2	2.50E+12	0	2.40E+04	6.66E+13	-0.48	7.78E+03

NUI Galway
OÉ Gaillimh

Chemical Kinetics

Reaction Rate Coefficients

Rate of production (consumption) of species **i** in process

$$\frac{dC_i}{dt} = \sum_{j=1}^{S} R_{ij} \qquad \rightleftharpoons \qquad R_i = \sum_{j}^{S} R_{ij} = \sum_{j}^{S} \nu_{ij} w_j$$

$$w_j = \left(k_j^+ \prod_{i=1}^{N} [c_i]^{\nu_{ij}^+} - k_j^- \prod_{i=1}^{N} [c_i]^{\nu_{ij}^-} \right)$$

*- rate of reaction **j***

$$k_j(T) = A_j T^{n_j} \exp(-E_{a,j} / RT)$$

- *coefficient of rate of reaction **j,***
  Arrhenius form

Example :

$$2H_2 + O_2 \underset{k^-}{\overset{k^+}{\rightleftarrows}} 2H_2O \,, \qquad R_{H_2} = 2\left(k^+[H_2]^2[O_2] - k^-[H_2O]^2\right)$$

Chemical Kinetics

Reaction Rate Coefficients

$$\frac{d(C)}{dt} \sim k[C]^{\nu} \Rightarrow k \sim 1/\left([C]^{\nu-1}\cdot t\right)$$

$$[X] = \frac{Nmolecules/mole}{V} \Rightarrow [\,k\,] \sim \left(\frac{V}{mole}\right)^{\nu-1}\frac{1}{c}$$

One body reaction

$A \rightarrow B$ $\qquad$ $\nu = 1$ $\qquad$ $[k_I] = [t^{-1}] = [s^{-1}]$

Two bodies reaction

$A + B \rightarrow D + \cdots$ $\qquad$ $\nu = 2$ $\qquad$ $[k_{II}] = \left[\frac{cm^3}{mol \cdot s}\right]$

Three bodies reaction

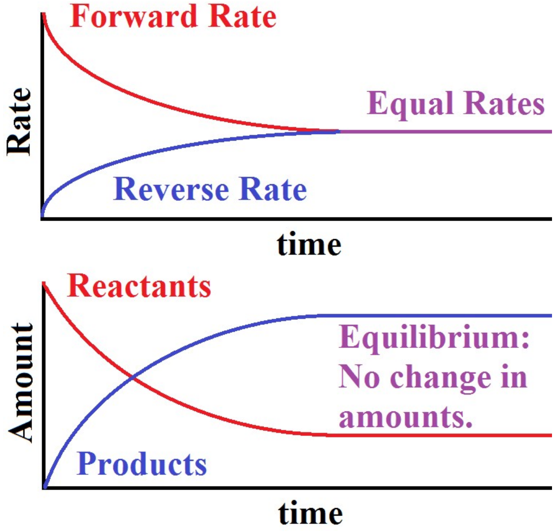
$A + B + C \rightarrow D + \cdots$ $\qquad$ $\nu = 3$ $\qquad$ $[k_{III}] = \left[\frac{cm^6}{mol^2 \cdot s}\right]$

Chemical Kinetics

Chemical Equilibrium

$$\sum_{k=1}^{K} \nu_{ki}^{+}\chi_k = \sum_{k=1}^{K} \nu_{ki}^{-}\chi_k$$

$$k_{fi}\prod_{k=1}^{K}[X_k]^{\nu'_{ki}} = k_{ri}\prod_{k=1}^{K}[X_k]^{\nu''_{ki}}$$



$$A \leftrightarrow B$$

$$K_p = \exp(-\Delta G_T^0 / RT)$$

$$\frac{k_{fi}}{k_{ri}} = \frac{\prod_{k=1}^{K}[X_k]^{\nu''_{ki}}}{\prod_{k=1}^{K}[X_k]^{\nu'_{ki}}} = K_p$$

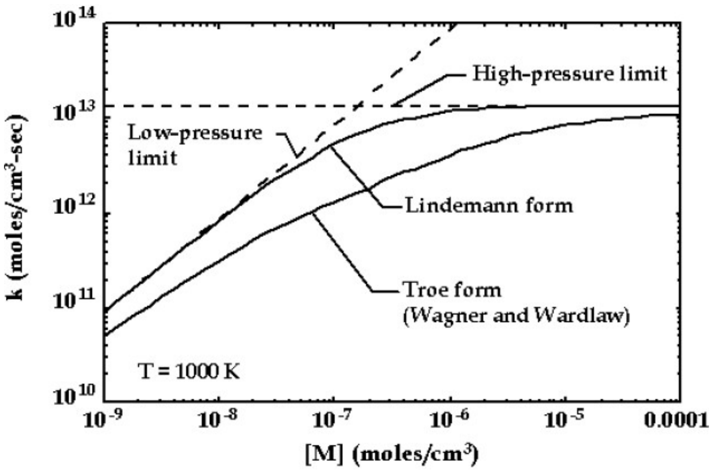
Thermodynamic Equilibrium which can be reached through chemical reactions is Chemical Equilibrium

$$\Delta G_T^0 = \Delta H^0 - T\Delta S^0$$

Chemical Kinetics

Pressure Dependent Reactions

Mono-molecular re-combination (Fall-off Reactions)
Example: Recombination reaction of methyl radicals



At high pressures we have a direct recombination reaction $CH_3 + CH_3 = C_2H_6$

At low pressures a third body collision is necessary to provide the activation energy $CH_3 + CH_3 + M = C_2H_6 + M$

Lindemann approximation
(assumes *F = 1)*

high pressure rate: $k_0 = A_0 T^{\beta_0} \exp(-E_0 / R_c T)$

low pressure rate: $k_\infty = A_\infty T^{\beta_\infty} \exp(-E_\infty / R_c T)$

any pressure: $k = k_\infty \left(\frac{p_r}{1 + p_r} \right) F; \quad p_r = \frac{k_0 [M]}{k_\infty}$

Troe approximation

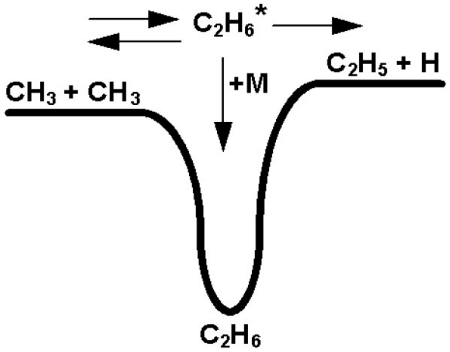
$$\log F = \left[1 + \left\{ \frac{\log p_r + c}{n - 0.14(\log p_r + c)} \right\}^2 \right]^{-1} \log F_{cent}$$

$$c = -0.4 - 0.67 \log F_{cent} \qquad n = 0.75 - 1.27 \log F_{cent}$$

$$F_{cent} = (1 - \alpha)\exp(-T / T^{***}) + \alpha \exp(-T / T^{**}) + \exp(-T^{**} / T)$$

Chemical Kinetics

Pressure Dependent Reactions



$$CH_3 + CH_3 \leftrightarrow C_2H_6{}^* \begin{cases} \rightarrow C_2H_5 + H \\ + M \rightarrow C_2H_6 \end{cases}$$

two competing reaction channels

Chemically activated bimolecular reactions with a rate coefficient described as

$$k = k_0 \left(\frac{p_r}{1 + p_r} \right) F;$$

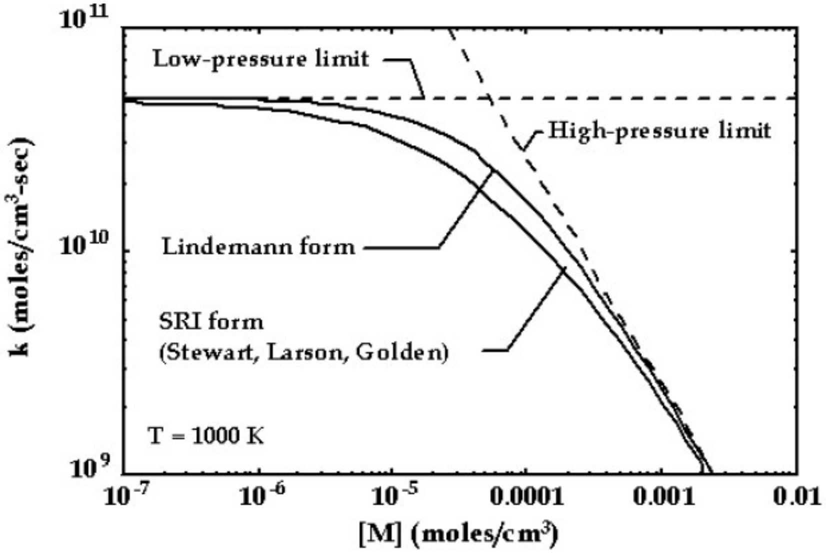
Example: Reaction of methyl radicals to form ethyl and hydrogen radicals which goes through activated ethane similarly as the previously discussed low pressure recombination reaction

With increasing pressure, deactivation collisions of activated ethane increase the rate of ethane formation while in parallel precluding dissociation to ethane and hydrogen radicals thus decrease this rate coefficient.

SRI approximation:

$$F = d \left[a \exp\left(\frac{-b}{T} \right) + \exp\left(\frac{-T}{c} \right) \right]^X T^e$$

$$X = \frac{1}{1 + (\log p_r)^2}$$



Pressure Dependent Reactions

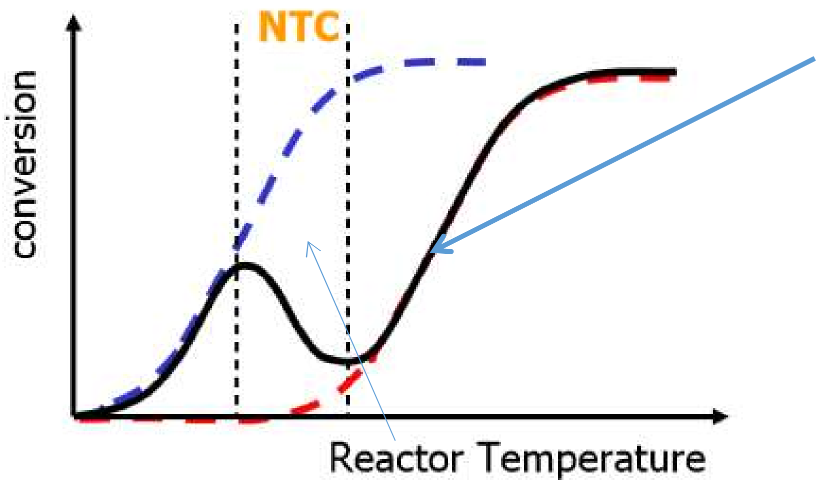
For both pressure dependent reactions, the factor F is an empirical correction coefficient which accounts for various effects of energy transfer efficiency by collisions of molecules. These include

- losses of vibrational energy due to anharmonicity of the potential,
- losses of vibrational modes for certain reactions
- energy dependency of the density of vibrational states
- rotational energies which aren’t taken into account in the simple approximation,
- reduction of this correction factor in cases where centrifugal barriers are present
- presence of internal rotors

Chemical Kinetics

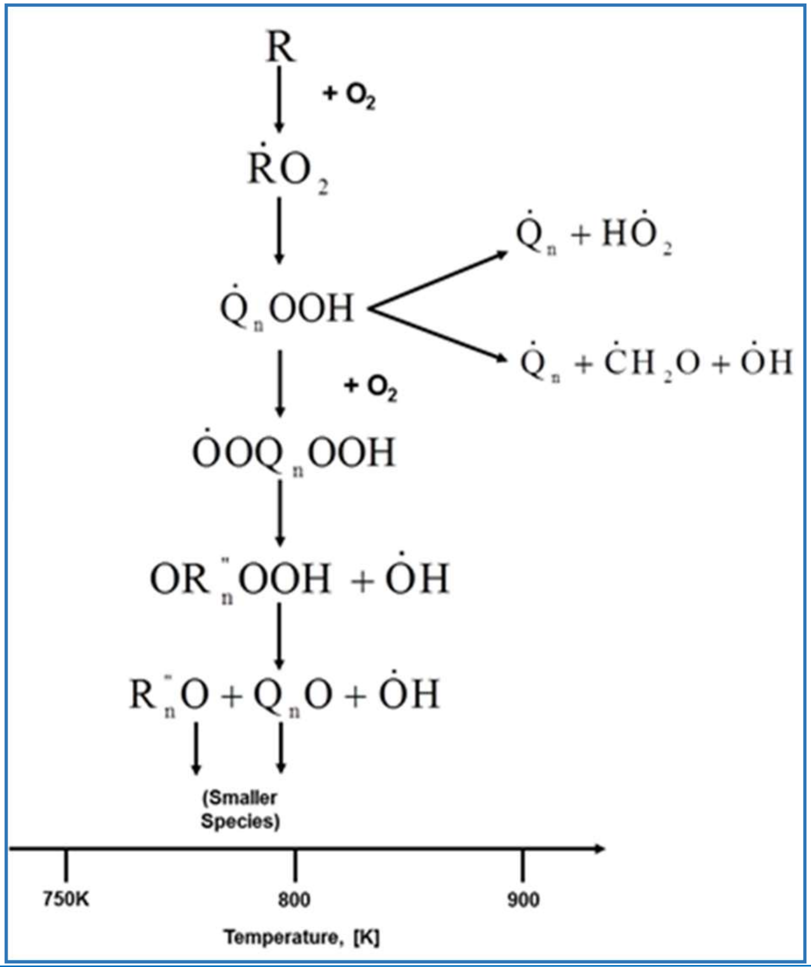
Specifics of Long Alkanes

H/C with n > 3 have negative temperature region (NTC)
(ignition delay increases with increasing temperature)



Low Temperature Oxidation

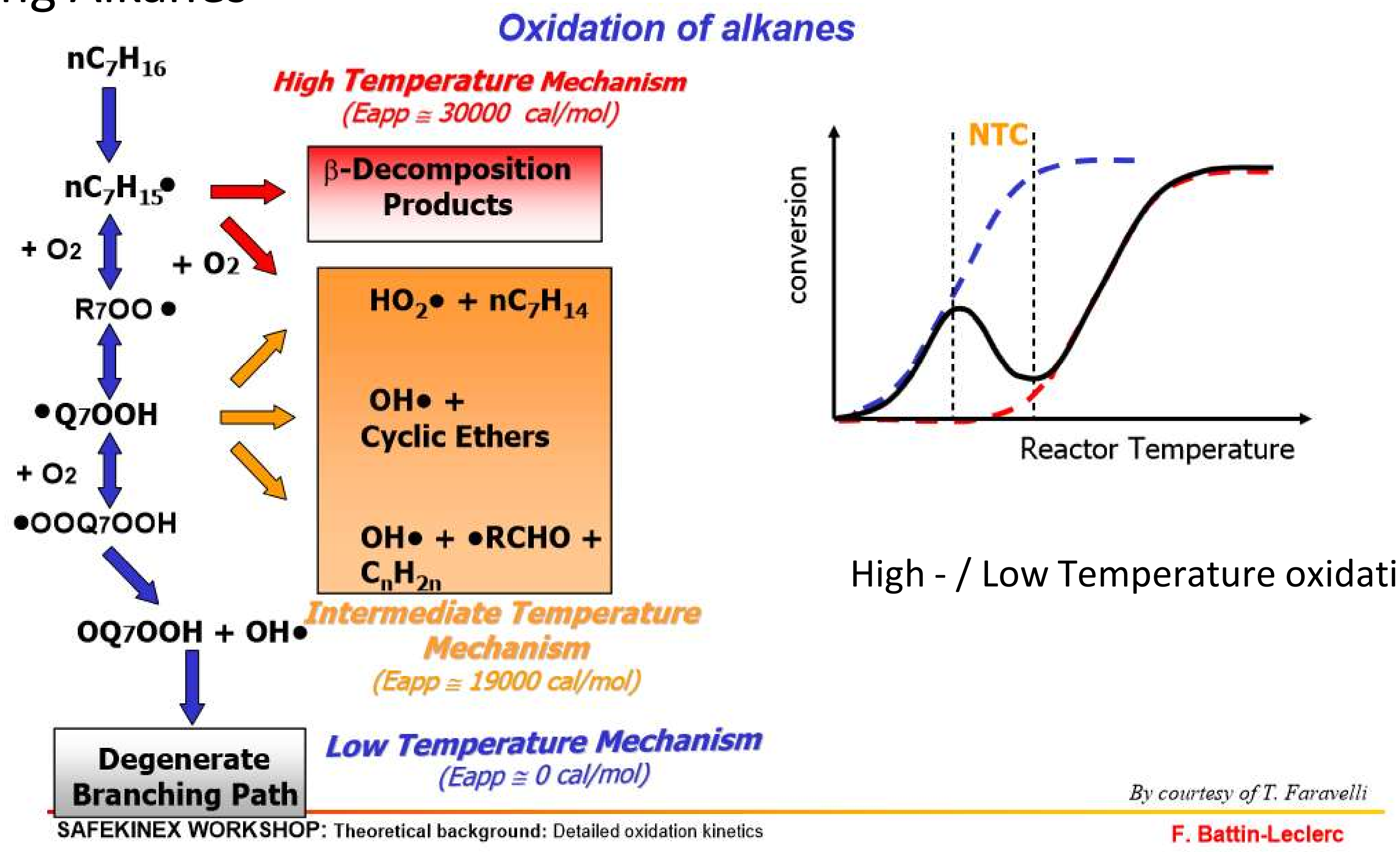
High Temperature Oxidation



Fuel Decomposition through reactions of the type 1) – 8)

Chemical Kinetics

Specifics of Long Alkanes



Oxidation of alkanes

High Temperature Mechanism
(Eapp ≅ 30000 cal/mol)

Intermediate Temperature Mechanism
(Eapp ≅ 19000 cal/mol)

Low Temperature Mechanism
(Eapp ≅ 0 cal/mol)

By courtesy of T. Faravelli

SAFEKINEX WORKSHOP: Theoretical background: Detailed oxidation kinetics

F. Battin-Leclerc

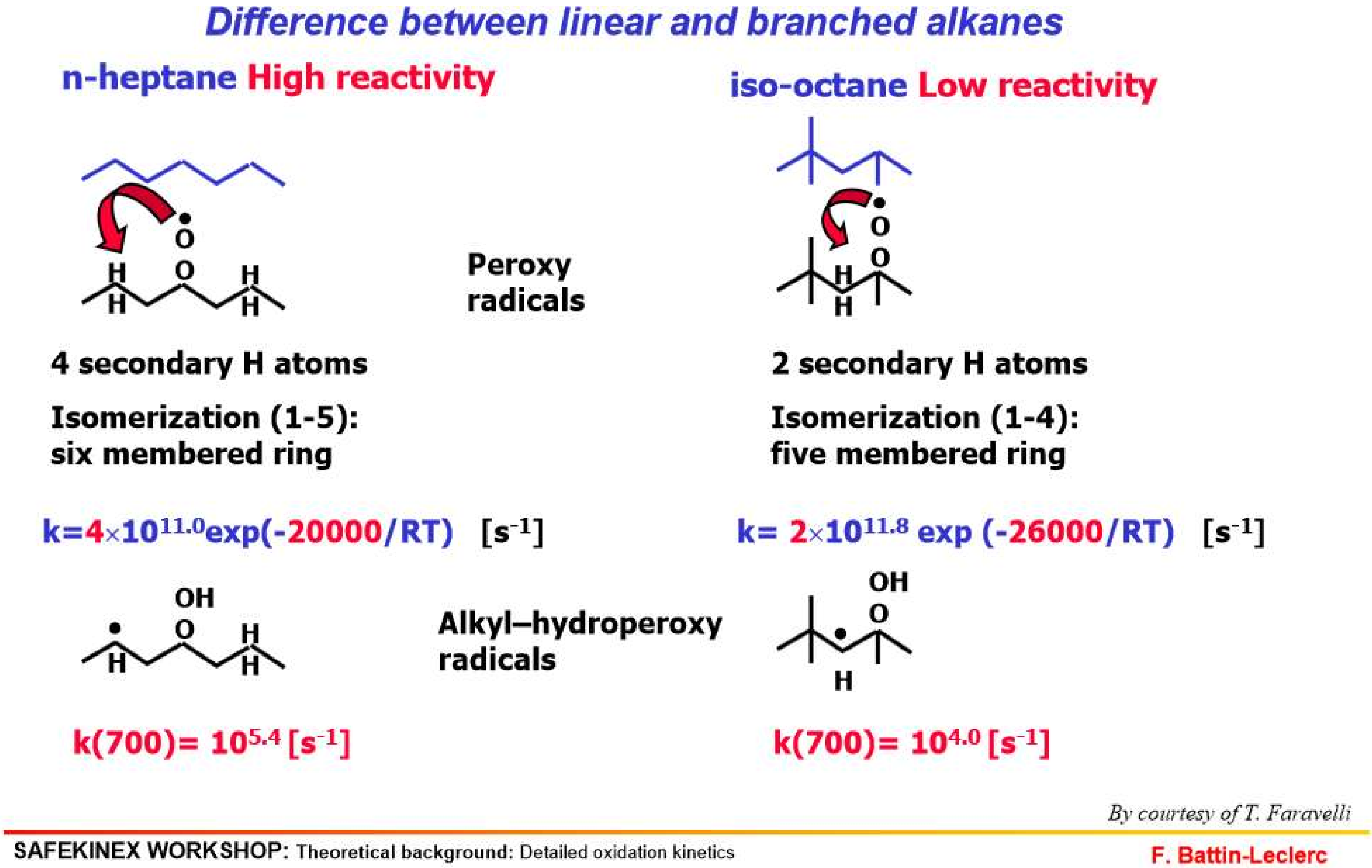
High - / Low Temperature oxidation

Chemical Kinetics

Specifics of Long Alkanes

Generally, isomers have a substantially lower reactivity (i.e. i-octane to avoid knock)

i-octane = -C8H18 = 2,2,4-trimethyl-pentane (5 carbon atoms with 2 methyl groups sitting on the 2nd C atom and a third one on the 4th .)



Difference between linear and branched alkanes

n-heptane High reactivity

iso-octane Low reactivity

Peroxy radicals

4 secondary H atoms

Isomerization (1-5): six membered ring

2 secondary H atoms

Isomerization (1-4): five membered ring

$k=4\times10^{11.0}\exp(-20000/RT)$ $[s^{-1}]$

$k= 2\times10^{11.8}\exp(-26000/RT)$ $[s^{-1}]$

Alkyl–hydroperoxy radicals

$k(700)= 10^{5.4}\,[s^{-1}]$

$k(700)= 10^{4.0}\,[s^{-1}]$

By courtesy of T. Faravelli

SAFEKINEX WORKSHOP: Theoretical background: Detailed oxidation kinetics

F. Battin-Leclerc

Chemical Kinetics

These very different reactions yield very large detailed chemical kinetic schemes which aren’t suited to be implemented in CFD tools to handle combustion problems.

As long as temperatures in the system are high enough chemical equilibrium may be assumed and then the situation can be treated such that you use a library of previously calculated equilibrium compositions depending on pressure, temperature and initial mixture composition (flamelet approach).

In case of low temperatures you normally can’t assume equilibrium anymore and you have to apply a so-called finite-rate chemistry approach and this requires a chemical mechanisms sufficiently small (typically < 20 reactions.

How do we come to reliable reduced kinetic mechanisms ?

What you should remember

- Explosive limits of H2/O2 mixtures
- General reaction mechanism (initiation, propagation and termination)
- Difference between light hydrocarbon (methane) and heavy hydrocarbon reactions
- NTC region for higher alkane combustion and its explanation
- What kind of pressure dependent reactions do you know ?
- What can you say about reaction rate and production rate at chemical equilibrium ?

Annex: Chemical Kinetics

Mechanism for Ammonium-perchlorate Decomposition

			Arrhenius parameters		
			A	b	Ea
1)	$HClO_4$	$\rightleftharpoons ClO_3^* + OH^*$	1.0 e14	0.0	39100
2)	$HClO_4 + HNO$	$\rightleftharpoons ClO_3^* + H_2O + NO^*$	1.5 e13	0.0	6000
3)	ClO_3^*	$\rightleftharpoons ClO^* + O_2$	1.7 e13	0.5	0.0
4)	$Cl2 + O_2 + M$	$\rightleftharpoons ClO_2^* + Cl^* + M^*$	6.0 e08	0.0	1200
5)	$ClO^* + NO^*$	$\rightleftharpoons Cl^* + NO_2^*$	6.78 e12	0.0	311
6)	$ClO^* + ClOH$	$\rightleftharpoons Cl_2 + HO_2^*$	1.0 e11	0,0	10000
7)	$ClOH + OH^*$	$\rightleftharpoons ClO^* + H_2O$	1.8 e13	0.0	0
8)	$HCl + OH^*$	$\rightleftharpoons Cl^* + H_2O$	5.0 e11	0.0	750
9)	$Cl2 + H^*$	$\rightleftharpoons HCl + Cl^*$	8.4 e13	0.0	1150
10)	$ClO^* + NH_3$	$\rightleftharpoons ClOH + NH_2^*$	6.0 e11	0.5	6400
11)	$NH_3 + Cl^*$	$\rightleftharpoons NH_2^* + HCl$	4.5 e11	0.5	100
12)	$NH_3 + OH^*$	$\rightleftharpoons NH_2^* + H_2O$	5.0 e07	1.6	955
13)	$NH_2^* + O_2$	$\rightleftharpoons HNO + OH^*$	3.0 e09	0.0	0
14)	$NH_2^* + NO^*$	$\rightleftharpoons H_2O + N_2$	6.2 e15	-1.3	0
15)	$HNO + OH^*$	$\rightleftharpoons NO^* + H_2O$	1.3 e07	1.9	-950
16)	$HNO + O_2$	$\rightleftharpoons NO_2^* + OH^*$	1.5 e13	0.0	10000
17)	$HNO + H^*$	$\rightleftharpoons H_2 + NO^*$	4.5 e11	0.7	660
18)	$NO^* + H^* + M$	$\rightleftharpoons HNO + M$	8.9 e19	-1.3	740
19)	$HO^*_2 + N_2$	$\rightleftharpoons HNO + OH^*$	2.7 e10	0.5	41800
20)	$NO^* + HO_2^*$	$\rightleftharpoons NO_2^* + OH^*$	2.11 e12	0.0	480
21)	$H^* + NO^*_2$	$\rightleftharpoons NO^* + OH^*$	3.47 e14	0.0	1480
22)	$H_2 + OH^*$	$\rightleftharpoons H_2O + H^*$	2.16 e08	1.5	3430

$$k = AT^b e^{-Ea/T}$$

ANNEX Chemical Kinetics

Mechanism for Ammonium-perchlorate / HTPB Reactions

1) $Cl_2 + O_2 + M \rightleftharpoons ClO_2^* + Cl^* + M$
2) $ClO^* + NO^* \rightleftharpoons Cl^* + NO^*_2$
3) $HCl + OH^* \rightleftharpoons Cl^* + H_2O$
4) $Cl2 + H^* \rightleftharpoons HCl + Cl^*$
5) $NH_3 + Cl^* \rightleftharpoons NH_2^* + HCl$
6) $NH_3 + OH^* \rightleftharpoons NH_2^* + H_2O$
7) $NH_2^* + O_2 \rightleftharpoons HNO + OH^*$
8) $NH_2^* + NO^* \rightleftharpoons H_2O + N_2$
9) $HNO + OH^* \rightleftharpoons NO^* + H_2O$
10) $HNO + O_2 \rightleftharpoons NO_2^* + OH^*$
11) $HNO + H^* \rightleftharpoons H_2 + NO^*$
12) $NO^* + H^* + M \rightleftharpoons HNO + M$
13) $HO^*_2 + N_2 \rightleftharpoons HNO + OH^*$
14) $NO^* + HO_2^* \rightleftharpoons NO_2^* + OH^*$
15) $H^* + NO^*_2 \rightleftharpoons NO^* + OH^*$
16) $H_2 + OH^* \rightleftharpoons H_2O + H^*$
17) $CH_4 + Cl^* \rightleftharpoons CH^*_3 + HCl$
18) $CH_4 + H^* \rightleftharpoons CH^*_3 + H_2$
19) $CH_4 + OH^* \rightleftharpoons CH^*_3 + H_2O$
20) $CH^*_3 + H^* + M \rightleftharpoons CH_4 + M$
21) $CO + OH^* \rightleftharpoons CO_2 + H^*$
22) $CO + ClO^* \rightleftharpoons CO_2 + Cl^*$
23) $CO + ClO^*_2 \rightleftharpoons CO_2 + ClO^*$
24) $H^* + O_2 \rightleftharpoons O^* + OH^*$
25) $CH_2^* + H_2 \rightleftharpoons CH^*_3 + H^*$
26) $CH_2^* + H^* + M \rightleftharpoons CH^*_3 + M$
27) $CH4 + O^* \rightleftharpoons CH^*_3 + OH^*$
28) $OH^+ + CH_3^* \rightleftharpoons CH^*_2 + H_2O$
29) $C_2H_4 + O2 \rightleftharpoons 2CO + 2H_2$
30) $Cl^* + HO^*_2 \rightleftharpoons ClO^* + OH^*$
31) $ClO^* + O^* \rightleftharpoons Cl^* + O_2$
32) $H^* + HCl \rightleftharpoons Cl^* + H_2$
33) $HCl + O^* \rightleftharpoons Cl^* + OH^*$
34) $Cl_2 + O^* \rightleftharpoons Cl^* + ClO^*$
35) $N_2O + M \rightleftharpoons N_2 + O^* + M$
36) $N_2O + OH^* \rightleftharpoons N_2 + HO^*_2$
37) $N_2O + O^* \rightleftharpoons 2NO^*$
38) $N_2O + O^* \rightleftharpoons N_2 + O_2$
39) $N_2O + H^* \rightleftharpoons N_2 + OH^*$
40) $2H^* + M \rightleftharpoons H_2 + M$
41) $2H^* + H_2 \rightleftharpoons 2H_2$
42) $2H^* + H_2O \rightleftharpoons H_2 + H_2O$
43) $2H^* + CO_2 \rightleftharpoons H_2 + CO_2$
44) $ClO^*_2 + NO^* \rightleftharpoons ClO^* + NO^*_2$
45) $Cl^* + ClO_2^* \rightleftharpoons 2ClO^*$
46) $ClO^* + ClO^* \rightleftharpoons Cl_2 + O_2$
47) $Cl^* + HO^*_2 \rightleftharpoons HCl + O_2$
48) $Cl^* + O_2^* + M \rightleftharpoons ClO^*_2 + M$
49) $NO^*_2 + O^* \rightleftharpoons NO^* + O_2$
50) $HNO + HNO \rightleftharpoons H_2O + N_2O$
51) $NO^*_2 + NO^*_2 \rightleftharpoons 2NO^* + O_2$
52) $Cl^* + N_2O \rightleftharpoons ClO^* + N_2$
53) $2OH^* \rightleftharpoons H_2O + O^*$
54) $NH_2^* + NO_2^* \rightleftharpoons H_2O + N_2O$
55) $HNO + NH_2^* \rightleftharpoons NH_3 + NO^*$
56) $ClO^* + HNO \rightleftharpoons HCl + NO^*_2$
57) $HCl + HO_2 \rightleftharpoons ClO^* + H_2O$
58) $NH_2^* + NO^* \rightleftharpoons H^* + N_2 + OH^*$
59) $NH_2^* + NH_2^* \rightleftharpoons NH^* + NH_3$
60) $NH^* + NO^* \rightleftharpoons N_2 + OH^*$
61) $NH^* + NO^* \rightleftharpoons H^* + N_2 + O^*$
62) $Cl^* + NH_2^* \rightleftharpoons HCl + NH^*$
63) $ClO_2^* + NH^* \rightleftharpoons ClO^* + HNO$
64) $N^* + NO_2^* \rightleftharpoons 2NO^*$
65) $N^* + N_2O \rightleftharpoons N_2 + NO$
66) $NH^* + OH^* \rightleftharpoons H_2O + N^*$
67) $NH^* + OH^* \rightleftharpoons H_2 + NO^*$
68) $NH^* + NH_2 \rightleftharpoons N^* + NH_3$
69) $HO_2^* + CH_3^* \rightleftharpoons O_2 + CH_4$
70) $CH_2 + CH_4 \rightleftharpoons 2CH_3^*$