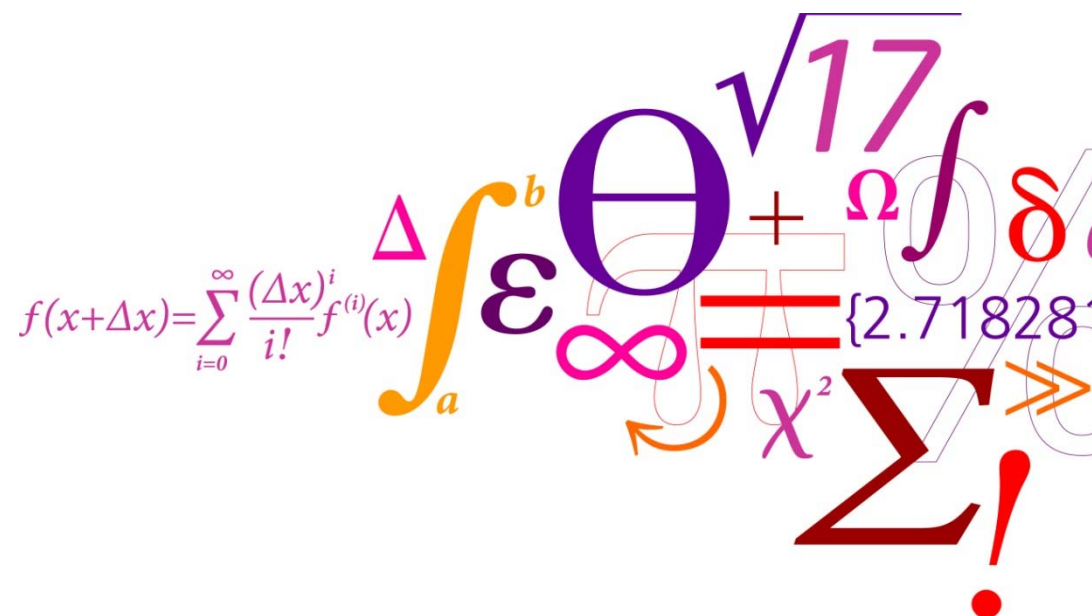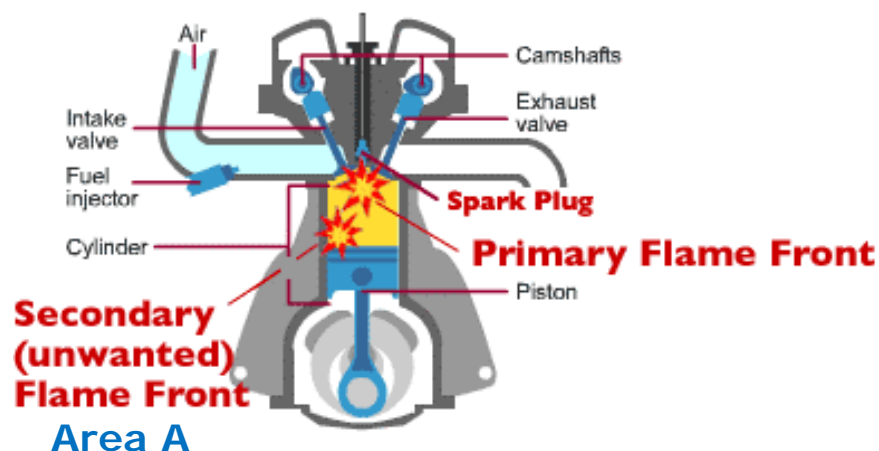# Chemical kinetics
Procida June 2015

Module 2

Module 2

- Reaction mechanisms (PG)
  - Understanding complex gas-phase reactions
  - Developing detailed chemical kinetic models
- Task 1: Oxidation of aromatic compounds
  - Introduction (AC)
  - Solving using OpenSMOKE++ (AC, PG)

Case: engine knock

Air
Camshafts
Intake valve
Exhaust valve
Fuel injector
Spark Plug
Cylinder
Primary Flame Front
Piston
Secondary (unwanted) Flame Front
Area A

Knock:

The gas in A ignites before the primary flame front arrives

- How fast does the gas in A ignite?
  - Composition
  - Temperature
  - Pressure
- How can we prevent knock?

Stable molecules and chain carriers

Hydrogen (H_2):
- Stable molecule
- Comparatively unreactive
- Can be stored in a box

Covalent bond in H_2
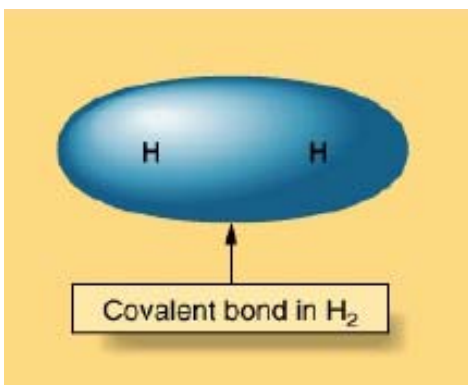
Hydrogen atom (H):
- Radical (unpaired electrons)
- Reactive
- Cannot be stored

Separated H atoms
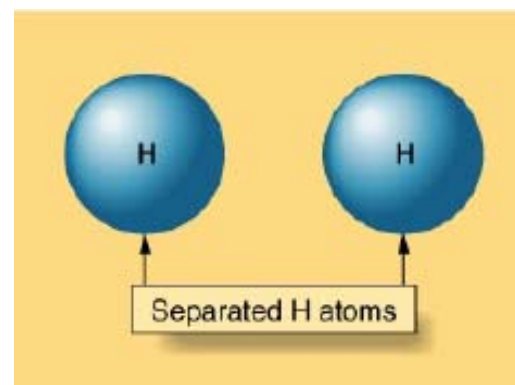
Chain carrier

Gas-phase processes

- Initiation
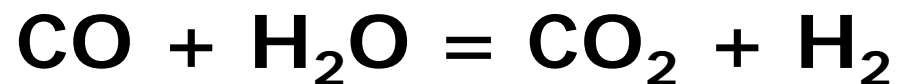 - Formation of the initial radicals

- Propagation / branching
  - Reactions preserving or increasing the number of radicals

- Termination
  - Reactions that act as a radical sink

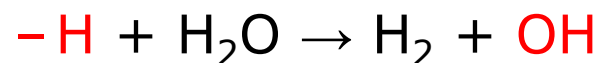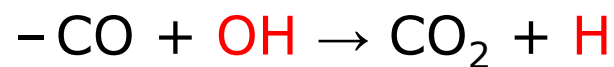# The water-gas shift reaction
$CO + H_2O = CO_2 + H_2$

- Initiation
  - $H_2O + O_2$ (trace) $\rightarrow$ OH + HO$_2$
- Propagation
  - $CO + OH \rightarrow CO_2 + H$
  - $H + H_2O \rightarrow H_2 + OH$
- Termination
  - $OH \rightarrow$ inert

Moist CO oxidation
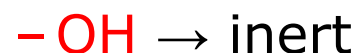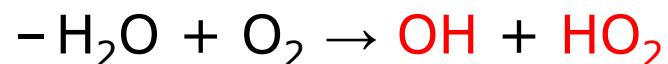
- Initiation
  - $H_2O + O_2 \rightarrow OH + HO_2$
- Propagation / branching
  - $CO + OH \rightarrow CO_2 + H$ (propagating)
  - $H + O_2 \rightarrow O + OH$ (branching)
  - $O + H_2O \rightarrow OH + OH$ (branching)
- Termination
  - $OH \rightarrow$ inert
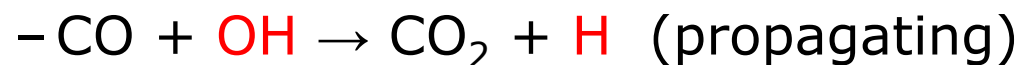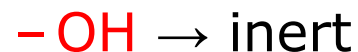
Case

Thought experiment
(Glassman, 1987)

Reactor of 1 cm^3
10^{19} molecules A
1 chain carrier R
10^8 collisions/sec

Question:
How long does it take
to consume all A molecules?

The importance of chain carriers
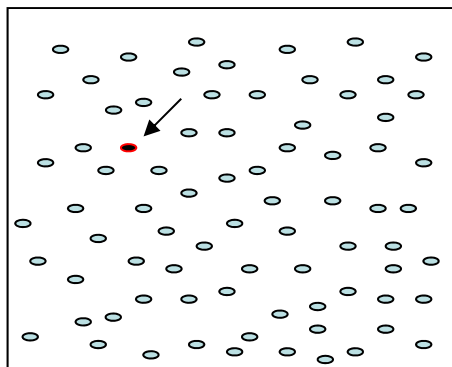
Thought experiment
(Glassman, 1987)

Reactor of 1 cm^3
10^{19} molecules A
1 chain carrier R
10^8 collisions/sec

Straight chain reaction:
A + R $\rightarrow$ B + R
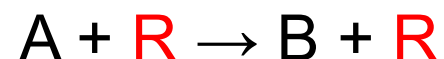
Consumption time:
t_{cons} ~ 30 years

The importance of chain carriers
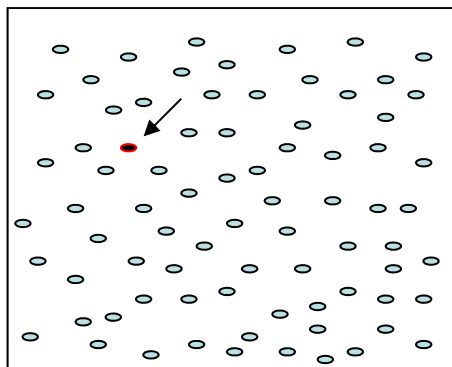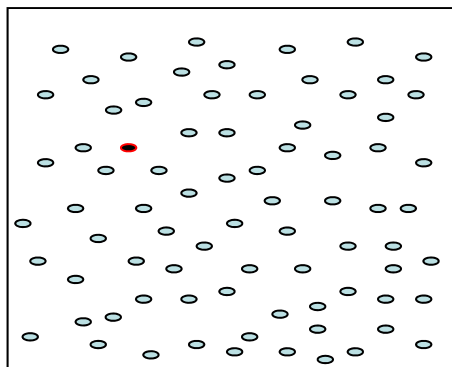
Thought experiment
(Glassman, 1987)

Reactor of 1 cm^3
10^{19} molecules A
1 chain carrier R
10^8 collisions/sec

Straight chain reaction:
A + R → B + R
Consumption time:
t_{cons} ~ 30 years

Chain-branching reaction:
A + R → B + R ⎫
     ...   } 99 steps
A + R → B + R ⎭
A + R → B + R + R
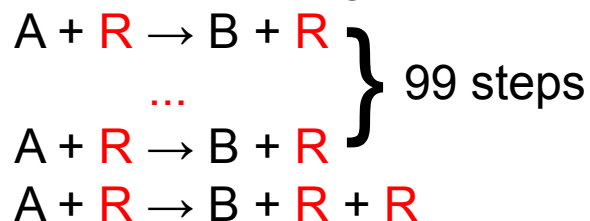
Consumption time:
t_{cons} ~ 50 μsec

The H$_2$ - O$_2$ system
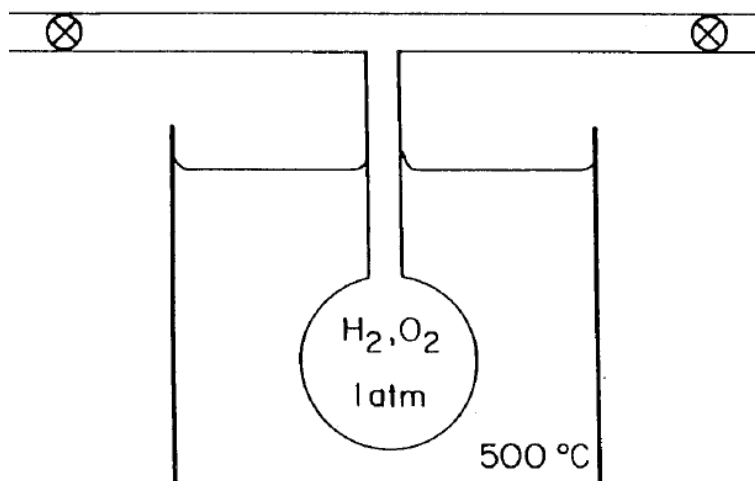
What happens?

- Initiation
  - H$_2$ + O$_2$ → H + HO$_2$
- Branching
  - H + O$_2$ → O + OH
  - O + H$_2$O → OH + OH
  - OH + H$_2$ → H$_2$O + H
- Termination
  - H → inert (wall)
  - H + O$_2$ + M → HO$_2$ + M
    HO$_2$ → inert (wall)
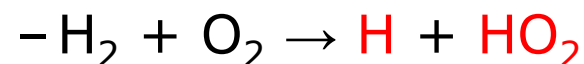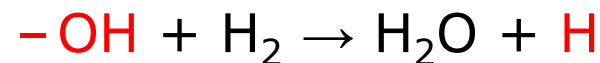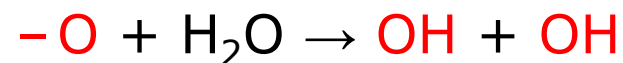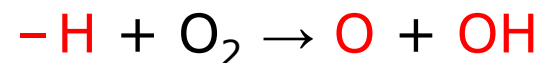
H$_2$ - O$_2$ explosion limits
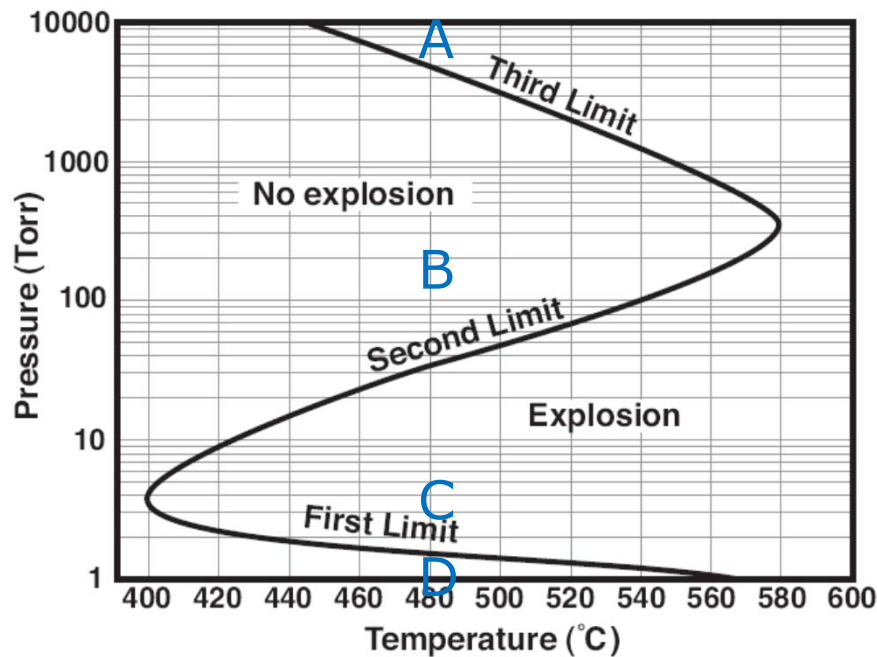
- A (no explosion)
  - H → inert (wall)
- B (explosion)
  - H + O$_2$ → O + OH
- C (no explosion)
  - H + O$_2$ + M → HO$_2$ + M
    HO$_2$ → inert (wall)
- D (explosion)
  - HO$_2$ + H$_2$ → H + H$_2$O$_2$
    (thermal explosion)

The hydrogen-oxygen reaction mechanism

no.	reaction	A	β	E_a
1	$O + OH \rightleftharpoons H + O_2$	2.0×10^{14}	-0.40	0
2	$O + H_2 \rightleftharpoons H + OH$	5.0×10^4	2.67	6 290
3	$OH + H_2 \rightleftharpoons H_2O + H$	2.1×10^8	1.52	3 450
4	$OH + OH \rightleftharpoons H_2O + O$	4.3×10^3	2.70	$-2 486$
5	$H + H + M \rightleftharpoons H_2 + M$	1.0×10^{18}	-1.00	0
	enhanced third-body efficiencies: $H_2O = 0$			
6	$H + H + H_2O \rightleftharpoons H_2 + H_2O$	6.0×10^{19}	-1.25	0
7	$H + O + M \rightleftharpoons OH + M$	6.2×10^{16}	-0.60	0
	enhanced third-body efficiencies: $H_2O = 5$			
8	$H + OH + M \rightleftharpoons H_2O + M$	1.6×10^{22}	-2.00	0
	enhanced third-body efficiencies: $H_2O = 5$			
9	$O + O + M \rightleftharpoons O_2 + M$	1.9×10^{13}	0.00	$-1 788$
	enhanced third-body efficiencies: $H_2O = 5$			
10	$H + O_2 + M \rightleftharpoons HO_2 + M$	2.1×10^{18}	-1.00	0
	enhanced third-body efficiencies: $N_2 = 0$, $H_2O = 10$			
11	$H + O_2 + N_2 \rightleftharpoons HO_2 + N_2$	6.7×10^{19}	-1.42	0
12	$HO_2 + H \rightleftharpoons H_2 + O_2$	4.3×10^{13}	0.00	1 411
13	$HO_2 + H \rightleftharpoons OH + OH$	1.7×10^{14}	0.00	875
14	$HO_2 + H \rightleftharpoons O + H_2O$	3.0×10^{13}	0.00	1 721
15	$HO_2 + O \rightleftharpoons OH + O_2$	3.3×10^{13}	0.00	0
16	$HO_2 + OH \rightleftharpoons H_2O + O_2$	1.9×10^{16}	-1.00	0
17	$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$	1.3×10^{11}	0.00	$-1 630$
	$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$	4.2×10^{14}	0.00	11 980
18	$H_2O_2 + M \rightleftharpoons OH + OH + M$	1.3×10^{17}	0.00	45 500
	enhanced third-body efficiencies: $H_2O = 5$			
19	$H_2O_2 + H \rightleftharpoons HO_2 + H_2$	1.7×10^{12}	0.00	3 755
20	$H_2O_2 + H \rightleftharpoons H_2O + OH$	1.0×10^{13}	0.00	3 576
21	$H_2O_2 + O \rightleftharpoons HO_2 + OH$	6.6×10^{11}	0.00	3 974
22	$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	7.8×10^{12}	0.00	1 330

$$k = A\, T^\beta \exp(-E_a/RT)$$

Hydrogen-air ignition
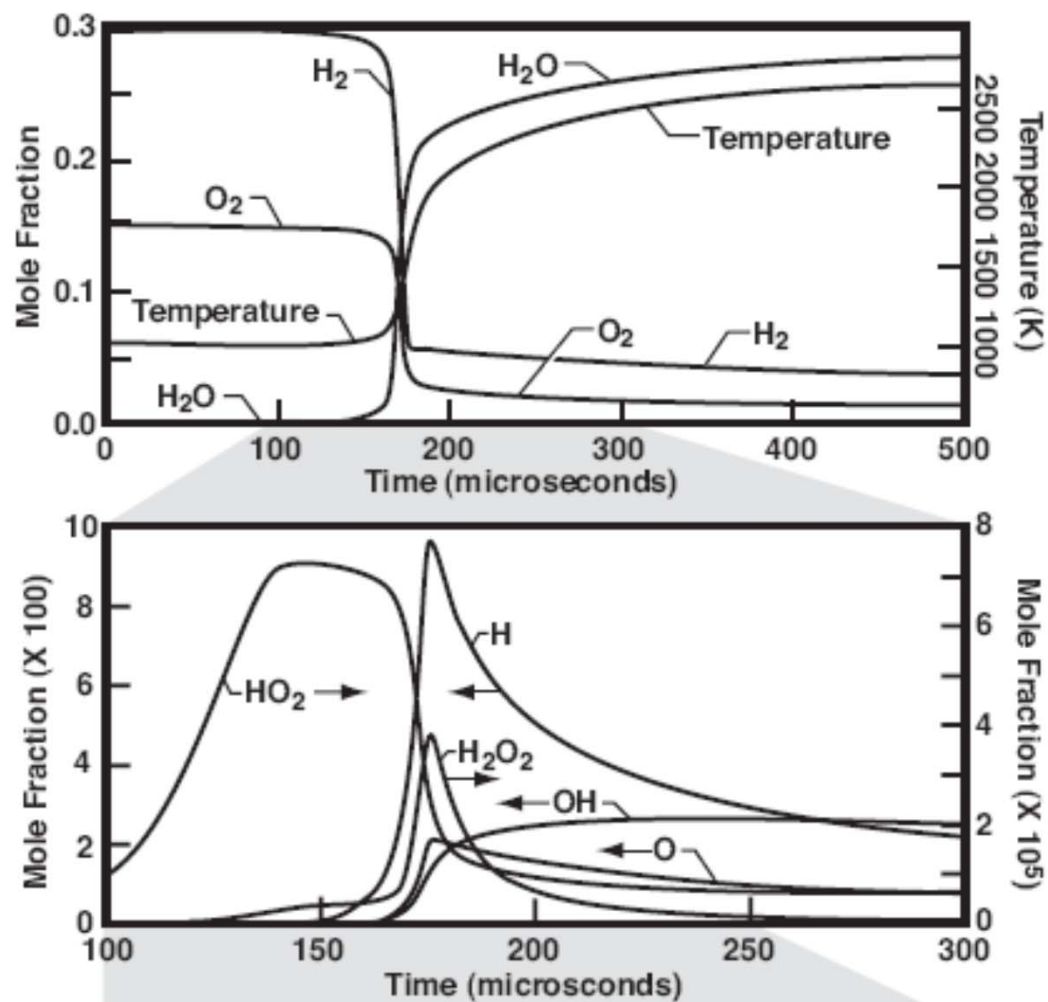
Thermal NO formation

- Mechanism for $[NO] \approx 0$:

$$O + N_2 \rightarrow NO + N \quad (1)$$
$$N + O_2 \rightarrow NO + O \quad (2)$$

- Formation rate of NO:

$$d[NO]/dt = k_1[O][N_2] + k_2[N][O_2]$$

- Steady-state assumption for N:

$$d[N]/dt = k_1[O][N_2] - k_2[N][O_2] = 0 \Leftrightarrow$$
$$[N]_{ss} = k_1[O][N_2] / k_2[O_2]$$

- Partial equilibrium assumption for $O_2 + M = O + O + M \quad (3)$:

$$K_{c,3} = [O]^2/[O_2] \Leftrightarrow [O]_{pe} = (K_{c,3}[O_2])^{1/2}$$

- Resulting expression:

$$d[NO]/dt = 2k_1 (K_{c,3}[O_2])^{1/2}[N_2]$$
$$= 1.3E15\exp(-67500/T) [O_2]^{1/2}[N_2]$$

Steady-state approximation

If B is consumed rapidly, then

rate of formation = rate of consumption

$$\frac{d[\mathrm{B}]}{d\mathrm{t}} = 0$$

Example: radicals like H, O, OH

Partial equilibrium assumption

If a reaction is rapid in both the forward and reverse direction,

it can be assumed in partial equilibrium:

$$A + B = C + D$$

Example: $OH + H_2 = H_2O + H$
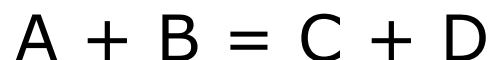
Formation of Thermal NO
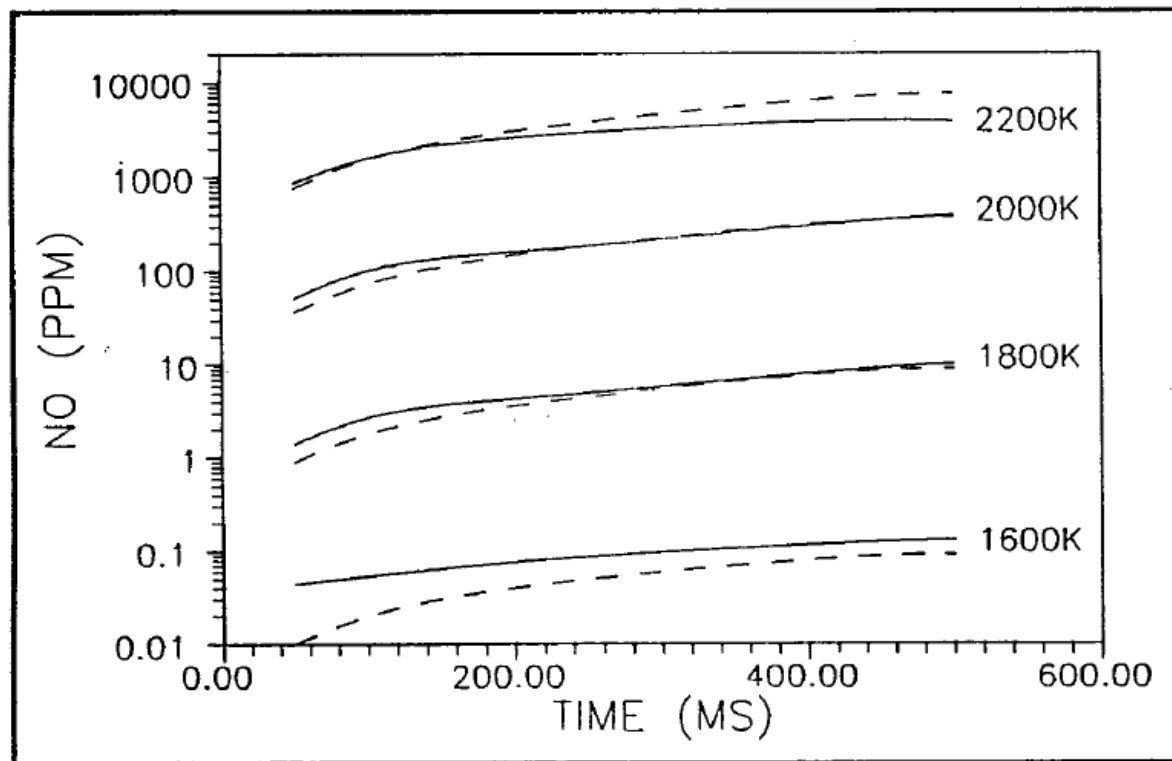
Solid lines: full model

Dashed lines: global model

$$[NO] = 1.3 \cdot 10^{15} \times \exp(-67650/T) \times [O_2]^{0.5}[N_2] \times t$$

Rate constant for N+NO = O+N$_2$
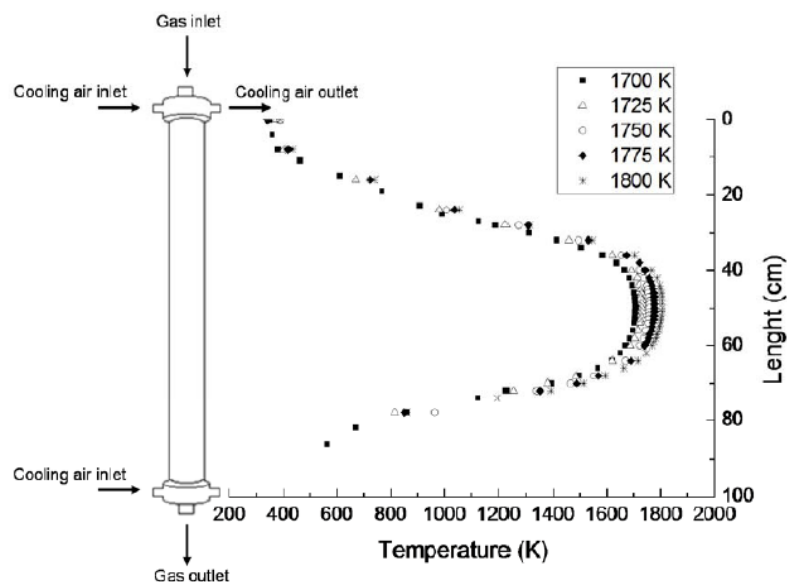
Flow reactor experiments:

N$_2$+O$_2$+trace H$_2$O, measure NO

k = 9.4E12 T$^{0.14}$ cm^3 mol^{-1} s^{-1}

Abian et al. (2015)
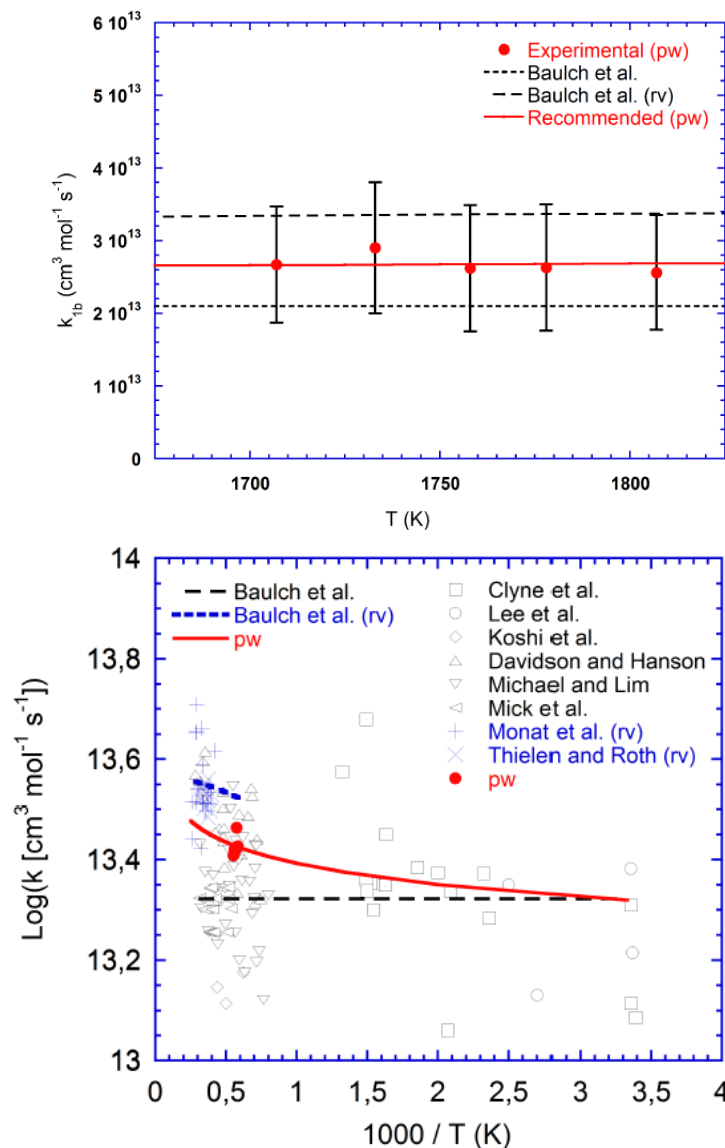
Case: engine knock

Area A
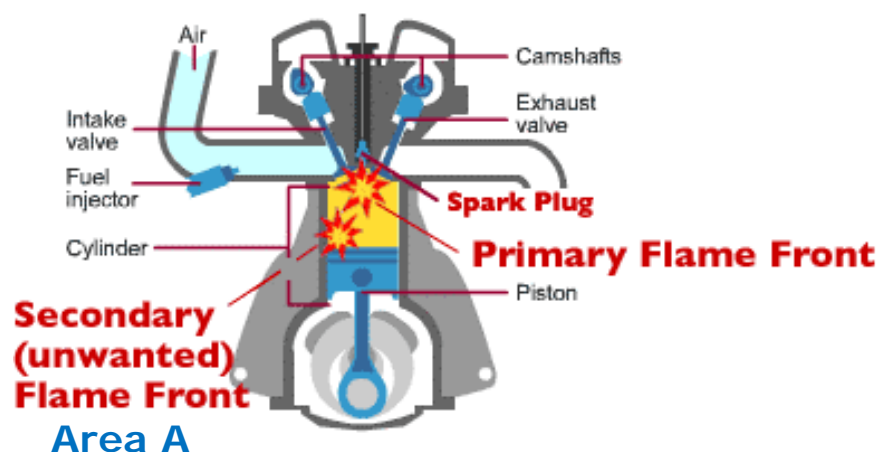
Knock:

The gas in A ignites before the primary flame front arrives

- How fast does the gas in A ignite?
  - Composition
  - Temperature
  - Pressure

- How can we prevent knock?

Assume moist CO oxidation

Moist CO oxidation

- Initiation

  $H_2O + O_2 \rightarrow OH + HO_2$

- Propagation / branching

  1. $CO + OH \rightarrow CO_2 + H$

  2. $H + O_2 \rightarrow O + OH$

  3. $O + H_2O \rightarrow OH + OH$

- Termination

  4. $OH \rightarrow$ inert
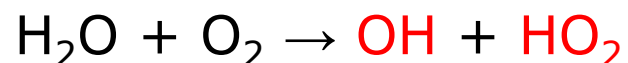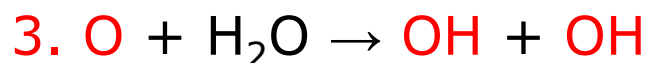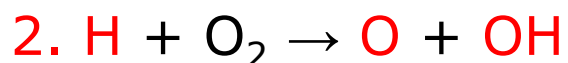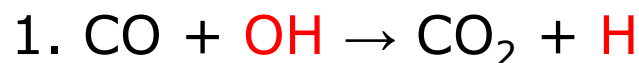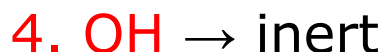
- H, O in steady-state:

- $d[OH]/dt = \{2k_1[CO]-k_4\}[OH]$

- If $d[OH]/dt > 0$: explosion

- Control knock:
  - Lower k_1
  - Increase k_4

Knock control

- Lower k_1:
  Lower temperature
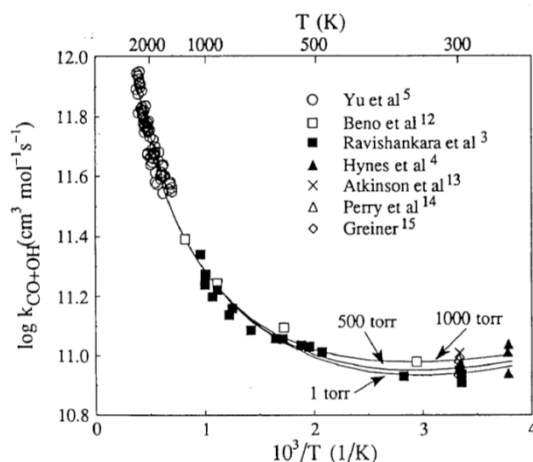
Figure 2. Arrhenius plot for the rate coefficient of reaction CO + OH; buffer gas is argon.

- Reduce end gas temperature
  - Lower compression ratio
  - Delay ignition

- Increase k_4:
  Use additives
  - Lead
  - Aromatic compounds
  - MTBE

Development of a chemical kinetic model

Reaction Mechanism: CH$_2$O Subset

Reaction subset for CH$_2$O. Rate constants for reactions 21–24 are reported elsewhere [24].

		A [cm, mole, s]	β	E$_a$ [cal/mole]	Source
1.	CH$_2$O + M $\rightleftharpoons$ HCO + H + M[a]	6.1E15	0.00	76900	[28]
2.	CH$_2$O + M $\rightleftharpoons$ CO + H$_2$ + M[a]	2.8E15	0.00	63800	[28]
3.	CH$_2$O + H $\rightleftharpoons$ HCO + H$_2$	5.7E07	1.90	2740	[5]
4.	CH$_2$O + O $\rightleftharpoons$ HCO + OH	1.8E13	0.00	3080	[31][b]
5.	CH$_2$O + OH $\rightleftharpoons$ HCO + H$_2$O	3.4E09	1.18	−447	[31][b]
6.	CH$_2$O + HO$_2$ $\rightleftharpoons$ HCO + H$_2$O$_2$	4.1E04	2.50	10200	[32]
7.	CH$_2$O + O$_2$ $\rightleftharpoons$ HCO + HO$_2$	5.0E04	3.00	39000	see text
8.	HCO + M $\rightleftharpoons$ H + CO + M[a]	4.8E17	−1.20	17700	[46]
9.	HCO + H $\rightleftharpoons$ CO + H$_2$	1.2E13	0.25	0	[24][b]
10.	HCO + O $\rightleftharpoons$ CO + OH	3.0E13	0.00	0	[34][b]
11.	HCO + O $\rightleftharpoons$ CO$_2$ + H	3.0E13	0.00	0	[34][b]
12.	HCO + OH $\rightleftharpoons$ CO + H$_2$O	1.0E14	0.00	0	[34][b]
13.	HCO + HO$_2$ $\rightleftharpoons$ CO$_2$ + OH + H	3.0E13	0.00	0	[31]
14.	HCO + O$_2$ $\rightleftharpoons$ CO + HO$_2$	3.4E12	0.00	0	[45]
15.	HCO + HCO $\rightleftharpoons$ CO + CH$_2$O	3.0E13	0.00	0	[29]
16.	CH$_2$O + NO$_2$ $\rightleftharpoons$ HCO + HONO	8.0E02	2.77	13730	[54][b]
17.	HCO + NO $\rightleftharpoons$ CO + HNO	7.0E13	−0.40	0	[44]
18.	HCO + HNO $\rightleftharpoons$ NO + CH$_2$O	6.0E11	0.00	2000	[54][b]
19.	HCO + NO$_2$ $\rightleftharpoons$ CO + HONO	1.2E23	−3.29	2355	[54][b]
20.	HCO + NO$_2$ $\rightleftharpoons$ H + CO$_2$ + NO	8.4E15	−0.75	1930	[54][b]
25.	NO$_2$ + HO$_2$ $\rightleftharpoons$ HONO + O$_2$	6.3E08	1.25	5000	[48]
26.	HNO + O$_2$ $\rightleftharpoons$ NO + HO$_2$	2.0E13	0.00	16000	[55]

[a] Enhanced third-body efficiencies: H$_2$O = 5.
[b] Adopted from Glarborg et al. [24]

Reaction mechanism: other format

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

Reaction			A_f	n_f	Ea_f	A_r	n_r	Ea_r
c2h5oh	=	c2h4+h2o	1.25E+14	0.1	6.70E+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

Slide courtesy of Henry Curran

Develop chemical kinetic model

- Identify relevant species
- Obtain thermodynamic properties
- Obtain transport properties
- Identify relevant reactions
- Obtain rate constants

Approach: establish N_2O subset

- Start with N_2O
- List possible N_2O reactions (dissociation, reaction with O/H radicals) and identify novel N-intermediates
    - $N_2O(+M) = N_2+O(+M)$
    - $N_2O+H = N_2+OH$
    - $N_2O+H = NH+NO$
    - $N_2O+O = N_2+O_2$
    - $N_2O+O = NO+NO$
    - $N_2O+OH = N_2+HO_2$
    - $N_2O+OH = HNO+NO$
- List possible NH reactions (dissociation, reaction with O/H radicals) and identify novel N-intermediates
- List possible NO reactions (dissociation, reaction with O/H radicals) and identify novel N-intermediates
- And so on

Thermochemistry in Chemkin format

$$\frac{C_p^o k}{R} = a_{1k} + a_{2k}T + a_{3k}T^2 + a_{4k}T^3 + a_{5k}T^4$$

$$\frac{H_k^o}{RT} = a_{1k} + \frac{a_{2k}}{2}T + \frac{a_{3k}}{3}T^2 + \frac{a_{4k}}{4}T^3 + \frac{a_{5k}}{5}T^4 + \frac{a_{6k}}{T}$$

$$\frac{S_k^o}{R} = a_{1k}lnT + a_{2k}T + \frac{a_{3k}}{2}T^2 + \frac{a_{4k}}{3}T^3 + \frac{a_{5k}}{4}T^4 + a_{7k}$$

Other thermodynamics properties are easily given in terms of C_p^o, H^o, and S^o

Slide courtesy of Henry Curran

NASA polynomials

```
THERMO
 300., 1000., 5000.
C6H5O        3/20/89 THERMC    6H   5O   1     0G    300.000   5000.000 1404.000      01
 1.57324764E+01 1.54394760E-02-5.31383756E-06 8.28591116E-10-4.82238305E-14          2
+1.76799222E+03-6.20052317E+01-3.73072513E+00 6.71840729E-02-5.88121307E-05          3
 2.61335718E-08-4.61968583E-12 4.31827564E+03 4.02213334E+01                         4
CH3OCH3      3/20/89 THERMC    2H   6O   1     0G    300.000   5000.000 1364.000      21
 8.43631162E+00 1.30235626E-02-4.45885307E-06 6.93233262E-10-4.02757540E-14          2
-2.62777965E+04-2.24530764E+01 1.53263200E+00 2.37669572E-02-8.14177550E-06          3
-5.29451929E-10 5.96605679E-13-2.32831259E+04 1.66340885E+01                         4
END
```

```
                        column numbers:


1        10        20        30        40        50        60        70        80
|         |         |         |         |         |         |         |         |
 23456789|123456789|123456789|123456789|123456789|123456789|123456789|123456789|


|<-name>||<-date->|<ref>|<---- elements --->G|<- Tlow >|<- Thi->|<- Tbk->|       21
|<--- a1 ---->|<---- a2 ---->|<---- a3 ---->|<---- a4 ---->|<---- a5 ---->|        2
|<--- a6 ---->|<----- a7 ---->|<---- a8 ---->|<---- a9 ---->|<---- a10 --->|       3
|<--- a11 --->|<---- a12 --->|<---- a13 --->|<---- a14 --->|                       4
```

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Thermochemical databases

Tables

JANAF Thermochemical Tables 3rd ed., vols. 1-2 , M.W. Chase, American Chemical Society, 1986, SELREF/QD516.D695 1986

Pedley, J. B.; Naylor, R. D.; Kirby, S. P. Thermochemical Data of Organic Compounds: Chapman & Hall, London, 1986.

Tables TRC (Thermodynamics Research Center) Thermodynamic Tables - Hydrocarbons - Department of Chemistry, Texas A&M University

On-line databases

NIST Webbook : http://webbook.nist.gov

Computational Chemistry Comparison and Benchmark Data Base http://srdata.nist.gov/cccbdb/

Active Thermochemical Tables (Branco Ruscic Argonne National Lab.) http://atct.anl.gov/Thermochemical%20Data/version%20Alpha%201.110/index.html

Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion (Burcat) : http://garfield.chem.elte.hu/Burcat/burcat.html

DTU Chemical Engineering, Technical University of Denmark

Slide courtesy of Pierre-Alexandre Glaude

Rate constants

- High accuracy
  - Experimental
  - High level theory
- Lower accuracy
  - Lower levels of theory
  - Analogy
  - Estimate

Kinetic experiments

- Microscopic

  Characterization of <u>elementary reaction</u>

    - Determine rate coefficients
    - Identify products

- Macroscopic

  Characterization of <u>process</u>

    - Identify mechanism
    - Validate model

Characterization of elementary reactions

REACTOR TYPE:
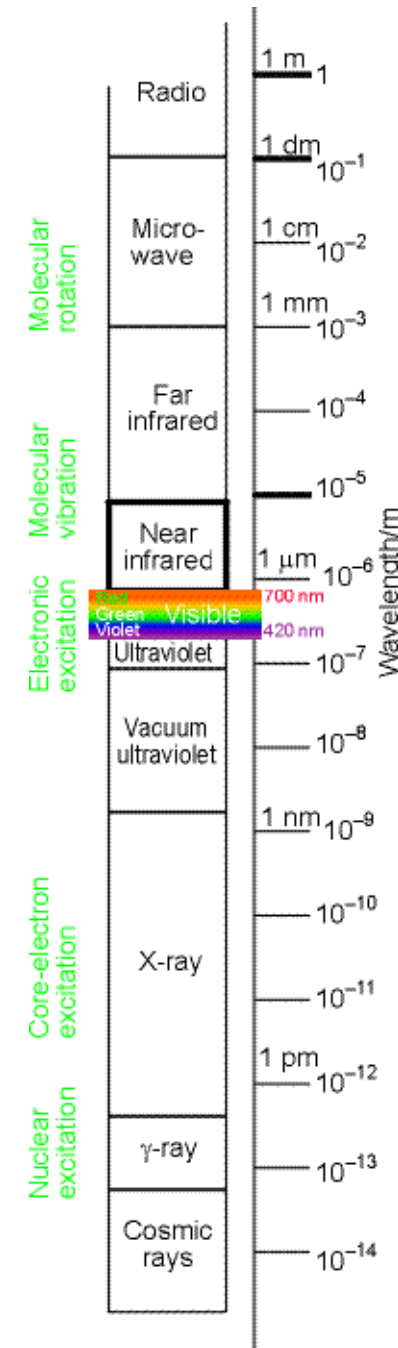
Batch reactor   Flow reactor

Which reactor type is best suited?
How are the radicals generated?
What reactor/excitation techniques will function?

X

Regions of the electromagnetic spectrum:

Types of excitation

Characterization of elementary reactions

REACTOR TYPE:

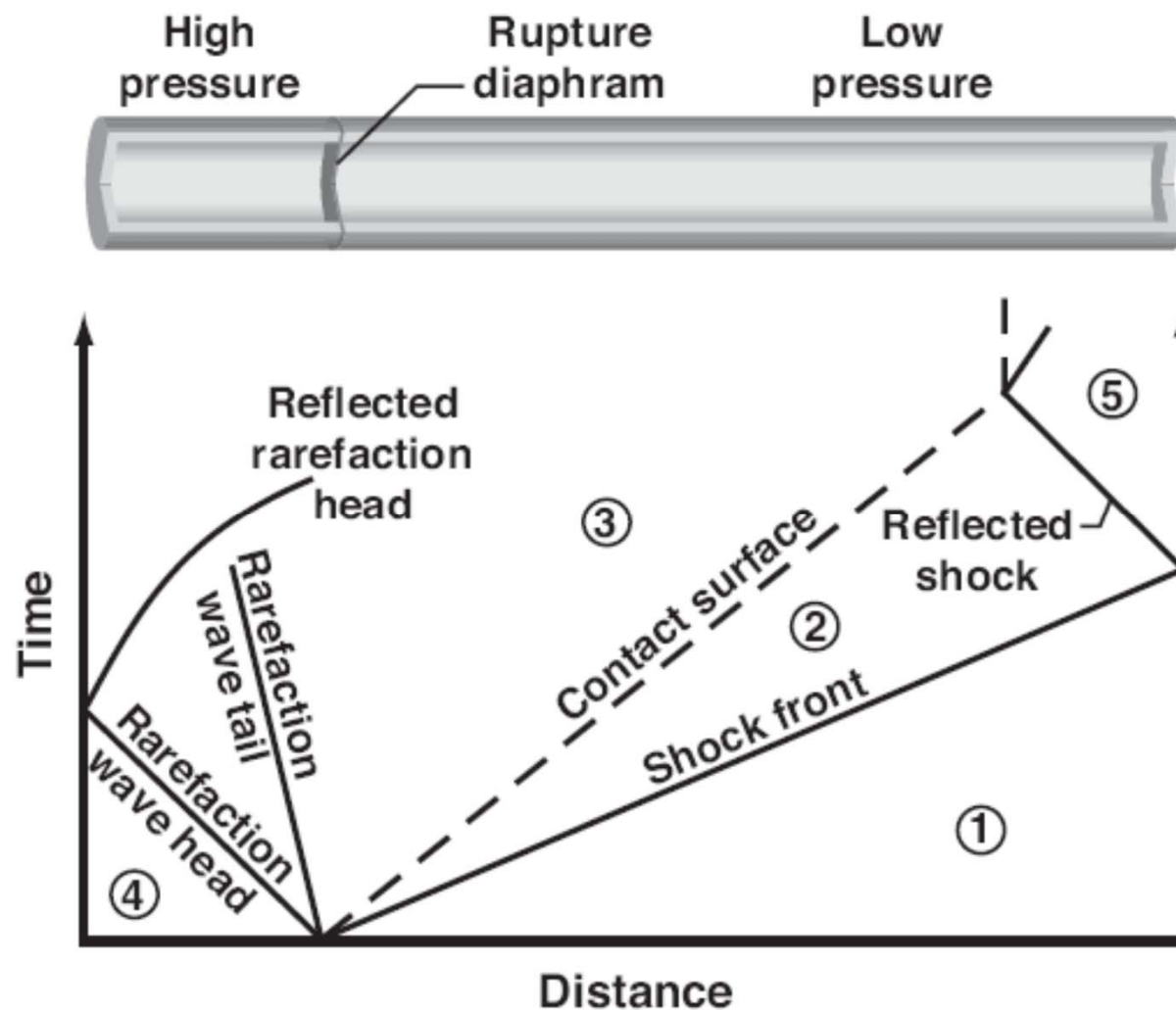Batch reactor

Flow reactor
(initial separation)

EXCITATION

Selective

Non-Selective

Photolysis

Discharge
Radiolysis
Thermal

Shock tube: thermal activation

Rate constants

➢ **Large number of reactions in a combustion mechanism**

➢ **Direct experimental determination often difficult for elementary reactions over a wide range of temperature and pressure**

➢ **Few experimental data, limited to light species**

➢ **Estimation methods:**

- **Collision theory (kinetic theory gas) pre-exponential A, radical combination**

- **correlations between structure and reactivity**

- **LFER (Linear Free Energy Relationships) ex: Evans-Polanyi**

- **methods based on the Transition State Theory (estimation of the TS)**

- **quantum calculation and TST**

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Rate constant databases

- **On-line databases**

  NIST Chemical Kinetics Database, Standard Reference Database 17

  http://kinetics.nist.gov/kinetics/index.jsp

- **Reviews**

  - **Baulch et al., Phys. Chem. Ref. Data, 34, 757 (2005)**
  - **Tsang and Hampson, J. Phys. Chem. Ref. Data 15:3 (1986)**
  - **Tsang, J. Phys. Chem. Ref. Data 20:221 (1991)**

- **On-line mechanisms:**

  - **Estimated rate constants for most reactions, to handle and mix carefully**
  - **GRI-mech, LLNL, Leeds, Konnov, NUIG, POLIMI, Jet-Surf, UCSD…**

- **Good website for general links: http://c3.nuigalway.ie/links.html**

Slide courtesy of Dr. Pierre-Alexandre Glaude