

# Kinetics of Combustion

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ME 6163: Combustion Engineering  
<http://zahurul.buet.ac.bd/ME6163/>



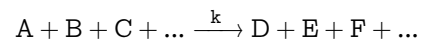
## Overview

- 1 Rate Laws
- 2 Elementary Reactions & Chain Reactions
  - Elementary Reactions
  - Chain Reactions



## Rate Laws

### Rate Laws & Reaction Order<sup>1</sup>



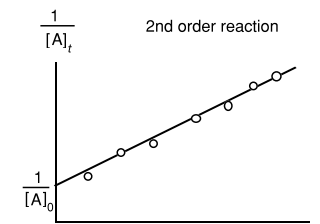
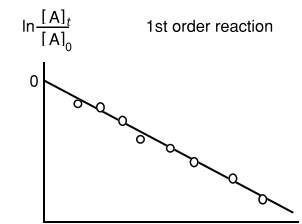
- Reaction Rate (RR) =  $\frac{d[A]}{dt} = -k[A]^a[B]^b[C]^c \dots$   
 $a, b, c, \dots$  are **reaction orders** wrt.  $A, B, C, \dots$ ,  
 $k$  is the **rate coefficient** of the reaction,  
the sum of all the exponents is the **overall reaction rate**.
- If some species are in excess,  $[B], [C], \dots$  remains constant,  
$$RR = \frac{d[A]}{dt} = -k[A]^a$$
- If the time behaviour is measured, the reaction order can be **determined**.

<sup>1</sup>J. Warnatz, U. Maas, and R. Dibble (2006). *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation*. 4th ed. Springer.



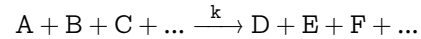
## Rate Laws

- For **first-order systems** ( $a = 1$ ):  $\ln \frac{[A]_t}{[A]_0} = -k(t - t_0)$   
 $[A]_0$  &  $[A]_t$  denote the concentration of species  $A$  at time  $t_0$  and  $t$ , respectively.
- For **second-order systems** ( $a = 2$ ):  $\frac{1}{[A]_t} - \frac{1}{[A]_0} = k(t - t_0)$
- For **third-order systems** ( $a = 3$ ):  $\frac{1}{[A]_t^2} - \frac{1}{[A]_0^2} = 2k(t - t_0)$



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Relation of Forward & Reverse Reactions<sup>2</sup>

- Forward reaction rate for production of A,

$$\frac{d[A]}{dt} = -k_f[A]^a[B]^b[C]^c \dots$$

- Reverse reaction rate for production of A,

$$\frac{d[A]}{dt} = k_b[D]^d[E]^e[F]^f \dots$$

- At chemical equilibrium, forward and backward reaction rates are same and no net reaction can be observed.

$$\Rightarrow -k_f[A]^a[B]^b[C]^c \dots = k_b[D]^d[E]^e[F]^f \dots$$

$\Rightarrow$  Equilibrium constant (based on concentration),  $K_c$

$$K_c \equiv \frac{k_f}{k_b} = \frac{[D]^d[E]^e[F]^f}{[A]^a[B]^b[C]^c}$$

<sup>2</sup>J. Warnatz, U. Maas, and R. Dibble (2006). *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation*. 4th ed. Springer.

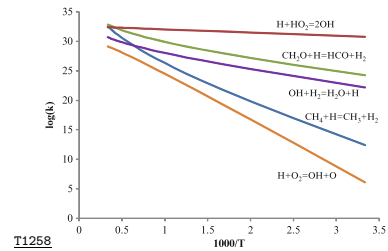
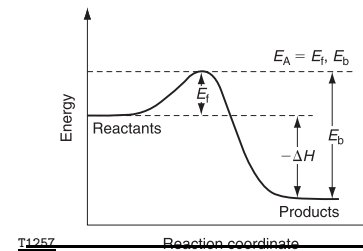
Temperature Dependence of Rate Coefficients<sup>3</sup>

**Arrhenius law:**  $k = A_o \exp\left(-\frac{E_a/R_u}{T}\right) = A_o \exp\left(-\frac{T_a}{T}\right)$

$A_o \equiv$  pre-exponential factor

$E_a \equiv$  activation energy, corresponds to an energy barrier which has to be overcome during reaction.

$T_a \equiv$  activation temperature,  $T_a \equiv E_a/R_u$



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<sup>3</sup>J. Warnatz, U. Maas, and R. Dibble (2006). *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation*. 4th ed. Springer.

Global One-step Reaction<sup>4</sup>

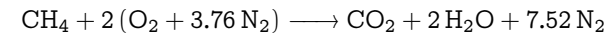
$$RR = A_o \exp\left(-\frac{E_a/R_u}{T}\right) [Fuel]^a [O_2]^b$$

Fuel	$A_o$	$E_a$ (kcal/mol)	a	b
$CH_4^*$	$1.3 \cdot 10^9$	48.4	-0.3	1.3
$CH_4$	$8.3 \cdot 10^5$	30	-0.3	1.3
$C_2H_6$	$1.1 \cdot 10^{12}$	30	0.1	1.65
$C_3H_8$	$8.6 \cdot 10^{11}$	30	0.1	1.65
$C_4H_{10}$	$7.4 \cdot 10^{11}$	30	0.15	1.6
$C_5H_{12}$	$6.4 \cdot 10^{11}$	30	0.25	1.5
$C_6H_{14}$	$5.7 \cdot 10^{11}$	30	0.25	1.5
$C_7H_{16}$	$5.1 \cdot 10^{11}$	30	0.25	1.5
$C_8H_{18}$	$4.6 \cdot 10^{11}$	30	0.25	1.5
$C_9H_{20}$	$4.2 \cdot 10^{11}$	30	0.25	1.5
$C_{10}H_{22}$	$3.8 \cdot 10^{11}$	30	0.25	1.5
$CH_3OH$	$3.2 \cdot 10^{11}$	30	0.25	1.5
$C_2H_5OH$	$1.5 \cdot 10^{12}$	30	0.15	1.6
$C_6H_6$	$2.0 \cdot 10^{11}$	30	-0.1	1.85
$C_7H_8$	$1.6 \cdot 10^{11}$	30	-0.1	1.85

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<sup>a</sup>Units of  $A_o$ :  $(\text{mol}/\text{cm}^3)^{1-a-b}/\text{s}$ .

<sup>4</sup>S. McAllister, J. Chen, and A. Fernandez-Pello (2011). *Fundamentals of Combustion Processes*. Springer.

Example: Methane Combustion at 1800 K<sup>5</sup>

- $RR = A_o \exp\left(-\frac{E_a/R_u}{T}\right) [Fuel]^a [O_2]^b$

- $A_o = 1.3 \times 10^9 \text{ mol}/\text{cm}^3$

- $E_a = 48.4 \text{ kcal}/\text{mol}$ ,  $R_u = 1.987 \text{ cal}/\text{mol}\cdot\text{K}$

- $a = -0.3$ ,  $b = 1.3$ ,  $[O_2] = 2[CH_4]$

- $\frac{d[CH_4]}{dt} = RR = 1.3 \times 10^9 \exp\left(-\frac{24358}{1800}\right) [CH_4]^{-0.3} (2[CH_4])^{1.3}$

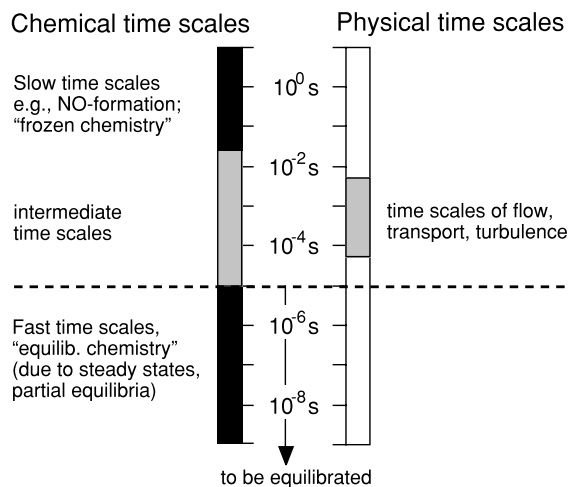
$$\Rightarrow \frac{d[CH_4]}{dt} = -4245.3[CH_4]$$

$$\Rightarrow \frac{[CH_4]}{[CH_4]_0} = \exp(-4245.3t)$$

- Reduction to 5%,  $\exp(-4245.3t) = 0.05 \rightarrow t = 0.71 \text{ ms}$

<sup>5</sup>S. McAllister, J. Chen, and A. Fernandez-Pello (2011). *Fundamentals of Combustion Processes*. Springer.

## Time Scales in Chemically Reacting Flow



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Pressure Dependence of Rate Coefficients<sup>6</sup>

$$RR = A_o \exp\left(-\frac{E_a/R_u}{T}\right) [Fuel]^a [O_2]^b$$

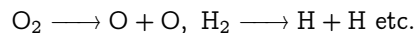
$$= A_o \exp\left(-\frac{E_a/R_u}{T}\right) [X_{fuel}]^a [X_{O_2}]^b \left(\frac{P/R_u}{T}\right)^{(a+b)} \propto P^{(a+b)}$$

- For one-step combustion chemistry model,  $(a + b)$  is always positive, ranging from 1.0 to 1.75.
- When the pressure of a combustion system is doubled, the reaction rate can increase threefold for the case  $a + b = 1.75$ .

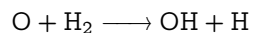
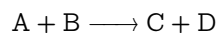
<sup>6</sup>S. McAllister, J. Chen, and A. Fernandez-Pello (2011). *Fundamentals of Combustion Processes*. Springer.

Elementary Reactions: Reaction Molecularity<sup>7</sup>

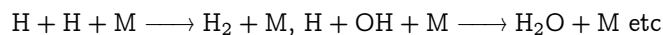
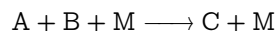
## 1 Unimolecular Reactions:



## 2 Bimolecular Reactions:



## 3 Termolecular Reactions:

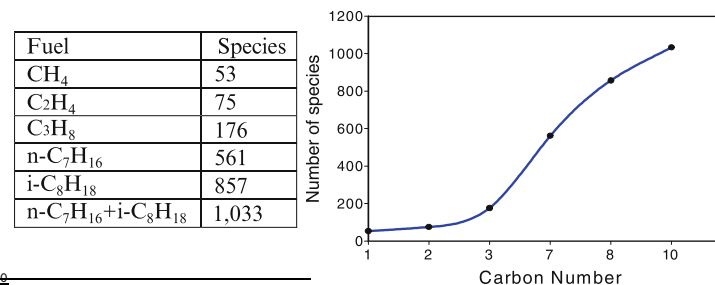


$M$  may be any molecule, widely known as third-body.

<sup>7</sup>S. Turns (2012). *An Introduction to Combustion: Concepts and Applications*. 3rd ed. McGraw-Hill.

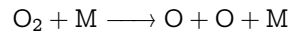
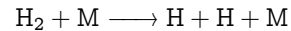
Four Types of Elementary Reactions in Combustion<sup>8</sup>

- 1 chain initiation
- 2 chain branching
- 3 chain propagating.
- 4 chain terminating or recombination

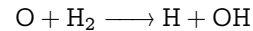
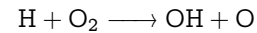


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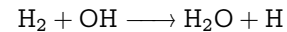
<sup>8</sup>S. McAllister, J. Chen, and A. Fernandez-Pello (2011). *Fundamentals of Combustion Processes*. Springer.

**1 Chain Initiation:**  $nR \xrightarrow{k_1} C$ 


M is a third-body with enough energy to break  $H_2$  or  $O_2$  bonds.

**2 Chain Branching:**  $R + C \xrightarrow{k_2} \alpha C + P$ 


produces two radical on the product side and consumes one on the reactant side. These reactions rapidly increase the pool of radicals.

**3 Chain Propagation:**  $R + C \xrightarrow{k_3} R + C$ 


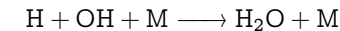
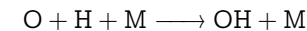
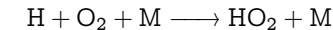
total number of radicals/charge-carriers ( $C$ ) remains same. This example is very important as it produces the most of the  $H_2O$  in  $H_2-O_2$  combustion.

$\Rightarrow R$  represents reactants,  $P$  represents stable products.


**4 Chain Termination or Recombination:**


gas termination

wall termination



- when sufficient radicals or third bodies are present, radicals can react themselves to recombine or react to form stable species.
- these reactions reduce the radical pool.

$$\frac{d[C]}{dt} = k_1[R]^n + (\alpha - 1)[R][C] - k_g[R]^2[C] - k_w[C]$$

$$= k_1[R]^n + k_2[R](\alpha - \alpha_c)[C]$$

$$\text{where, } \alpha_c \equiv 1 + \frac{k_g[R]^2 + k_w}{k_2[R]}$$

$[C]$  varies exponentially with time, growing for  $(\alpha - \alpha_c) > 0$  and decaying otherwise.


 Branched-Chain Explosion / Chain Reactions<sup>9</sup>

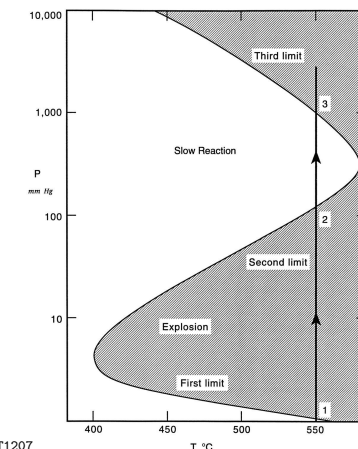
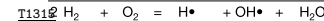
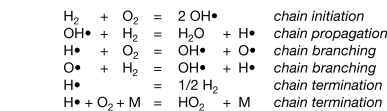
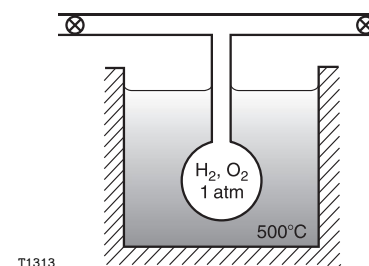
- Branched-chain explosion, when  $\alpha_c \geq \alpha$ .
- Explosion is favoured for small  $\alpha_c$ , which corresponds to situations of fast chain-branching reactions (large  $k_2$ ) and/or slow chain-termination reactions (small  $k_g$  and  $k_w$ ).
- Since  $[R]$  is proportional to the system pressure  $P$ :

$$\alpha_c \rightarrow 1 + \frac{k_w}{k_2[R]} \rightarrow \infty, \text{ as } P \rightarrow 0$$

$$\alpha_c \rightarrow 1 + \frac{k_g[R]}{k_2} \rightarrow \infty, \text{ as } P \rightarrow \infty$$

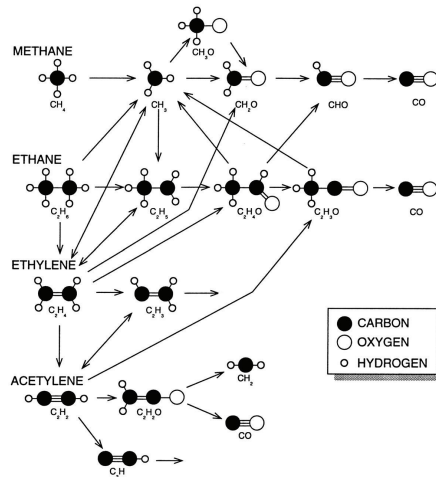
- As  $P \rightarrow 0$ , gas density decreases and chain cycle becomes less efficient because it requires the collision between two molecules.
- As  $P \rightarrow \infty$ , the increase in density favours the three-body gas termination reaction as compared to the two-body chain-branching reaction.

<sup>9</sup>C. Law (2006). *Combustion Physics*. Cambridge University Press.


 H<sub>2</sub> - O<sub>2</sub> Explosion Limits<sup>10</sup>


<sup>10</sup>S. Turns (2012). *An Introduction to Combustion: Concepts and Applications*. 3rd ed. McGraw-Hill.



Complex Elementary C/H/O Reaction Paths<sup>11</sup>

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<sup>11</sup>E. Keating (2007). *Applied Combustion*. 2nd ed. Taylor & Francis.Flammability and Explosion Limits<sup>12</sup>

Mixture	Lean		Rich		Stoichiometric
	Flammability	Explosion	Flammability	Explosion	
H <sub>2</sub> -air	4	18	74	59	29.8
CO-O <sub>2</sub>	16	38	94	90	66.7
CO-air	12.5		74		29.8
NH <sub>3</sub> -O <sub>2</sub>	15	25	79	75	36.4
C <sub>3</sub> H <sub>8</sub> -O <sub>2</sub>	2	3	55	37	16.6
CH <sub>4</sub> -air	5.3		15		9.51
C <sub>2</sub> H <sub>6</sub> -air	3.0		12.5		5.66
C <sub>3</sub> H <sub>8</sub> -air	2.2		9.5		4.03
C <sub>4</sub> H <sub>10</sub> -air	1.9		8.5		3.13

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<sup>12</sup>D. Winterbone (1997). *Advanced Thermodynamics for Engineers*. Arnold.

## References I

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