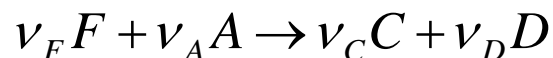


# Chemical Kinetics

First and Second Laws of thermodynamics are used to predict the final equilibrium state of the products after the reaction is complete.

**Chemical kinetics** deals with how fast the reaction proceeds.

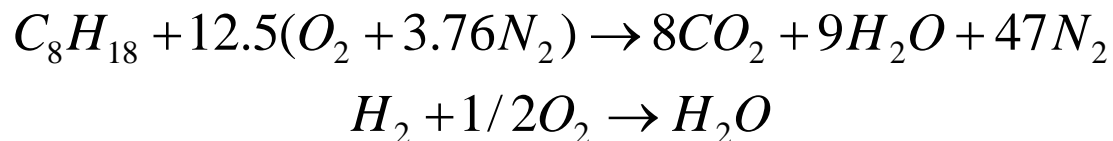


How fast the fuel is consumed is of interest, the **reaction rate**  $\omega'''$  is defined as:

$$\omega''' = -\frac{d[F]}{dt}$$

where [ F ] refers to the fuel concentration (kmol/m<sup>3</sup> or kg/m<sup>3</sup>), negative sign due to the fact that the fuel is consumed.

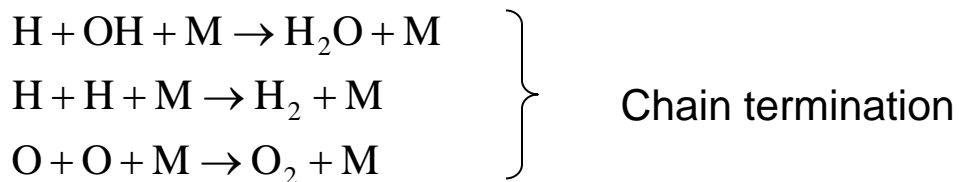
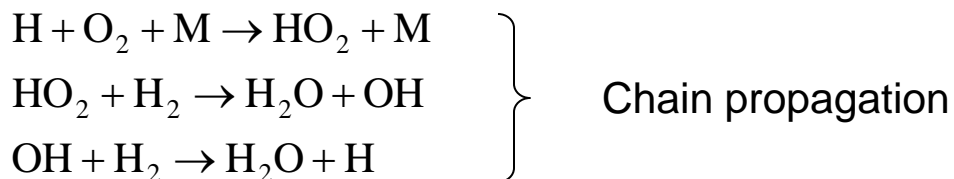
**Global (or overall) reactions** describe the initial and final states:



## Reaction Mechanism

In reality the reaction proceeds through elementary reactions in a chain process known as **chain reactions**

The global hydrogen-oxygen reaction proceeds via the following elementary reactions, collectively known as a **reaction mechanism**:



( $M$  is any species present that acts as a collision partner)

## Law of Mass Action

The **law of mass action** states that for an elementary reaction the reaction rate is proportional to the product of the concentrations of the reactants present raised to a power equal to the corresponding stoichiometric coefficient. The constant of proportionality is called the **reaction rate constant  $k$** .

$$\frac{d[A_i]}{dt} = (v_i'' - v_i')k \prod_{j=1}^n [A_j]^{v_j'}$$

where  $\prod_{j=1}^n [A_j]^{v_j'} = [A_1]^{v_1'} \cdot [A_2]^{v_2'} \cdot [A_3]^{v_3'} \cdots [A_n]^{v_n'}$

the overall order of the reaction is given by  $\sum_{j=1}^n v_j'$

For  $m$  simultaneous equations:

$$\frac{d[A_i]}{dt} = \sum_{l=1}^m (v_{i,l}'' - v_{i,l}')k_l \prod_{j=1}^n [A_j]^{v_{j,l}'}$$

## Law of Mass Action

Applying the law of mass action to the reaction  $H + H + H \xrightarrow{k} H_2 + H$

$$\frac{d[A_1]}{dt} = (v_1'' - v_1')k[A_1]^{v_1'} \cdot [A_2]^{v_2'} \quad \text{Recall } n = 2$$

$$A_1 = H \quad \frac{d[H]}{dt} = (1 - 3)k[H]^3 \cdot [H_2]^0 = -2k[H]^3$$

$$\frac{d[A_2]}{dt} = (v_2'' - v_2')k[A_2]^{v_1'} \cdot [A_2]^{v_2'}$$

$$A_2 = H_2 \quad \frac{d[H_2]}{dt} = (1 - 0)k[H]^3 \cdot [H_2]^0 = k[H]^3$$

$$\text{note } k[H]^3 = \boxed{-\frac{1}{2} \frac{d[H]}{dt} = \frac{d[H_2]}{dt}}$$

## Reaction Rate Theory

Kinetic theory of gases is used to come up with the following expression for the elementary reaction rate constant, first proposed by Arrhenius

$$k = AT^b \exp\left(-\frac{E_a}{RT}\right)$$

where  $A$  and  $b$  are the rate coefficients,  $E_a$  is the activation energy and  $\bar{R}$  is the universal gas constant.

Therefore, for the reaction  $H + H + H \xrightarrow{k} H_2 + H$  the reaction rate is

$$\frac{d[H_2]}{dt} = k[H]^3 = AT^b \exp\left(-\frac{E_a}{RT}\right) \cdot [H]^3$$

The values of  $a$ ,  $b$  and  $E_a$  are tabulated for different reactions.

This expression indicates that molecular hydrogen is produced faster at higher temperature and at a higher atomic hydrogen concentration.

# Rate Coefficients for H<sub>2</sub>-O<sub>2</sub> Reactions

Reactions	$A$ ((cm <sup>3</sup> /gmol) <sup>n-1</sup> /s)*	$b$	$E_a$ (kJ/gmol)	Temperature range (K)
H + O <sub>2</sub> → OH + O	1.2 · 10 <sup>17</sup>	-0.91	69.1	300-2,500
OH + O → O <sub>2</sub> + H	1.8 · 10 <sup>13</sup>	0	0	300-2,500
O + H <sub>2</sub> → OH + H	1.5 · 10 <sup>7</sup>	2.0	31.6	300-2,500
OH + H <sub>2</sub> → H <sub>2</sub> O + H	1.5 · 10 <sup>8</sup>	1.6	13.8	300-2,500
H + H <sub>2</sub> O → OH + H <sub>2</sub>	4.6 · 10 <sup>8</sup>	1.6	77.7	300-2,500
O <sub>2</sub> + H <sub>2</sub> O → OH + OH	1.5 · 10 <sup>10</sup>	1.14	72.2	300-2,500
H + H + M → H <sub>2</sub> + M				
M = Ar (low P)	6.4 · 10 <sup>17</sup>	-1.0	0	300-5,000
M = H <sub>2</sub> (low P)	0.7 · 10 <sup>16</sup>	-0.6	0	100-5,000
H <sub>2</sub> + M → H + H + M				
M = Ar (low P)	2.2 · 10 <sup>14</sup>	0	402	2,500-8,000
M = H <sub>2</sub> (low P)	8.8 · 10 <sup>14</sup>	0	402	2,500-8,000
H + OH + M → H <sub>2</sub> O + M				
M = H <sub>2</sub> O (low P)	1.4 · 10 <sup>23</sup>	-2.0	0	1,000-3,000
H <sub>2</sub> O + M → H + OH + M				
M = H <sub>2</sub> O (low P)	1.6 · 10 <sup>17</sup>	0	478	2,000-5,000
O + O + M → O <sub>2</sub> + M				
M = Ar (low P)	1.0 · 10 <sup>17</sup>	-1.0	0	300-5,000
O <sub>2</sub> + M → O + O + M				
M = Ar (low P)	1.2 · 10 <sup>14</sup>	0	451	2,000-10,000

\*  $n$  is the reaction order