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.

$$\nu_F F + \nu_A A \rightarrow \nu_C C + \nu_D D$$

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

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

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

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

$$C_8H_{18} + 12.5(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 47N_2$$

$$H_2 + 1/2O_2 \rightarrow H_2O$$

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**:

$$\left. H_2 + M \rightarrow H + H + M \right\} \quad \text{Chain initiation}$$

$$\left. \begin{array}{l} \mathrm{H + O_2 + M \rightarrow HO_2 + M} \\ \mathrm{HO_2 + H_2 \rightarrow H_2O + OH} \\ \mathrm{OH + H_2 \rightarrow H_2O + H} \end{array} \right\} \quad \text{Chain propagation}$$

$$\left. \begin{array}{l} \mathrm{H + O_2 \rightarrow OH + O} \\ \mathrm{H_2 + O \rightarrow OH + H} \end{array} \right\} \quad \text{Chain branching}$$

$$\left. \begin{array}{l} \mathrm{H + OH + M \rightarrow H_2O + M} \\ \mathrm{H + H + M \rightarrow H_2 + M} \\ \mathrm{O + O + M \rightarrow O_2 + M} \end{array} \right\} \quad \text{Chain termination}$$

(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***.

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

$$\text{where} \quad \prod_{j=1}^{n}[A_j]^{\nu_j'} = [A_1]^{\nu_1'} \cdot [A_2]^{\nu_2'} \cdot [A_3]^{\nu_3'} \cdots [A_n]^{\nu_n'}$$

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

For m simultaneous equations:

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

Law of Mass Action

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

$$\frac{d[A_1]}{dt} = (\nu_1'' - \nu_1')k[A_1]^{\nu_1'} \cdot [A_2]^{\nu_2'}$$

Recall n = 2

$A_1 = H$

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

$$\frac{d[A_2]}{dt} = (\nu_2'' - \nu_2')k[A_2]^{\nu_1'} \cdot [A_2]^{\nu_2'}$$

$A_2 = H_2$

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

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

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

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 $H + H + H \xrightarrow{\mathrm{k}} H_2 + H$ the reaction rate is

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

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 H2-O2 Reactions

Reactions	A $((cm^3/gmol)^{n-1}/s)$*	b	E_a (kJ/gmol)	Temperature range (K)
$H + O_2 \rightarrow OH + O$	$1.2 \cdot 10^{17}$	−0.91	69.1	300–2,500
$OH + O \rightarrow O_2 + H$	$1.8 \cdot 10^{13}$	0	0	300–2,500
$O + H_2 \rightarrow OH + H$	$1.5 \cdot 10^{7}$	2.0	31.6	300–2,500
$OH + H_2 \rightarrow H_2O + H$	$1.5 \cdot 10^{8}$	1.6	13.8	300–2,500
$H + H_2O \rightarrow OH + H_2$	$4.6 \cdot 10^{8}$	1.6	77.7	300–2,500
$O + H_2O \rightarrow OH + OH$	$1.5 \cdot 10^{10}$	1.14	72.2	300–2,500
$H + H + M \rightarrow H_2 + M$				
$M = Ar$ (low P)	$6.4 \cdot 10^{17}$	−1.0	0	300–5,000
$M = H_2$ (low P)	$0.7 \cdot 10^{16}$	−0.6	0	100–5,000
$H_2 + M \rightarrow H + H + M$				
$M = Ar$ (low P)	$2.2 \cdot 10^{14}$	0	402	2,500–8,000
$M = H_2$ (low P)	$8.8 \cdot 10^{14}$	0	402	2,500–8,000
$H + OH + M \rightarrow H_2O + M$				
$M = H_2O$ (low P)	$1.4 \cdot 10^{23}$	−2.0	0	1,000–3,000
$H_2O + M \rightarrow H + OH + M$				
$M = H_2O$ (low P)	$1.6 \cdot 10^{17}$	0	478	2,000–5,000
$O + O + M \rightarrow O_2 + M$				
$M = Ar$ (low P)	$1.0 \cdot 10^{17}$	−1.0	0	300–5,000
$O_2 + M \rightarrow O + O + M$				
$M = Ar$ (low P)	$1.2 \cdot 10^{14}$	0	451	2,000–10,000

* n is the reaction order