Chemical Kinetics

One (elementary) step reaction

\[ \sum_{i=1}^{N} \nu'_i M_i \rightarrow \sum_{i=1}^{N} \nu''_i M_i \]

\( N \) is the number of species
\( \nu'_i, \nu''_i \) are the stoichiometric coefficients
\( \nu'_i = 0 \) if \( i \) is not a reactant
\( \nu''_i = 0 \) if \( i \) is not a product

Example:

\[ \text{H}_2 + \text{O}_2 \rightarrow 2 \text{OH} \]

\( N = 3 \)
\( \text{H}_2 \ (i = 1) : \quad \nu'_1 = 1 \quad \nu''_1 = 0 \)
\( \text{O}_2 \ (i = 2) : \quad \nu'_2 = 1 \quad \nu''_2 = 0 \)
\( \text{OH} \ (i = 3) : \quad \nu'_3 = 0 \quad \nu''_3 = 2 \)
\[
\sum_{i=1}^{N} \nu'_i \mathcal{M}_i \rightarrow \sum_{i=1}^{N} \nu''_i \mathcal{M}_i
\]

there is a relation between the change in the number of moles of each species; i.e., for any two species \(i\) and \(j\)

\[
\frac{dn_i}{\nu''_i - \nu'_i} = \frac{dn_j}{\nu''_j - \nu'_j}
\]

If \(\dot{\omega}_i\) is the time rate of change of the concentration of species \(i\) (moles, per unit volume per second), i.e., \(\dot{\omega}_i = dC_i/dt\), then

\[
\frac{\dot{\omega}_i}{\nu''_i - \nu'_i} = \frac{\dot{\omega}_j}{\nu''_j - \nu'_j}
\]

or

\[
\frac{\dot{\omega}_i}{\nu''_i - \nu'_i} = \frac{\dot{\omega}_j}{\nu''_j - \nu'_j} = \omega
\]

and we may the common ratio \(\omega\), which is species independent, as the reaction rate (moles per unit volume per second)

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**Law of Mass Action**

phenomenological law that was verified experimentally

the reaction rate is proportional to the products of the concentrations reactants

\[
\omega = k(T) \prod_{i=1}^{N} C_i^{\nu'_i}
\]

(specific) reaction rate constant

the units of \(k\) depend on the reaction order \(n = \sum \nu'_i\)

and is [concentration\(^{(n-1)}\), time\(^{-1}\)]

**example**

\[
\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}
\]

\[
\frac{\dot{\omega}_{\text{H}_2\text{O}}}{2} = \frac{\dot{\omega}_{\text{CO}_2}}{1} = \frac{\dot{\omega}_{\text{CH}_4\text{O}_2}}{1} = -\frac{\dot{\omega}_{\text{O}_2}}{2} = \omega
\]

\[
\omega = k C_{\text{CH}_4} C_{\text{O}_2}^2
\]

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Chemical reaction involving $M$ elementary steps

$$\sum_{i=1}^{N} \nu'_{i,j} M_i \rightarrow \sum_{i=1}^{N} \nu''_{i,j} M_i \quad j = 1, 2, \ldots, M$$

where forward and backward reactions are written as separate steps

net rate of production of species $i$ \( \hat{\omega}_i = \sum_{j=1}^{M} \hat{\omega}_{i,j} \)

$$\hat{\omega}_i = \sum_{j=1}^{M} (\nu''_{i,j} - \nu'_{i,j}) \omega_j$$

where \( \omega_j \) is the reaction rate of the elementary step $j$, namely

$$\omega_j = k(T) \prod_{i=1}^{N} C_i^{\nu'_{i,j}}$$

Chain reaction - hydrogen-bromine reaction

$$\begin{align*}
\text{Br}_2 + M & \xrightarrow{k_1} 2\text{Br} + M \\
\text{Br} + \text{H}_2 & \xrightarrow{k_2} \text{HBr} + \text{H} \\
\text{H} + \text{Br}_2 & \xrightarrow{k_3} \text{HBr} + \text{Br} \quad \Rightarrow \quad \text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr} \\
\text{H} + \text{HBr} & \xrightarrow{k_4} \text{Br} + \text{H}_2 \\
2\text{Br} + M & \xrightarrow{k_5} \text{Br}_2 + M
\end{align*}$$

$$\hat{\omega}_i = \sum_{j=1}^{5} (\nu''_{i,j} - \nu'_{i,j}) \omega_j \quad \omega_j = k(T) \prod_{i=1}^{5} C_i^{\nu'_{i,j}}$$

for example

$$\hat{\omega}_{\text{Br}_2} = \frac{dC_{\text{Br}_2}}{dt} = 2k_1 C_{\text{Br}_2} - k_2 C_{\text{Br}_4} C_{\text{H}_2} + k_3 C_{\text{H}} C_{\text{Br}_2} + k_4 C_{\text{H}} C_{\text{HBr}} - 2k_5 C_{\text{Br}}^2$$
Two of the important questions in chemical kinetics are

- determine all the elementary steps by which a given chemical reaction actually proceeds
- determine the specific rate constant for each step

### Reaction Mechanisms

- First order decomposition reaction
- One step opposing reactions
- Chain reaction
- Reduced mechanisms modeling
First order decomposition reaction

\[ A \xrightarrow{k} B \]

\[ \frac{dC_A}{dt} = kC_A \quad C_A(0) \text{ given} \]

\[ C_A = C_A(0)e^{-kt} \]

\[ t = \frac{1}{k} \ln \left( \frac{C_A(0)}{C_A} \right) \quad \Rightarrow \quad t_c \sim \frac{1}{k} \]

characteristic time scale

large \( k \) corresponds to a small time scale or very fast reaction
this is a source of stiffness in the differential equations

One step opposing reaction

\[ A \xrightarrow{k_f} B \quad B \xrightarrow{k_b} A \]

\[ \frac{dC_A}{dt} = -k_f C_A + k_b C_B \quad C_A(0) \text{ specified, } C_B(0) = 0 \]

\[ \frac{dC_B}{dt} = k_f C_A - k_b C_B \]

\[ \frac{d}{dt} \mathbf{C} = \mathbf{M} \cdot \mathbf{C} \quad \mathbf{M} = \begin{pmatrix} -k_f & k_b \\ k_f & -k_b \end{pmatrix} \quad \mathbf{C} = \begin{pmatrix} C_A \\ C_B \end{pmatrix} \]

\[ \mathbf{C} = \mathbf{V}_1 e^{\lambda_1 t} + \mathbf{V}_2 e^{\lambda_2 t} \]

there are two characteristic times, corresponding to \( \lambda_1^{-1} \) and \( \lambda_2^{-1} \)
\[
\begin{vmatrix}
-k_f - \lambda & k_b \\
k_f & -k_b - \lambda
\end{vmatrix} = 0 \quad \Rightarrow \quad \lambda_1 = 0, \quad \lambda_2 = -(k_f + k_b)
\]

\[
\begin{pmatrix}
C_A \\
C_B
\end{pmatrix} = \begin{pmatrix}
C_A(0) \\
C_B(0)
\end{pmatrix} \left( \begin{array}{cc}
k_f & k_b \\
k_f + k_b & -1
\end{array} \right) e^{-(k_f + k_b)t} \]

\[
\begin{pmatrix}
C_A \\
C_B
\end{pmatrix} = C_A^{eq} \left( \begin{array}{cc}
1/k_f & 0 \\
0 & 1
\end{array} \right) + C_B^{eq} \left( \begin{array}{cc}
1 & 0 \\
0 & 1
\end{array} \right) e^{-(k_f + k_b)t}
\]

where

\[
C_A^{eq} = \frac{k_b}{k_f + k_b} C_A(0), \quad C_B^{eq} = \frac{k_f}{k_f + k_b} C_A(0)
\]

the characteristic times are \( t_1 = \infty \) and \( t_2 = (k_f + k_b)^{-1} \) corresponding to the reciprocal of the eigenvalues; i.e., \( \frac{1}{\lambda_1} \) and \( \frac{1}{\lambda_2} \)

at equilibrium, \( k_f C_A^{eq} - k_b C_B^{eq} = 0 \)

In fact, for this simple system, one easily see that

\[
\frac{d}{dt} [C_A + C_B] = 0
\]

\[
\frac{d}{dt} [k_f C_A - k_b C_B] = -(k_f + k_b)[k_f C_A - k_b C_B]
\]

\[
\begin{align*}
z_1 &= C_A + C_B \\
z_2 &= k_f C_A - k_b C_B
\end{align*}
\]

\[
\frac{d}{dt} \begin{pmatrix} z_1 \\ z_2 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & -(k_f + k_b) \end{pmatrix} \begin{pmatrix} z_1 \\ z_2 \end{pmatrix}
\]

\[
\begin{align*}
z_1 &= z_1(0) e^0 \\
z_2 &= z_2(0) e^{-(k_f + k_b)t}
\end{align*}
\]

when \( k_f + k_b \gg 1 \), the characteristic times are

\( t_1 = 0 \) (slow time) and \( t_2 = (k_f + k_b)^{-1} \) (fast time)

\( C_A + C_B \) is a conserved quantity,

\( k_f C_A - k_b C_B \approx 0 \) almost all the time
Chain Reaction
Hydrogen-Bromine Reaction
any halogen molecule (F₂, Cl₂ or I₂) may replace Br₂

\[ \text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr} \]

\[
\begin{align*}
\text{Br}_2 + \text{M} & \xrightarrow{k_1} 2\text{Br} + \text{M} \quad \text{chain initiating} \\
\text{Br} + \text{H}_2 & \xrightarrow{k_2} \text{HBr} + \text{H} \\
\text{H} + \text{Br}_2 & \xrightarrow{k_3} \text{HBr} + \text{Br} \\
\text{H} + \text{HBr} & \xrightarrow{k_4} \text{Br} + \text{H}_2 \\
2\text{Br} + \text{M} & \xrightarrow{k_5} \text{Br}_2 + \text{M} \quad \text{chain terminating}
\end{align*}
\]

the intermediates H, Br are the chain carriers

\[
\begin{align*}
\frac{dC_{\text{HBr}}}{dt} &= k_2 C_{\text{Br}} C_{\text{H}_2} + k_3 C_{\text{H}} C_{\text{Br}_2} - k_4 C_{\text{H}} C_{\text{HBr}} \\
\frac{dC_{\text{H}}}{dt} &= k_2 C_{\text{Br}} C_{\text{H}_2} - k_3 C_{\text{H}} C_{\text{Br}_2} - k_4 C_{\text{H}} C_{\text{HBr}} \\
\frac{dC_{\text{Br}_2}}{dt} &= 2k_1 C_{\text{Br}_2} - k_2 C_{\text{Br}} C_{\text{H}_2} + k_3 C_{\text{H}} C_{\text{Br}_2} + k_4 C_{\text{H}} C_{\text{HBr}} - 2k_5 C_{\text{Br}}^2 \\
\frac{dC_{\text{H}_2}}{dt} &= -k_2 C_{\text{Br}} C_{\text{H}_2} + k_4 C_{\text{H}} C_{\text{HBr}} \\
\frac{dC_{\text{Br}_2}}{dt} &= -k_1 C_{\text{Br}_2} - k_3 C_{\text{H}} C_{\text{Br}_2} + k_5 C_{\text{Br}}^2.
\end{align*}
\]
We are faced with a set of $N$ nonlinear coupled differential equations (for spatially homogeneous system, as discussed here, these are ODEs), with $N$ generally a large number.

The description of the combustion of real fuels may involve 1000 species or more, involved in a complex network of elementary steps that add up to few thousands. For example, the detailed kinetic mechanism of the primary reference fuel (PRF) contains 1034 species participating in 4236 elementary reactions.

Attempts are made to model the overall reaction with fewer species and a smaller number of steps.

Recent simulations show that the computational work scales approximately as $N^2$, so that an order of magnitude reduction in computational cost would be achieved by reducing $N$ (using 1000 species instead of 50 will increase the cost by a factor of 400).

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The objectives of “reduced mechanism modeling” are to
- provide insight and understanding how the complex chemistry affects the burning process,
- enable numerical simulations by reducing the computational requirements (memory, stiffness, computational cycles)

Strategies:
- Intuition and experience
- Sensitivity analysis
- Steady-state and partial equilibrium approximations
- Novel computational methodologies, such as Intrinsic Low-Dimensional Manifold (ILDM), Computational Singular Perturbation (CSP), Global Quasilinearization (GQL), etc.
### Steady State Approximation

\[ \begin{align*}
\text{Br}_2 + M & \xrightarrow{k_3} 2\text{Br} + M \\
\text{Br} + \text{H}_2 & \xrightarrow{k_2} \text{HBr} + \text{H} \\
\text{H} + \text{Br}_2 & \xrightarrow{k_3} \text{HBr} + \text{Br} \\
\text{H} + \text{HBr} & \xrightarrow{k_4} \text{Br} + \text{H}_2 \\
2\text{Br} + M & \xrightarrow{k_5} \text{Br}_2 + M
\end{align*} \]

Radicals form and react very rapidly (at nearly equal rates) such that their concentrations remain nearly constant.

\[ \begin{align*}
\frac{dC_{\text{Br}}}{dt} & \approx 0 \\
\frac{dC_{\text{H}}}{dt} & \approx 0
\end{align*} \]

Rate of formation of HBr

\[ \frac{dC_{\text{HBr}}}{dt} = k_2 C_{\text{Br}} C_{\text{H}_2} + k_3 C_{\text{H}} C_{\text{Br}_2} - k_4 C_{\text{H}} C_{\text{HBr}} \]
\[
\frac{dC_H}{dt} \approx 0 \Rightarrow k_2 C_{Br} C_{H_2} - k_3 C_H C_{Br_2} - k_4 C_H C_{HBr} = 0
\]

\[
\frac{dC_{Br}}{dt} \approx 0 \Rightarrow 2k_1 C_{Br_2} - k_2 C_{Br} C_{H_2} + k_3 C_H C_{Br_2} + k_4 C_H C_{HBr} - 2k_5 C_{Br_2}^2 = 0
\]

Algebraic equations for \( C_H \) and \( C_{Br} \):

\[
C_{Br} = \sqrt{\frac{k_1}{k_5} C_{Br_2}^{1/2}} \quad C_H = \frac{k_2 \sqrt{k_1/k_5} C_{H_2}}{k_3 C_{Br_2} + k_4 C_{HBr}}
\]

\[
\Rightarrow \frac{dC_{HBr}}{dt} = \frac{2k_2 \sqrt{k_1/k_5} C_{H_2} C_{Br_2}^{1/2}}{1 + (k_4/k_3) C_{HBr} C_{Br_2}}
\]

different from the expression

\[
\frac{dC_{HBr}}{dt} = 2k_0 C_{H_2} C_{Br_2} \quad \text{for the global reaction } \text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr}
\]

\[
\frac{dC_{HBr}}{dt} \approx 2k_0 C_{H_2} C_{Br_2}^{1/2} \quad \text{when } k_4/k_3 \ll 1; \quad (k_0 = k_2 \sqrt{k_1/k_5})
\]

- Reaction rate is not necessarily of the form \( \sim P \prod_{i=1}^{N} C_i^{n_i} \) as for elementary steps.
- Reaction rate for the global reaction may be approximated using an expression of the form

\[
\omega = k \prod_{i=1}^{N} C_i^{n_i} \quad i = \text{reactants only}
\]

\( n_i \) is the reaction order w.r.t. species \( i \), which does not have to be an integer (and could be negative), determined empirically.

\( n = \sum n_i \) is the overall reaction order.
Partial Equilibrium Approximation

Unlike the steady-state approximation, which refers to a particular species, the partial equilibrium approximation pertains to a particular reaction. If step $s$ of a reaction mechanism proceeds at a rate $k_f^{(s)}$, i.e.,

$$\sum_{i=1}^{N} \nu_{r,i} M_i \xrightarrow{k_f^{(s)}} \sum_{i=1}^{N} \nu_{s,i} M_i$$

and its backward step at a rate $k_b^{(s)}$, i.e.,

$$\sum_{i=1}^{N} \nu_{s,i} M_i \xrightarrow{k_b^{(s)}} \sum_{i=1}^{N} \nu_{r,i} M_i$$

the approximation is expressed as

$$k_f^{(s)} \prod_{i=1}^{N} C_i^{\nu_{r,i}} \approx k_b^{(s)} \prod_{i=1}^{N} C_i^{\nu_{s,i}}$$

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Novel computational methodologies

Set of nonlinear coupled ODEs

$$\frac{dC}{dt} = F(C)$$

$C(0) = C_0$

$C = (C_1, C_2, \ldots, C_N)^T$
\[
\frac{d\mathbf{C}}{dt} = \mathbf{F}(\mathbf{C})
\]

Linearize \(\mathbf{F}(\mathbf{C})\) near the equilibrium state \(\mathbf{C}_{eq}\)

\[
\mathbf{F}(\mathbf{C}) \approx \mathbf{F}(\mathbf{C}_{eq}) + \mathbf{J} \cdot \mathbf{C}
\]

\(\mathbf{J} = \left( \frac{\partial F_i}{\partial C_j} \right)_{eq}\) is the Jacobian at the equilibrium state

Examine the dynamics of the linearized system

\[
\frac{d\mathbf{C}}{dt} = \mathbf{J} \cdot \mathbf{C}
\]

\((\mathbf{J} - \lambda \mathbf{I})\mathbf{v} = 0\) \(\lambda_n\) eigenvalues \(\mathbf{v}_n\) eigenvectors

We can diagonalize the matrix \(\mathbf{J}\), using \(\mathbf{V}\) (formed by the eigenvectors) and its inverse \(\mathbf{V}^{-1} = \tilde{\mathbf{V}}\). The elements of the resulting diagonal matrix \(\Lambda = \tilde{\mathbf{V}} \mathbf{J} \mathbf{V}\) are the eigenvalues \(\lambda_n\).

\[
\frac{d\mathbf{C}}{dt} = \mathbf{V} \Lambda \tilde{\mathbf{V}} \cdot \mathbf{C}
\]

\(\tilde{\mathbf{V}} \frac{d\mathbf{C}}{dt} = \Lambda \tilde{\mathbf{V}} \cdot \mathbf{C}\)

\[
\mathbf{z} \equiv \tilde{\mathbf{V}} \mathbf{C} \quad \Rightarrow \quad \frac{dz}{dt} = \Lambda z
\]

\[
\frac{dz_i}{dt} = \lambda_i z_i \quad i = 1, \ldots, n
\]

If the eigenvalues are ordered by their magnitude \(\lambda_{m+1} > \lambda_m\), the large/small eigenvalues correspond to the slow/fast times and we can split the system into the fast modes that determine the slow intrinsic manifold and the slow modes that describes the dynamics that remain to be solved.
\[ J = V \Lambda V, \quad V^{-1} = \tilde{V}, \]

\[
V = \begin{pmatrix}
v_1 & \cdots & v_m & v_{m+1} & \cdots & v_n
\end{pmatrix} = \begin{pmatrix} V_s & V_f \end{pmatrix},
\]

\[
\Lambda = \begin{pmatrix}
\lambda_{(1)} & 0 & 0 & \cdots & 0 \\
0 & \lambda_{(m)} & 0 & \cdots & 0 \\
0 & 0 & \lambda_{(m+1)} & \cdots & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots \\
0 & 0 & 0 & \cdots & \lambda_{(n)}
\end{pmatrix} = \begin{pmatrix} \Lambda_s & 0 \\
0 & \Lambda_f \end{pmatrix},
\]

The eigenvalues are ordered by their magnitude \( \lambda_{m+1} > \lambda_m \).

\[
\tilde{V} = \begin{pmatrix}
-v_1 & - & - & - & - \\
\vdots & - & - & - & - \\
-v_m & - & - & - & - \\
\vdots & \cdots & \cdots & \cdots & \cdots \\
-v_n & - & - & - & -
\end{pmatrix} = \begin{pmatrix} \tilde{V}_s \\
\tilde{V}_f \end{pmatrix}.
\]

\[
z \equiv \tilde{V} C \quad \Rightarrow \quad \frac{dz}{dt} = \Lambda z
\]

\[
\frac{dz_i}{dt} = \lambda_i z_i \quad i = 1, \ldots, n
\]

\[
z_s = \tilde{V}_s C \quad \frac{dz_s}{dt} = \Lambda_s z_s \quad \text{slow dynamics that need to be solved for}
\]

\[
z_f = \tilde{V}_f C \quad 0 = \Lambda_f z_f \quad \text{determined the low intrinsic manifold}
\]
Simple* hydrogen-oxygen kinetics mechanism

\[ H_2, H, O, OH, H_2O, N_2 \]

\[
\begin{align*}
O + H_2 & \rightleftharpoons H + OH \\
H_2 + OH & \rightarrow H_2O + H \\
O + H_2O & \rightleftharpoons 2OH \\
H_2 + M & \rightarrow 2H + M \\
O + H + M & \rightarrow OH + M \\
H + OH + M & \rightarrow H_2O + M
\end{align*}
\]

Ren et al. (J. Chem. Phys; 2006)

The times at which the first reaction event commences, and that at which the system relaxes onto its equilibrium are approximately \(10^{-9}\) s and \(10^{-3}\) s.

* Representation of \(H_2/O_2\) chemistry would involve \(O_3\), \(HO_2\), \(H_2O_2\) as well as \(NO\) and related species.

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Al-Khateeb et al. (J. Chem. Phys; 2009)
Specific Reaction-Rate Constant

The Arrhenius Law \[ k(T) = BT^\alpha e^{-E/RT} \]
the pre-exponential factor has a weak temperature dependence, with \(-1 < \alpha \leq 2\). The coefficient \(B\) is the frequency factor, and \(E\) is the activation energy.

The probability that a molecule possesses energy \(\geq E\) is proportional to \(\exp\left(-\frac{E}{RT}\right)\). The exponential factor in the reaction rate \(\omega\) represents the fraction of collisions between reactant molecules for which products can be formed.

The reaction rate of a elementary reaction

\[ \sum_{i=1}^{N} \nu_i' M_i \rightarrow \sum_{i=1}^{N} \nu_i'' M_i \]

\[ \omega = BT^\alpha e^{-E/RT} \prod_{i=1}^{N} C_i^{\nu_i'} \]