Lecture 3
Chemical Kinetics

An elementary step reaction may be expressed in the form

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

$N$ - number of species  \hspace{1cm} $\nu'_i = 0$ if $i$ is not a reactant
$\nu'_i, \nu''_i$ - stoichiometric coefficients \hspace{1cm} $\nu''_i = 0$ if $i$ is not a product

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

$$\frac{\dot{\omega}_j}{\nu''_j - \nu'_j} = \frac{\dot{\omega}_j}{\nu''_j - \nu'_j} \quad \text{for any } i, j$$

$$\frac{\dot{\omega}_i}{\nu''_i - \nu'_i} = \frac{\dot{\omega}_j}{\nu''_j - \nu'_j} = \omega \quad \text{reaction rate}$$

the reaction rate $\omega$, which is species independent, is the rate of consumption (moles per unit volume per second) of any species for which $\nu'_i - \nu''_i = 1$.  

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

If \( \omega_i \) is the time rate of change of the mass of species \( i \) mass, per unit volume per second)

\[
\omega_i = (\nu''_i - \nu'_i) W_i \quad \text{mass/volume} \cdot \text{s}
\]

\[
\sum_{i=1}^{N} \omega_i = \omega \sum_{i=1}^{N} (\nu''_i - \nu'_i) W_i = 0
\]

**Law of Mass Action** - phenomenological law, verified experimentally

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

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

\( k \) is the (specific) reaction rate constant; its units depend on the reaction order \( n = \sum \nu'_i \), and is \{concentration\(^{n-1}\) \cdot time\(^{-1}\) \}.

The representation of methane oxidation \( \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \) is a gross simplification. It is seldom that the original reactants interact among themselves in a single step and produce the final product. In most cases, there are large number of steps with intermediate species involved before the final formation of products.

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 \( i \)

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

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

\[
\omega_j = k_j(T) \prod_{i=1}^{N} C_i^{\nu'_{i,j}}
\]
Chain reaction - hydrogen-bromine reaction

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

Note that summing all the reactions, after multiplying the second by 2, yields the overall step.

\[ \omega_i = \sum_{j=1}^{5} (\nu_{i,j} - \nu_{i,j}') \omega_j \quad \omega_j = k_j(T) \prod_{i=1}^{5} C_i^{\nu_{i,j}'} \]

for example

\[ \dot{\omega}_{\text{Br}} = \frac{dC_{\text{Br}}}{dt} = 2k_1C_{\text{Br}_2} - k_2C_{\text{Br}_2}C_{\text{H}_2} + k_3C_{\text{H}}C_{\text{Br}_2} + k_4C_{\text{H}}C_{\text{HBr}} - 2k_5C_{\text{Br}}^2 \]

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Chemical Kinetics

Two of the important questions of chemical kinetics studies:

- determine all the elementary steps involved in a given chemical reaction
- determine the specific rate constant for each elementary step

Reaction Mechanisms

- First order decomposition reaction
- Second order reactions
- One step opposing reactions
- Chain reactions
- Reduced mechanisms modeling (steady state and partial equilibrium approximations, new computational methodologies)
First order decomposition reaction

\[ A \xrightarrow{k} B \]

such as \( O_2 \rightarrow 2O \), or \( OH \rightarrow O + H \)

\[ \frac{dC_A}{dt} = -kC_A \quad C_{A_0} \text{ given} \]

\[ C_A = C_{A_0} e^{-kt} \]

\[ t = \frac{1}{k} \ln \left[ \frac{C_{A_0}}{C_A} \right] \]

\[ t_c \sim \frac{1}{k} \]

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

Experimental determination of \( k \)

Second order reactions

(a) \( A + B \xrightarrow{k} C + D \)

such as \( H + O_2 \rightarrow OH + O \)

\( \text{or } O_3 + CO \rightarrow CO_2 + 2O \)

\[ \frac{dC_A}{dt} = -kC_AC_B \quad C_{A_0} \& C_{B_0} \text{ given} \]

\[ \frac{dC_B}{dt} = -kC_AC_B \]

\[ C_{A_0} - C_A = C_{B_0} - C_B \]

\[ \frac{dC_A}{dt} = -kC_A(C_{A_0} - C_{B_0} - C_A) \]

\[ C_A = \frac{C_{A_0}}{C_{B_0}} (C_A - C_{A_0} + C_{B_0}) e^{-(C_{B_0} - C_{A_0})kt} \]

\[ C_A = \frac{C_{A_0}(C_{A_0} - C_{B_0})}{C_{A_0} - C_{B_0} e^{(C_{A_0} - C_{B_0})kt}} \]

\[ C_A = C_{A_0} - C_{B_0} (1 - e^{C_{A_0}kt}) \text{ if } C_{A_0} \gg C_{B_0} \]
(b) \[ 2A + M \xrightarrow{k} B \]
such as \[ 2O + M \rightarrow O_2 + M \]
M third body, \( C_M \approx \text{const.} \)

\[ \frac{dC_A}{dt} = -kC_A^2 \]
\[ C_A = \frac{C_A(0)}{1 + C_A(0)kt} \]

\[ t = \frac{1}{k} \left[ \frac{1}{C_A} - \frac{1}{C_A(0)} \right] \]

---

**One step opposing reaction**

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

\[ \frac{dC_A}{dt} = -k_fC_A + k_bC_B \]
\[ \text{\( C_A(0) \) specified, \( C_B(0) = 0 \) } \]

\[ \frac{dC_B}{dt} = k_fC_A - k_bC_B \]

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

\[ C = V_1e^{\lambda_1t} + V_2e^{\lambda_2t} \]

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

\[
\begin{pmatrix}
C_A \\
C_B
\end{pmatrix} =
\begin{pmatrix}
C_A(0) \\
C_B(0)
\end{pmatrix} + \frac{k_b}{k_f + k_b} \begin{pmatrix} 1 \\ -1 \end{pmatrix} e^{-(k_f + k_b)t}
\]

as \( t \to \infty \)

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

\[
\begin{pmatrix}
C_A \\
C_B
\end{pmatrix} = \begin{pmatrix}
C_A^\text{eq} \\
C_B^\text{eq}
\end{pmatrix} + C_B^\text{eq} \begin{pmatrix} 1 \\ -1 \end{pmatrix} e^{-(k_f + k_b)t}
\]

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

at equilibrium,

\[
k_f C_A^\text{eq} - k_b C_B^\text{eq} = 0
\]

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

\[
\begin{align*}
\frac{dC_A}{dt} &= -k_f C_A + k_b C_B \\
\frac{dC_B}{dt} &= k_f C_A - k_b C_B
\end{align*}
\]

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

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

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

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

\[
\begin{align*}
\frac{dz_1}{dt} &= 0 \\
\frac{dz_2}{dt} &= -(k_f + k_b)z_2
\end{align*}
\]

\[
z_1 = z_1(0) e^{0t} \quad z_2 = z_2(0) e^{-(k_f + k_b)t}
\]

The characteristic times are:

\( t_1 = \lambda_1^{-1} = \infty \) (slow time) and \( t_2 = \lambda_2^{-1} = (k_f + k_b)^{-1} \) (fast time)

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

\[ C_A + C_B \text{ is a conserved quantity} \]

When \( k_f + k_b \gg 1 \), the quantity \( k_f C_A - k_b C_B \approx 0 \) almost all the time; i.e., the system is almost all the time in equilibrium \( k_f C_A^{eq} - k_b C_B^{eq} = 0 \)

The system can be approximated (almost all the time) by
\[ C_A + C_B = C_A(0) \]
\[ k_f C_A - k_b C_B \approx 0 \]

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**Chain Reaction**

Hydrogen-Bromine Reaction

any halogen molecule (F\(_2\), Cl\(_2\) or I\(_2\)) may replace Br\(_2\)

\[ H_2 + Br_2 \rightarrow 2 HBr \]

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

the intermediates H, Br are the chain carriers
\[
\begin{align*}
\text{Br}_2 + M & \underset{k_1}{\rightarrow} 2\text{Br} + M \\
\text{Br} + \text{H}_2 & \underset{k_2}{\rightarrow} \text{HBr} + \text{H} \\
\text{H} + \text{Br}_2 & \underset{k_3}{\rightarrow} \text{HBr} + \text{Br} \quad \Rightarrow \quad \text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr} \\
\text{H} + \text{HBr} & \underset{k_4}{\rightarrow} \text{Br} + \text{H}_2 \\
2\text{Br} + M & \underset{k_5}{\rightarrow} \text{Br}_2 + M
\end{align*}
\]

\[\frac{dC_{\text{HBr}}}{dt} = k_2 C_{\text{Br}} C_{\text{H}_2} + k_3 C_{\text{H}} C_{\text{Br}_2} - k_4 C_{\text{H}} C_{\text{HBr}}\]

\[\frac{dC_{\text{H}}}{dt} = k_2 C_{\text{Br}} C_{\text{H}_2} - k_3 C_{\text{H}} C_{\text{Br}_2} - k_4 C_{\text{H}} C_{\text{HBr}}\]

\[\frac{dC_{\text{Br}}}{dt} = 2k_1 C_{\text{Br}_2} - k_2 C_{\text{Br}} C_{\text{H}_2} + k_3 C_{\text{H}} C_{\text{Br}_2} + k_4 C_{\text{H}} C_{\text{HBr}} - 2k_5 C_{\text{Br}}^2\]

\[\frac{dC_{\text{H}_2}}{dt} = -k_2 C_{\text{Br}} C_{\text{H}_2} + k_4 C_{\text{H}} C_{\text{HBr}}\]

\[\frac{dC_{\text{Br}_2}}{dt} = -k_1 C_{\text{Br}_2} - k_3 C_{\text{H}} C_{\text{Br}_2} + k_5 C_{\text{Br}}^2\]

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 thousands species, involved in a complex network of elementary steps that may add up to few thousands. For example, the detailed kinetic mechanism of the important diesel reference fuel n-hexadecane (n-C$_{16}$H$_{34}$) can include 2,100 chemical species and 8,300 individual reactions$^1$.

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...
Methane oxidation

A reduced scheme involving 31 steps out of more than 200 steps (Warnatz 1984)

### Steady State Approximation

\[
\begin{align*}
\text{Br}_2 + M & \xrightarrow{k_4} 2\text{Br} + M \\
\text{Br} + \text{H}_2 & \xrightarrow{k_3} \text{HBr} + \text{H} \\
\text{H} + \text{Br}_2 & \xrightarrow{k_5} \text{HBr} + \text{Br} \quad \Rightarrow \quad \text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr} \\
\text{H} + \text{HBr} & \xrightarrow{k_4} \text{Br} + \text{H}_2 \\
2\text{Br} + M & \xrightarrow{k_4} \text{Br}_2 + M \\
\frac{dC_{\text{Br}}}{dt} &= 2k_1 C_{\text{Br}_2} - k_2 C_{\text{Br}} C_{\text{H}_2} + k_3 C_{\text{H}} C_{\text{Br}} + k_4 C_{\text{H}} C_{\text{HBr}} - 2k_5 C_{\text{Br}}^2 \\
2k_1 C_{\text{Br}_2} + k_3 C_{\text{H}} C_{\text{Br}_2} + k_4 C_{\text{H}} C_{\text{HBr}} &\approx k_5 C_{\text{Br}} C_{\text{H}} + 2k_5 C_{\text{Br}}^2 \\
\omega_{\text{Br}_2}^+ &\approx \omega_{\text{Br}_2}^- \\
\Rightarrow \quad \frac{dC_{\text{Br}}}{dt} &\approx 0
\end{align*}
\]

The steady-state approximation states that \(\omega_{\text{Br}_2}^+\) and \(\omega_{\text{Br}_2}^-\) are both large compared with \(dC_{\text{Br}}/dt\) so that effectively \(dC_{\text{Br}}/dt \approx 0\). Radicals form and react very rapidly (at nearly equal rates) such that their concentrations remains nearly constant.

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\[
\frac{dC_{Br}}{dt} \approx 0 \Rightarrow 2k_1C_{Br2} - k_2C_{Br}C_{H2} + k_3C_HC_{Br2} + k_4C_HC_{HBr} - 2k_5C_{Br}^2 = 0
\]

Similarly, for the other radicals

\[
\frac{dC_{H}}{dt} \approx 0 \Rightarrow k_2C_{Br}C_{H2} - k_3C_HC_{Br2} - k_4C_HC_{HBr} = 0
\]

\[
\frac{dC_{Br}}{dt} \approx 0 \Rightarrow 2k_1C_{Br2} - k_2C_{Br}C_{H2} + k_3C_HC_{Br2} + k_4C_HC_{HBr} - 2k_5C_{Br}^2 = 0
\]

\[
C_{Br} = \sqrt{\frac{k_1}{k_5}C_{Br2}^{1/2}} \quad C_{H} = \frac{k_2\sqrt{k_1/k_5}C_{H2}C_{Br2}^{1/2}}{k_3C_{Br2} + k_4C_{HBr}}\]

algebraic equations for \(C_{H}\) and \(C_{Br}\)

Rate of formation of HBr

\[
\frac{dC_{HBr}}{dt} = k_2C_{Br}C_{H2} + k_3C_HC_{Br2} - k_4C_HC_{HBr}
\]

\[
\Rightarrow \frac{dC_{HBr}}{dt} = \frac{2k_2\sqrt{k_1/k_5}C_{H2}C_{Br2}^{1/2}}{1 + (k_4/k_3)C_{HBr}C_{Br2}^{-1}}
\]

different from the expression

\[
\frac{dC_{HBr}}{dt} = 2k_0C_{H2}C_{Br2} \text{ for the global reaction } \text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr}
\]

\[
\frac{dC_{HBr}}{dt} \approx 2k_0C_{H2}C_{Br2}^{1/2} \quad \text{when } k_4/k_3 \ll 1; \quad (k_0 = k_2\sqrt{k_1/k_5})
\]
• Reaction rate for a global reaction step is not necessarily of the form
  \( \prod_{i=1}^{N} C_i^{n_i} \) as for elementary steps

• Reaction rate for the global reaction may be approximated using an expression of the form
  \[ \omega = k \prod_{i=1}^{N} C_i^{n_i} \]
  \( i \) 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), and is determined empirically

\( n = \sum_i n_i \) is the overall reaction order.

Note, however that in the rate of consumption/production

\[ \hat{\omega}_i = (\nu_i^c - \nu_i^b) \omega = (\nu_i^c - \nu_i^b) k \prod_{i=1}^{N} C_i^{n_i} \]

\( i = 1, 2, \ldots, N \)

the stoichiometric coefficients appear to properly identify the number of moles
of each reactant involved in the chemical reaction

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**Partial Equilibrium Approximation**

Unlike the steady-state approximation, which refers to a particular species, the partial equilibrium approximation pertains to a particular reaction. It should include the forward and backward steps of any reaction that pertains partial equilibrium. The forward an backward rates are large such that their difference contribute significantly to \( dC_i/dt \). Hence, if step \( s \) of a reaction mechanism proceeds at a rate \( k_f^{(s)} \), i.e.,

\[ \sum_{i=1}^{N} \nu_{i,s}^c M_i \overset{k_f^{(s)}}{\rightarrow} \sum_{i=1}^{N} \nu_{i,s}^b M_i \]

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

\[ \sum_{i=1}^{N} \nu_{i,s}^b M_i \overset{k_f^{(s)}}{\rightarrow} \sum_{i=1}^{N} \nu_{i,s}^c M_i \]

the approximation is expressed as

\[ k_f^{(s)} \prod_{i=1}^{N} C_i^{\nu_{i,s}^c} - k_b^{(s)} \prod_{i=1}^{N} C_i^{\nu_{i,s}^b} \approx 0 \]
Novel computational methodologies

Set of nonlinear coupled ODEs

\[
\begin{align*}
\frac{d\mathbf{C}}{dt} &= \mathbf{F}(\mathbf{C}) \\
\mathbf{C}(0) &= \mathbf{C}_0
\end{align*}
\]

\[
\mathbf{C} = (C_1, C_2, \ldots, C_n)^T
\]

Phase space

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

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

\( \mathbf{J} \) is the Jacobian at the equilibrium state, i.e., \( J_{ij} = \left( \frac{\partial F_i}{\partial C_j} \right)_{eq} \)

Examine the dynamics of the linearized system (rename \( \mathbf{C} - \mathbf{C}_{eq} \) as \( \mathbf{C} \))

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

\[
\mathbf{C} = \mathbf{v} e^{\lambda t} \Rightarrow (\mathbf{J} - \lambda \mathbf{I}) \mathbf{v} = 0 \quad \lambda_n \text{ - eigenvalues, } \mathbf{v}_n \text{ - eigenvectors}
\]

We can diagonalize the matrix \( \mathbf{J} \), using \( \mathbf{V} \) (formed by the eigenvectors) and its inverse \( \mathbf{V}^{-1} \equiv \mathbf{\tilde{V}} \).

Note that not every matrix \( \mathbf{J} \) can be diagonalized; it depends if \( \mathbf{J} \) has \( n \)-linearly independent eigenvectors.
\[ V = \begin{pmatrix} v_1 & \cdots & v_m & v_{m+1} & \cdots & v_n \end{pmatrix} \quad \Lambda = \begin{pmatrix} \lambda_1 & 0 & \cdots & 0 \\ 0 & \lambda_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & \cdots & \cdots & \lambda_n \end{pmatrix} \]

\[(J - \lambda I) v = 0 \quad \text{is equivalent to} \quad J V = \Lambda\]

\[ \tilde{V} \equiv V^{-1} \quad \Rightarrow \quad \tilde{V} J V = \tilde{V} \Lambda \tilde{V} = \Lambda \]

\[ V = \begin{pmatrix} \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \end{pmatrix} \]

We have diagonalized the matrix \( J \), using \( V \) and its inverse \( V^{-1} \equiv \tilde{V} \). The elements of the resulting diagonal matrix \( \Lambda = \tilde{V} J V \) are the eigenvalues \( \lambda_n \).

\[ \Lambda = \tilde{V} J V \quad \Rightarrow \quad J = V \Lambda \tilde{V} \]

We have diagonalized the matrix \( J \), using \( V \) and its inverse \( V^{-1} \equiv \tilde{V} \). The elements of the resulting diagonal matrix \( \Lambda = \tilde{V} J V \) are the eigenvalues \( \lambda_n \).

\[ \frac{dC}{dt} = J C = (V \Lambda \tilde{V}) C \]

\[ \tilde{V} \frac{dC}{dt} = (\Lambda \tilde{V}) C = \Lambda (\tilde{V} C) \]

\[ z \equiv \tilde{V} C \quad \Rightarrow \quad \begin{cases} \frac{dz}{dt} = \Lambda z \\ \frac{dz_i}{dt} = \lambda_i z_i \quad i = 1, \ldots, n \end{cases} \]

\[ z_i = z_i(0) e^{\lambda_i t} \quad i = 1, \ldots, n \]
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 (corresponding to the smaller eigenvalues) that determine the low intrinsic manifold and the slow modes that describes the dynamics that remain to be solved.

$$\begin{align*}
\mathbf{z}_f &= \mathbf{\tilde{V}}_f \mathbf{C} \\
\mathbf{z}_s &= \mathbf{\tilde{V}}_s \mathbf{C} \\
0 &\approx \Lambda_f \mathbf{z}_f \\
d\mathbf{z}_s/dt &= \Lambda_s \mathbf{z}_s
\end{align*}$$

$\mathbf{z}_f$ determine the low intrinsic manifold.

$\mathbf{z}_s$ slow dynamics; needs to be solved.
Simple example

$$\begin{align*}
A & \xrightarrow{k_1} B \\
B & \xrightarrow{k_2} D \\
\frac{dC_A}{dt} &= -k_1 C_A \\
\frac{dC_B}{dt} &= k_1 C_A - k_2 C_B \\
\frac{dC_D}{dt} &= k_2 C_D \\
\begin{vmatrix}
-k_1 - \lambda & 0 & 0 \\
k_1 & -k_2 - \lambda & 0 \\
0 & k_2 & -\lambda
\end{vmatrix} &= 0 \implies
\begin{align*}
\lambda_1 &= 0 \\
\lambda_2 &= -k_2 \\
\lambda_3 &= -k_1
\end{align*}
\end{align*}$$

$$\begin{align*}
\mathbf{v}_1 &= \begin{pmatrix} 0 \\ 0 \end{pmatrix} \\
\mathbf{v}_2 &= \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\
\mathbf{v}_2 &= \begin{pmatrix} k_1 - k_2 \\ -k_1 \\ k_2 \end{pmatrix}
\end{align*}$$

$$\mathbf{V} = \begin{pmatrix} 0 & 0 & k_1 - k_2 \\
0 & 1 & -k_1 \\
1 & -1 & k_2 \end{pmatrix} \quad \text{inverse of } \mathbf{V} \quad \mathbf{V}^{-1} = \begin{pmatrix} 1 & 1 & 1 \\
\frac{k_1}{k_1 - k_2} & 1 & 0 \\
\frac{1}{k_1 - k_2} & 0 & 0 \end{pmatrix}
$$

verify that $\mathbf{V} \mathbf{V}^{-1} = \mathbf{I}$

$$z \equiv \mathbf{VC} = \begin{pmatrix} C_1 + C_2 + C_3 \\
\frac{k_1 C_1}{k_1 - k_2} + C_2 \\
\frac{C_1}{k_1 - k_2} \end{pmatrix} \implies
\begin{align*}
\frac{dz_1}{dt} &= 0 \\
\frac{dz_2}{dt} &= -k_2 z_2 \\
\frac{dz_3}{dt} &= -k_1 z_3
\end{align*}$$
\[ \frac{dz_1}{dt} = 0 \]
\[ \frac{dz_2}{dt} = -k_2 z_2 \]
\[ \frac{dz_3}{dt} = -k_1 z_3 \]

The combination \( C_1 + C_2 + C_3 \) is conserved at all times.

The combination \( \frac{k_1 C_1}{k_1 - k_2} + C_2 \) evolves on a time scale \( \sim k_2^{-1} \).

\( C_1 \) evolves on a time scale \( \sim k_1^{-1} \).

---

**Case I.** \( k_1 \gg k_2 \)

If \( k_1 \gg 1 \), then \( C_1 \approx 0 \), namely A reacts very rapidly and converts to B, which then reacts slowly to produce C.

\( C_1 = 0, \quad C_2 = \alpha_2 e^{-k_2 t}, \quad C_3 = \alpha_1 - \alpha_2 e^{-k_2 t} \).

**Case II.** \( k_2 \gg k_1 \)

\( C_2 \approx \frac{k_1 C_1}{k_1 - k_2} \), so that once produced B converts very fast to C, but the first reaction proceeds slower and

\( C_1 = \alpha_3 e^{-k_1 t}, \quad C_2 = \frac{\alpha_3 k_1}{k_2 - k_1} e^{-k_1 t}, \quad C_3 = \alpha_1 - \frac{\alpha_3 k_2}{k_2 - k_1} e^{-k_1 t} \).
**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 \(\exp(-E/RT)\). The exponential factor in the reaction rate \(\omega\) represents the fraction of collisions between reactant molecules for which products can be formed.

\(-(\Delta H)\) is the heat of reaction

The reaction rate of an elementary reaction
\[
\sum_{i=1}^{N} \nu_i' M_i \rightarrow \sum_{i=1}^{N} \nu_i'' M_i
\]

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

The reaction rate of a mechanism involving \(M\) elementary steps
\[
\sum_{i=1}^{N} \nu_{i,j}' M_i \rightarrow \sum_{i=1}^{N} \nu_{i,j}'' M_i \quad j = 1, 2, \ldots, M
\]

\[\omega = \sum_{j=1}^{M} B_j T^\alpha e^{-E_j/RT} \prod_{i=1}^{N} c_i^{\nu_{i,j}'}\]

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The species and energy equations (equal \(c_p\), Fick’s diffusion)

\[
\rho c_p \frac{DT}{Dt} - \nabla \cdot (\lambda \nabla T) = \frac{Dp}{Dt} + \Phi - \sum_{i=1}^{N} \omega_i h_i^0
\]

\[
\rho \frac{DY_i}{Dt} - \nabla \cdot (\rho D_i \nabla Y_i) = \omega_i, \quad i = 1, 2, \ldots, N - 1
\]

We have seen that the net production/consumption (moles per unit volume per second) for a one step (elementary) reaction is given by

\[
\dot{\omega}_i = (\nu_i'' - \nu_i') \omega = (\nu_i'' - \nu_i') k \prod_{i=1}^{N} C_{ni} \quad i = 1, 2, \ldots, N
\]

where \(\nu_i'\) in the exponents may be replaced with empirical \(n_i\), as necessary.

The time rate of change of the mass of species \(i\) (grams, per unit volume per second), is given by

\[
\rho \frac{DY_i}{Dt} - \nabla \cdot (\rho D_i \nabla Y_i) = (\nu_i'' - \nu_i') \omega, \quad i = 1, 2, \ldots, N - 1
\]

The term \(\sum \omega_i h_i^0\) appearing in the energy equation

\[
\sum_{i=1}^{N} \omega_i h_i^0 = \omega \sum_{i=1}^{N} (\nu_i'' - \nu_i') W_i h_i^0 = -Q \omega
\]

difference between the heat of formation of the products and reactants (negative for exothermic reactions)

is the total heat released, or the heat of combustion

\[
\rho c_p \frac{DT}{Dt} - \nabla \cdot (\lambda \nabla T) = \frac{Dp}{Dt} + \Phi + Q \omega
\]

Note that when using the energy equation in the form

\[
\rho c_p \frac{DT}{Dt} = \frac{Dp}{Dt} + \Phi + \nabla \cdot (\lambda \nabla T) + \sum_{i=1}^{N} \rho c_p Y_i \nabla \cdot \nabla T + \sum_{i=1}^{N} h_i \omega_i
\]

\(-\sum_{i=1}^{N} h_i \omega_i\) is often referred to as the heat release, instead of \(-\sum_{i=1}^{N} h_i'' \omega_i\); it differs from \(Q\) defined earlier when the net distinct contributions of the sensible enthalpies is not small

\[
\sum_{i=1}^{N} h_i \omega_i = \sum_{i=1}^{N} h_i'' \omega_i + \omega \sum_{i=1}^{N} (\nu_i'' - \nu_i') W_i \int_{T_0}^{T} c_p dT
\]

equal 0 when all \(c_p\) are equal