7. Branched Chain Reactions

\( \text{\textit{H}_2\text{-O}_2 \text{ System}} \)

The hydrogen-oxygen mixture explodes by the following mechanism.

\[
\Delta n(\text{chain carrier})
\]

\[
\begin{align*}
\text{O}_2 + \text{H} & \rightarrow \text{O} + \text{OH} \quad \text{(reaction-1, } k_1) +1 \quad \text{chain branching} \\
\text{H}_2 + \text{O} & \rightarrow \text{H} + \text{OH} \quad \text{(reaction-2, } k_2) +1 \quad \text{chain branching} \\
\text{H}_2 + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{H} \quad \text{(reaction-3, } k_3) \pm0 \quad \text{chain propagation}
\end{align*}
\]

\[
\text{net: } 2 \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH} + \text{H} \quad (\text{... no way to eliminate chain carriers})
\]

- Once chain carriers (H, OH, or O) are formed, the reaction self-multiplies the chain carriers.
  \( \rightarrow \text{Branched Chain Reaction} \)

At the initial stage of reactions, \([\text{O}_2]\) and \([\text{H}_2]\) can be assumed to be constants.

By using \(r_1 = k_1[\text{O}_2], \ r_2 = k_2[\text{H}_2], \ \text{and } r_3 = k_3[\text{H}_2]\), the rate equation system can be written as

\[
x = Ax
\]

where \(x = \begin{bmatrix} \text{[H]} \\ \text{[O]} \\ \text{[OH]} \end{bmatrix}\) and \(A = \begin{bmatrix}
-r_1 & r_2 & r_3 \\
1 & -r_2 & 0 \\
1 & r_2 & -r_3
\end{bmatrix}\)

**Exercise 7.1**

1) Write the eigen equation for the matrix \(A\) in Eq. (7.1), in the form of a cubic equation,

\[
a\lambda^3 + b\lambda^2 + c\lambda + d = 0.
\]

2) Show that the matrix \(A\) has a positive eigenvalue.  (Note that \(r_1, r_2, r_3 > 0\).)

**Solution to exercise 7.1**

1) The eigen equation is

\[
f(\lambda) = \begin{vmatrix}
-\lambda_1 - \lambda & r_2 & r_3 \\
1 & -\lambda_2 - \lambda & 0 \\
1 & r_2 & -\lambda_3 - \lambda
\end{vmatrix}
\]

\[
= \lambda^3 + (r_1 + r_2 + r_3)\lambda^2 + r_2r_3\lambda - 2r_1r_2r_3 = 0.
\]

2) Since \(r_1, r_2, \text{ and } r_3\) are positive,

\[
f(0) = -2r_1r_2r_3 < 0 \text{ and } f(\lambda) \text{ monotonically increases with } \lambda \text{ at } \lambda > 0.
\]

\[
\Rightarrow f(\lambda) = 0 \text{ has a root } > 0.
\]

**Chain Explosion**

General solution to (7.1)

\[
x = S \begin{bmatrix}
a_1 e^{\lambda_1 t} \\
a_2 e^{\lambda_2 t} \\
a_3 e^{\lambda_3 t}
\end{bmatrix} = a_1 s_1 e^{\lambda_1 t} + a_2 s_2 e^{\lambda_2 t} + a_3 s_3 e^{\lambda_3 t} \quad (7.2)
\]

\[
\lambda < 0 : \text{Converging term} \\
\lambda = 0 : \text{Constant term} \\
\lambda > 0 : \text{Diverging term}
\]

- Reaction system with \(\lambda_{\text{max}} > 0\)
  \(\rightarrow\) the system self-multiplies the chain carriers and results in the **Chain Explosion**.
Exercise 7.2

The figures show the numerical solution for the rate equations for reactions 1–3 for the 2:1 H₂-O₂ mixture at \( T = 1000 \text{ K} \), \( p = 1.01 \text{ kPa} \), \([\text{O}]_0 = 1.46 \times 10^{-11} \text{ mol m}^{-3}\) and \([\text{OH}]_0 = 1.22 \times 10^{-10} \text{ mol m}^{-3}\). The coefficients for the solution (7.2) at this condition are shown below.

\[
x = \begin{bmatrix} [\text{H}] \\ [\text{O}] \\ [\text{OH}] \end{bmatrix} = a_1 s_1 e^{\lambda_1 t} + a_2 s_2 e^{\lambda_2 t} + a_3 s_3 e^{\lambda_3 t} \
\tag{7.2}
\]

| \(i\) | \(\lambda_i \/ s^{-1}\) | \(|\lambda_i| \/ \text{ms}\) | \(a_i \/ 10^{10} \text{ mol m}^{-3}\) |
|---|---|---|---|
| 1 | 3.63 \times 10^3 | 0.275 | 1.17 |
| 2 | -2.20 \times 10^4 | 0.0455 | 0.02 |
| 3 | -9.93 \times 10^4 | 0.0101 | 1.67 |
| s_i | 0.994 | 0.872 | -0.711 |
| | 0.105 | -0.482 | 0.020 |
| | 0.041 | -0.088 | 0.703 |

1) Calculate \([\text{H}]\) and \([\text{O}]\) at \( t = 0.2, 0.6 \) and \( 1.0 \) ms from eq. (7.2) with coefficients given above ignoring the minor terms for \(\lambda_2\) and \(\lambda_3\), and plot them in figure (a).
2) Interpret the physical meanings of \(\lambda_1\) and \(s_1\) in figure (a).
3) Interpret the physical meanings of \(\lambda_3\) and \(s_3\) in figure (b).

### Solution to exercise 7.2

1) See the figure above.
2) \(\lambda_1\) is the first order rate of exponential growth of \([\text{H}], [\text{O}], \) and \([\text{OH}]\) and \(s_1\) represents the ratio of the concentrations of \([\text{H}], [\text{O}], \) and \([\text{OH}]\).
3) \(\lambda_3\) is the first order decay of \([\text{H}]\) and \([\text{OH}]\) in the initial stage of reactions. \(s_3\) represents the amplitudes.

* \(a_2\) is relatively small and it is difficult to distinguish the contribution of this term in these figures.