7. Branched Chain Reactions

⟨H_2-O_2 System⟩

The hydrogen-oxygen mixture explodes by the following mechanism.

		Δn(chain carrier)	
O_2 + **H** → **O** + **OH**	(reaction-1, k_1)	**+1**	chain branching
H_2 + **O** → **H** + **OH**	(reaction-2, k_2)	**+1**	chain branching
H_2 + **OH** → H_2O + **H**	(reaction-3, k_3)	±0	chain propagation

net: 2 H_2 + O_2 → H_2O + **OH** + **H** (? ... no way to eliminate chain carriers)

- Once chain carriers (H, OH, or O) are formed, the reaction self-multiplies the chain carriers.
  → Branched Chain Reaction

At the initial stage of reactions, [O_2] and [H_2] can be assumed to be constants.
By using $r_1 = k_1[O_2]$, $r_2 = k_2[H_2]$, and $r_3 = k_3[H_2]$, the rate equation system can be written as

$$\dot{\mathbf{x}} = \mathbf{A}\mathbf{x} \tag{7.1}$$

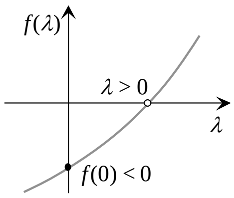
where $\mathbf{x} = \begin{pmatrix} [H] \\ [O] \\ [OH] \end{pmatrix}$ and $\mathbf{A} = \begin{pmatrix} -r_1 & r_2 & r_3 \\ r_1 & -r_2 & 0 \\ r_1 & r_2 & -r_3 \end{pmatrix}$

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 $f(\lambda) = -\begin{vmatrix} -r_1-\lambda & r_2 & r_3 \\ r_1 & -r_2-\lambda & 0 \\ r_1 & r_2 & -r_3-\lambda \end{vmatrix}$
$= \lambda^3 + (r_1 + r_2 + r_3)\lambda^2 + r_2r_3\lambda - 2r_1r_2r_3 = 0.$
2) Since r_1, r_2, and r_3 are positive,
$f(0) = -2r_1r_2r_3 < 0$ and
$f(\lambda)$ monotonically increases with λ at $\lambda > 0$.
→ $f(\lambda) = 0$ has a root > 0.



⟨Chain Explosion⟩

General solution to (7.1)

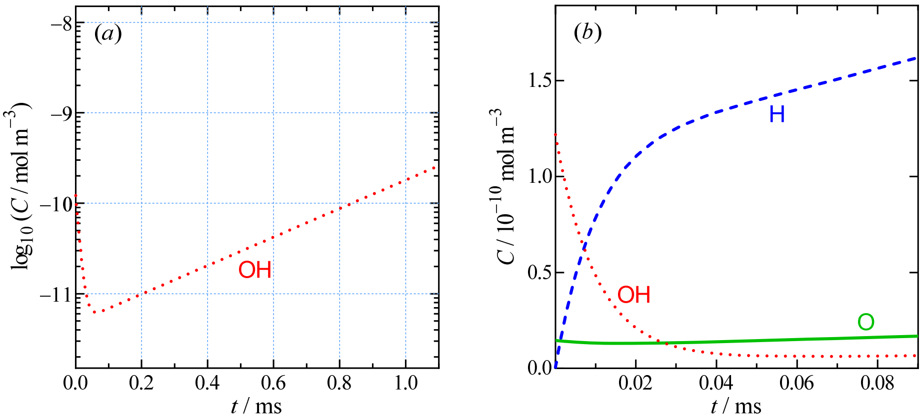
$$\mathbf{x} = \mathbf{S}\begin{pmatrix} a_1 e^{\lambda_1 t} \\ a_2 e^{\lambda_2 t} \\ a_3 e^{\lambda_3 t} \end{pmatrix} = a_1\mathbf{s}_1 e^{\lambda_1 t} + a_2\mathbf{s}_2 e^{\lambda_2 t} + a_3\mathbf{s}_3 e^{\lambda_3 t} \tag{7.2}$$

$\lambda < 0$: Converging term
$\lambda = 0$: Constant term
$\lambda > 0$: Diverging term

- Reaction system with $\lambda_{max} > 0$
  → the system self-multiplies the chain carriers and results in the Chain Explosion.

〈Eigenvalues and Eigenvectors〉

Exercise 7.2



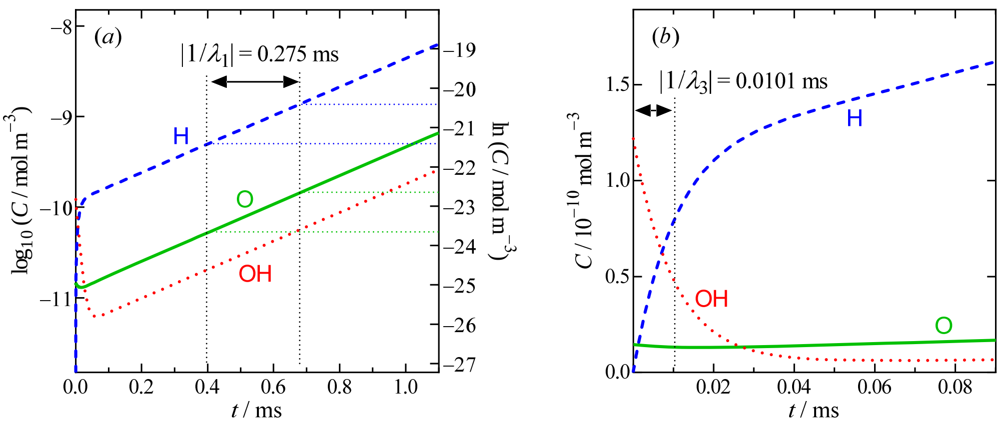
The figures show the numerical solution for the rate equations for reactions 1–3 for the 2:1 H_2-O_2 mixture at T = 1000 K, p = 1.01 kPa, $[O]_0 = 1.46\times10^{-11}$ mol m^{-3} and $[OH]_0 = 1.22\times10^{-10}$ mol m^{-3}. The coefficients for the solution (7.2) at this condition are shown below.

$$\mathbf{x} = \begin{pmatrix} [H] \\ [O] \\ [OH] \end{pmatrix} = a_1\mathbf{s}_1 e^{\lambda_1 t} + a_2\mathbf{s}_2 e^{\lambda_2 t} + a_3\mathbf{s}_3 e^{\lambda_3 t} \tag{7.2}$$

i	1	2	3
λ_i / s^{-1}	3.63×10^3	-2.20×10^4	-9.93×10^4
$\lvert\lambda_i^{-1}\rvert$ / ms	0.275	0.0455	0.0101
a_i / 10^{-10} mol m^{-3}	1.17	0.02	1.67
$\mathbf{s}_i$	$\begin{pmatrix} 0.994 \\ 0.105 \\ 0.041 \end{pmatrix}$	$\begin{pmatrix} 0.872 \\ -0.482 \\ -0.088 \end{pmatrix}$	$\begin{pmatrix} -0.711 \\ 0.020 \\ 0.703 \end{pmatrix}$

1) Calculate [H] and [O] at t = 0.2, 0.6 and 1.0 ms from eq. (7.2) with coefficients given above ignoring the minor terms for λ_2 and λ_3, and plot them in figure (a).
2) Interpret the physical meanings of λ_1 and $\mathbf{s}_1$ in figure (a).
3) Interpret the physical meanings of λ_3 and $\mathbf{s}_3$ in figure (b).

Solution to exercise 7.2



1) See the figure above.
2) λ_1 is the first order rate of exponential growth of [H], [O], and [OH] and $\mathbf{s}_1$ represents the ratio of the concentrations of [H], [O], and [OH].
3) λ_3 is the first order decay of [H] and [OH] in the initial stage of reactions. $\mathbf{s}_1$ represents the amplitudes.

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