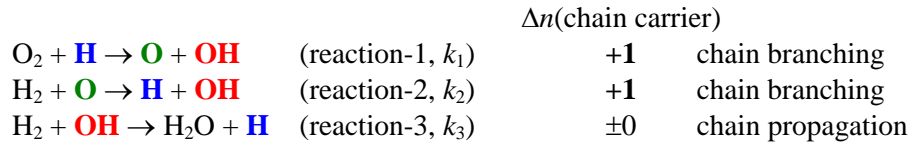


7. Branched Chain Reactions

⟨H₂-O₂ System⟩

The hydrogen-oxygen mixture explodes by the following mechanism.



net: 2 H₂ + O₂ → H₂O + **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, [O₂] and [H₂] can be assumed to be constants.

By using r₁ = k₁[O₂], r₂ = k₂[H₂], and r₃ = k₃[H₂], the rate equation system can be written as

$$\dot{\mathbf{x}} = \mathbf{A}\mathbf{x} \quad (7.1)$$

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

Exercise 7.1

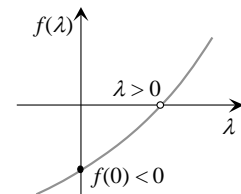
- 1) Write the eigen equation for the matrix **A** in Eq. (7.1), in the form of a cubic equation, $a\lambda^3 + b\lambda^2 + c\lambda + d = 0$.
- 2) Show that the matrix **A** has a positive eigenvalue. (Note that r₁, r₂, r₃ > 0.)

Solution to exercise 7.1

$$1) \text{ The eigen equation is } f(\lambda) = - \begin{vmatrix} -r_1 - \lambda & r_2 & r_3 \\ r_1 & -r_2 - \lambda & 0 \\ r_1 & r_2 & -r_3 - \lambda \end{vmatrix}$$

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

- 2) Since r₁, r₂, and r₃ are positive,
f(0) = -2r₁r₂r₃ < 0 and
f(λ) monotonically increases with λ at λ > 0.
→ f(λ) = 0 has a root > 0.



⟨Chain Explosion⟩

General solution to (7.1)

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

λ < 0 : Converging term

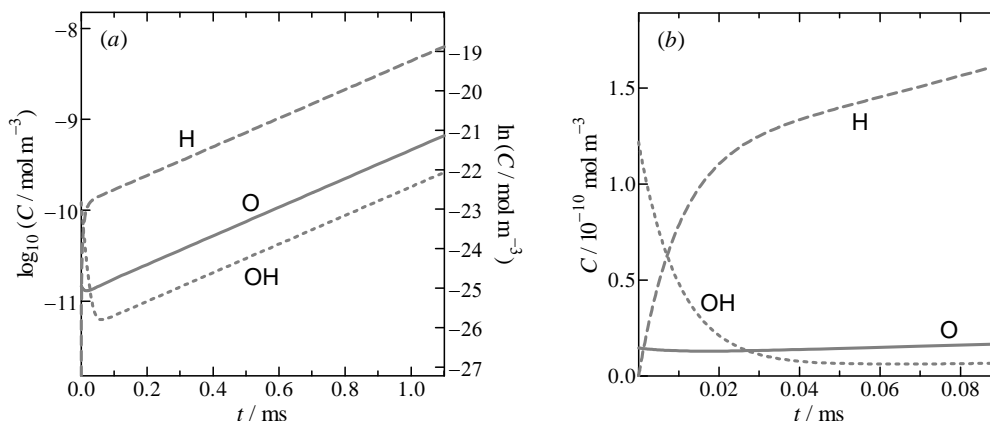
λ = 0 : Constant term

λ > 0 : Diverging term

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

Eigenvalues and Eigenvectors

Exercise 7.2



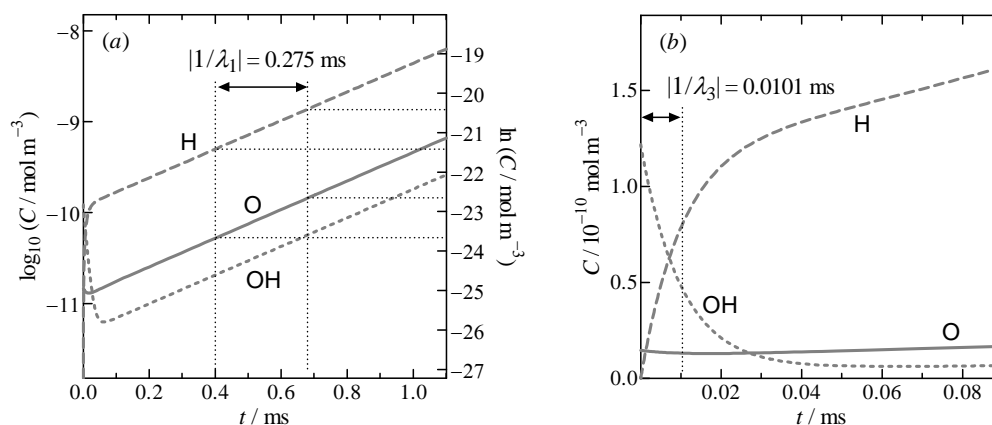
The figures show the numerical solution for the rate equations for reactions 1–3 for the 2:1 $\text{H}_2\text{-O}_2$ mixture at $T = 1000 \text{ K}$, $p = 1.01 \text{ kPa}$, $[\text{O}]_0 = 1.46 \times 10^{-11} \text{ mol m}^{-3}$ and $[\text{OH}]_0 = 1.22 \times 10^{-10} \text{ mol m}^{-3}$. The coefficients for the solution (7.2) at this condition are shown below.

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

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

- Interpret the physical meanings of λ_1 and \mathbf{s}_1 in figure (a).
- Interpret the physical meanings of λ_3 and \mathbf{s}_3 in figure (b).

Solution to exercise 7.2



- 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].
- 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.