6. Straight Chain Reactions

⟨Cl₂-H₂ System⟩

The chlorine-hydrogen mixture explodes by the following mechanism after the photolytic initiation (Cl₂ + $h\nu \rightarrow 2$ Cl).

$$H_2 + \mathbf{Cl} \rightarrow HCl + \mathbf{H}$$
 (reaction-1, k_1)
 $Cl_2 + \mathbf{H} \rightarrow HCl + \mathbf{Cl}$ (reaction-2, k_2)

net:
$$H_2 + Cl_2 \rightarrow 2 HCl$$

- Once chain carriers (Cl or H) are formed, the reaction continues to proceed.
 - → Chain Reaction

The rate equation system is

$$\frac{d[Cl]}{dt} = -k_1[H_2][Cl] + k_2[Cl_2][H]$$
(6.1)

$$\frac{d[H]}{dt} = k_1[H_2][Cl] - k_2[Cl_2][H]$$
(6.2)

At the initial stage of reactions, [H₂] and [Cl₂] can be assumed to be constants.

By using x = [C1], y = [H], $r_1 = k_1[H_2]$, and $r_2 = k_2[Cl_2]$, the rate equation system can be simplified as

$$\dot{\mathbf{x}} = \mathbf{A}\mathbf{x}$$
where $\mathbf{x} = \begin{pmatrix} x \\ y \end{pmatrix}$ and $\mathbf{A} = \begin{pmatrix} -r_1 & r_2 \\ r_1 & -r_2 \end{pmatrix}$

The general solution to Eq. (6.3) is

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

$$(6.4)$$

where $\mathbf{S} = (\mathbf{s}_1 \ \mathbf{s}_2)$, λ_1 and λ_2 are the eigenvalues, and \mathbf{s}_1 and \mathbf{s}_2 are the corresponding eigenvectors of \mathbf{A} .

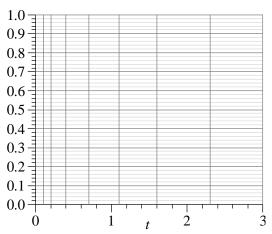
The coefficients a_1 and a_2 can be calculated from the initial condition, $\mathbf{x} = \mathbf{x}_0$ at t = 0, as

$$\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \mathbf{S}^{-1} \mathbf{x}_0$$
 (6.5)

Exercise 6.1

- 1) Derive the solution to the differential equation system (6.3) for the initial condition, $\mathbf{x}_0 = \begin{pmatrix} c_0 \\ 0 \end{pmatrix}$.
- 2) Fill the following table of the solution for $r_1 = 1$, $r_2 = 2$, and $c_0 = 1$, and then plot it.

t	X	У
0	1	0
0.1	0.91	0.09
0.2	0.85	0.15
0.4	0.77	0.23
0.7	0.71	0.29
1.1	0.68	0.32
1.6	0.67	0.33
2.3	0.67	0.33
3	0.67	0.33



Solution to exercise 6.1

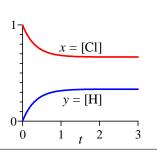
1) The eigen equation is $\begin{vmatrix} -r_1 - \lambda & r_2 \\ r_1 & -r_2 - \lambda \end{vmatrix} = \lambda \left\{ \lambda + \left(r_1 + r_2 \right) \right\} = 0.$

The eigenvalues are $\lambda_1 = 0$ and $\lambda_2 = -(r_1 + r_2)$, and

corresponding eigenvectors are $\mathbf{s}_1 = \begin{pmatrix} r_2 \\ r_1 \end{pmatrix}$ and $\mathbf{s}_2 = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$.

The solution is $\mathbf{x} = \frac{c_0}{r_1 + r_2} \begin{bmatrix} r_2 \\ r_1 \end{bmatrix} + \begin{pmatrix} r_1 \\ -r_1 \end{pmatrix} \exp \left\{ -(r_1 + r_2)t \right\}$

2) As shown in the figure to the right.



(Eigenvalues and Eigenvectors)

• Eigenvalues represent rates of changes as $\exp(\lambda t)$.

 $\lambda < 0$: Converge (with time constant $|\lambda_2^{-1}| = 1/3$)

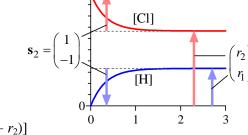
 $\lambda = 0$: Constant (steady state)

 $(\lambda > 0 : Diverge)$

• Corresponding Eigenvectors represent the amplitude.

 $\mathbf{s}_1 = \begin{pmatrix} r_2 \\ r_1 \end{pmatrix}$: Amplitude of constant part $\exp(0t) = 1$

 $\mathbf{s}_2 = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$: Amplitude of converging part $\exp[-(r_1 + r_2)]$



• Cl₂-H₂ reaction : $\lambda_1 = 0$ and $\lambda_2 < 0 \rightarrow$ exponential decay (λ_2) to a steady state (λ_1)

(Steady State)

Exercise 6.2

- 1) By assuming the steady states for both [Cl] and [H], derive the ratio of the steady-state concentrations, [Cl]_{ss} / [H]_{ss}. in terms of r_1 and r_2 where $r_1 = k_1[H_2]$ and $r_2 = k_2[Cl_2]$.
- 2) Then, derive the steady-state concentrations [Cl]_{ss} and [H]_{ss} in terms of c_0 , r_1 , and r_2 by using [Cl]_{ss} + [H]_{ss} = c_0 .

Solution to exercise 6.2

- 1) (6.1) = 0 or $(6.2) = 0 \rightarrow r_1[C1]_{ss} = r_2[H]_{ss}$. Thus, $[C1]_{ss} / [H]_{ss} = r_2 / r_1$
- 2) $[C1]_{ss} = \frac{c_0 r_2}{r_1 + r_2}$ and $[H]_{ss} = \frac{c_0 r_1}{r_1 + r_2}$.

* This is the constant part of the solution of Exercise. 6.1

(Thermal Explosion)

- Ultimately, the Cl₂-H₂ mixture explodes by self-heating, i.e., thermal feedback.
 - $H_2 + Cl_2 \rightarrow 2$ HCl is exothermic by 185 kJ mol⁻¹.
 - Rate constants increases with temperature (cf. Arrhenius equation).