6. Straight Chain Reactions

⟨Cl_2-H_2 System⟩

The chlorine-hydrogen mixture explodes by the following mechanism after the photolytic initiation ($Cl_2 + h\nu \rightarrow 2\,Cl$).

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

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

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

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

At the initial stage of reactions, $[H_2]$ and $[Cl_2]$ can be assumed to be constants.
By using $x = [Cl]$, $y = [H]$, $r_1 = k_1[H_2]$, and $r_2 = k_2[Cl_2]$, the rate equation system can be simplified as

$$\dot{\mathbf{x}} = \mathbf{A}\mathbf{x} \qquad (6.3)$$

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

$$\mathbf{x} = \mathbf{S}\begin{pmatrix} a_1 e^{\lambda_1 t} \\ a_2 e^{\lambda_2 t} \end{pmatrix} = a_1 \mathbf{s}_1 e^{\lambda_1 t} + a_2 \mathbf{s}_2 e^{\lambda_2 t} \qquad (6.4)$$

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

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

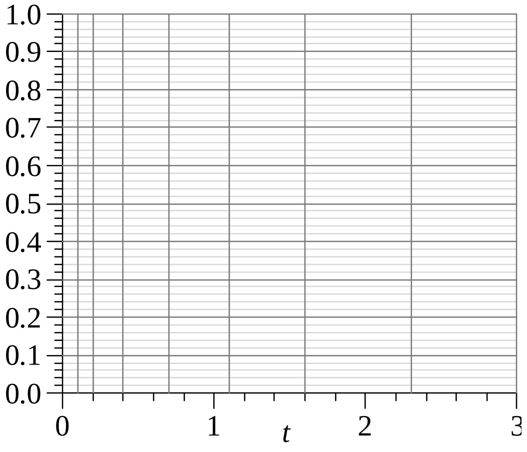
$$\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \mathbf{S}^{-1}\mathbf{x}_0 \qquad (6.5)$$

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	y
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

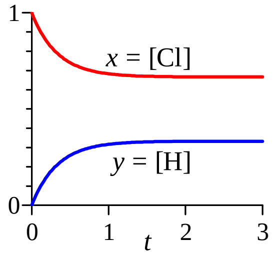
1) The eigen equation is $\begin{vmatrix} -r_1-\lambda & r_2 \\ r_1 & -r_2-\lambda \end{vmatrix} = \lambda\{\lambda+(r_1+r_2)\}=0$.

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 $\mathbf{s}_2 = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$.

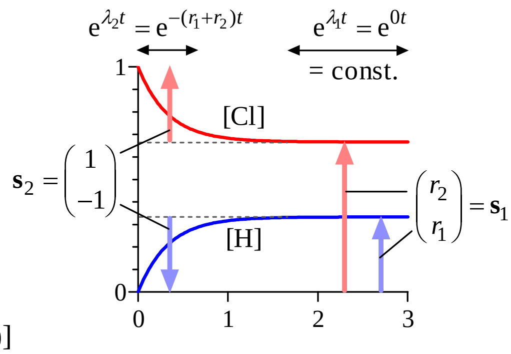
The solution is $\mathbf{x} = \frac{c_0}{r_1+r_2}\left[\begin{pmatrix} r_2 \\ r_1 \end{pmatrix} + \begin{pmatrix} r_1 \\ -r_1 \end{pmatrix} \exp\{-(r_1+r_2)t\}\right]$.

2) As shown in the figure to the right.



⟨Eigenvalues and Eigenvectors⟩

- Eigenvalues represent rates of changes as exp(λt).
  - $\lambda < 0$: 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[$-(r_1 + r_2)$]



- Cl_2-H_2 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 $\rightarrow$ $r_1[Cl]_{ss} = r_2[H]_{ss}$. Thus, $[Cl]_{ss} / [H]_{ss} = r_2 / r_1$

2) $[Cl]_{ss} = \frac{c_0 r_2}{r_1 + r_2}$ 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 Cl_2-H_2 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).