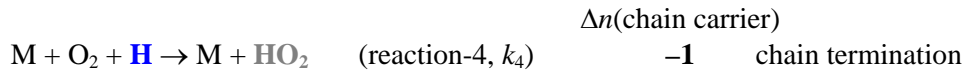# 8. Explosion Limits and Numerical Analysis

⟨Explosion Limits⟩

With reactions 1–3 only, the H_2-O_2 mixture should explode at any T and p, but the actual mixture shows explosion limits.   For better description, we should add the following reaction.

$$\Delta n(\text{chain carrier})$$

$$M + O_2 + \mathbf{H} \rightarrow M + \mathbf{HO_2} \qquad (\text{reaction-4, } k_4) \qquad -1 \qquad \text{chain termination}$$

Here "M" means the any molecule, including H_2, O_2, N_2 *etc.*, and it means that the rate of reaction depends on the total concentration, [M] (or total pressure).

Exercise 8.1

1) Write the matrix $\mathbf{A}$ of the differential equation system $\dot{\mathbf{x}} = \mathbf{A}\mathbf{x}$ consisting of reactions 1–4.   Assume constant $[O_2]$, $[H_2]$, and [M] and use constants, r_1, r_2, r_3, and $r_4 = k_4[O_2][M]$.
2) Write the eigen equation for the matrix $\mathbf{A}$.
3) Determine the conditions of r_1 to r_4 for $\lambda_{max} < 0$, $\lambda_{max} = 0$, and $\lambda_{max} > 0$.
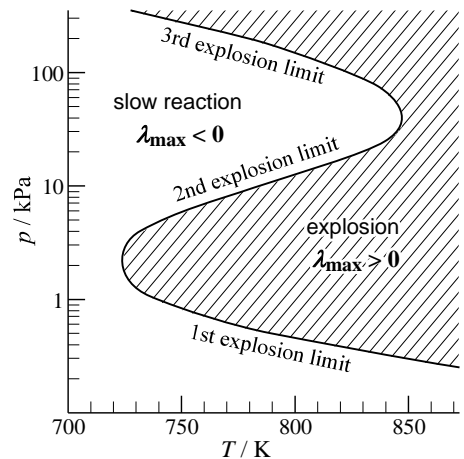

Explosion limits of H_2-O_2 (2:1) mixture

Solution to exercise 8.1

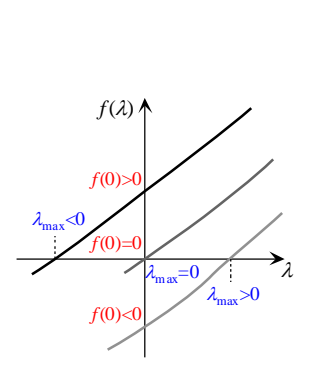1) $\mathbf{A} = \begin{pmatrix} -r_1 - r_4 & r_2 & r_3 \\ r_1 & -r_2 & 0 \\ r_1 & r_2 & -r_3 \end{pmatrix}$

2) The eigen equation is $f(\lambda) = - \begin{vmatrix} -r_1 - r_4 - \lambda & r_2 & r_3 \\ r_1 & -r_2 - \lambda & 0 \\ r_1 & r_2 & -r_3 - \lambda \end{vmatrix}$

$= \lambda^3 + (r_1 + r_2 + r_3 + r_4)\lambda^2 + (r_2 r_3 + r_3 r_4 + r_4 r_2)\lambda + r_2 r_3 (r_4 - 2r_1) = 0$.

3) Similarly to Exercise 7.1, $f(\lambda)$ monotonically increases with λ at $\lambda > 0$.   So, the necessary conditions are:
$r_4 > 2r_1 : f(0) > 0$ and $\lambda_{max} < 0$
$r_4 = 2r_1 : f(0) = 0$ and $\lambda_{max} = 0$
$r_4 < 2r_1 : f(0) < 0$ and $\lambda_{max} > 0$

⟨H_2-O_2 Explosion Limits⟩

• Explosion limits $\leftrightarrow \lambda_{max} = 0$
2nd Limit: $\lambda_{max} = 0$ in Exercise 8.1   ... $r_4 = 2r_1 \rightarrow k_4[M] = 2k_1$
1st Limit: appears by including heterogeneous removal of chain carriers
3rd Limit: appears by including further reactions of HO_2 and self-heating effect

⟨Sensitivity Analysis⟩

Definition of the normalized sensitivity coefficient for the concentration of i-th chemical species with respect to the rate constant for the j-th reaction is

$$S(c_i, k_j) = \frac{k_j}{c_i} \frac{\partial c_i}{\partial k_j} = \frac{\partial \ln c_i}{\partial \ln k_j} \qquad (8.1)$$

where c_i is the concentration of i-th chemical species and k_j is the rate constant for the j-th reaction.

⟨Contribution Analysis⟩

The contribution of j-th reaction to the formation of i-th species is defined as

$$\chi(i, j) = \frac{\upsilon_f(i, j)}{\sum_j \upsilon_f(i, j)} \qquad (8.2)$$

where $\upsilon_f(i, j)$ is the rate of formation of i-th species by the j-th reaction.

⟨Example for Cl$_2$-H$_2$⟩

For the Cl$_2$-H$_2$ system considered in section 6,

$$H_2 + Cl \rightarrow HCl + H \qquad (k_1) \quad r_1 = k_1[H_2]$$
$$Cl_2 + H \rightarrow HCl + Cl \qquad (k_2) \quad r_2 = k_2[Cl_2]$$

As derived in Exercise 6.2, the steady-state concentrations for the condition, $[Cl] + [H] = c_0$ are,

$$[Cl]_{ss} = \frac{c_0 r_2}{r_1 + r_2} \quad \text{and} \quad [H]_{ss} = \frac{c_0 r_1}{r_1 + r_2} \tag{8.3}$$

Exercise 8.2

1) Derive an expression of $\dfrac{d[HCl]}{dt}$ for the steady-state condition in terms of r_1, r_2, and c_0.

   Then, write an expression for [HCl] for the steady-state condition and [HCl] = 0 at $t = 0$.
2) Derive the normalized sensitivity coefficient for [HCl] with respect to r_1, S([HCl], r_1), by differentiating the expression for [HCl] derived above, partially with respect to r_1.   Similarly, derive the normalized sensitivity coefficient for [HCl] with respect to r_2, S([HCl], r_2).
3) Calculate the values of S([HCl], r_1) and S([HCl], r_2) for 1:1 mixture of Cl$_2$ and H$_2$ at 298 K.   At this temperature, $k_1 = 9.8 \times 10^3$ m^3 mol^{-1} s^{-1} and $k_2 = 1.2 \times 10^7$ m^3 mol^{-1} s^{-1}.
4) Calculate the contributions to the formation of HCl by reactions 1 and 2, χ(HCl, 1) and χ(HCl, 2), respectively.

Solution to exercise 8.2

1) $\dfrac{d[HCl]}{dt} = r_1[Cl]_{ss} + r_2[H]_{ss} = \dfrac{2c_0 r_1 r_2}{r_1 + r_2}$

   $[HCl] \approx \dfrac{2c_0 r_1 r_2}{r_1 + r_2} t$

2) $\dfrac{\partial[HCl]}{\partial r_1} = 2c_0 r_2 \dfrac{\partial[r_1 / (r_1 + r_2)]}{\partial r_1} t = \dfrac{2c_0 r_2^2}{(r_1 + r_2)^2} t \;\rightarrow\; S([HCl], r_1) = \dfrac{r_2}{r_1 + r_2}.$

   Similarly, $S([HCl], r_2) = \dfrac{r_1}{r_1 + r_2}.$

3) Since $[Cl_2] = [H_2]$, $S([HCl], r_1) = \dfrac{k_2[Cl_2]}{r_1[H_2] + k_2[Cl_2]} = \dfrac{k_2}{k_1 + k_2} = 0.9992 \approx 1$

   $S([HCl], r_2) = \dfrac{k_1}{k_1 + k_2} \qquad\qquad = 0.0008 \approx 0$

   * For this case, since $r_2 \gg r_1$, Eq. (8.4) becomes $[HCl] \approx 2c_0 r_1 t$.

4) Rates of formation of HCl via reactions 1 and 2 are $r_1[Cl]_{ss} = \dfrac{c_0 r_1 r_2}{r_1 + r_2}$ and $r_2[H]_{ss} = \dfrac{c_0 r_1 r_2}{r_1 + r_2}$,

   which are the same.   Thus χ(HCl, 1) = 0.5 and χ(HCl, 2) = 0.5.

[Rate-Determining Step]
- Both reactions 1 and 2 equally contribute HCl formation.
- Reaction 1 is the rate-determining step for this system.