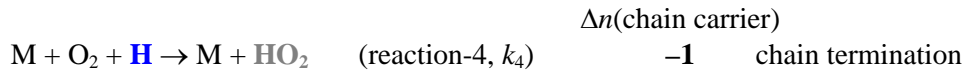


8. Explosion Limits and Numerical Analysis

⟨Explosion Limits⟩

With reactions 1–3 only, the H₂-O₂ mixture should explode at any T and p , but the actual mixture shows explosion limits. For better description, we should add the following reaction.



Here "M" means the any molecule, including H₂, O₂, N₂ etc., and it means that the rate of reaction depends on the total pressure.

Exercise 8.1

- Write the matrix \mathbf{A} of the differential equation system $\dot{\mathbf{x}} = \mathbf{A}\mathbf{x}$ consisting of reactions 1–4. Assume constant [O₂], [H₂], and [M] and use constants, r_1 , r_2 , r_3 , and $r_4 = k_4[\text{O}_2][\text{M}]$.
- Write the eigen equation for the matrix \mathbf{A} .
- Determine the conditions of r_1 to r_4 for $\lambda_{\max} < 0$, $\lambda_{\max} = 0$, and $\lambda_{\max} > 0$.

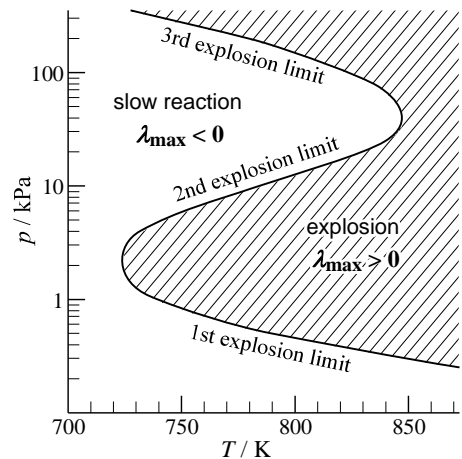
Solution to exercise 8.1

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

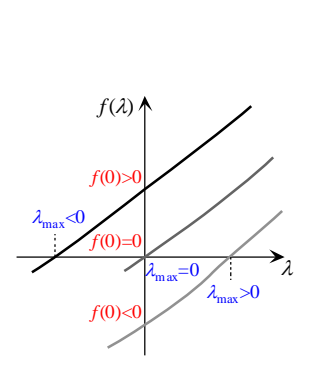
$$2) \text{ The eigen equation is } f(\lambda) = - \begin{vmatrix} -r_1 - r_4 - \lambda & r_2 & r_3 \\ r_1 & -r_2 - \lambda & 0 \\ r_1 & r_2 & -r_3 - \lambda \end{vmatrix}$$

$$= \lambda^3 + (r_1 + r_2 + r_3 + r_4)\lambda^2 + (r_2r_3 + r_3r_4 + r_4r_2)\lambda + r_2r_3(r_4 - 2r_1) = 0.$$

- 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 $\lambda_{\max} > 0$



Explosion limits of H₂-O₂ (2:1) mixture



⟨H₂-O₂ Explosion Limits⟩

- Explosion limits $\leftrightarrow \lambda_{\max} = 0$
- 2nd Limit: $\lambda_{\max} = 0$ in Exercise 8.1 ... $r_4 = 2r_1 \rightarrow k_4[\text{M}] = 2k_1$
- 1st Limit: appears by including heterogeneous removal of chain carriers
- 3rd Limit: appears by including further reactions of HO₂ 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

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

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

$$\chi(i, j) = \frac{v_f(i, j)}{\sum_j v_f(i, j)} \quad (8.2)$$

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

Example for Cl₂-H₂

For the Cl₂-H₂ system considered in section 6,



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

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

Exercise 8.2

- 1) Derive an expression of $\frac{d[\text{HCl}]}{dt}$ for the steady-state condition in terms of r_1 , r_2 , and c_0 .
Then, write an expression for $[\text{HCl}]$ for the steady-state condition and $[\text{HCl}] = 0$ at $t = 0$.
- 2) Derive the normalized sensitivity coefficient for $[\text{HCl}]$ with respect to r_1 , $S([\text{HCl}], r_1)$, by differentiating the expression for $[\text{HCl}]$ derived above, partially with respect to r_1 . Similarly, derive the normalized sensitivity coefficient for $[\text{HCl}]$ with respect to r_2 , $S([\text{HCl}], r_2)$.
- 3) Calculate the values of $S([\text{HCl}], r_1)$ and $S([\text{HCl}], r_2)$ for 1:1 mixture of Cl₂ and H₂ at 298 K. At this temperature, $k_1 = 9.8 \times 10^3 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_2 = 1.2 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
- 4) Calculate the contributions to the formation of HCl by reactions 1 and 2, $\chi(\text{HCl}, 1)$ and $\chi(\text{HCl}, 2)$, respectively.

Solution to exercise 8.2

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

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

$$2) \quad \frac{\partial[\text{HCl}]}{\partial r_1} = 2c_0 r_2 \frac{\partial[r_1 / (r_1 + r_2)]}{\partial r_1} t = \frac{2c_0 r_2^2}{(r_1 + r_2)^2} t \rightarrow S([\text{HCl}], r_1) = \frac{r_2}{r_1 + r_2}$$

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

$$3) \quad \text{Since } [\text{Cl}_2] = [\text{H}_2], \quad S([\text{HCl}], r_1) = \frac{k_2[\text{Cl}_2]}{r_1[\text{H}_2] + k_2[\text{Cl}_2]} = \frac{k_2}{k_1 + k_2} = 0.9992 \approx 1$$

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

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

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

which are the same. Thus $\chi(\text{HCl}, 1) = 0.5$ and $\chi(\text{HCl}, 2) = 0.5$.

[Rate-Determining Step]

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