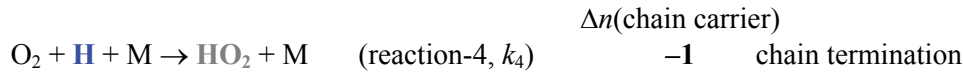


## 8. Explosion Limits and Numerical Analysis

### 〈Explosion Limits〉

With reactions 1–3, the H<sub>2</sub>-O<sub>2</sub> mixture should explode at any  $T$  and  $p$ , but the actual mixture shows the explosion limits. For better understanding, we should add the following reaction.



Here "M" means the any molecule, including H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> etc, and it indicates that the rate of reaction depends on the total pressure. Then, with  $r_4 = k_4[\text{O}_2][\text{M}]$ , the matrix  $\mathbf{A}$  becomes,

$$\mathbf{A} = \begin{pmatrix} -r_1 - r_4 & r_2 & r_3 \\ r_1 & -r_2 & 0 \\ r_1 & r_2 & -r_3 \end{pmatrix} \quad (8.1)$$

### Exercise 8.1

- 1) Write the eigen equation for the matrix  $\mathbf{A}$  in Eq. (8.1).
- 2) Determine the conditions of  $r_1$  to  $r_4$  for  $\lambda_{\max} < 0$ ,  $\lambda_{\max} = 0$ , and  $\lambda_{\max} > 0$ .

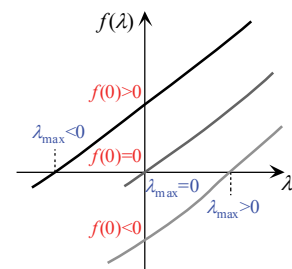
#### Solution to exercise 8.1

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

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

- 2) Similarly to Exercise 7.1,  $f(\lambda)$  monotonically increases with  $\lambda$  at  $\lambda > 0$ . So, the necessary conditions are:

$$\begin{aligned} r_4 > 2r_1 &: f(0) > 0 \text{ and } \lambda_{\max} < 0 \\ r_4 = 2r_1 &: f(0) = 0 \text{ and } \lambda_{\max} = 0 \\ r_4 < 2r_1 &: f(0) < 0 \text{ and } \lambda_{\max} > 0 \end{aligned}$$



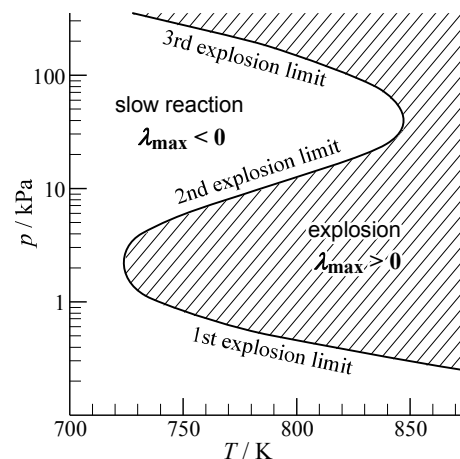
- Explosion limit  $\leftrightarrow \lambda_{\max} = 0$

### 〈H<sub>2</sub>-O<sub>2</sub> Explosion Limits〉

2nd Limit:  $\lambda_{\max} = 0$  in Exercise 8.1

1st Limit: appears by including heterogeneous removal of chain carriers

3rd Limit: appears by including further reactions of HO<sub>2</sub> 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

$$S_{ij} = \frac{k_j}{c_i} \frac{\partial c_i}{\partial k_j} = \frac{\partial \ln c_i}{\partial \ln k_j} \quad (8.2)$$

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

$$\chi_{ij} = \frac{r_{ij}}{\sum_j r_{ij}} \quad (8.3)$$

where  $r_{ij}$  is the rate of formation of  $i$ -th species by the  $j$ -th reaction.

### 〈Example for Cl<sub>2</sub>-H<sub>2</sub>〉

For the Cl<sub>2</sub>-H<sub>2</sub> system considered in section 6,



the steady-state concentrations for the initial conditions,  $[\text{Cl}]_0 = c_0$  and  $[\text{H}]_0 = 0$ , are

$$[\text{Cl}]_{\text{ss}} = \frac{c_0 r_2}{r_1 + r_2} \quad \text{and} \quad [\text{H}]_{\text{ss}} = \frac{c_0 r_1}{r_1 + r_2} \quad (8.4)$$

as derived in Exercise 6.2. The rate of formation of HCl in the steady state is

$$\frac{d[\text{HCl}]}{dt} = r_1[\text{Cl}]_{\text{ss}} + r_2[\text{H}]_{\text{ss}} = \frac{2c_0 r_1 r_2}{r_1 + r_2} \quad (8.5)$$

Thus, the concentration of HCl can be approximated by

$$[\text{HCl}] \approx \frac{2c_0 r_1 r_2}{r_1 + r_2} t \quad (8.6)$$

### Exercise 8.2

- 1) Derive the normalized sensitivity coefficient for [HCl] with respect to  $r_1$ ,  $S([\text{HCl}], r_1)$ , by differentiating Eq. (8.6) partially with respect to  $r_1$ . Similarly, derive the normalized sensitivity coefficient for [HCl] with respect to  $r_2$ ,  $S([\text{HCl}], r_2)$ .
- 2) Calculate the values of  $S([\text{HCl}], r_1)$  and  $S([\text{HCl}], r_2)$  for 1:1 mixture of Cl<sub>2</sub> and H<sub>2</sub> at 298 K. At this temperature,  $k_1 = 9.8 \times 10^3 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $k_2 = 1.2 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .
- 3) 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

$$1) \quad \frac{\partial [\text{HCl}]}{\partial r_1} = 2c_0 r_2 \frac{\partial [r_1 / (r_1 + r_2)]}{\partial r_1} t = \frac{2c_0 r_2^2}{(r_1 + r_2)^2} t \rightarrow S([\text{HCl}], r_1) = \frac{r_2}{r_1 + r_2}.$$

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

$$2) \quad \text{Since } [\text{Cl}_2] = [\text{H}_2], \quad S([\text{HCl}], r_1) = \frac{k_2[\text{Cl}_2]}{r_1[\text{H}_2] + k_2[\text{Cl}_2]} = \frac{k_2}{k_1 + k_2} = 0.9992 \approx 1$$

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

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

$$3) \quad \text{Rates of formation of HCl via reactions 1 and 2 are } r_1[\text{Cl}]_{\text{ss}} = \frac{c_0 r_1 r_2}{r_1 + r_2} \quad \text{and} \quad r_2[\text{H}]_{\text{ss}} = \frac{c_0 r_1 r_2}{r_1 + r_2},$$

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.