

12.B.2.2. Stability of Nonlinear Chemical Reactions

Consider the chemical reaction [see §S2.D]



where the convention is

$$v_1, v_2 \leq 0 \quad \& \quad v_3, v_4 \geq 0$$

The rate equation is [c.f. (2.228)]

$$\begin{aligned} \frac{\partial c_3}{\partial t} &= k_1 c_1^{|v_1|} c_2^{|v_2|} - k_2 c_3^{v_3} c_4^{v_4} \\ &= k_1 c_1^{|v_1|} c_2^{|v_2|} \left(1 - \frac{k_2 c_3^{v_3} c_4^{v_4}}{k_1 c_1^{|v_1|} c_2^{|v_2|}} \right) \end{aligned} \quad (12.29)$$

with [see (2.235)]

$$c_j = \frac{n_j}{V} \quad J^c = \frac{1}{V} \frac{d\xi}{dt} = \frac{1}{V v_j} \frac{dn_j}{dt} = \frac{1}{v_j} \frac{dc_j}{dt} \quad (12.29a)$$

For a system of ideal gases, the affinity

$$A \equiv \sum_j \mu_j v_j$$

is given by [see (2.244)]

$$A = RT \ln \left(K(T, P) \frac{c_3^{v_3} c_4^{v_4}}{c_1^{|v_1|} c_2^{|v_2|}} \right) \quad (12.30)$$

where $K(T, P)$ is independent of the concentrations c_j .

Consider now the thermodynamic equilibrium state. To begin [see (2.239)],

$$A = 0 \quad (12.30a)$$

Since it must be a steady state (i.e., time-independent),

$$J^c = 0 \quad \leftrightarrow \quad \frac{dc_j}{dt} = 0 \forall j \quad (12.30b)$$

Note that by (12.29a), if $\frac{dc_j}{dt} = 0$ for one value of j , then $\frac{dc_j}{dt} = 0$ for all values of j .

Putting (12.30a-b) into (12.22) then gives

$$\mathcal{P} = 0 \quad (12.30c)$$

which means the entropy S^0 is time-independent, as expected.

Putting (12.30b) into (12.29) gives

$$J^c = 0 \quad \leftrightarrow \quad k_1 c_{10}^{|v_1|} c_{20}^{|v_2|} = k_2 c_{30}^{v_3} c_{40}^{v_4} \quad (12.30d)$$

where the subscript 0 is used to denote equilibrium values.

Setting $A = 0$ in (12.30) gives

$$A = 0 \quad \leftrightarrow \quad K(T, P) \frac{c_{30}^{v_3} c_{40}^{v_4}}{c_{10}^{|v_1|} c_{20}^{|v_2|}} = 1 \quad (12.30e)$$

Combining (12.30d & e) gives

$$K(T, P) = \frac{c_{10}^{|v_1|} c_{20}^{|v_2|}}{c_{30}^{v_3} c_{40}^{v_4}} = \frac{k_2}{k_1} \quad (12.30f)$$

Since $K(T, P)$ is independent of the concentrations, (12.30f) is valid for all cases so that (12.30) becomes

$$A = R T \ln \left(\frac{k_2}{k_1} \frac{c_3^{v_3} c_4^{v_4}}{c_1^{|v_1|} c_2^{|v_2|}} \right) \quad (12.30g)$$

which can be inverted to give

$$\frac{c_3^{v_3} c_4^{v_4}}{c_1^{|v_1|} c_2^{|v_2|}} = \frac{k_1}{k_2} e^{A/R T}$$

so that (12.29) becomes

$$\begin{aligned} \frac{\partial c_3}{\partial t} &= k_1 c_1^{|v_1|} c_2^{|v_2|} \left(1 - e^{A/R T} \right) \\ &= v_3 J^c \end{aligned} \quad (12.31) \quad [(12.29a) \text{ used. }]$$

which clearly shows that

$$J^c = 0 \quad \leftrightarrow \quad A = 0 \quad (12.31a)$$

is the only steady state.

As will be shown in Exercise 12.1, one can create local steady states by imposing constraints on the system. By definition, the entropy of a local steady state is at a local maximum at all times. Hence, the entropy around the local steady state takes the form

$$S = S_{\text{local}}^0 + \delta S_{\text{local}} + \delta^2 S_{\text{local}} + \dots \quad (12.32)$$

where $S_{\text{local}}^0 < S^0$ is the (time-independent) entropy of the steady state and

$$\delta S_{\text{local}} = 0 \quad \text{and} \quad \delta^2 S_{\text{local}} \leq 0 \quad (12.32a)$$

Using (2.177) of §2.H.2, we have

$$\delta^2 S_{\text{local}} = -\frac{1}{2 T} \int d^3 r \left[\sum_{i,j=1}^N \left(\frac{\partial \mu_i}{\partial c_j} \right)_{P, T, \{c_k \neq c_j\}} \delta c_i \delta c_j \right] \leq 0 \quad (12.33)$$

where we have replaced the sum over cells with a volume integral.

Taking the time derivative of (12.33) gives

$$\frac{d \delta^2 S_{\text{local}}}{d t} = -\frac{1}{2 T} \int d^3 r \left[\sum_{i,j=1}^N \left(\frac{\partial \mu_i}{\partial c_j} \right)_{P, T, \{c_k \neq c_j\}}^0 \left(\frac{d \delta c_i}{d t} \delta c_j + \delta c_i \frac{d \delta c_j}{d t} \right) \right] \quad (12.34a)$$

Using

$$\mu_i = \left(\frac{\partial g}{\partial c_i} \right)_{P, T, \{c_k \neq c_i\}} \quad g = \frac{G}{V} = \text{Gibbs energy per unit volume}$$

we have

$$\left(\frac{\partial \mu_i}{\partial c_j} \right)_{P, T, \{c_k \neq c_j\}}^0 = \left(\frac{\partial^2 g}{\partial c_j \partial c_i} \right)_{P, T, \{c_k \neq c_i, c_j\}}^0 = \left(\frac{\partial \mu_j}{\partial c_i} \right)_{P, T, \{c_k \neq c_i\}}^0$$

so that (12.34a) becomes

$$\frac{d \delta^2 S_{\text{local}}}{d t} = -\frac{1}{T} \int d^3 r \sum_{i,j=1}^N \left(\frac{\partial \mu_i}{\partial c_j} \right)_{P, T, \{c_k \neq c_j\}}^0 \frac{d \delta c_i}{d t} \delta c_j \quad (12.34)$$

Using (12.24), we have

$$\frac{d \delta c_i}{d t} = \sum_{\alpha=1}^r v_{i\alpha} \delta J_{\alpha}^c \quad (12.35)$$

Similarly, (12.24a) gives

$$\delta A_{\alpha} = \sum_{j=1}^N v_{j\alpha} \delta \mu_j \quad (12.37)$$

Since μ_i is a function of T, P & $\{c_j\}$, we have

$$\delta \mu_i = \sum_{j=1}^N \left(\frac{\partial \mu_i}{\partial c_j} \right)_{P, T, \{c_k \neq c_j\}}^0 \delta c_j \quad (12.36)$$

(12.34) thus gives

$$\begin{aligned} \frac{d \delta^2 S_{\text{local}}}{d t} &= -\frac{1}{T} \int d^3 r \sum_{i=1}^N \delta \mu_i \frac{d \delta c_i}{d t} && [(12.36) \text{ used. }] \\ &= -\frac{1}{T} \int d^3 r \sum_{\alpha=1}^r \sum_{i=1}^N \delta \mu_i v_{i\alpha} \delta J_{\alpha}^c && [(12.35) \text{ used. }] \\ &= -\frac{1}{T} \int d^3 r \sum_{\alpha=1}^r \delta A_{\alpha} \delta J_{\alpha}^c \\ &= -\frac{1}{T} \int d^3 r \sum_{\alpha=1}^{r_{\text{uc}}} \delta A_{\alpha} \delta J_{\alpha}^c && [(12.37) \text{ used. }] \end{aligned} \quad (12.38)$$

where the sum runs over only r_{uc} unconstrained affinities because $\delta A_{\alpha} = 0$ for the constrained ones.

In view of (12.32a), $\delta^2 S_{\text{local}}$ is a Lyapunov function if

$$\frac{d \delta^2 S_{\text{local}}}{d t} > 0 \quad (12.38a)$$

The entropy production itself is given by (12.22) as

$$\mathcal{P} = -\frac{1}{T} \int d^3 r \sum_{\alpha=1}^r J_{\alpha}^c A_{\alpha} \quad (12.39)$$

with the excess entropy production due to fluctuations in the forces given by (12.23) as

$$\delta_X \mathcal{P} = -\frac{1}{T} \int d^3 r \sum_{\alpha=1}^r J_{\alpha}^c \delta A_{\alpha} \quad (12.40)$$

Analogous to (12.30a-b), the thermodynamic equilibrium state is specified by

$$J_{\alpha}^c = 0 \quad \text{and} \quad A_{\alpha}^0 = 0 \quad \forall \alpha \quad (12.40a)$$

Keeping one or more forces (i.e., affinities) fixed at some finite values can create one or more local steady states. Similar to the thermodynamic equilibrium state, the unconstrained fluxes vanish at these local steady states. Therefore, the unconstrained fluxes near the steady states can be expanded as

$$J_{\alpha}^c = \delta J_{\alpha}^c + \delta^2 J_{\alpha}^c + \dots \quad (12.41)$$

Since $\delta A_{\alpha} = 0$ for the constrained reactions, putting (12.41) into (12.40) gives

$$\delta_X \mathcal{P} = -\frac{1}{T} \int d^3 r \sum_{\alpha=1}^{r_{\text{uc}}} \delta J_{\alpha}^c \delta A_{\alpha} \quad (12.42)$$

$$= \frac{d \delta^2 S_{\text{local}}}{dt} \quad [(12.38) \text{ used. }]$$

Note that if $J_{\alpha}^{c_0}, A_{\alpha}^0 \neq 0$ for some α , then by (12.39), $\mathcal{P} \neq 0$. In order to keep S_{local}^0 time-independent, the system is necessarily an open one so that any excess entropy generated is immediately transported out of the system.

Exercise 12.1.

Consider the autocatalytic nonlinear chemical reaction



Assuming an ideal gas system, the affinity can be written as [see (12.30g)]

$$A = RT \ln \left(\frac{k_2}{k_1} \frac{c_X^2}{c_B c_X} \right) = RT \ln \left(\frac{k_2}{k_1} \frac{c_X}{c_B} \right) \quad (1b)$$

- (a) When all concentrations are allowed to vary freely, what steady states can occur? Are they stable? What is the state of thermodynamic equilibrium?
- (b) Hold $c_B = c_B^0$ by allowing the B molecules to flow in and out of the system. Determine if the resultant steady states are stable.

For further discussions, read p.732 of Reichl's text.

Answer (a)

The rates of reaction for (1a) are obtained by writing it as



where X' is the auto-catalysis with

$$c_{X'} \equiv c_X \rightarrow \frac{d c_{X'}}{dt} = \frac{d c_X}{dt}$$

(1c) then gives

$$\begin{aligned} J^c &= -\frac{d c_B}{dt} = -\left(-k_1 c_B c_{X'} + k_2 c_X c_{X'} \right)_{c_{X'}=c_X} = -\left(-k_1 c_B c_X + k_2 c_X^2 \right) \\ &= \frac{d c_X}{dt} = \left(k_1 c_B c_{X'} - k_2 c_X c_{X'} \right)_{c_{X'}=c_X} = k_1 c_B c_X - k_2 c_X^2 \end{aligned} \quad (1)$$

The steady states are given by

$$J^c = 0 \quad \rightarrow \quad k_1 c_B c_X - k_2 c_X^2 = 0 \quad (1d)$$

with solutions

$$\bar{c}_X = 0 \quad \bar{c}_B = \text{arbitrary} \quad (1e)$$

or

$$\bar{c}_X = \frac{k_1}{k_2} \bar{c}_B \quad (1f)$$

Solution (1e) indicates a system with only B molecules and hence no chemical reaction. It is therefore

of no interest to us.

Solution (1f) has an affinity [see (1b)]

$$\bar{A} = RT \ln \left(\frac{k_2 \bar{c}_X}{k_1 \bar{c}_B} \right) = 0 \quad (1g)$$

which means it is the thermodynamic equilibrium state.

Answer (b)

Setting $c_B = c_B^0$ turns the steady states (1e-f) into

$$\bar{c}_X = 0 \quad \bar{c}_B = c_B^0 \quad (2a)$$

and

$$\bar{c}_X = \frac{k_1}{k_2} c_B^0 \quad \bar{c}_B = c_B^0 \quad (2b)$$

Consider now a small fluctuation δc_X about \bar{c}_X so that

$$c_X = \bar{c}_X + \delta c_X$$

(1) gives

$$\begin{aligned} \delta J^c &= k_1 c_B^0 \delta c_X - 2 k_2 c_X \delta c_X \\ &\approx (k_1 c_B^0 - 2 k_2 \bar{c}_X) \delta c_X \end{aligned} \quad (2c)$$

(1b) gives

$$\delta A = \frac{RT}{c_X} \delta c_X \approx \frac{RT}{\bar{c}_X} \delta c_X \quad (2d)$$

Assuming the system to be uniform in space, (12.42) gives

$$\begin{aligned} \delta_X \mathcal{P} &= -\frac{V}{T} \delta J^c \delta A \\ &\approx -VR \left(\frac{k_1 c_B^0 - 2 k_2 \bar{c}_X}{\bar{c}_X} \right) (\delta c_X)^2 \end{aligned} \quad (2)$$

If a steady state is stable, we must have $\delta_X \mathcal{P} > 0$ since \mathcal{P} is minimal at a stable steady state.

For steady state (2a), (2) becomes

$$\delta_X \mathcal{P} = -\lim_{\bar{c}_X \rightarrow 0} \frac{VR k_1 c_B^0 (\delta c_X)^2}{\bar{c}_X} < 0$$

which means the state is unstable.

For steady state (2b), (2) becomes

$$\begin{aligned} \delta_X \mathcal{P} &\approx -VR \left(\frac{k_1 c_B^0 - 2 k_2 \frac{k_1}{k_2} c_B^0}{\frac{k_1}{k_2} c_B^0} \right) (\delta c_X)^2 \\ &= VR k_2 (\delta c_X)^2 > 0 \end{aligned}$$

which means the state is stable.