

## 12.D.1. The Brusselator - A Nonlinear Chemical Model

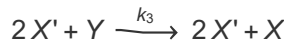
Read Reichl's introduction on p.735 of his text.

The **Brusselator** is one of the simplest chemical models that support oscillations in both space (traveling waves) and time (**chemical clock**). It consists of a chain reaction of 4 steps:



To ensure the indicated (1-way) directions of the reactions,  $A$  &  $B$  are usually kept in abandon supply, while  $D$  &  $E$  are removed as soon as they appear. The system is thus held far away from thermodynamic equilibrium.

With the 3rd equation re-written as



the rate equations for (12.50) are

$$\begin{aligned}
 J_1^c &= \frac{d c_X^{(1)}}{d t} = k_1 c_A \\
 &= -\frac{d c_A}{d t} = -(-k_1 c_A)
 \end{aligned}
 \tag{12.50a}$$

$$\begin{aligned}
 J_2^c &= \frac{d c_Y^{(2)}}{d t} = \frac{d c_D}{d t} = k_2 c_B c_X \\
 &= -\frac{d c_B}{d t} = -\frac{d c_X^{(2)}}{d t} = -(-k_2 c_B c_X)
 \end{aligned}
 \tag{12.50b}$$

$$\begin{aligned}
 J_3^c &= \frac{d c_X^{(3)}}{d t} = (k_3 c_X^2 c_Y)_{c_X=c_X} = k_3 c_X^2 c_Y \\
 &= -\frac{d c_Y^{(3)}}{d t} = -(-k_3 c_X^2 c_Y)_{c_X=c_X} = -(-k_3 c_X^2 c_Y)
 \end{aligned}
 \tag{12.50c}$$

$$\begin{aligned}
 J_4^c &= \frac{d c_E}{d t} = k_4 c_X \\
 &= -\frac{d c_X^{(4)}}{d t} = -(-k_4 c_X)
 \end{aligned}
 \tag{12.50d}$$

Note that for chemicals that appear in multiple reactions, a superscript ( $\alpha$ ) is used to mark its rate in the  $\alpha^{\text{th}}$  reaction. The total rates for  $X$  and  $Y$  are

$$\begin{aligned}
 \frac{d c_X}{d t} &= \frac{d c_X^{(1)}}{d t} + \frac{d c_X^{(2)}}{d t} + \frac{d c_X^{(3)}}{d t} + \frac{d c_X^{(4)}}{d t} \\
 &= k_1 c_A - k_2 c_B c_X + k_3 c_X^2 c_Y - k_4 c_X
 \end{aligned}
 \tag{12.51a}$$

$$\frac{d c_Y}{d t} = \frac{d c_Y^{(2)}}{d t} + \frac{d c_Y^{(3)}}{d t}$$

$$= k_2 c_B c_X - k_3 c_X^2 c_Y \tag{12.51b}$$

If we include effects of diffusion, (12.51a-b) become [c.f. (5.45) of §5.C.2]

$$\frac{\partial c_X}{\partial t} = k_1 c_A - k_2 c_B c_X + k_3 c_X^2 c_Y - k_4 c_X + D_X' \nabla_r^2 c_X \tag{12.51}$$

$$\frac{\partial c_Y}{\partial t} = k_2 c_B c_X - k_3 c_X^2 c_Y + D_Y' \nabla_r^2 c_Y \tag{12.52}$$

where  $D_j'$  is the coefficient of diffusion for the  $j$ -type molecules. Note that in the absence of chemicals, (12.51-2) take the usual form of diffusion equation (5.45). In the absence of diffusion,  $c_j$  are independent of position so that  $\frac{\partial c_j}{\partial t} = \frac{d c_j}{d t}$  and (12.53-4) are the same as (12.51a-b).

(12.51-2) can be put into a simpler form

$$\frac{\partial X}{\partial \tau} = A - (B + 1) X + X^2 Y + D_X \nabla_r^2 X \tag{12.53}$$

$$\frac{\partial Y}{\partial \tau} = B X - X^2 Y + D_Y \nabla_r^2 Y \tag{12.54}$$

where

$$\begin{aligned} \tau &= k_2 t & D_j &= \frac{D_j'}{k_4} \\ X &= \sqrt{\frac{k_3}{k_4}} c_X & Y &= \sqrt{\frac{k_3}{k_4}} c_Y \\ A &= \frac{k_1}{k_4} \sqrt{\frac{k_3}{k_4}} c_A & B &= \frac{k_2}{k_4} c_B \end{aligned} \tag{12.54a}$$

For spatially uniform steady states, (12.53-4) simplify to

$$0 = A - (B + 1) X + X^2 Y \tag{12.54b}$$

$$0 = B X - X^2 Y \tag{12.54c}$$

(12.54c) gives

$$X = 0 \quad \text{or} \quad X Y = B$$

For  $X = 0$ , (12.54b) gives

$$A = 0$$

which is uninteresting since the reaction chain cannot be started.

For  $X Y = B$ , (12.54b) becomes

$$0 = A - (B + 1) X + X B$$

$$\rightarrow X_0 = A \quad \& \quad Y_0 = \frac{B}{A} \tag{12.55}$$

where the subscript 0 is used to indicate that this is a spatially uniform steady state that is the counterpart to the thermodynamic equilibrium state when the reverse reactions in (12.50) are allowed. By gradually increasing the magnitudes of the rate constants  $k_\alpha$  of the reverse reactions, one can trace state (12.55) back to any thermodynamic equilibrium state. These spatially uniform steady states thus form the **thermodynamic branch** of steady state solutions.

We wish to find the conditions under which the thermodynamic branch becomes unstable and there occurs a bifurcation (or phase transition) to a state that oscillates in space or time.

As usual, the stability of a steady state can be analyzed using linear stability theory. For the state (12.55), we set

$$X(r, \tau) = X_0 + \delta x(r, \tau) = A + \delta x \quad (12.56)$$

$$Y(r, \tau) = Y_0 + \delta y(r, \tau) = \frac{B}{A} + \delta y \quad (12.57)$$

Putting (12.56-7) into (12.53-4) then gives, to 1st order in  $\delta x$  &  $\delta y$ ,

$$\begin{aligned} \frac{\partial \delta x}{\partial \tau} &= -(B+1) \delta x + X_0^2 \delta y + (2X_0 \delta x) Y_0 + D_X \nabla_r^2 \delta x \\ &= (B-1 + D_X \nabla_r^2) \delta x + A^2 \delta y \end{aligned} \quad (12.58)$$

$$\begin{aligned} \frac{\partial \delta y}{\partial \tau} &= B \delta x - X_0^2 \delta y - (2X_0 \delta x) Y_0 + D_Y \nabla_r^2 \delta y \\ &= -B \delta x + (-A^2 + D_Y \nabla_r^2) \delta y \end{aligned} \quad (12.59)$$