Two different types of kinetics, where the initial rate increases faster or slower than the reactant concentration, can coexist on bell-shaped kinetic dependencies

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Online Resource 4

Calculating the Jacobian Mapping $G:\mathbb{R}_{+}^{2}\to\mathbb{R}^{2}$ (Theorem 4)

From the equalities (2.12), (2.13), (4.5) follows

$$x_1 = -\frac{\left(-2y_3^3K_7 + (-K_7K_3 - K_1K_m - K_7K_2)y_3^2 + K_my_3y_2K_3 + K_mK_3K_2(y_2+K_1)\right)\left(y_3^2K_7 + ((K_7+y_2)K_3 + K_1K_m)y_3 + K_mK_3(y_2+K_1)\right)}{K_mK_2(y_3+K_3)(K_1K_m+y_3K_7)K_3}, \tag{1}$$

$$x_2 = -\frac{y_2\left(-2y_3^4K_7 + ((-3K_7-K_1)K_m - K_7(K_3+K_2))y_3^3 - 2K_m\left(K_1K_m + \left(K_7 - \frac{1}{2}y_2\right)K_3 + K_7K_2\right)y_3^2 + (((y_2-K_1)K_3 - K_2K_1)K_m + K_3K_2(y_2-K_7+K_1))K_my_3 + K_m^2K_3K_2y_2\right)}{K_mK_2(y_3+K_3)(K_1K_m+y_3K_7)} \tag{2}$$

Using formulas (1)-(2), we calculate partial derivatives:

$$\frac{\partial x_1}{\partial y_2} = \frac{2y_3^4K_7 + ((K_7+K_1)K_m + K_7(K_3+K_2))y_3^3 - 2K_my_3^2K_3y_2 - (((K_1+2y_2)K_3 + K_2K_1)K_m + K_2K_3(K_1+K_7+2y_2))K_my_3 - 2K_m^2K_3K_2(y_2+K_1)}{(y_3+K_3)K_2K_m(K_1K_m+y_3K_7)} \tag{3}$$

$$\begin{aligned}\frac{\partial x_1}{\partial y_3} = {} & \frac{1}{K_mK_2(y_3+K_3)^2(K_1K_m+y_3K_7)^2K_3}\Bigg(\left(2K_7^2(y_2+K_7)y_3^3 + 4K_7\left(K_1K_7 + \frac{3}{4}y_2\left(-\frac{1}{3}y_2+K_1\right)\right)K_my_3^2 + 2K_1K_m^2(-y_2^2+K_1K_7)y_3 - y_2(K_1K_m + K_2(K_1-K_7))(y_2+K_1)K_m^2\right)K_3^3 \\ & + \Bigg((7y_2K_7^2 + 10K_7^3)y_3^4 + 22K_7\left(\left(\left(\frac{1}{11}y_2+K_1\right)K_7 + \frac{6}{11}K_1y_2\right)K_m + \frac{1}{11}K_7K_2(y_2+K_7)\right)y_3^3 + 14\Bigg(\left(\left(K_1^2 + \frac{2}{7}K_1y_2 + \frac{1}{14}y_2^2\right)K_7 + \frac{3}{14}y_2\left(-\frac{1}{3}y_2+K_1\right)K_1\right)K_m \\ & + \frac{2}{7}K_7K_2\left(K_1+\frac{1}{4}y_2\right)(y_2+K_7)\Bigg)K_my_3^2 + 2K_m^2\left(K_1^3K_m + K_7K_2(y_2+K_1)^2\right)y_3 + K_1K_m^3K_2y_2(y_2+K_1)\Bigg)K_3^2 + 4\Bigg(\left(y_2K_7^2 + \frac{7}{2}K_7^3\right)y_3^3 + 8K_7\Bigg(\left(\left(K_1+\frac{1}{32}y_2\right)K_7 \\ & + \frac{7}{32}K_1y_2\right)K_m + \frac{1}{8}\left(\frac{1}{4}y_2+K_7\right)K_7K_2\Bigg)y_3^2 + \frac{11}{2}K_1\left(\left(\left(\frac{1}{11}y_2+K_1\right)K_7 + \frac{1}{11}K_1y_2\right)K_m + \frac{4}{11}\left(\frac{1}{4}y_2+K_7\right)K_7K_2\right)K_my_3 + \left(K_1^2K_m + K_7K_2\left(K_1+\frac{1}{4}y_2\right)\right)K_1K_m^2\Bigg)y_3^2K_3 + 2 \\ & y_3^3(K_1K_m+y_3K_7)^2(K_1K_m + 3y_3K_7 + K_7K_2)\Bigg)\end{aligned} \tag{4}$$

$$\frac{\partial x_2}{\partial y_2} = \frac{2y_3^4K_7 + ((3K_7+K_1)K_m + K_7(K_3+K_2))y_3^3 + 2(K_1K_m + (K_7-y_2)K_3 + K_7K_2)K_my_3^2 - (((-K_1+2y_2)K_3 - K_2K_1)K_m + K_3K_2(-K_7+K_1+2y_2))K_my_3 - 2K_m^2K_3K_2y_2}{K_mK_2(y_3+K_3)(K_1K_m+y_3K_7)} \tag{5}$$

$$\begin{aligned}\frac{\partial x_2}{\partial y_3} = {} & -\frac{1}{K_2(y_3+K_3)^2(K_1K_m+y_3K_7)^2K_m}\Bigg(\Big(-K_1\left(2K_1y_3^2 + 4K_1y_3K_3 + K_3((K_1-y_2)K_3 + K_2(K_1+y_2))\right)K_m^3 + \Big(-2K_1(3K_7+K_1)y_3^3 + (((-y_2-12K_1)K_7 + K_1y_2 - 3K_1^2)K_3 \\ & - K_7K_2K_1)y_3^2 - 4K_3\left(K_1\left(K_7-\frac{1}{2}y_2\right)K_3 + \left(K_1+\frac{1}{2}y_2\right)K_2K_7\right)y_3 + K_3^2K_2(K_1+y_2)(-K_7+K_1)\Big)K_m^2 - 4K_7\Bigg(\left(\frac{7}{4}K_1 + \frac{3}{4}K_7\right)y_3^3 + \Bigg(\left(3K_1 + \frac{3}{2}K_7\right)K_3 + \frac{1}{2}K_1K_2\Bigg)y_3 \\ & + K_3\left(\left(\frac{1}{2}K_7 + \frac{3}{4}K_1 - \frac{1}{4}y_2\right)K_3 + \left(\frac{1}{4}K_7 + K_1 + \frac{1}{4}y_2\right)K_2\right)\Bigg)y_3^2K_m - 2\left(2y_3^2 + \left(\frac{7}{2}K_3 + \frac{1}{2}K_2\right)y_3 + K_3(K_3+K_2)\right)K_7^2y_3^3\Bigg)y_2\Bigg)\end{aligned} \tag{6}$$

The Jacobian mapping $G:\mathbb{R}_+^2 \to \mathbb{R}^2$, by definition, is

$$\Im(G) = \det\left(\frac{\partial x_i}{\partial y_j}\right)_{\substack{i=1,2\\ j=2,3}},$$

therefore, using the formulas (3)-(6), we obtain

$$\Im(G) = -\frac{AB}{C}, \tag{7}$$

where

$$A = 2(K_2+K_3+2y_3)\left(K_1K_m^2 + K_7y_3^2\right) + 2\left[(K_1+3K_7)y_3^2 + 2K_7(K_2+K_3)y_3 - K_2K_3(K_1-K_7)\right]K_m \tag{8}$$

$$B = 3K_7 y_3^4 \left(K_1 K_m + K_7 K_3 + K_7 y_3\right) + \left(3K_1 - 2y_2\right) K_7 K_3 K_m y_3^3 + K_m^2 K_3^2 y_2 \left[y_2 y_3 + K_2\left(y_2 + K_1\right)\right] + \\ + \left[\left(K_1 - y_2\right) K_3 K_m + \left(K_1 K_m + K_7 K_3\right) y_3 + K_7 y_3^2\right]\left(K_1 K_m + K_7 K_3 + K_7 K_2\right) y_3^2 \tag{9}$$

$$C = K_3 \left(K_1 K_m + K_7 y_3\right)^2 \left(K_3 + y_3\right)^2 K_2^2 K_m^2$$

Let us prove that if y_3 is given by the formula (4.7) and y_2 by the formula (4.6), then the factors A and B are positive.

Consider first the multiplier A. It follows from formula (4.7) that $y_3 = r + w$, where r is the single positive root of the cubic equation

$$2K_7 r^3 + \left(K_1 K_m + \left(K_2 + K_3\right) K_7\right) r^2 - K_1 K_2 K_3 K_m = 0, \tag{10}$$

and w is some non-negative number.

Replacing y_3 in formula (8) with the sum $r + w$, we get

$$A = 2r\left(r + 2w + 2K_m\right)\left[K_1 K_m + \left(K_2 + K_3 + 3w\right) K_7\right] + 2\left(K_2 + K_3 + 2w\right)\left(K_1 K_m^2 + K_7 w^2\right) + \\ + \left[4K_7 w\left(K_2 + K_3\right) + 2K_2 K_3\left(K_7 - K_1\right) + 2w^2\left(3K_7 + K_1\right)\right] K_m + 2K_7 r^2\left(2r + 3w + 3K_m\right) \tag{11}$$

From equality (10) express r^3:

$$r^3 = \frac{K_1 K_2 K_3 K_m - \left(K_1 K_m + \left(K_2 + K_3\right) K_7\right) r^2}{2K_7}, \tag{12}$$

and replace r^3 in formula (11) with the right side of formula (12). After the transformations, we get

$$A = \left[w\left(2K_2 + 2K_3 + 3w + 6r\right)\left(2K_m + w\right) + 2r\left(2K_2 + 2K_3 + 3r\right)\left(K_m + w\right)\right] K_7 + \\ + 2K_1 K_m\left[\left(K_2 + K_3 + 2r + 2w\right) K_m + w\left(w + 2r\right)\right] + \left[w\left(w^2 + 6r(w + r)\right) + 2K_2 K_3 K_m\right] K_7 \tag{13}$$

Since $w \geq 0$, it follows from equality (13) that $A > 0$, which was required to be proved.

Consider now the factor B. Since y_3 is given by formula (4.7) and y_2 by formula (4.6), these values and also y_1 given by formula (4.5) are positive. Therefore, the x_1, x_2, x_3 values calculated from the formulas (2.12), (2.13), (2.14) are also positive, and therefore the formulas (3.1) are correct. Further, we take into account that there is an equality (4.4), and, therefore, the value of x_3 can be calculated according to the formula:

$$x_3 = \frac{\left\{\left(K_7 y_3^3 + \frac{1}{2}Ey_3^2 - \frac{1}{2}K_1K_2K_3K_m\right)\left(2K_m y_3 + y_3^2 - D\right) + K_2K_3K_m\left[C + \frac{1}{2}\left(x_1 + x_2\right)\left(y_3^2 + D\right)\right]\right\} y_3}{K_m K_2 K_3 (K_m + y_3)(K_2 + y_3)(K_3 + y_3)} \quad (14)$$

where $C = \left[y_3\left(K_2 + K_3 + y_3\right) + \left(K_2 x_1 + K_3 x_2 + K_2 K_3\right)\right]\left(K_m + y_3\right)$;

$D = K_2K_3 - (K_2 + K_3)K_m$; $E = K_7\left(K_2 + K_3\right) + K_1K_m$

Replacing x_3 in formulas (3.1) with the right side of formula (14) we obtain

$$y_1 = \frac{2K_7 y_3^3 + \left(K_1K_m + K_7\left(K_2 + K_3\right)\right)y_3^2 - K_2K_3K_m\left(K_1 + x_2 - x_1\right)}{2K_2K_m\left(K_3 + y_3\right)}, \quad (15)$$

$$y_2 = \frac{2K_7 y_3^3 + \left(K_1K_m + K_7\left(K_2 + K_3\right)\right)y_3^2 - K_2K_3K_m\left(K_1 + x_1 - x_2\right)}{2K_2K_m\left(K_3 + y_3\right)}. \quad (16)$$

Replacing y_2 in equality (9) with the right side of formula (16), we have

$$\begin{aligned} B = {} & 2K_7^2 y_3^6 + \frac{1}{4}\left[3\left(K_2^2 + 6K_2K_3 + K_3^2\right)K_7^2 + 3K_1K_m\left(6K_7(K_2 + K_3) + K_1K_m\right)\right]y_3^4 + \\ & + \left[\left(K_2K_3K_7^2 + K_1^2K_m^2\right)\left(K_2 + K_3\right) + K_1K_m\left(K_2^2 + 7K_2K_3 + K_3^2\right)K_7\right]y_3^3 + \\ & + \frac{3}{2}\left(K_2K_3K_1K_m + 2K_7y_3^3\right)\left[K_7\left(K_2 + K_3\right) + K_1K_m\right]y_3^2 + \frac{1}{4}K_2^2K_3^2K_m^2\left[\left(x_2 - x_1\right)^2 - K_1^2\right] \end{aligned} \quad (17)$$

Since the values y_1, y_2 are positive, inequality follows from equality (15), (16)

$$\frac{1}{2}K_1K_2K_3K_m < K_7 y_3^3 + \frac{1}{2}\left(K_1K_m + K_7\left(K_2 + K_3\right)\right)y_3^2,$$

therefore, by replacing the expression $\frac{1}{4}K_1^2K_2^2K_3^2K_m^2$ on the right side of formula (17) with a larger value

$$\left(K_7 y_3^3 + \frac{1}{2}\left(K_1K_m + K_7\left(K_2 + K_3\right)\right)y_3^2\right)^2$$

we finally obtain

$$\begin{aligned}
B > K_7^2 y_3^6 + \frac{1}{2}\Big[\left(K_2^2 + 8K_2K_3 + K_3^2\right)K_7^2 + K_1K_m\left(8K_7(K_2 + K_3) + K_1K_m\right)\Big]y_3^4 + \\
+\Big[\left(K_2K_3K_7^2 + K_1^2K_m^2\right)\left(K_2 + K_3\right) + K_1K_m\left(K_2^2 + 7K_2K_3 + K_3^2\right)K_7\Big]y_3^3 + \\
+\frac{1}{2}\left(3K_2K_3K_1K_m + 4K_7y_3^3\right)\left[K_7\left(K_2 + K_3\right) + K_1K_m\right]y_3^2 + \frac{1}{4}K_2^2K_3^2K_m^2\left(x_1 - x_2\right)^2
\end{aligned}$$

i.e. the factor B is positive, which is what was required to be proven.