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

Journal of Mathematical Chemistry

P.F. Zhuk[a], S.O. Karakhim[b,*]

[a] National Aviation University, Liubomyra Huzara Ave, 1, Kyiv 03058, Ukraine
e-mail: petro_zhuk@ukr.net (P.F. Zhuk)

[b] Palladin Institute of Biochemistry of the National Academy of Sciences of Ukraine, 9 Leontovicha Street, Kyiv 01054, Ukraine
e-mail: ksa1957@ukr.net; laserlab@biochem.kiev.ua (S.O. Karakhim)

* Corresponding author:
e-mail: ksa1957@ukr.net; laserlab@biochem.kiev.ua (S.O. Karakhim)

Online Resource 2

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

From the equalities (2.13), (2.14), (4.2) follows

$$x_2 = -\frac{2\left(\left(\frac{1}{2} K_3+y_1\right) K_7 y_3^2+\frac{1}{2}(K_3+y_1)(K_7 K_2+K_1 K_m) y_3-\frac{1}{2} K_m K_2 (y_1^2-K_1 K_3)\right)(y_3^2 K_7+(K_1 K_m+K_2 (K_7+y_1)) y_3+K_m K_2 (K_1+y_1))}{K_2 (y_3 K_7+K_m (K_1+y_1))(K_1 K_m+y_3 K_7) K_3}, \tag{1}$$

$$\begin{aligned} x_3 = {} & -\frac{1}{K_3 (K_1 K_m+y_3 K_7+K_m y_1) K_2 (K_1 K_m+y_3 K_7)}\Big(2\Big(-\frac{1}{2} y_1^3 K_2^2 K_m+K_2\Big(y_3^2 K_7+\Big(\Big(-K_7+\frac{1}{2} K_1\Big) K_m+\frac{1}{2} K_7 K_2\Big) y_3-K_m^2 K_1\Big) y_1^2+\Big(y_3^2 K_7+\Big(\frac{1}{2} K_1 K_m+\frac{1}{2} K_2 K_3\Big) y_3 \\ & -\frac{1}{2} K_2 ((K_1+K_3) K_m-K_2 K_3)\Big)(K_1 K_m+y_3 K_7) y_1+\frac{1}{2} y_3 K_3 (K_1 K_m+y_3 K_7)^2\Big) y_3\Big) \end{aligned} \tag{2}$$

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

$$\begin{aligned} \frac{\partial x_2}{\partial y_1} = {} & \frac{1}{K_3 (K_1 K_m+y_3 K_7) K_2 (y_3 K_7+K_m (K_1+y_1))^2}\Big(-2 y_3^5 K_7^3-5\Big(\Big(K_1-\frac{1}{5} K_3\Big) K_m+\frac{1}{5} K_2 (3 K_7+K_3+4 y_1)\Big) K_7^2 y_3^4-4\Big(\Big(-\frac{1}{2} K_3+K_1\Big) K_1 K_m^2+\frac{1}{2} K_2\Big(\Big(\frac{7}{2} K_1-\frac{1}{2} K_3+y_1\Big) K_7 \\ & +(3 y_1+K_3) K_1+y_1^2\Big) K_m+\frac{1}{4} K_2^2 K_7 (K_7+2 y_1+K_3)\Big) K_7 y_3^3-K_m (K_1^2 (-K_3+K_1) K_m^2+((5 K_1^2+(-2 K_3+2 y_1) K_1+y_1^2) K_7+((2 y_1+K_3) K_1+y_1^2) K_1) K_2 K_m+2 \\ & K_2^2 K_7 (K_7 K_1+(K_3+y_1) K_1-y_1^2)) y_3^2-K_m^2 K_2 (K_1^2 (-K_3+K_1) K_m+K_2 ((K_1+y_1)(K_1-3 y_1) K_7+K_3 K_1^2-3 K_1 y_1^2-2 y_1^3)) y_3+2 K_m^3 K_2^2 y_1 (K_1+y_1)^2\Big) \end{aligned} \tag{3}$$

$$\begin{aligned} \frac{\partial x_2}{\partial y_3} = {} & \frac{1}{K_2 K_3 (K_1 K_m+y_3 K_7)^2 (y_3 K_7+K_1 K_m+y_1 K_m)^2}(2 y_3^5 K_7^4 K_3+y_1 K_1^4 K_m^4 K_2+2 K_3 K_1^4 K_m^4 y_3+2 y_3^4 K_7^3 y_1^2 K_2+4 y_3^5 K_7^4 y_1+2 y_3^4 K_7^4 K_3 K_2+15 y_3^4 K_7^3 y_1 K_1 K_m+20 y_3^3 K_7^2 y_1 K_1^2 K_m^2+14 y_3^3 \\ & K_7^2 y_1^2 K_1 K_m^2+12 K_3 K_1^2 K_m^2 K_2 y_3^2 K_7^2+8 K_3 K_1^3 K_m^3 K_2 y_3 K_7+10 K_3 K_1^2 K_m^3 K_2 y_3 K_7 y_1+12 K_3 K_1^2 K_m^2 y_3^3 K_7^2+7 K_3 K_1^2 K_m^3 y_3^2 K_7 y_1+2 y_1^2 K_7^2 K_2^2 y_3^2 K_1 K_m+2 y_1^2 K_7 K_2^2 y_3 K_1^2 K_m^2+2 y_1^3 K_7 \\ & K_2^2 y_3 K_1 K_m^2+y_1 K_7^3 K_2^2 y_3^2 K_1 K_m+2 y_1 K_7^2 K_2^2 y_3 K_1^2 K_m^2+4 y_1^2 K_7^2 K_2^2 y_3 K_1 K_m^2+11 y_1 K_1^3 K_m^3 y_3^2 K_7+6 y_3^4 K_7^3 y_1^2 K_m+2 y_1 K_1^4 K_m^4 y_3+10 y_1^2 K_1^2 K_m^3 y_3^2 K_7+3 y_1^2 K_7 K_2^2 K_m^3 K_1^2+3 y_1^3 K_7 K_2^2 \\ & K_m^3 K_1+y_1^2 K_7^3 K_2^2 K_m y_3^2+2 y_1^3 K_7^2 K_2^2 K_m^2 y_3+16 y_1 K_1^2 K_m^2 K_2 y_3^2 K_7^2+8 y_1 K_1^3 K_m^3 K_2 y_3 K_7+10 y_1^2 K_1^2 K_m^3 K_2 y_3 K_7+15 y_1^2 K_1 K_m^2 K_2 y_3^2 K_7^2+2 y_1^3 K_1 K_m^3 K_2 y_3 K_7+4 y_3^3 K_7^2 K_3 K_2 y_1 K_1 K_m \\ & +5 y_3^2 K_7 K_3 K_2 y_1 K_1^2 K_m^2+4 y_3^2 K_7 K_3 K_2 y_1^2 K_1 K_m^2+y_3^4 K_7^3 K_3 K_2 y_1+2 y_3^3 K_7^2 K_3 K_2 y_1^2 K_m+11 y_3^2 K_7^2 K_3 K_m^2 K_2 y_1 K_1-K_m^3 K_2^2 y_1^4 K_1-K_m^3 K_2^2 y_1^3 K_1^2+2 K_3 K_1^3 K_m^4 y_3 y_1+2 K_3 K_1^4 K_m^4 K_2 \\ & +2 y_3 K_7 K_3 K_m^3 K_2 y_1^2 K_1+4 y_3^3 K_7^3 K_3 K_m K_2 y_1+y_3^2 K_7^2 K_3 K_m^2 K_2 y_1^2+3 K_3 K_1^3 K_m^4 K_2 y_1+12 y_3^3 K_7^3 y_1 K_2 K_1 K_m+6 y_3^3 K_7^3 y_1^2 K_2 K_m+2 y_1^3 K_7^2 K_2^2 y_3^2 K_m+8 y_3^4 K_7^3 K_3 K_1 K_m+3 y_3^4 \\ & K_7^3 K_3 y_1 K_m+8 y_3^3 K_7^3 K_3 K_2 K_1 K_m+2 y_1^2 K_1^3 K_m^4 y_3+y_3^2 K_7^2 y_1^3 K_m^2 K_2+K_3 K_7^2 K_2^2 y_3^2 y_1 K_1 K_m+2 K_3 K_7 K_2^2 y_3 y_1 K_1^2 K_m^2+2 K_3 K_7 K_2^2 y_3 y_1^2 K_1 K_m^2+K_3 K_7^2 K_2^2 y_3^2 y_1^2 K_m+8 y_3^3 K_7^2 y_1^2 K_2 K_1 K_m \\ & +2 K_3 K_1^3 K_m^3 y_3 K_2 y_1+2 K_3 K_1^2 K_m^3 y_3 K_2 y_1^2+K_3 K_1^2 K_m^4 K_2 y_1^2+y_1 K_7 K_2^2 K_m^3 K_1^3+8 y_1^2 K_1^2 K_m^2 y_3^2 K_2 K_7+2 y_1^2 K_1^3 K_m^3 y_3 K_2+2 y_1^3 K_1^2 K_m^3 y_3 K_2+8 y_3^3 K_7^2 K_3 K_1 K_m^2 y_1+3 y_3^4 K_7^4 y_1 K_2+4 \\ & y_3^3 K_7^2 y_1^3 K_2 K_m+8 K_3 K_1^3 K_m^3 y_3^2 K_7+y_1^2 K_1^3 K_m^4 K_2+7 y_3^2 K_7 y_1^3 K_2 K_1 K_m^2+K_m^3 K_2^2 K_1^3 K_3 y_1+K_m^3 K_2^2 K_1^2 K_3 y_1^2+K_7 K_m^3 K_2^2 y_1^4) \end{aligned} \tag{4}$$

$$\begin{aligned} \frac{\partial x_3}{\partial y_1} = {} & \frac{1}{K_3 (K_1 K_m+y_3 K_7+K_m y_1)^2 K_2 (K_1 K_m+y_3 K_7)}(y_3 (-y_3^2 K_7^2 K_2^2 K_3+2 K_2 y_1^2 y_3 K_m^2 K_7+K_m y_3^3 K_3 K_7^2+2 K_1 K_m^2 K_2 K_3 y_3 K_7+y_3 K_3 K_1^2 K_m^3+4 K_2 y_1 K_m^3 K_1^2+2 K_2 y_1^2 K_m^3 K_1-2 K_2^2 y_1 y_3^2 K_7^2 \\ & -2 K_2 y_1^2 y_3^2 K_7 K_m+8 K_2 y_1 y_3 K_m^2 K_7 K_1+4 K_2 y_1 y_3^2 K_m K_7^2-2 K_2 y_1 y_3 K_1^2 K_m^2-2 K_1 K_m y_3^2 K_2 K_3 K_7+2 K_1^2 K_m^2 K_2 y_3 K_7-y_3^3 K_7^2 K_2 K_3-5 K_1 K_m y_3^3 K_7^2-4 K_1^2 K_m^2 y_3^2 K_7-4 K_2 y_1 y_3^3 K_7^2 \\ & +3 y_1^2 K_2^2 K_m^2 K_1+K_1^2 K_m^3 K_2 K_3-K_1^2 K_m^2 K_2^2 K_3-2 y_3^4 K_7^3+2 y_1^3 K_2^2 K_m^2-K_1^3 K_m^3 y_3+K_1^3 K_m^3 K_2+2 y_1^2 K_2^2 K_m y_3 K_7-6 K_2 y_1 y_3^2 K_7 K_1 K_m-K_2 y_1^2 y_3 K_1 K_m^2-2 K_2^2 y_1 y_3 K_7 K_1 K_m-K_1^2 \\ & K_m^2 y_3 K_2 K_3-2 K_1 K_m K_2^2 K_3 y_3 K_7+y_3^2 K_7^2 K_2 K_1 K_m+y_3^2 K_7^2 K_2 K_m K_3+2 y_3^2 K_3 K_1 K_m^2 K_7)) \end{aligned} \tag{5}$$

$$\begin{aligned} \frac{\partial x_3}{\partial y_3} = {} & \frac{1}{K_3 (K_1 K_m+y_3 K_7+K_m y_1)^2 K_2 (K_1 K_m+y_3 K_7)^2}(-4 y_1 y_3^5 K_7^4-2 y_3^5 K_3 K_7^4-8 K_2 y_1^2 y_3^2 K_1^2 K_m^2 K_7-2 K_2 y_1^3 y_3 K_1^2 K_m^3-8 y_3^4 K_3 K_7^3 K_1 K_m-2 K_2 y_1^2 y_3 K_1^3 K_m^3-2 K_2^2 y_1^2 y_3^2 K_7^2 K_1 K_m-10 y_1^2 \\ & K_1^2 K_m^3 y_3^2 K_7-2 K_2^2 y_1^2 y_3 K_7 K_1^2 K_m^2-14 y_1^2 K_1 K_m^2 y_3^3 K_7^2-y_1 K_1^3 K_m^3 K_2^2 K_3-8 K_2 y_1^2 y_3^3 K_7^2 K_1 K_m-11 y_1 K_1^3 K_m^3 y_3^2 K_7-20 y_1 K_1^2 K_m^2 y_3^3 K_7^2+6 K_2 y_1^2 y_3 K_m^3 K_7 K_1^2-7 K_2 y_1^3 y_3^2 K_7 K_m^2 K_1 \\ & -4 K_2 y_1^3 y_3^3 K_7^2 K_m+4 K_2 y_1^3 y_3 K_m^3 K_7 K_1+2 K_2 y_1^3 y_3^2 K_m^2 K_7^2+3 K_2 y_1^2 y_3^2 K_m^2 K_7^2 K_1+y_1^2 K_1^2 K_m^4 K_2 K_3-y_1 y_3^4 K_7^3 K_2 K_3-2 y_1^3 K_2^2 K_m^2 K_1 y_3 K_7+y_1 K_1 K_m^2 K_2 K_3 y_3^2 K_7^2+2 y_1 K_1^2 \\ & K_m^3 K_2 K_3 y_3 K_7-2 y_1^2 K_1 K_m^2 K_2^2 K_3 y_3 K_7-y_1^2 K_1^2 K_m^3 K_2^2 K_3+y_1 K_1^3 K_m^4 K_2 K_3-2 y_1 K_1^2 K_m^2 K_2^2 K_3 y_3 K_7-2 y_1^2 K_1^2 K_m^3 y_3 K_2 K_3-4 y_1^2 K_1 K_m^2 y_3^2 K_2 K_3 K_7+y_1 K_1^2 K_m^2 K_2 y_3^2 K_7^2-15 y_1 y_3^4 \\ & K_7^3 K_1 K_m+2 y_1 K_1^3 K_m^3 K_2 y_3 K_7-4 y_1 K_1 K_m y_3^3 K_2 K_3 K_7^2-2 y_1 K_1^3 K_m^3 y_3 K_2 K_3-5 y_1 K_1^2 K_m^2 y_3^2 K_2 K_3 K_7-y_1^2 y_3^2 K_7^2 K_2^2 K_3 K_m-2 y_3 K_3 K_1^3 K_m^4 y_1-3 y_3^4 K_3 K_7^3 K_m y_1-12 y_3^3 K_3 K_1^2 K_m^2 K_7^2 \\ & -y_1 K_1 K_m K_2^2 K_3 y_3^2 K_7^2-8 y_3^3 K_3 K_7^2 K_m^2 y_1 K_1-7 y_3^2 K_3 K_1^2 K_m^3 K_7 y_1-2 y_1^2 y_3^3 K_7^2 K_2 K_3 K_m+2 y_1^2 K_1 K_m^3 K_2 K_3 y_3 K_7+y_1^2 y_3^2 K_7^2 K_2 K_m^2 K_3-8 y_3^2 K_3 K_1^3 K_m^3 K_7-2 K_2 y_1^2 y_3^4 K_7^3+y_1^4 K_2^2 \\ & K_m^3 K_1-2 K_2^2 y_1^3 K_7^2 K_m y_3^2+y_1^3 K_2^2 K_m^3 K_1^2+3 K_2 y_1^2 K_m^4 K_1^3-2 y_1 K_1^4 K_m^4 y_3+2 K_2 y_1^3 K_m^4 K_1^2-2 y_1^2 K_1^3 K_m^4 y_3-2 y_3 K_3 K_1^4 K_m^4+y_1 K_1^4 K_m^4 K_2-6 y_1^2 y_3^4 K_7^3 K_m) \end{aligned} \tag{6}$$

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

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

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

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

where

$$A = 2K_7^2(K_3+3y_1)y_3^4 + 4\left(\frac{1}{2}K_7K_2 + K_1K_m\right)K_7(K_3+2y_1)y_3^3 + 2\left(K_1^2(K_3+y_1)K_m + 2K_7K_2\left(K_1y_1 + K_1K_3 - y_1^2\right)\right)K_my_3^2 + 2K_1K_m^2K_2\left(K_1K_3 - y_1^2\right)y_3 + 2K_2^2K_m^2y_1^2(y_1+K_1) \tag{8}$$

$$B = y_3^2K_7^2 + 2K_7\left(\left(\frac{1}{2}K_3 + K_1 + \frac{3}{2}y_1\right)K_m - \frac{1}{2}K_2(K_3+y_1)\right)y_3 + K_m\left(K_1(K_1+K_3+2y_1)K_m - K_2\left(K_1K_3 - y_1^2\right)\right), \tag{9}$$

$$C = K_2\left(K_1K_m + y_3K_7 + K_my_1\right)^2\left(K_1K_m + y_3K_7\right)^2K_3^2.$$

Replace in formulas (8)-(9), y_1 with $y^* + z$, where y^* is the only positive root of the quadratic equation with respect to the variable y:

$$K_mK_2y^2 - \left(2K_7y_3^2 + K_1K_my_3 + K_7K_2y_3\right)y - K_3K_7y_3^2 - K_3K_2K_7y_3 - K_1K_3K_my_3 - K_1K_3K_2K_m = 0,$$

and z is an arbitrary positive number. Then

$$\begin{aligned}A = {}& \frac{1}{K_mK_2}\Bigg(\Bigg(\Bigg(\left(\left((2z+K_3)K_1+3z^2\right)K_m^2 + 3\left(z+\frac{1}{3}K_1+\frac{1}{3}K_3\right)K_7y_3K_m + y_3^2K_7^2\right)K_2^2 + \left(K_1(K_1+z+K_3)K_m^2 + 2\left(\frac{5}{2}K_1+z+\frac{1}{2}K_3\right)K_7y_3K_m + 4y_3^2K_7^2\right)y_3K_2 + 3y_3^4K_7^2 + y_3^2K_1^2K_m^2 \\ & + 4y_3^3K_7K_1K_m\Bigg)\sqrt{4y_3^4K_7^2 + \left(4K_7K_1K_m + 4K_7^2K_2\right)y_3^3 + \left(K_7^2K_2^2 + 2K_7K_m(2K_3+K_1)K_2 + K_1^2K_m^2\right)y_3^2 + 4K_2K_3K_m(K_7K_2+K_1K_m)y_3 + 4K_m^2K_2^2K_1K_3} + \Bigg(\Big(2K_1^2K_3 + 2z(z \\ & + 3K_3)K_1 + 2z^3\Big)K_m^3 + 3\left(\left(\frac{2}{3}z+\frac{5}{3}K_3\right)K_1 + z(2K_3+z)\right)K_7y_3K_m^2 + 3\left(z+\frac{1}{3}K_1+K_3\right)K_7^2y_3^2K_m + y_3^3K_7^3\Bigg)K_2^3 + \Bigg(\Big(\big((2z+5K_3)K_1 + z(6K_3+z)\big)K_1K_m^3 + 2\Big(K_1^2 + (6z \\ & + 6K_3)K_1 + z(z+3K_3)\Big)K_7y_3K_m^2 + 12\left(\frac{2}{3}K_1+z+\frac{7}{12}K_3\right)K_7^2y_3^2K_m + 6y_3^3K_7^3\Bigg)y_3K_2^2 + 3\Bigg(\left(z+\frac{1}{3}K_1+K_3\right)K_1^2K_m^3 + 4\left(\frac{2}{3}K_1+z+\frac{7}{12}K_3\right)K_7y_3K_1K_m^2 + \frac{10}{3}\Big(\frac{2}{5}K_3 \\ & + \frac{9}{5}K_1+z\Big)K_7^2y_3^2K_m + \frac{11}{3}y_3^3K_7^3\Bigg)y_3^2K_2 + 11y_3^5K_7^2K_1K_m + 6y_3^6K_7^3 + 6K_7y_3^4K_1^2K_m^2 + y_3^3K_1^3K_m^3\Bigg)\end{aligned} \tag{10}$$

$$\begin{aligned}B = {}& \frac{1}{2}\frac{1}{K_mK_2}\Bigg(\Big(2K_1K_m^2 + \big((K_1+3K_7)y_3 + 2zK_2\big)K_m + 2 \\ & y_3^2K_7\Big)\sqrt{4y_3^4K_7^2 + \left(4K_7K_1K_m + 4K_7^2K_2\right)y_3^3 + \left(K_7^2K_2^2 + 2K_7K_m(2K_3+K_1)K_2 + K_1^2K_m^2\right)y_3^2 + 4K_2K_3K_m(K_7K_2+K_1K_m)y_3 + 4K_m^2K_2^2K_1K_3} + 4\Bigg(\frac{1}{2}y_3K_1 + \Bigg(\frac{1}{2}K_1 + z \\ & + \frac{1}{2}K_3\Bigg)K_2\Bigg)K_1K_m^3 + \Big(K_1(K_1+7K_7)y_3^2 + 2\big((3z+3K_1+K_3)K_7 + K_1(z+K_3)\big)K_2y_3 + 2z^2K_2^2\Big)K_m^2 + 4K_7\left(\left(K_1+\frac{3}{2}K_7\right)y_3 + K_2\left(z+\frac{5}{4}K_7+\frac{1}{4}K_1+\frac{1}{2}K_3\right)\right)y_3^2K_m + 2y_3^3 \\ & K_7^2(2y_3+K_2)\Bigg)\end{aligned} \tag{11}$$

and it is obvious that the Jacobian mapping G is positive for the points $y = (y_1, y_3) \in \mathbb{R}_+^2$, in which y_1 is given by the formula (5.3).