Kinetic Plasticity and the Determination of Product Ratios for Kinetic Schemes Leading to Multiple Products Without Rate Laws: New Methods Based on Directed Graphs

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Supplementary Material

1. Solution of Scheme 3 by the Laplace transform method.

The set of differential equations describing Scheme 3 are

$$x'(t) + (k_1 + k_3)x(t) - k_2 y(t) = 0$$
$$y'(t) + (k_2 + k_4)y(t) - k_1 x(t) = 0$$
$$p_x'(t) - k_3 x(t) = 0$$
$$p_y'(t) - k_4 y(t) = 0$$

Taking Laplace transforms of both sides of each equation and using the initial conditions at time zero $[X]_0 = a$, $[Y]_0 = b$, $[P_X]_0 = 0$, and $[P_Y]_0 = 0$ results in

$$\begin{bmatrix} s+k_1+k_3 & -k_2 & 0 & 0 \\ -k_1 & s+k_2+k_4 & 0 & 0 \\ -k_3 & 0 & s & 0 \\ 0 & -k_4 & 0 & s \end{bmatrix} \begin{bmatrix} x(s) \\ y(s) \\ p_x(s) \\ p_y(s) \end{bmatrix} = \begin{bmatrix} a \\ b \\ 0 \\ 0 \end{bmatrix}$$

The determinant of the left-hand matrix is

$$D = (s+k_1+k_3)(s+k_2+k_4)s^2 - k_2 k_1 s^2 = s^2(s+\gamma_1)(s+\gamma_2)$$

where $\gamma_1 + \gamma_2 = k_1 + k_2 + k_3 + k_4$ and $\gamma_1\gamma_2 = k_1k_4 + k_2k_3 + k_3k_4$.

Solving the matrix equation yields

$$x(s) = \frac{1}{D}\begin{vmatrix} a & -k_2 & 0 & 0 \\ b & s+k_2+k_4 & 0 & 0 \\ 0 & 0 & s & 0 \\ 0 & -k_4 & 0 & s \end{vmatrix} = \frac{a(s+k_2+k_4)+bk_2}{(s+\gamma_1)(s+\gamma_2)}$$

$$y(s)=\frac{1}{D}\begin{vmatrix} s+k_1+k_3 & a & 0 & 0 \\ -k_1 & b & 0 & 0 \\ -k_3 & 0 & s & 0 \\ 0 & 0 & 0 & s \end{vmatrix}=\frac{b(s+k_1+k_3)+ak_1}{(s+\gamma_1)(s+\gamma_2)}$$

$$p_x(s)=\frac{1}{D}\begin{vmatrix} s+k_1+k_3 & -k_2 & a & 0 \\ -k_1 & s+k_2+k_4 & b & 0 \\ -k_3 & 0 & 0 & 0 \\ 0 & -k_4 & 0 & s \end{vmatrix}=\frac{ak_3(s+k_2+k_4)+bk_2k_3}{s(s+\gamma_1)(s+\gamma_2)}$$

$$p_y(s)=\frac{1}{D}\begin{vmatrix} s+k_1+k_3 & -k_2 & 0 & a \\ -k_1 & s+k_2+k_4 & 0 & b \\ -k_3 & 0 & s & 0 \\ 0 & -k_4 & 0 & 0 \end{vmatrix}=\frac{bk_4(s+k_1+k_3)+ak_1k_4}{s(s+\gamma_1)(s+\gamma_2)}$$

From tables of inverse Laplace transforms the time dependent product concentration functions are given by

$$[P_X](t)=\frac{bk_2k_3+ak_3(k_2+k_4)}{\gamma_1\gamma_2}-\left\{\frac{bk_2k_3+ak_3(k_2+k_4-\gamma_1)}{\gamma_1(\gamma_2-\gamma_1)}\right\}\exp(-\gamma_1 t)$$
$$+\left\{\frac{bk_2k_3+ak_3(k_2+k_4-\gamma_2)}{\gamma_2(\gamma_2-\gamma_1)}\right\}\exp(-\gamma_2 t)$$

$$[P_Y](t)=\frac{ak_1k_4+bk_4(k_1+k_3)}{\gamma_1\gamma_2}-\left\{\frac{ak_1k_4+bk_4(k_1+k_3-\gamma_1)}{\gamma_1(\gamma_2-\gamma_1)}\right\}\exp(-\gamma_1 t)$$
$$+\left\{\frac{ak_1k_4+bk_4(k_1+k_3-\gamma_2)}{\gamma_2(\gamma_2-\gamma_1)}\right\}\exp(-\gamma_2 t)$$

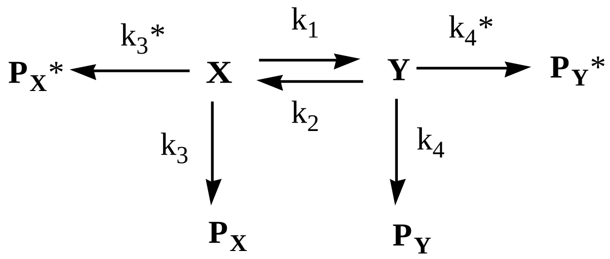
The final product ratio at infinite time is then given by

$$\frac{[P_X]_\infty}{[P_Y]_\infty}=\left(\frac{k_3}{k_4}\right)\frac{bk_2+a(k_2+k_4)}{ak_1+b(k_1+k_3)}$$

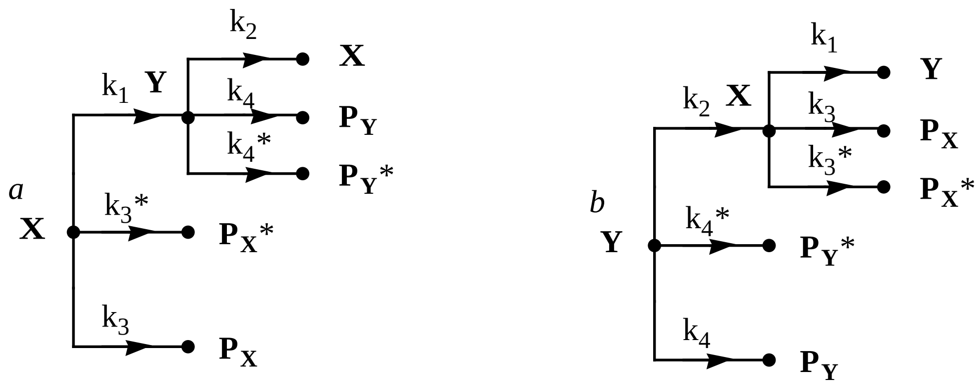
which is identical to eq. [1].

2. Solution of kinetic schemes in reference 11 by the digraph method using path divergent trees

<u>Scheme S1</u>



Path divergent trees:



For target PX:

$$a\left(\frac{k_3}{k_3+k_3^*+k_1}\right)+b\left(\frac{k_2}{k_2+k_4^*+k_4}\right)\left(\frac{k_3}{k_3+k_3^*+k_1}\right)=\left(\frac{k_3}{k_3+k_3^*+k_1}\right)\left[a+b\left(\frac{k_2}{k_2+k_4^*+k_4}\right)\right]$$

For target PX*:

$$a\left(\frac{k_3^*}{k_1+k_3+k_3^*}\right)+b\left(\frac{k_2}{k_2+k_4+k_4^*}\right)\left(\frac{k_3^*}{k_1+k_3+k_3^*}\right)=\left(\frac{k_3^*}{k_1+k_3+k_3^*}\right)\left[a+b\left(\frac{k_2}{k_2+k_4+k_4^*}\right)\right]$$

For target PY:

$$b\left(\frac{k_4}{k_4+k_4^*+k_2}\right)+a\left(\frac{k_1}{k_1+k_3^*+k_3}\right)\left(\frac{k_4}{k_4+k_4^*+k_2}\right)=\left(\frac{k_4}{k_4+k_4^*+k_2}\right)\left[b+a\left(\frac{k_1}{k_1+k_3^*+k_3}\right)\right]$$

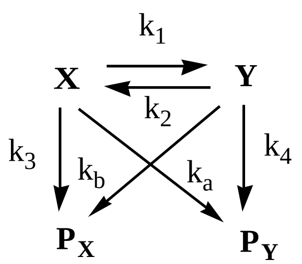
For target PY*:

$$b\left(\frac{k_4^*}{k_2+k_4+k_4^*}\right)+a\left(\frac{k_1}{k_1+k_3+k_3^*}\right)\left(\frac{k_4^*}{k_2+k_4+k_4^*}\right)=\left(\frac{k_4^*}{k_2+k_4+k_4^*}\right)\left[b+a\left(\frac{k_1}{k_1+k_3+k_3^*}\right)\right]$$

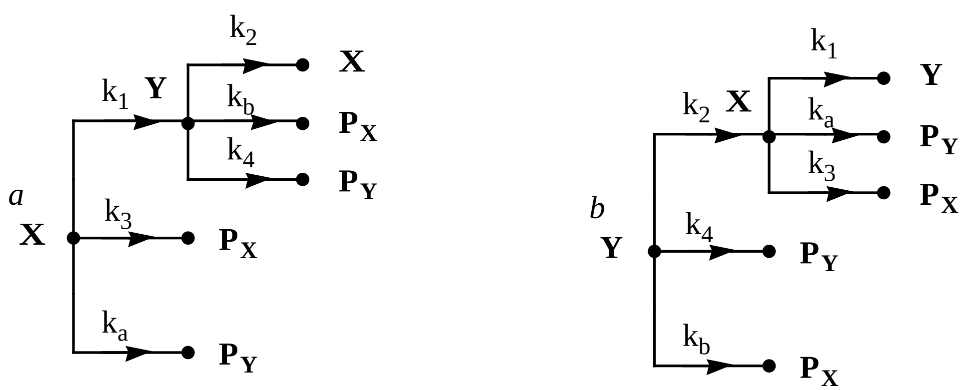
$$\frac{[P_X]_\infty}{[P_Y]_\infty}=\left(\frac{k_3}{k_4}\right)\left(\frac{(a+b)k_2+a\left(k_4+k_4^*\right)}{(a+b)k_1+b\left(k_3+k_3^*\right)}\right) \qquad \frac{[P_X^*]_\infty}{[P_Y^*]_\infty}=\left(\frac{k_3^*}{k_4^*}\right)\left(\frac{(a+b)k_2+a\left(k_4+k_4^*\right)}{(a+b)k_1+b\left(k_3+k_3^*\right)}\right)$$

$$\frac{[P_X]_\infty}{[P_X^*]_\infty}=\left(\frac{k_3}{k_3^*}\right) \qquad \frac{[P_Y]_\infty}{[P_Y^*]_\infty}=\left(\frac{k_4}{k_4^*}\right)$$

Scheme S2



Path divergent trees:



For target PX:

$$a\left(\frac{k_3}{k_1+k_3+k_a}\right)+a\left(\frac{k_3}{k_1+k_3+k_a}\right)\left(\frac{k_b}{k_2+k_4+k_b}\right)+b\left(\frac{k_b}{k_2+k_4+k_b}\right)+b\left(\frac{k_b}{k_2+k_4+k_b}\right)\left(\frac{k_3}{k_1+k_3+k_a}\right)$$

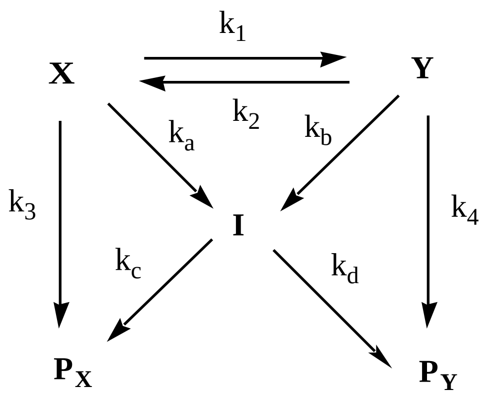
$$=a\left(\frac{k_3}{k_1+k_3+k_a}\right)\left[1+\left(\frac{k_b}{k_2+k_4+k_b}\right)\right]+b\left(\frac{k_b}{k_2+k_4+k_b}\right)\left[1+\left(\frac{k_3}{k_1+k_3+k_a}\right)\right]$$

For target PY:

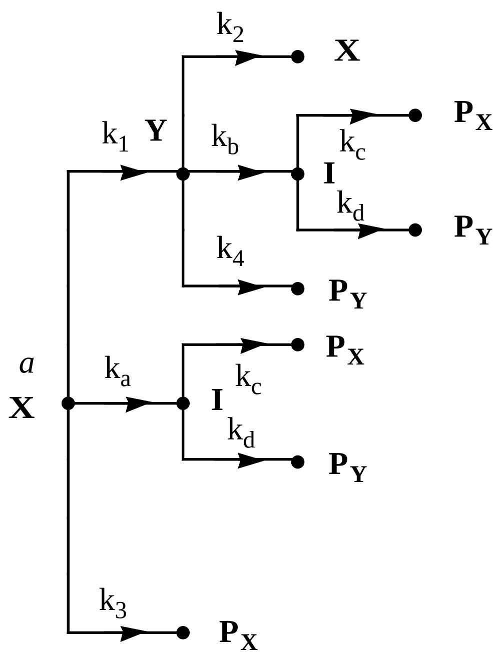
$$a\left(\frac{k_a}{k_1+k_3+k_a}\right)+a\left(\frac{k_a}{k_1+k_3+k_a}\right)\left(\frac{k_4}{k_2+k_4+k_b}\right)+b\left(\frac{k_4}{k_2+k_4+k_b}\right)+b\left(\frac{k_4}{k_2+k_4+k_b}\right)\left(\frac{k_a}{k_1+k_3+k_a}\right)$$
$$=a\left(\frac{k_a}{k_1+k_3+k_a}\right)\left[1+\left(\frac{k_a}{k_2+k_4+k_b}\right)\right]+b\left(\frac{k_4}{k_2+k_4+k_b}\right)\left[1+\left(\frac{k_a}{k_1+k_3+k_a}\right)\right]$$

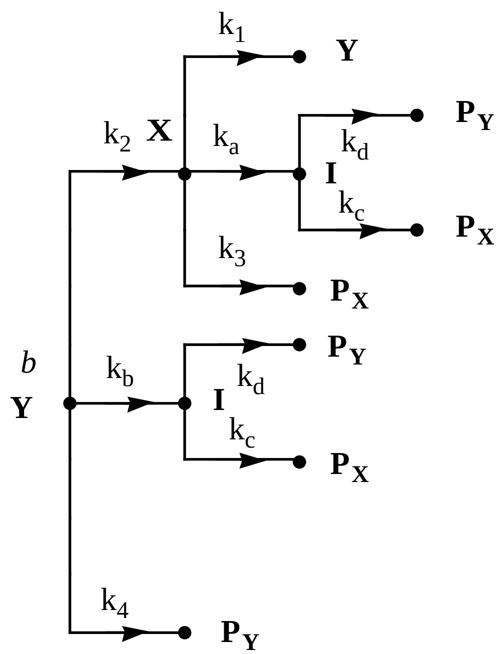
$$\frac{[P_X]_\infty}{[P_Y]_\infty}=\frac{(a+b)(k_1k_b+k_2k_3+k_3k_b)+bk_ak_b+ak_3k_4}{(a+b)(k_2k_a+k_1k_4+k_4k_a)+ak_ak_b+bk_3k_4}$$

<u>Scheme S3</u>



Path divergent trees:





For target PX:

$$a\left(\frac{k_3}{k_1+k_3+k_a}\right)\left[1+\frac{k_c}{k_c+k_d}\left(1+\frac{k_b}{k_2+k_4+k_b}\right)\right]$$
$$+b\left[\left(\frac{k_b}{k_2+k_4+k_b}\right)\left(\frac{k_c}{k_c+k_d}\right)+\left(\frac{k_2}{k_2+k_4+k_b}\right)\left[\left(\frac{k_3}{k_1+k_3+k_a}\right)+\left(\frac{k_a}{k_1+k_3+k_a}\right)\left(\frac{k_c}{k_c+k_d}\right)\right]\right]$$

For target PY:

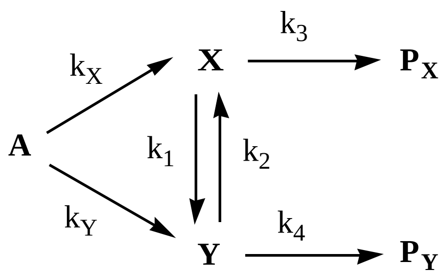
$$b\left(\frac{k_4}{k_2+k_4+k_b}\right)\left[1+\frac{k_d}{k_c+k_d}\left(1+\frac{k_a}{k_1+k_3+k_a}\right)\right]$$
$$+a\left[\left(\frac{k_a}{k_1+k_3+k_a}\right)\left(\frac{k_d}{k_c+k_d}\right)+\frac{k_1}{k_1+k_3+k_a}\left[\left(\frac{k_4}{k_2+k_4+k_b}\right)+\left(\frac{k_b}{k_2+k_4+k_b}\right)\left(\frac{k_d}{k_c+k_d}\right)\right]\right]$$

$$\frac{[P_X]_\infty}{[P_Y]_\infty}=\frac{(k_c+k_d)\varepsilon_1+k_c\phi}{(k_c+k_d)\varepsilon_2+k_d\phi}$$

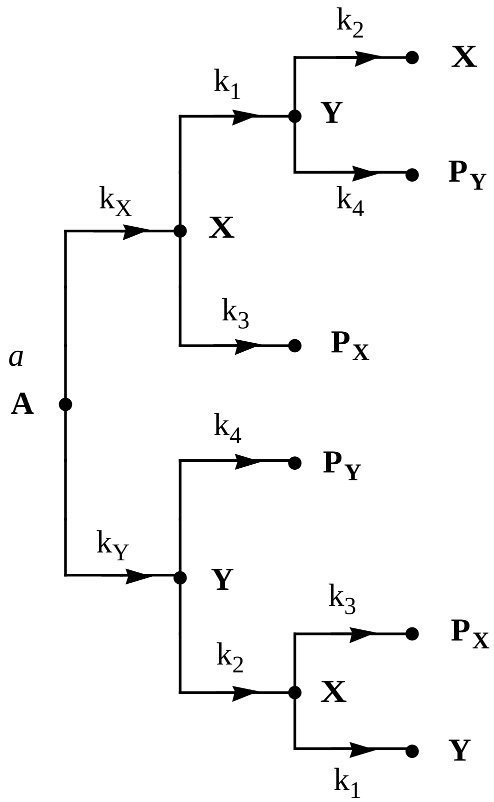
where

$$\varepsilon_1=k_2k_3(a+b)+ak_3(k_4+k_b)$$
$$\varepsilon_2=k_1k_4(a+b)+bk_4(k_3+k_a)$$
$$\phi=(a+b)(k_1k_b+k_2k_a+k_ak_b)+bk_3k_b+ak_4k_a$$

Scheme S4



Path divergent trees:



For target PX:

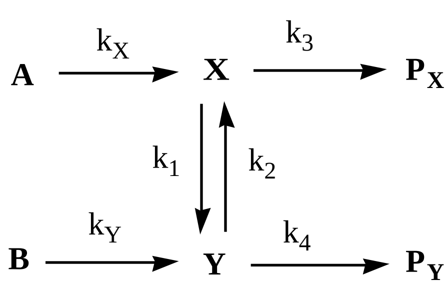
$$a\left(\frac{k_X}{k_X+k_Y}\right)\left(\frac{k_3}{k_1+k_3}\right)+a\left(\frac{k_Y}{k_X+k_Y}\right)\left(\frac{k_2}{k_2+k_4}\right)\left(\frac{k_3}{k_1+k_3}\right)=a\left(\frac{k_3}{k_1+k_3}\right)\left(\frac{1}{k_X+k_Y}\right)\left[k_X+\left(\frac{k_2k_Y}{k_2+k_4}\right)\right]$$

For target PY:

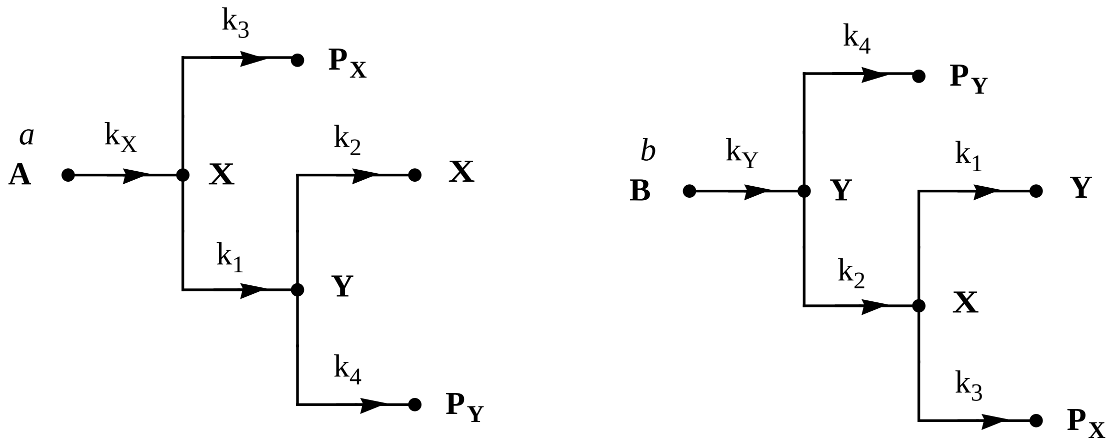
$$a\left(\frac{k_Y}{k_X+k_Y}\right)\left(\frac{k_4}{k_2+k_4}\right)+a\left(\frac{k_X}{k_X+k_Y}\right)\left(\frac{k_1}{k_1+k_3}\right)\left(\frac{k_4}{k_2+k_4}\right)=a\left(\frac{k_4}{k_2+k_4}\right)\left(\frac{1}{k_X+k_Y}\right)\left[k_Y+\left(\frac{k_1k_X}{k_1+k_3}\right)\right]$$

$$\frac{[P_X]_\infty}{[P_Y]_\infty}=\left(\frac{k_3}{k_4}\right)\frac{k_X(k_2+k_4)+k_2k_Y}{k_Y(k_1+k_3)+k_1k_X}$$

<u>Scheme S5</u>



Path divergent trees:



For target PX:

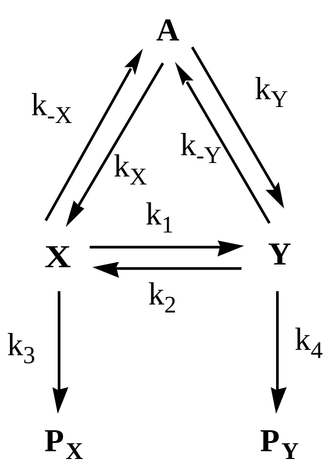
$$ak_X\left(\frac{k_3}{k_1+k_3}\right)+bk_Y\left(\frac{k_2}{k_2+k_4}\right)\left(\frac{k_3}{k_1+k_3}\right)=\left(\frac{k_3}{k_1+k_3}\right)\left[ak_X+bk_Y\left(\frac{k_2}{k_2+k_4}\right)\right]$$

For target PY:

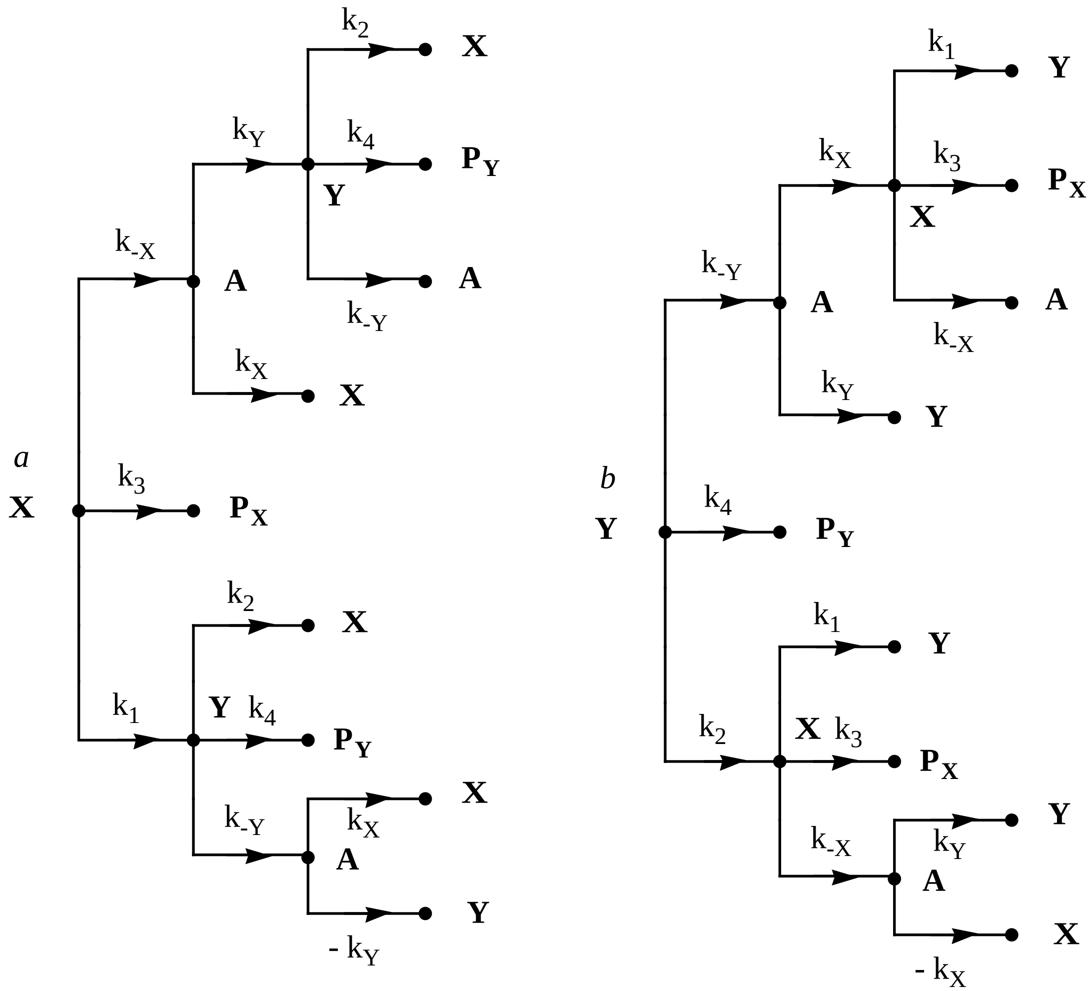
$$bk_Y\left(\frac{k_4}{k_2+k_4}\right)+ak_X\left(\frac{k_1}{k_1+k_3}\right)\left(\frac{k_4}{k_2+k_4}\right)=\left(\frac{k_4}{k_2+k_4}\right)\left[bk_Y+ak_X\left(\frac{k_1}{k_1+k_3}\right)\right]$$

$$\frac{[P_X]_\infty}{[P_Y]_\infty}=\left(\frac{k_3}{k_4}\right)\frac{ak_X(k_2+k_4)+bk_Yk_2}{bk_Y(k_1+k_3)+ak_Xk_1}$$

<u>Scheme S6</u>



Path divergent trees:



For target PX:

$$a\left(\frac{k_3}{k_1+k_3+k_{-X}}\right)+b\left(\frac{k_2}{k_2+k_4+k_{-Y}}\right)\left(\frac{k_3}{k_1+k_3+k_{-X}}\right)+b\left(\frac{k_{-Y}}{k_2+k_4+k_{-Y}}\right)\left(\frac{k_X}{k_X+k_Y}\right)\left(\frac{k_3}{k_1+k_3+k_{-X}}\right)$$

$$=\left(\frac{k_3}{k_1+k_3+k_{-X}}\right)\left[a+b\left(\left(\frac{k_2}{k_2+k_4+k_{-Y}}\right)+\left(\frac{k_{-Y}}{k_2+k_4+k_{-Y}}\right)\left(\frac{k_X}{k_X+k_Y}\right)\right)\right]$$

$$=\left(\frac{k_3}{k_1+k_3+k_{-X}}\right)\left[a+\frac{b}{k_2+k_4+k_{-Y}}\left(k_2+\frac{k_X k_{-Y}}{k_X+k_Y}\right)\right]$$

For target PY:

$$b\left(\frac{k_4}{k_2+k_4+k_{-Y}}\right)+a\left(\frac{k_1}{k_1+k_3+k_{-X}}\right)\left(\frac{k_4}{k_2+k_4+k_{-Y}}\right)+a\left(\frac{k_{-X}}{k_1+k_3+k_{-X}}\right)\left(\frac{k_Y}{k_X+k_Y}\right)\left(\frac{k_4}{k_2+k_4+k_{-Y}}\right)$$

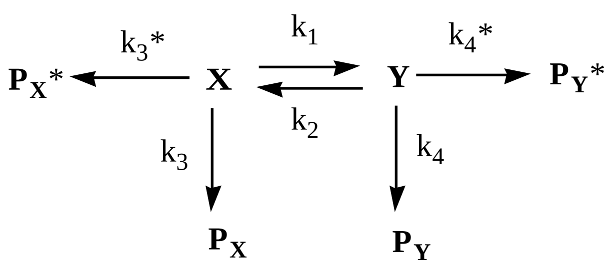
$$=\left(\frac{k_4}{k_2+k_4+k_{-Y}}\right)\left[b+a\left(\left(\frac{k_1}{k_1+k_3+k_{-X}}\right)+\left(\frac{k_{-X}}{k_1+k_3+k_{-X}}\right)\left(\frac{k_Y}{k_X+k_Y}\right)\right)\right]$$

$$=\left(\frac{k_4}{k_2+k_4+k_{-Y}}\right)\left[b+\frac{a}{k_1+k_3+k_{-X}}\left(k_1+\frac{k_Y k_{-X}}{k_X+k_Y}\right)\right]$$

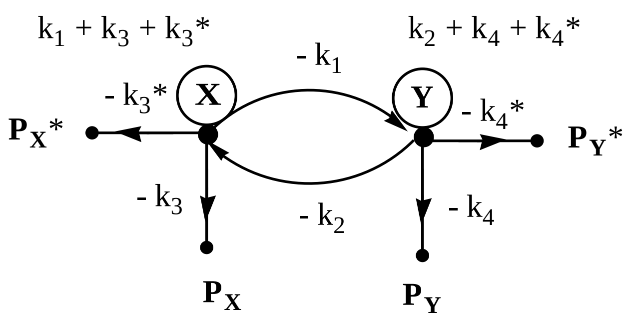
$$\frac{[P_X]_\infty}{[P_Y]_\infty}=\left(\frac{k_3}{k_4}\right)\frac{(a+b)\left[k_2(k_X+k_Y)+k_X k_{-Y}\right]+ak_4(k_X+k_Y)+ak_Y k_{-Y}}{(a+b)\left[k_1(k_X+k_Y)+k_Y k_{-X}\right]+bk_3(k_X+k_Y)+bk_X k_{-X}}$$

3. Solution of kinetic schemes in reference 11 by the modified Chou digraph method.

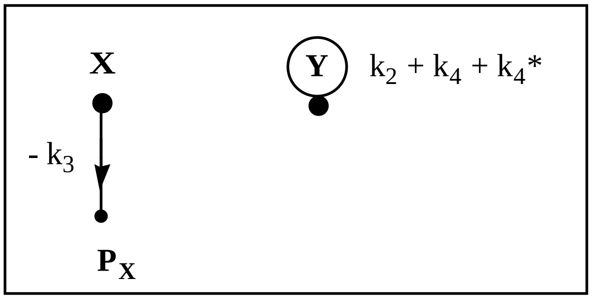
Scheme S1

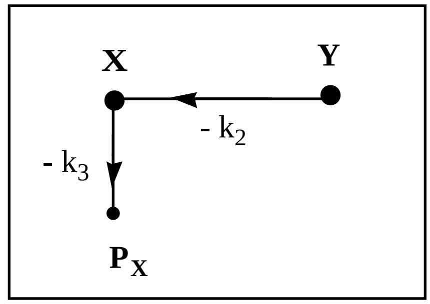


Digraph:

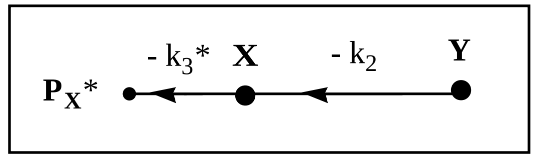


Subgraphs:

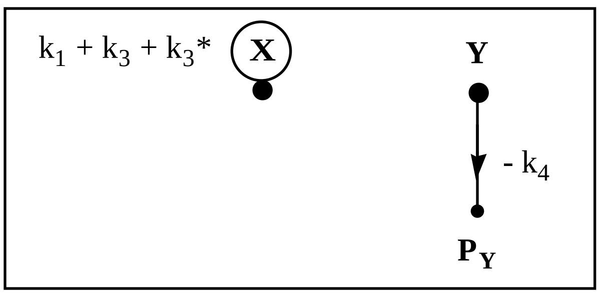


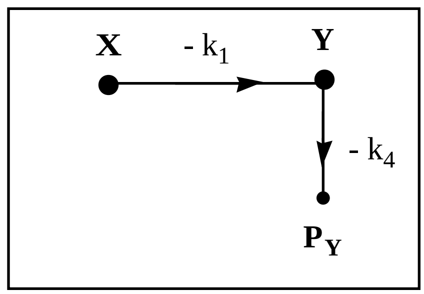


$$\left[P_X\right]_\infty \to a(-1)^{3+1+1}(-k_3)\left(k_2+k_4+k_4^*\right)+b(-1)^{3+0+1}k_2k_3 = k_3\left\{a\left(k_2+k_4+k_4^*\right)+bk_2\right\}$$

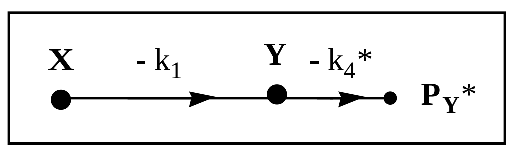


$$\left[P_X^*\right]_\infty \to a(-1)^{3+1+1}\left(-k_3^*\right)\left(k_2+k_4+k_4^*\right)+b(-1)^{3+0+1}k_2k_3^* = k_3^*\left\{a\left(k_2+k_4+k_4^*\right)+bk_2\right\}$$





$$\left[P_Y\right]_\infty \to b(-1)^{3+1+1}(-k_4)\left(k_1+k_3+k_3^*\right)+a(-1)^{3+0+1}k_1k_4 = k_4\left\{b\left(k_1+k_3+k_3^*\right)+ak_1\right\}$$

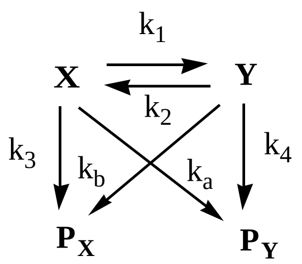


$$\left[P_Y^*\right]_\infty \to b(-1)^{3+1+1}\left(-k_4^*\right)\left(k_1+k_3+k_3^*\right)+a(-1)^{3+0+1}k_1k_4^* = k_4^*\left\{b\left(k_1+k_3+k_3^*\right)+ak_1\right\}$$

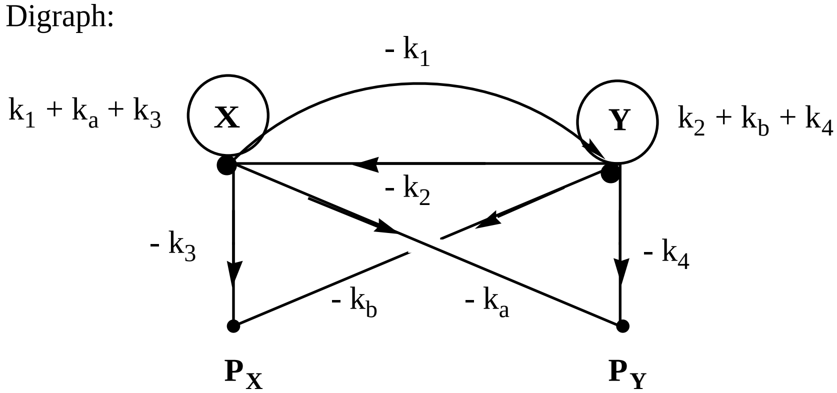
$$\frac{\left[P_X\right]_\infty}{\left[P_Y\right]_\infty} = \left(\frac{k_3}{k_4}\right)\left(\frac{(a+b)k_2+a\left(k_4+k_4^*\right)}{(a+b)k_1+b\left(k_3+k_3^*\right)}\right) \qquad \frac{\left[P_X^*\right]_\infty}{\left[P_Y^*\right]_\infty} = \left(\frac{k_3^*}{k_4^*}\right)\left(\frac{(a+b)k_2+a\left(k_4+k_4^*\right)}{(a+b)k_1+b\left(k_3+k_3^*\right)}\right)$$

$$\frac{\left[P_X\right]_\infty}{\left[P_X^*\right]_\infty} = \left(\frac{k_3}{k_3^*}\right) \qquad \frac{\left[P_Y\right]_\infty}{\left[P_Y^*\right]_\infty} = \left(\frac{k_4}{k_4^*}\right)$$

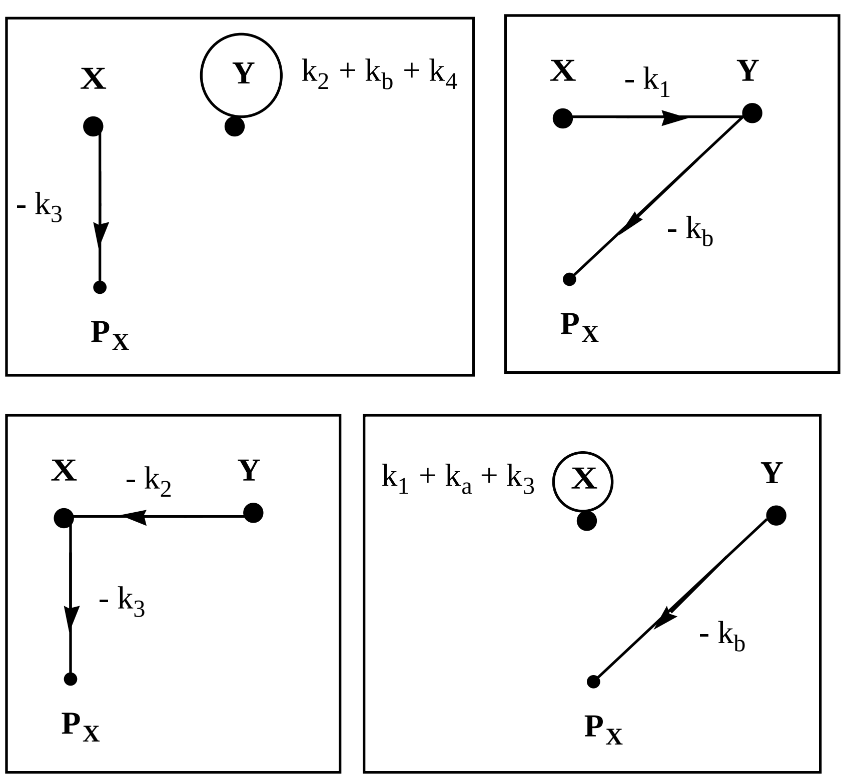
Scheme S2



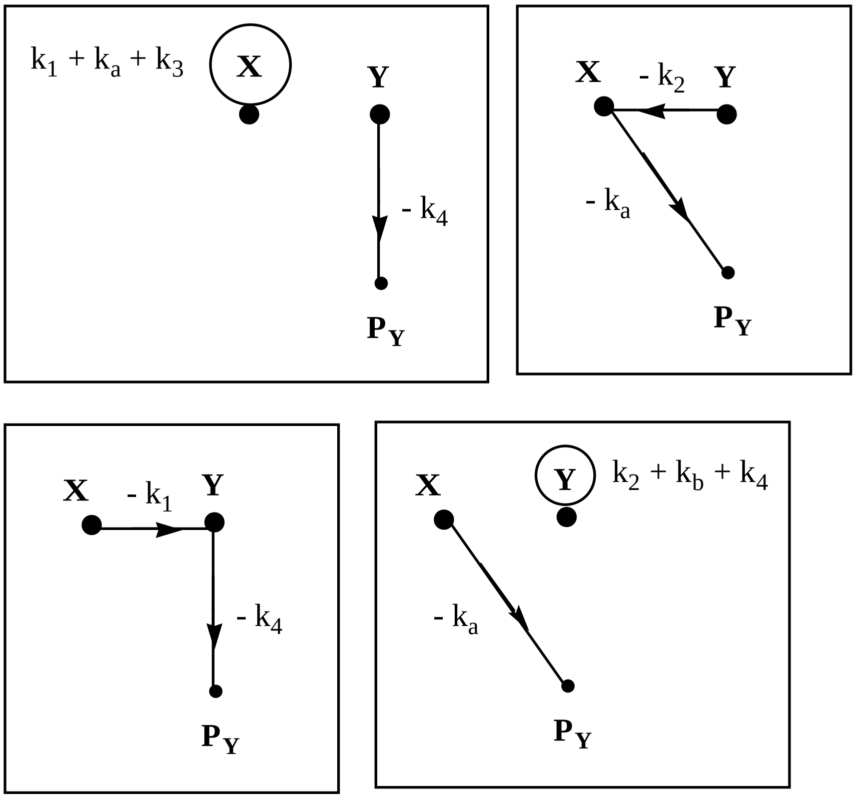
Digraph:



Subgraphs:

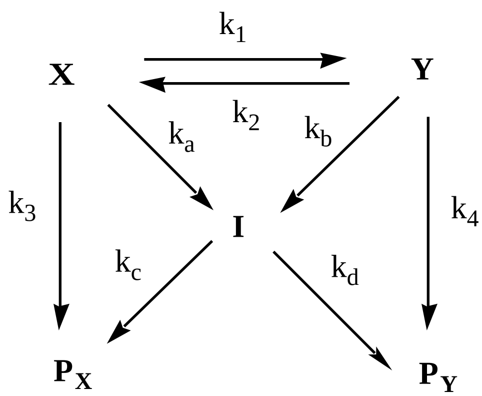


$$[P_X]_\infty \to a(-1)^{3+1+1}(-k_3)(k_2+k_4+k_b)+a(-1)^{3+0+1}k_1k_b+b(-1)^{3+0+1}k_2k_3$$
$$+b(-1)^{3+1+1}(-k_b)(k_1+k_3+k_a)$$
$$=a[k_3(k_2+k_4+k_b)+k_1k_b]+b[k_2k_3+k_b(k_1+k_3+k_a)]$$
$$=(a+b)(k_1k_b+k_2k_3+k_3k_b)+bk_ak_b+ak_3k_4$$

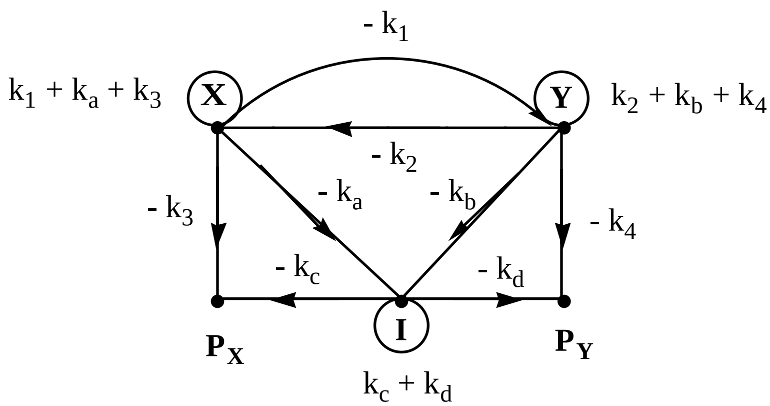


$$[P_Y]_\infty \to b(-1)^{3+1+1}(-k_4)(k_1+k_3+k_a)+b(-1)^{3+0+1}k_2k_a+a(-1)^{3+0+1}k_1k_4$$
$$+a(-1)^{3+1+1}(-k_a)(k_2+k_4+k_b)$$
$$=b[k_4(k_1+k_3+k_a)+k_2k_a]+a[k_1k_4+k_a(k_2+k_4+k_b)]$$
$$=(a+b)(k_2k_a+k_1k_4+k_4k_a)+ak_ak_b+bk_3k_4$$
$$\frac{[P_X]_\infty}{[P_Y]_\infty}=\frac{(a+b)(k_1k_b+k_2k_3+k_3k_b)+bk_ak_b+ak_3k_4}{(a+b)(k_2k_a+k_1k_4+k_4k_a)+ak_ak_b+bk_3k_4}$$

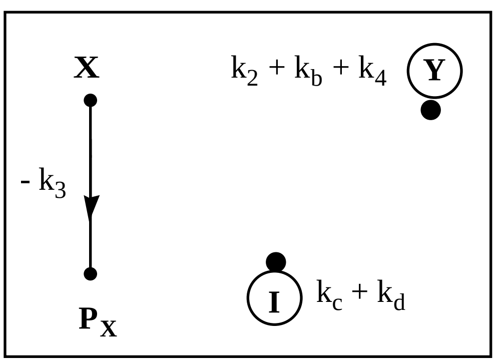
Scheme S3

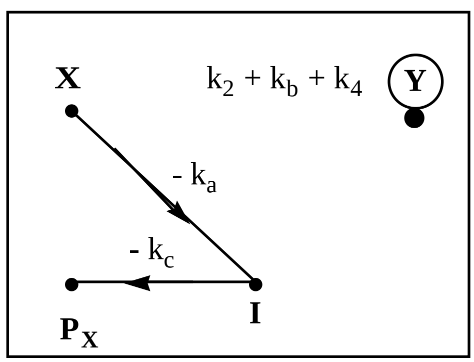


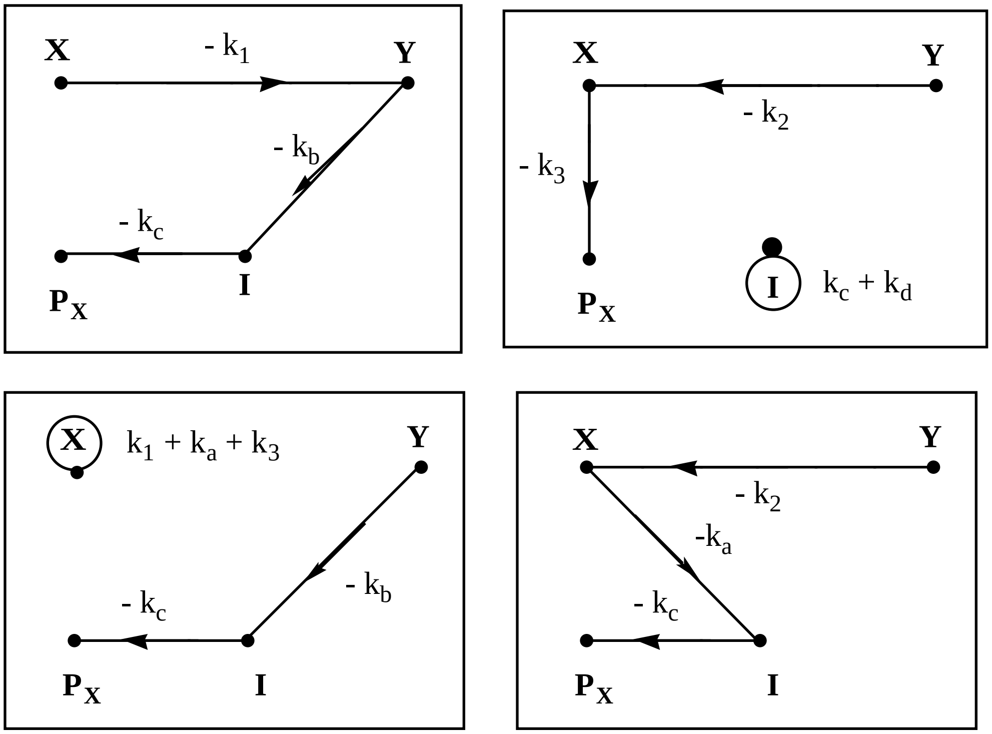
Digraph:



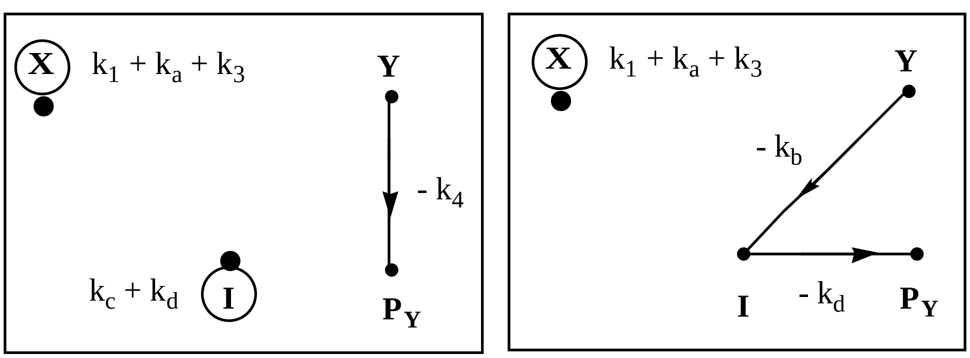
Subgraphs:

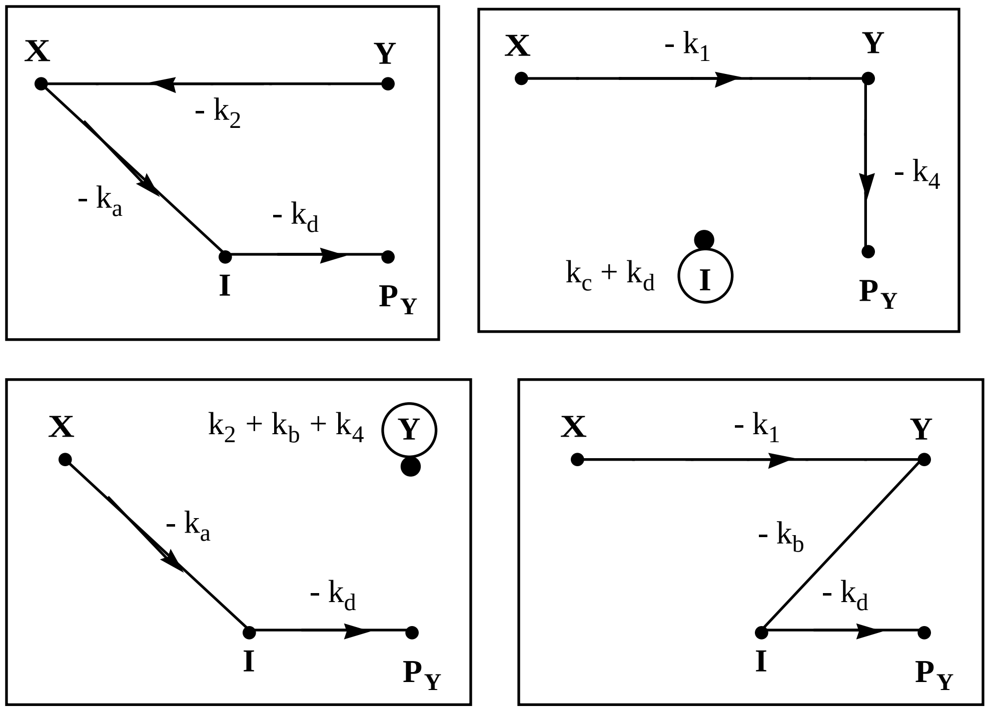






$$
\begin{aligned}
[P_X]_\infty \to\ & a(-1)^{4+2+1}(-k_3)(k_c+k_d)(k_2+k_4+k_b)+a(-1)^{4+1+1}k_ak_c(k_2+k_4+k_b)+a(-1)^{4+0+1}(-k_1k_bk_c)\\
& +b(-1)^{4+1+1}k_2k_3(k_c+k_d)+b(-1)^{4+1+1}k_bk_c(k_1+k_3+k_a)+b(-1)^{4+0+1}(-k_2k_ak_c)\\
& = a(k_2+k_4+k_b)\big(k_3(k_c+k_d)+k_ak_c\big)+ak_1k_bk_c+b\big(k_2k_3(k_c+k_d)+k_bk_c(k_1+k_3+k_a)+k_2k_ak_c\big)\\
& = (a+b)\big(k_2k_3(k_c+k_d)+k_bk_c(k_1+k_3+k_a)+k_2k_ak_c\big)+a\big(k_3k_4(k_c+k_d)+k_4k_ak_c+k_3k_bk_d\big)
\end{aligned}
$$





$$
\begin{aligned}
[P_Y]_\infty \to\; & b(-1)^{4+2+1}(-k_4)(k_c+k_d)(k_1+k_3+k_a) + b(-1)^{4+1+1}k_b k_d(k_1+k_3+k_a) + b(-1)^{4+0+1}(-k_2 k_a k_d) \\
& + a(-1)^{4+1+1}k_1 k_4(k_c+k_d) + a(-1)^{4+1+1}k_a k_d(k_2+k_4+k_b) + a(-1)^{4+0+1}(-k_1 k_b k_d) \\
& = b(k_1+k_3+k_a)\big(k_4(k_c+k_d)+k_b k_d\big) + b k_2 k_a k_d + a\big(k_1 k_4(k_c+k_d) + k_a k_d(k_2+k_4+k_b) + k_1 k_b k_d\big) \\
& = (a+b)\big(k_1 k_4(k_c+k_d) + k_a k_d(k_2+k_4+k_b) + k_1 k_b k_d\big) + b\big(k_3 k_4(k_c+k_d) + k_3 k_b k_d + k_4 k_a k_c\big)
\end{aligned}
$$

$$
\frac{[P_X]_\infty}{[P_Y]_\infty} = \frac{(k_c+k_d)\varepsilon_1 + k_c\phi}{(k_c+k_d)\varepsilon_2 + k_d\phi}
$$

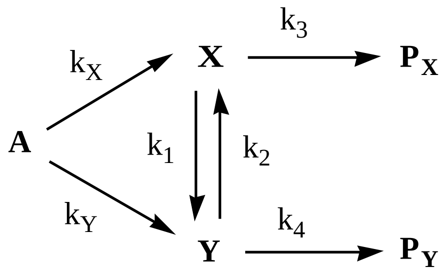
where

$$\varepsilon_1 = k_2 k_3(a+b) + a k_3(k_4+k_b)$$

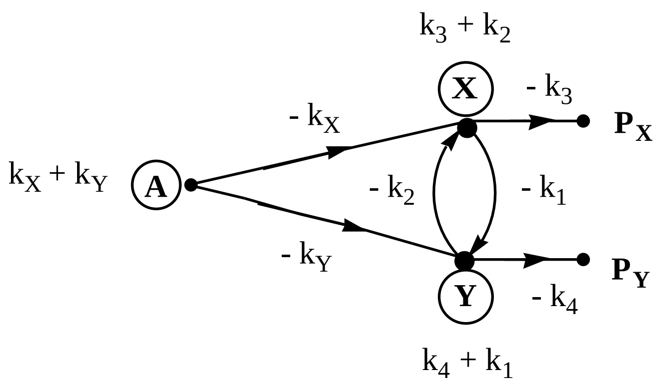
$$\varepsilon_2 = k_1 k_4(a+b) + b k_4(k_3+k_a)$$

$$\phi = (a+b)(k_1 k_b + k_2 k_a + k_a k_b) + b k_3 k_b + a k_4 k_a$$

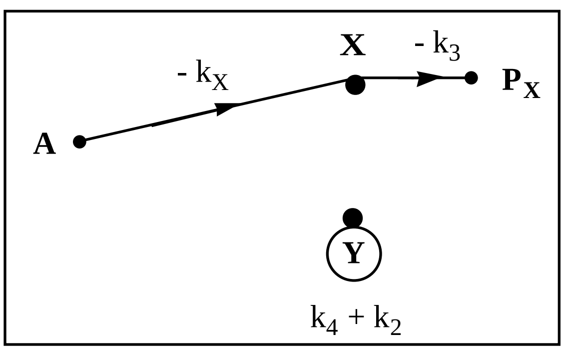
Scheme S4

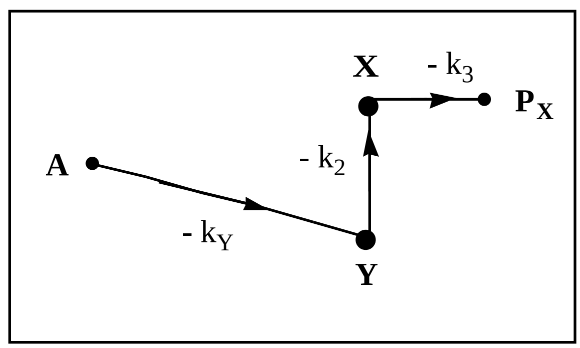


Digraph:

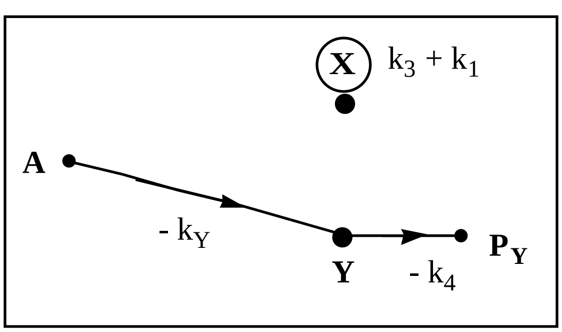


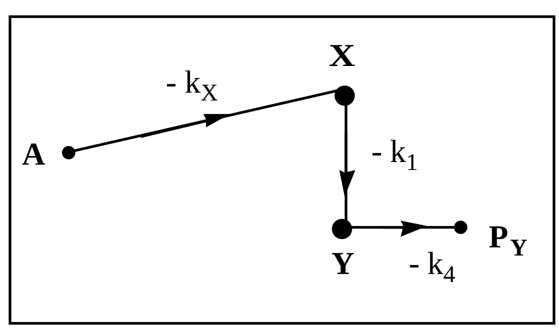
Subgraphs:





$$[P_X]_\infty \rightarrow a(-1)^{4+1+1} k_3 k_X (k_2 + k_4) + a(-1)^{4+0+1}(-k_2 k_3 k_Y) = a k_3 [k_X (k_2 + k_4) + k_2 k_Y]$$

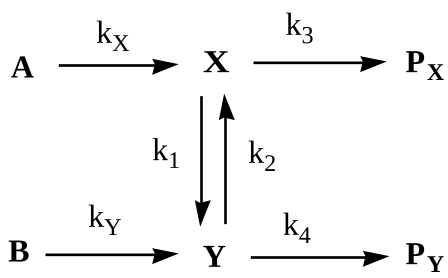




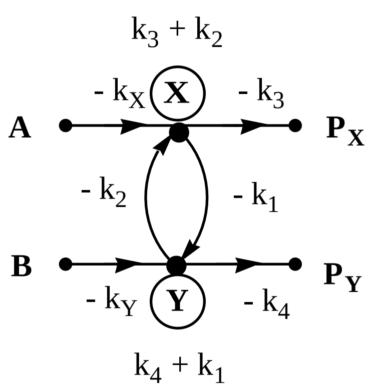
$$[P_X]_\infty \rightarrow a(-1)^{4+1+1} k_4 k_Y (k_1 + k_3) + a(-1)^{4+0+1}(-k_1 k_4 k_X) = a k_4 [k_Y (k_1 + k_3) + k_1 k_X]$$

$$\frac{[P_X]_\infty}{[P_Y]_\infty} = \left(\frac{k_3}{k_4}\right)\frac{k_X(k_2+k_4)+k_2k_Y}{k_Y(k_1+k_3)+k_1k_X}$$

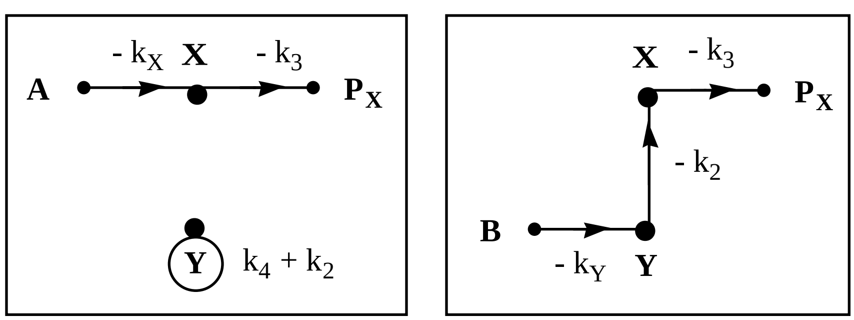
Scheme S5



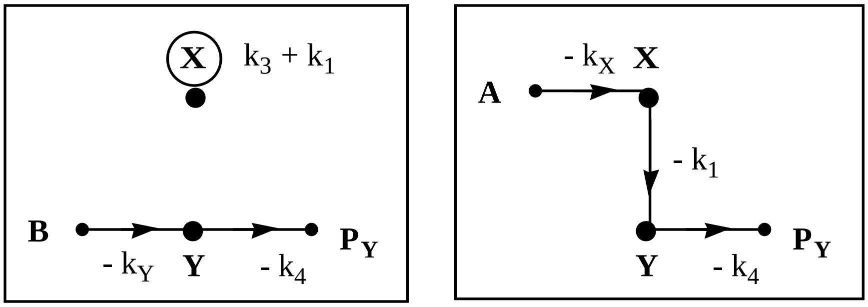
Digraph:



Subgraphs:



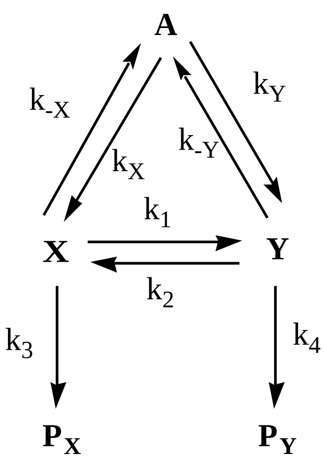
$$[P_X]_\infty \rightarrow a(-1)^{4+1+1}k_3k_X(k_2+k_4)+b(-1)^{4+0+1}(-k_2k_3k_Y) = k_3\{ak_X(k_2+k_4)+bk_2k_Y\}$$



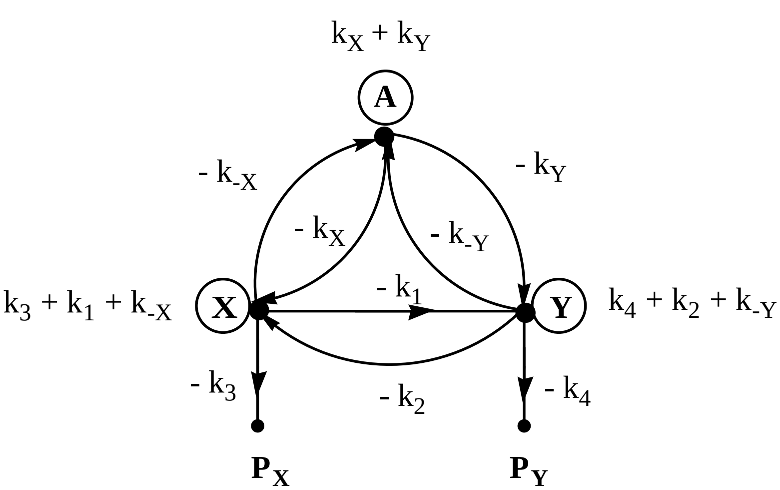
$$[P_X]_\infty \to b(-1)^{4+1+1} k_4 k_Y (k_1 + k_3) + a(-1)^{4+0+1}(-k_1 k_4 k_X) = k_4\{bk_Y(k_1 + k_3) + ak_1 k_X\}$$

$$\frac{[P_X]_\infty}{[P_Y]_\infty} = \left(\frac{k_3}{k_4}\right)\frac{ak_X(k_2 + k_4) + bk_Y k_2}{bk_Y(k_1 + k_3) + ak_X k_1}$$

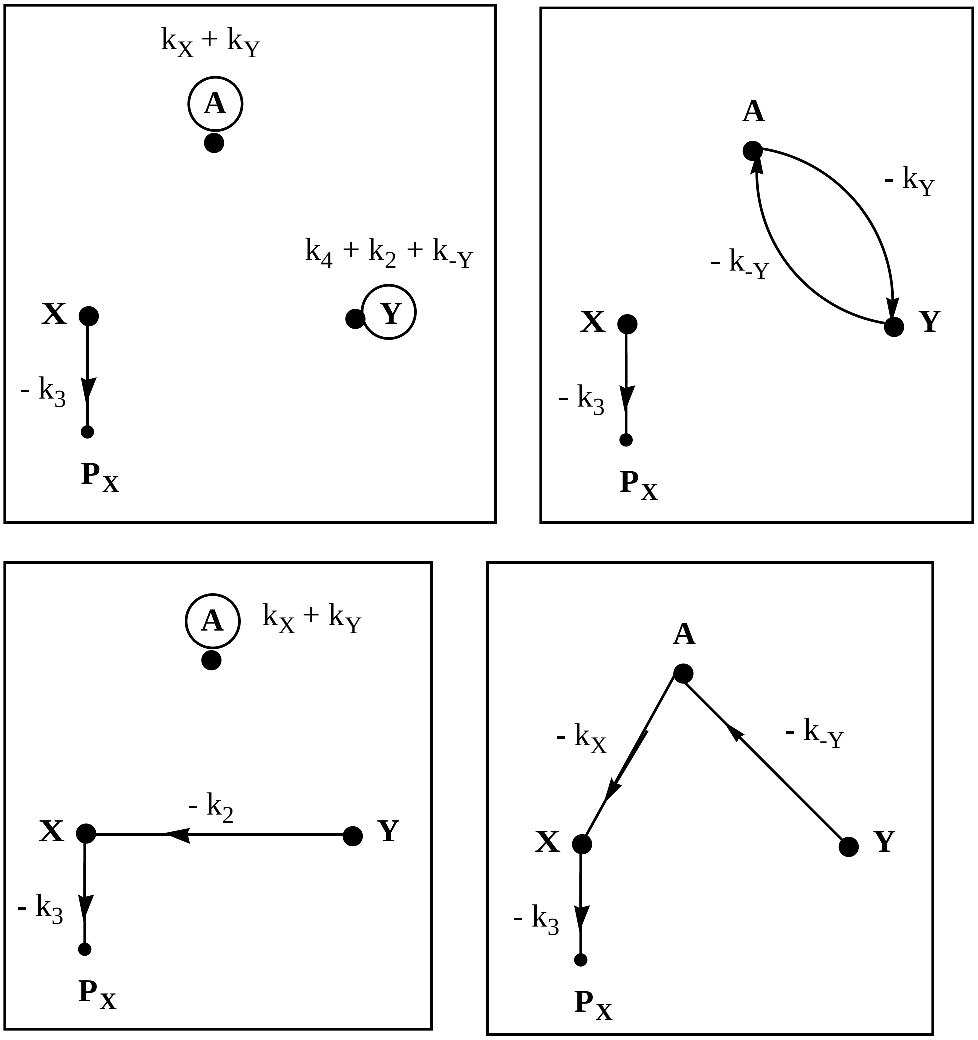
<u>Scheme S6</u>



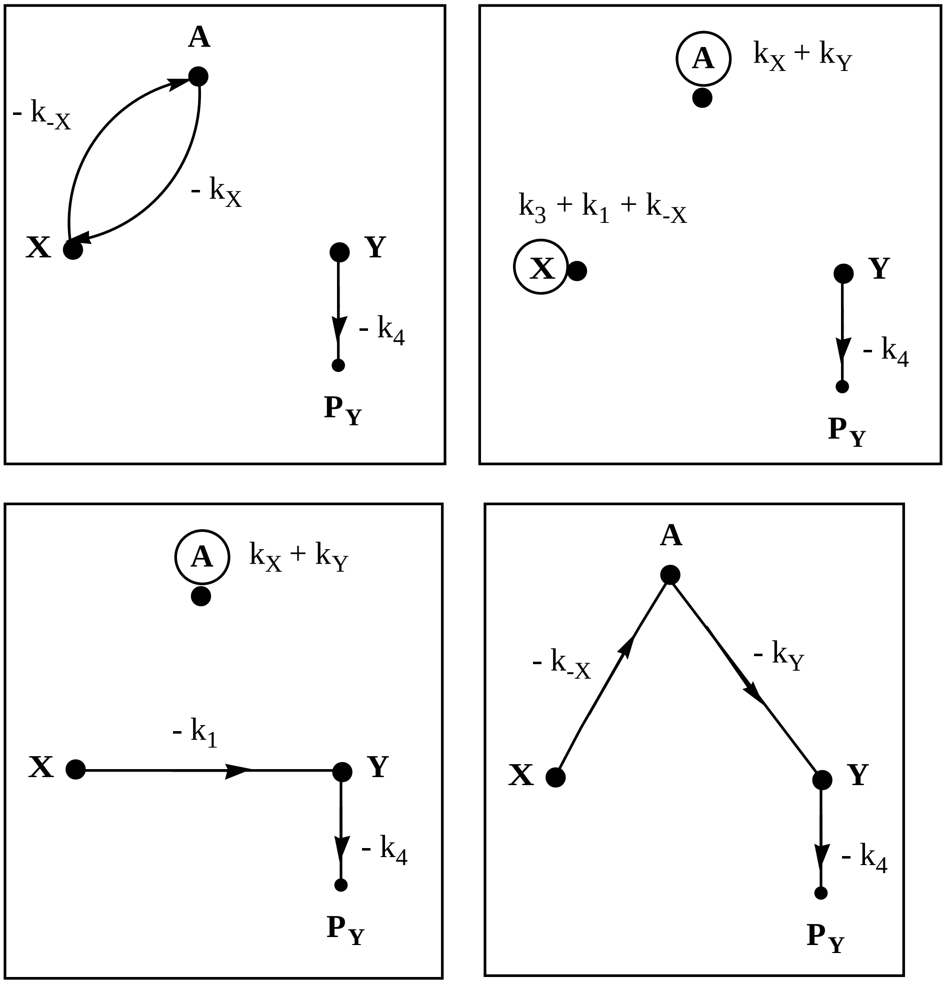
Digraph:



Subgraphs:



$$
\begin{aligned}
[P_X]_\infty \to\ & a(-1)^{4+2+1}(-k_3)(k_X+k_Y)(k_2+k_4+k_{-Y}) + a(-1)^{4+1+1}(-k_3 k_Y k_{-Y}) \\
& + b(-1)^{4+1+1} k_2 k_3 (k_X+k_Y) + b(-1)^{4+0+1}(-k_3 k_X k_{-Y}) \\
& = k_3\left\{a\left[(k_X+k_Y)(k_2+k_4+k_{-Y}) + k_Y k_{-Y}\right] + b\left[k_2(k_X+k_Y) + k_X k_{-Y}\right]\right\} \\
& = k_3\left\{(a+b)\left[k_2(k_X+k_Y) + k_X k_{-Y}\right] + a k_4 (k_X+k_Y) + a k_Y k_{-Y}\right\}
\end{aligned}
$$

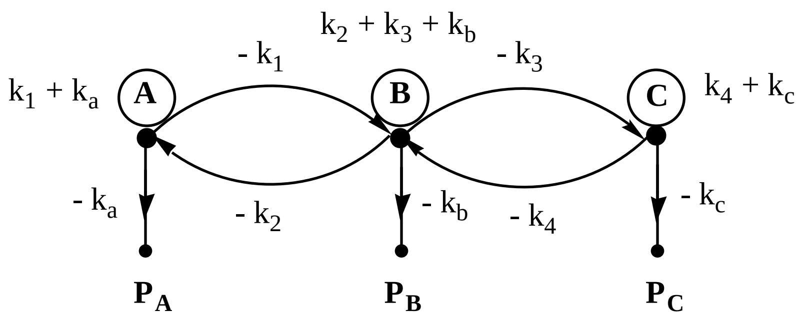


$$
\begin{aligned}
[P_Y]_\infty \rightarrow\ & b(-1)^{4+2+1}(-k_4)(k_X + k_Y)(k_1 + k_3 + k_{-X}) + b(-1)^{4+1+1}(-k_4 k_X k_{-X}) \\
& + a(-1)^{4+1+1} k_1 k_4 (k_X + k_Y) + a(-1)^{4+0+1}(-k_4 k_Y k_{-X}) \\
& = k_4 \left\{ b\left[(k_X + k_Y)(k_1 + k_3 + k_{-X}) + k_X k_{-X}\right] + a\left[k_1(k_X + k_Y) + k_Y k_{-X}\right]\right\} \\
& = k_4 \left\{ (a+b)\left[k_1(k_X + k_Y) + k_Y k_{-X}\right] + b k_3 (k_X + k_Y) + b k_X k_{-X} \right\}
\end{aligned}
$$

$$
\frac{[P_X]_\infty}{[P_Y]_\infty} = \left(\frac{k_3}{k_4}\right) \frac{(a+b)\left[k_2(k_X + k_Y) + k_X k_{-Y}\right] + a k_4 (k_X + k_Y) + a k_Y k_{-Y}}{(a+b)\left[k_1(k_X + k_Y) + k_Y k_{-X}\right] + b k_3 (k_X + k_Y) + b k_X k_{-X}}
$$

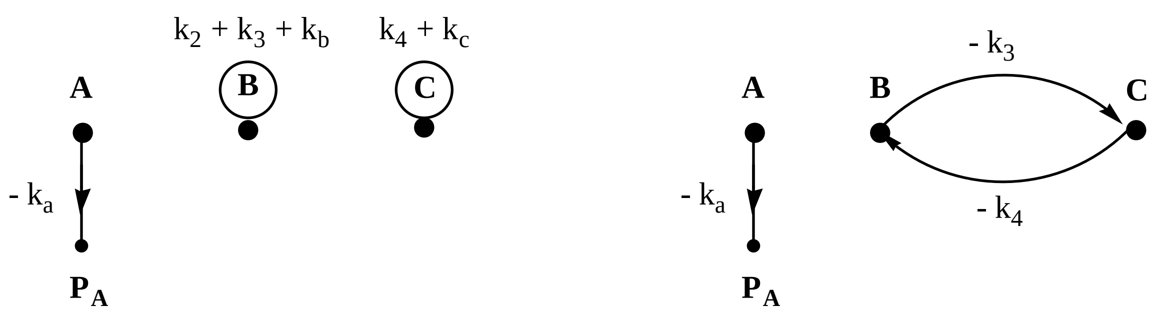
4. Solution of Scheme 6 by the modified Chou digraph method.

Digraph:



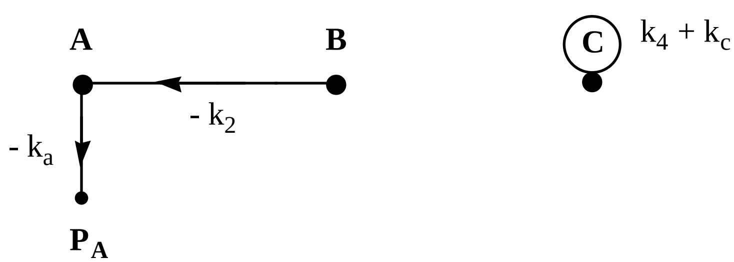
<u>Subgraphs:</u> target is P_A

Contribution from A



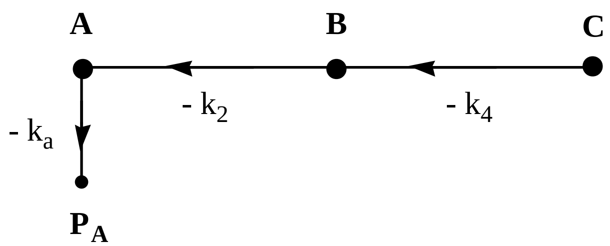
$$a\left\{(-1)^{4+2+1}(-k_a)(k_2+k_3+k_b)(k_4+k_c)+(-1)^{4+1+1}(-k_a k_3 k_4)\right\}$$
$$= ak_a\left\{(k_2+k_3+k_b)(k_4+k_c)-k_3k_4\right\}$$
$$= ak_a\left\{(k_2+k_b)(k_4+k_c)+k_3k_c\right\}$$

Contribution from B



$$b\left\{(-1)^{4+1+1}k_a k_2(k_4+k_c)\right\}=bk_a k_2(k_4+k_c)$$

Contribution from C



$$c\left\{(-1)^{4+0+1}\left(-k_a k_2 k_4\right)\right\} = c k_a k_2 k_4$$

Overall contribution to P_A from A, B, and C is found by summing above individual contributions:

$$[P_A]_\infty \rightarrow k_a\left\{a\left[(k_2 + k_a)(k_4 + k_c) + k_3 k_c\right] + b k_2 (k_4 + k_c) + c k_2 k_4\right\}$$

<u>Target product is P_C:</u>

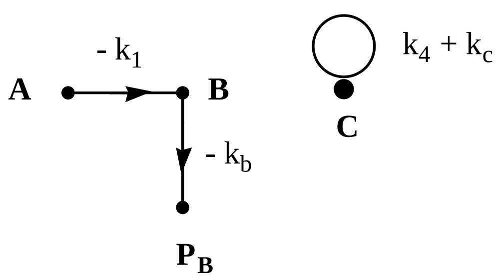
Overall contribution to P_C is found using transposition of variables:

$a \Leftrightarrow c$
$k_a \Leftrightarrow k_c$
$k_1 \Leftrightarrow k_4$
$k_2 \Leftrightarrow k_3$

$$[P_C]_\infty \rightarrow k_c\left\{c\left[(k_1 + k_a)(k_3 + k_c) + k_2 k_a\right] + b k_3 (k_1 + k_a) + a k_1 k_3\right\}$$

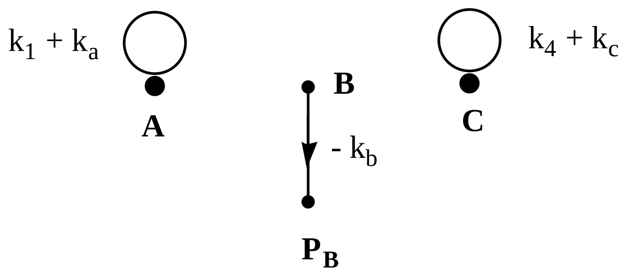
<u>Subgraphs:</u> target is P_B

Contribution from A



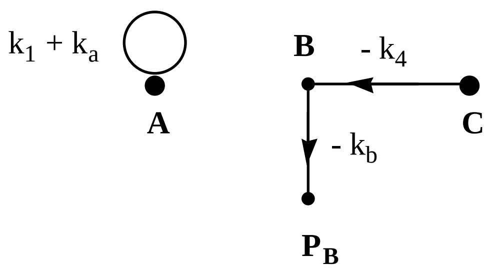
$$a\left\{(-1)^{4+1+1}(k_b k_1)(k_c + k_4)\right\} = a k_b k_1 (k_c + k_4)$$

Contribution from B



$$b\left\{(-1)^{4+2+1}(-k_b)(k_a+k_1)(k_c+k_4)\right\} = bk_b(k_a+k_1)(k_c+k_4)$$

Contribution from C



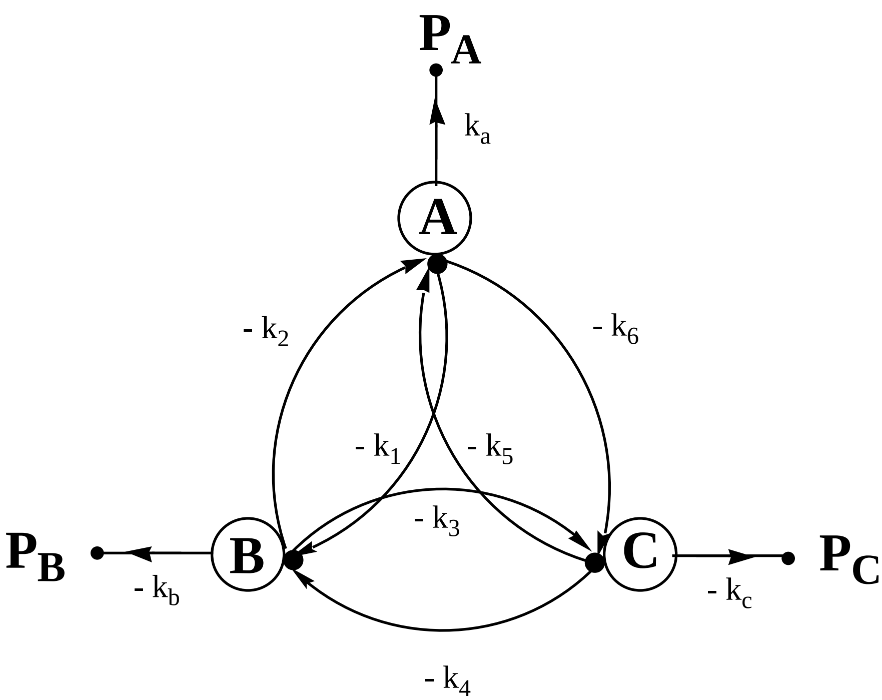
$$c\left\{(-1)^{4+1+1}(k_bk_4)(k_a+k_1)\right\} = ck_bk_4(k_a+k_1)$$

Overall contribution to P_B from A, B, and C is found by summing above individual contributions:

$$[P_B]_\infty \rightarrow k_b\left\{ak_1(k_4+k_c) + b(k_4+k_c)(k_1+k_a) + ck_4(k_1+k_a)\right\} \text{x}$$

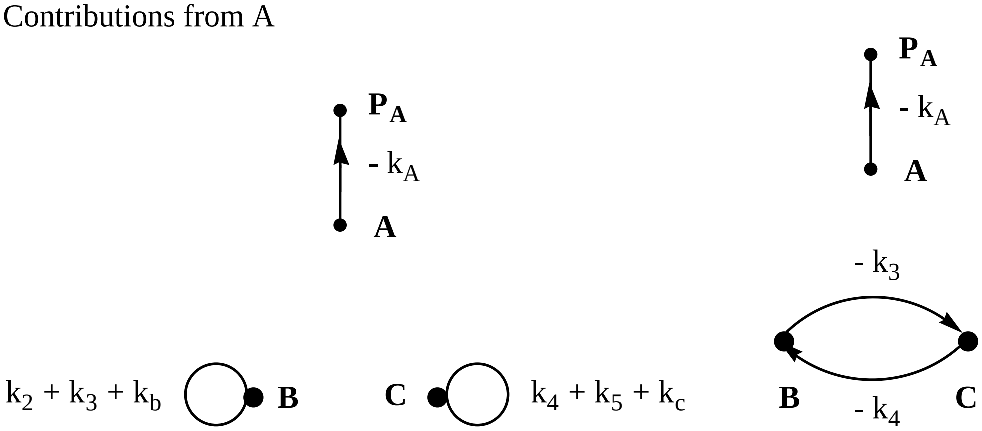
5. Solution of Scheme 7 by the modified Chou digraph method.

<u>Digraph:</u>



Subgraphs: target is P_A

Contributions from A

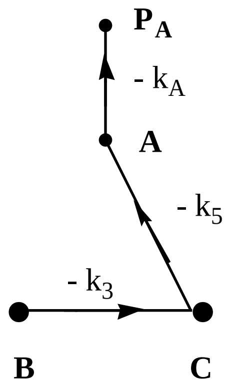


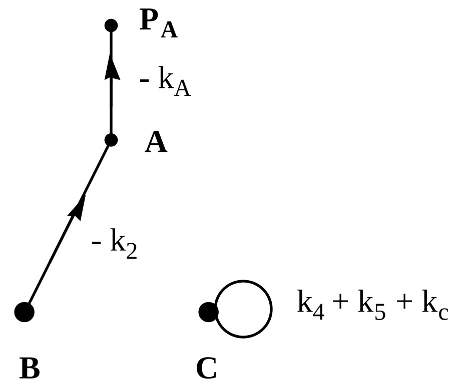
$$a\left\{(-1)^{4+2+1}(-k_a)(k_2+k_3+k_b)(k_4+k_5+k_c)+(-1)^{4+1+1}(-k_a k_3 k_4)\right\}$$

$$=ak_a\left\{(k_2+k_3+k_b)(k_4+k_5+k_c)-k_3k_4\right\}$$

$$=ak_a\left\{(k_2+k_b)(k_4+k_5+k_c)+k_3(k_5+k_c)\right\}$$

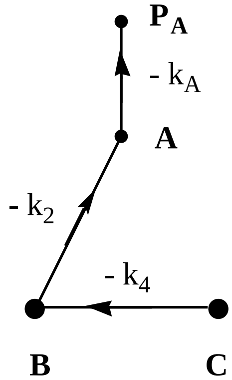
Contributions from B

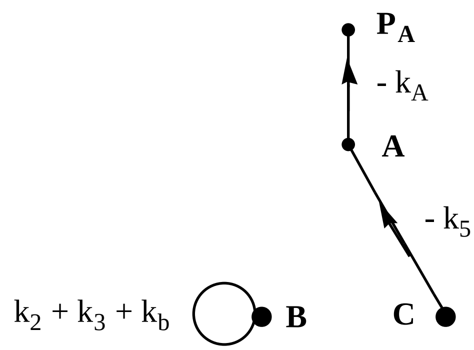




$$b\left\{(-1)^{4+0+1}\left(-k_a k_3 k_5\right)+(-1)^{4+1+1} k_a k_2\left(k_4+k_5+k_c\right)\right\}$$
$$=b k_a\left\{k_2\left(k_4+k_5+k_c\right)+k_3 k_5\right\}$$

Contributions from C





$$c\left\{(-1)^{4+0+1}\left(-k_a k_2 k_4\right)+(-1)^{4+1+1} k_a k_5\left(k_2+k_3+k_b\right)\right\}$$
$$=c k_a\left\{k_5\left(k_2+k_3+k_b\right)+k_2 k_4\right\}$$

Overall contribution to P_A from A, B, and C is found by summing above individual contributions:

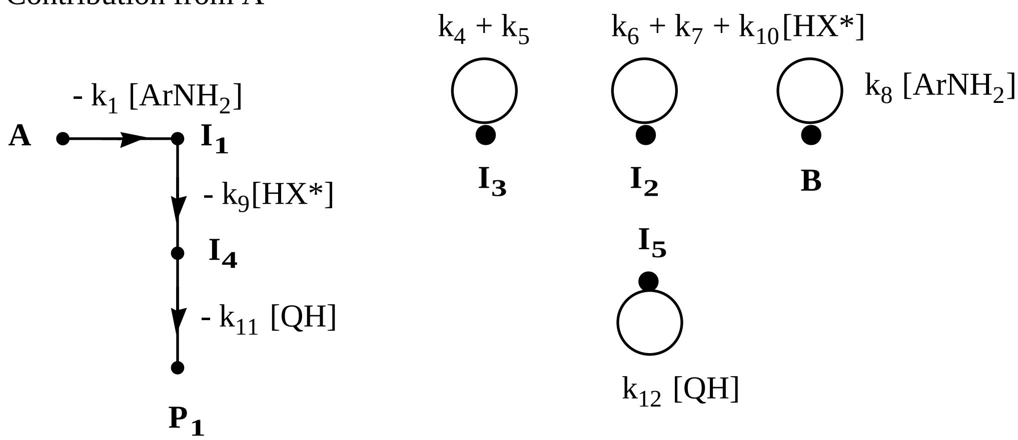
$$\left[P_A\right]_\infty \rightarrow k_a\left\{a\left[\left(k_2+k_b\right)\left(k_4+k_5+k_c\right)+k_3\left(k_5+k_c\right)\right]\right.$$
$$\left.+b\left[k_2\left(k_4+k_5+k_c\right)+k_3 k_5\right]+c\left[k_5\left(k_2+k_3+k_b\right)+k_2 k_4\right]\right\}$$

Contributions to P_B from A, B, and C and to P_C from A, B, and C are found in a similar fashion.

6. Subgraphs of digraph in Fig. 10.

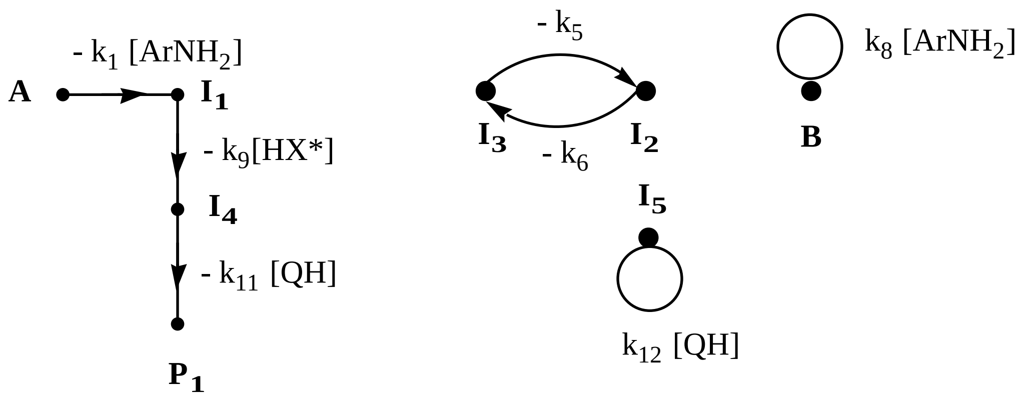
Target product is P_1:

Contribution from A



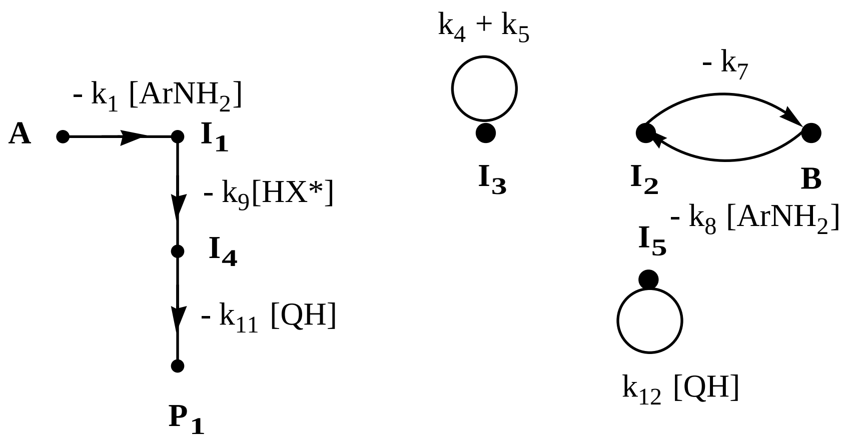
$$[A]_0(-1)^{8+4+1}(-k_1k_8k_9k_{11}k_{12})[ArNH_2]^2\left[HX^*\right][QH]^2(k_4+k_5)\left(k_6+k_7+k_{10}\left[HX^*\right]\right)$$

$$=[A]_0\,k_1k_8k_9k_{11}k_{12}(k_4+k_5)\left(k_6+k_7+k_{10}\left[HX^*\right]\right)[ArNH_2]^2\left[HX^*\right][QH]^2$$



$$[A]_0(-1)^{8+3+1}(-k_1k_5k_6k_8k_9k_{11}k_{12})[ArNH_2]^2\left[HX^*\right][QH]^2$$

$$=-[A]_0k_1k_5k_6k_8k_9k_{11}k_{12}[ArNH_2]^2\left[HX^*\right][QH]^2$$



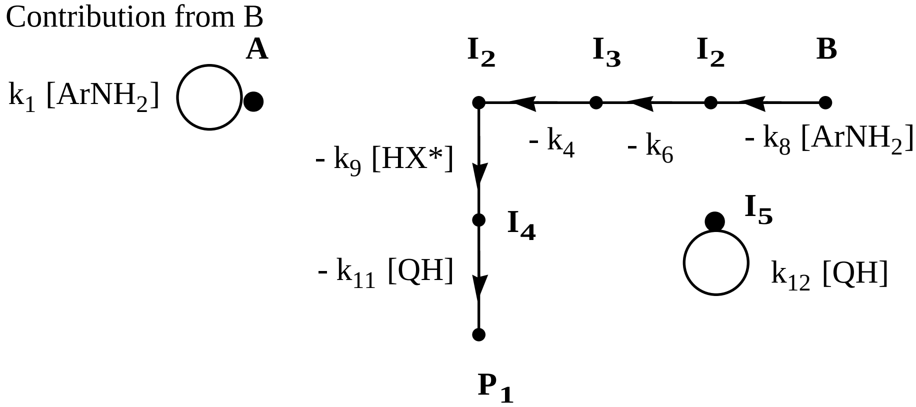
$$[A]_0(-1)^{8+3+1}(-k_1k_7k_8k_9k_{11}k_{12})(k_4+k_5)[ArNH_2]^2\left[HX^*\right][QH]^2$$

$$=-[A]_0k_1k_7k_8k_9k_{11}k_{12}(k_4+k_5)[ArNH_2]^2\left[HX^*\right][QH]^2$$

Overall contribution to P_1 from A is found by summing above individual contributions:

$$[A]_0k_1k_8k_9k_{11}k_{12}\left(k_4k_6+k_{10}\left[HX^*\right](k_4+k_5)\right)$$

Contribution from B



$$[B]_0(-1)^{7+1+1}(-k_1k_4k_6k_8k_9k_{11}k_{12})[ArNH_2]^2[QH]^2\left[HX^*\right]$$

$$=[B]_0\,k_1k_4k_6k_8k_9k_{11}k_{12}[ArNH_2]^2[QH]^2\left[HX^*\right]$$

Overall contribution to P_1:

$$[P_1]_\infty\to k_1k_8k_9k_{11}k_{12}[ArNH_2]^2[QH]^2\left[HX^*\right]\left\{[A]_0\left(k_4k_6+k_{10}\left[HX^*\right](k_4+k_5)\right)+[B]_0k_4k_6\right\}$$

<u>Target product is P_2:</u>

Overall contribution to P_2 is found using transposition of variables:

$$[A]_0 \Leftrightarrow [B]_0$$
$$k_1[ArNH_2] \Leftrightarrow k_8[ArNH_2]$$
$$k_2 \Leftrightarrow k_7$$
$$k_3 \Leftrightarrow k_6$$
$$k_4 \Leftrightarrow k_5$$
$$k_9\left[HX^*\right] \Leftrightarrow k_{10}\left[HX^*\right]$$
$$k_{11}[QH] \Leftrightarrow k_{12}[QH]$$

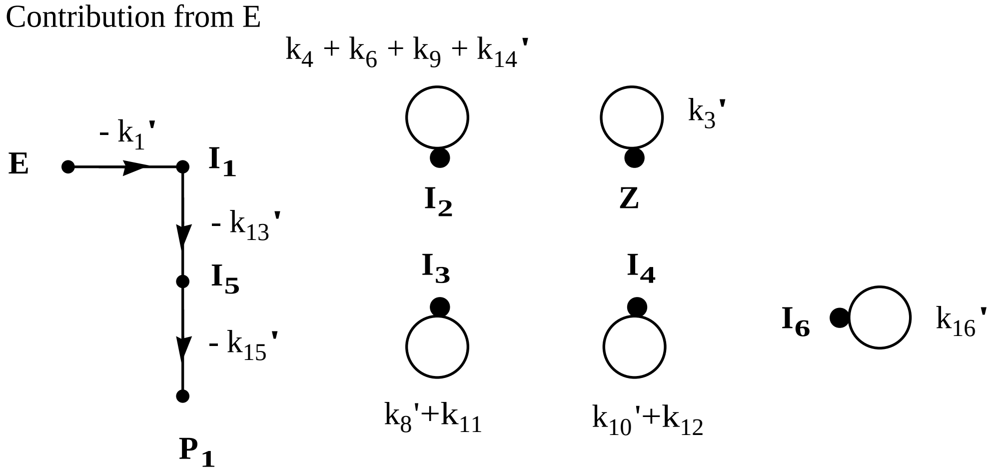
$$[P_2]_\infty \to k_1k_8k_{10}k_{11}k_{12}[ArNH_2]^2[QH]^2\left[HX^*\right]\left\{[B]_0\left(k_3k_5 + k_9\left[HX^*\right](k_4 + k_5)\right) + [A]_0\, k_3k_5\right\}$$

Dividing the contributions to P_1 and P_2 leads to eq. [30] for the final product ratio.

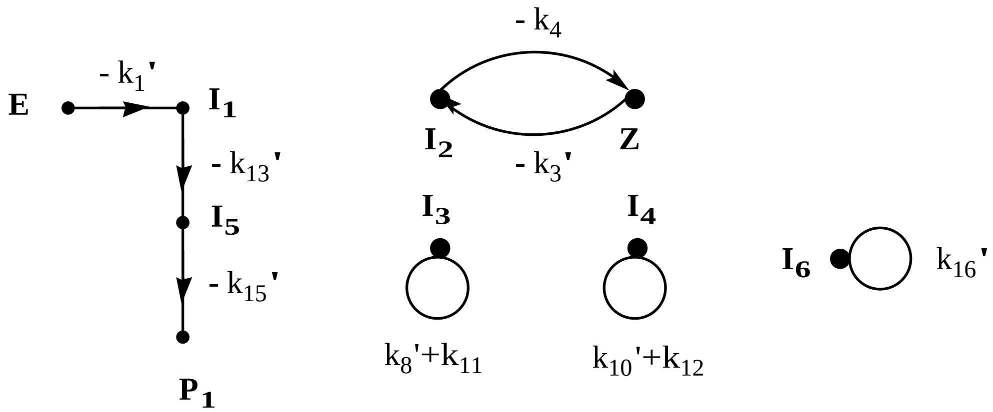
7. Subgraphs of digraph in Fig. 12.

Target product is P_1:

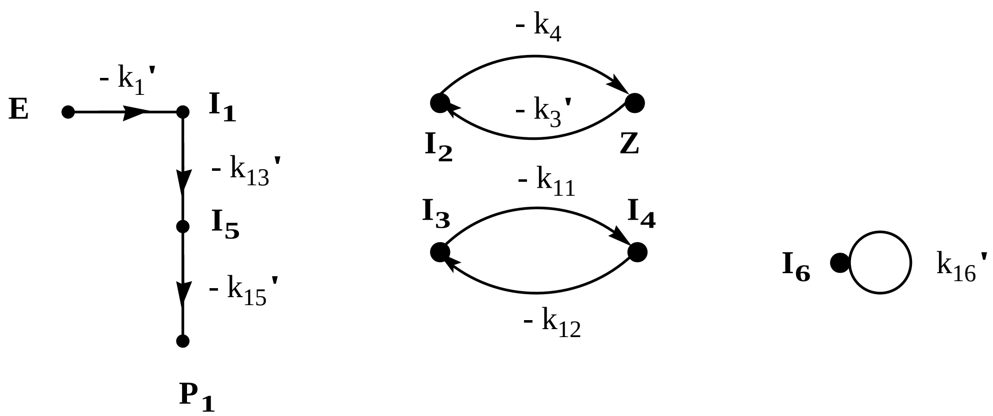
Contribution from E



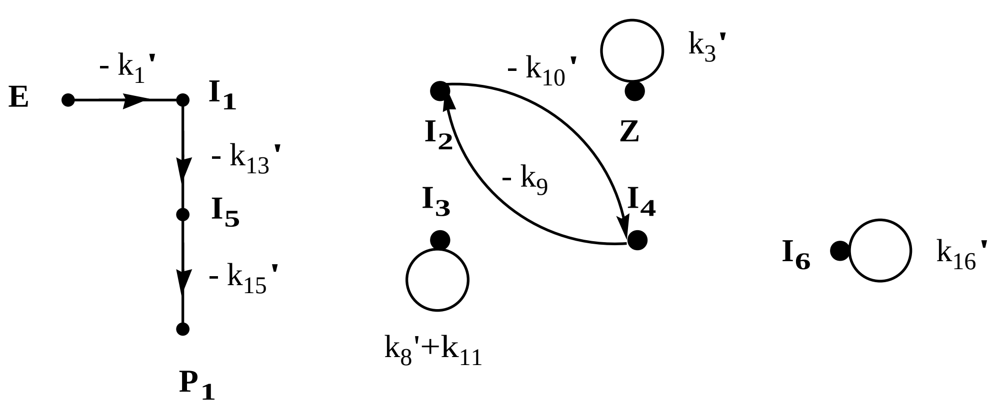
$$[E]_0(-1)^{9+5+1}\left(-k_1'\, k_3'\, k_{13}'\, k_{15}'\, k_{16}'\right)\left(k_4 + k_6 + k_9 + k_{14}'\right)\left(k_8' + k_{11}\right)\left(k_{10}' + k_{12}\right)$$
$$= [E]_0 k_1'\, k_3'\, k_{13}'\, k_{15}'\, k_{16}'\left(k_4 + k_6 + k_9 + k_{14}'\right)\left(k_8' + k_{11}\right)\left(k_{10}' + k_{12}\right)$$



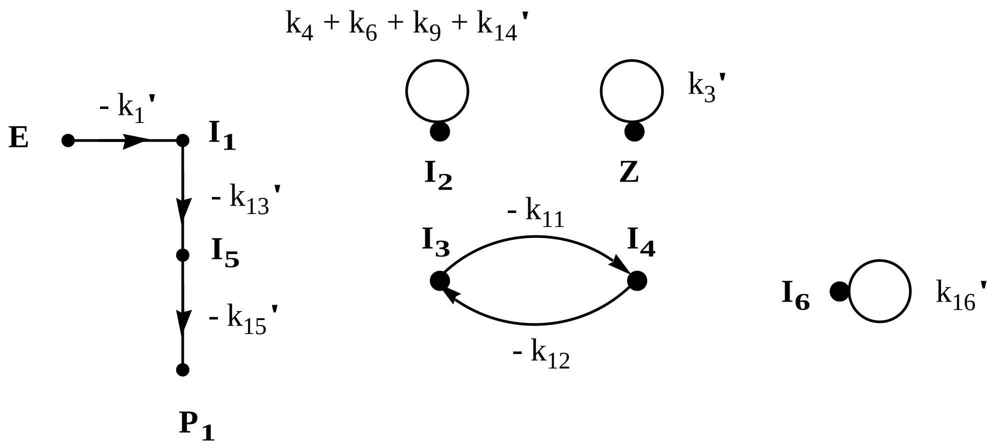
$$[E]_0(-1)^{9+4+1}(-k_1' k_3' k_4 k_{13}' k_{15}' k_{16}')(k_8' + k_{11})(k_{10}' + k_{12})$$
$$= -[E]_0 k_1' k_3' k_4 k_{13}' k_{15}' k_{16}' (k_8' + k_{11})(k_{10}' + k_{12})$$



$$[E]_0(-1)^{9+3+1}(-k_1' k_3' k_4 k_{11} k_{12} k_{13}' k_{15}' k_{16}')$$
$$= [E]_0 k_1' k_3' k_4 k_{11} k_{12} k_{13}' k_{15}' k_{16}'$$



$$[E]_0(-1)^{9+4+1}(-k_1' k_3' k_9 k_{10}' k_{12} k_{13}' k_{15}' k_{16}')(k_8' + k_{11})$$
$$= -[E]_0 k_1' k_3' k_9 k_{10}' k_{12} k_{13}' k_{15}' k_{16}' (k_8' + k_{11})$$

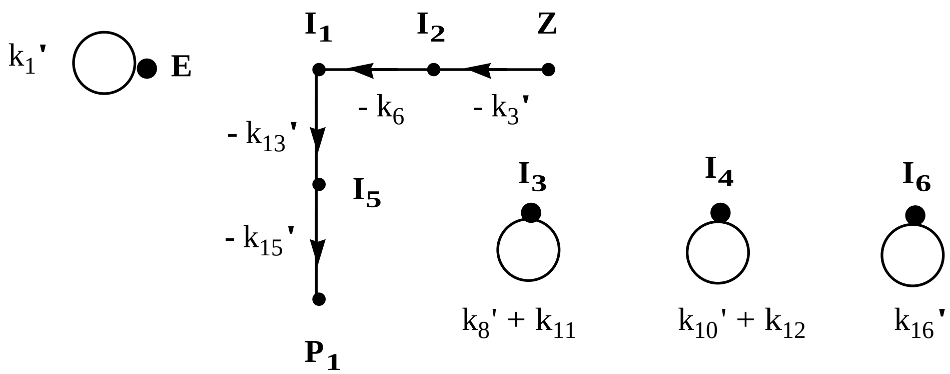


$$[E]_0(-1)^{9+4+1}(-k_1' k_3' k_{11} k_{12} k_{13}' k_{15}' k_{16}')(k_4+k_6+k_9+k_{14}')$$
$$=-[E]_0 k_1' k_3' k_{11} k_{12} k_{13}' k_{15}' k_{16}'(k_4+k_6+k_9+k_{14}')$$

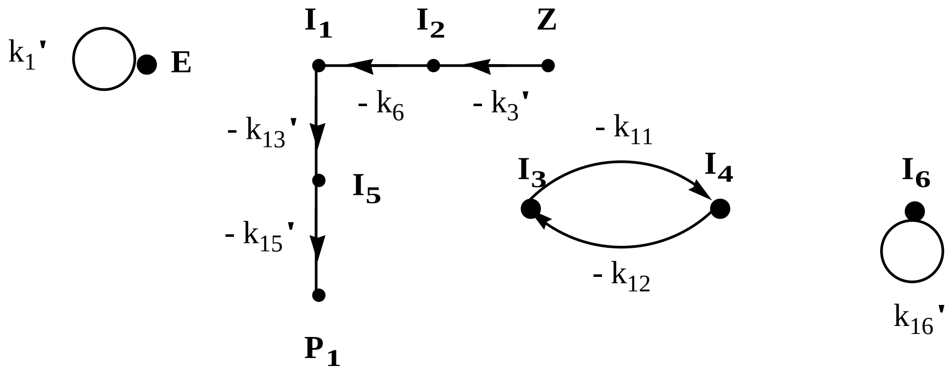
Overall contribution to P_1 from E is found by summing above individual contributions:

$$[E]_0 k_1' k_3' k_{13}' k_{15}' k_{16}'\{(k_6+k_{14}')(k_8' k_{10}'+k_{10}' k_{11}+k_8' k_{12})+k_8' k_9 k_{12}\}$$

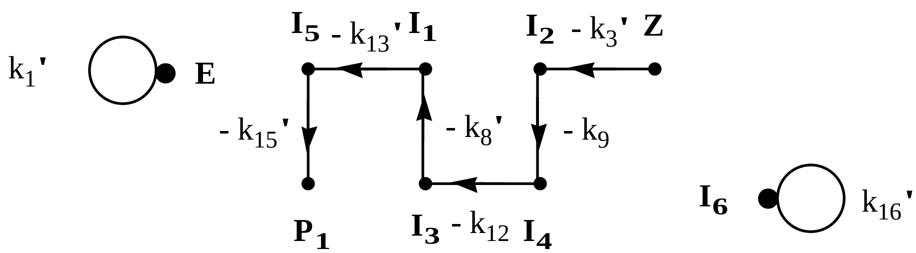
Contribution from Z



$$[Z]_0(-1)^{9+4+1} k_1' k_3' k_6 k_{13}' k_{15}' k_{16}'(k_8'+k_{11})(k_{10}'+k_{12})$$
$$=[Z]_0 k_1' k_3' k_6 k_{13}' k_{15}' k_{16}'(k_8'+k_{11})(k_{10}'+k_{12})$$



$$[Z]_0 (-1)^{9+3+1} k_1' k_3' k_6 k_{11} k_{12} k_{13}' k_{15}' k_{16}'$$
$$= -[Z]_0 k_1' k_3' k_6 k_{11} k_{12} k_{13}' k_{15}' k_{16}'$$



$$[Z]_0 (-1)^{9+2+1} k_1' k_3' k_8' k_9 k_{12} k_{13}' k_{15}' k_{16}'$$
$$= [Z]_0 k_1' k_3' k_8' k_9 k_{12} k_{13}' k_{15}' k_{16}'$$

Overall contribution to P_1 from Z is found by summing above individual contributions:

$$[Z]_0 k_1' k_3' k_{13}' k_{15}' k_{16}' \left\{ k_6 \left(k_8' k_{10}' + k_{10}' k_{11} + k_8' k_{12} \right) + k_8' k_9 k_{12} \right\}$$

Overall contribution to P_1:

$$[P_1]_\infty \rightarrow k_1' k_3' k_{13}' k_{15}' k_{16}' \left\{ \left([E]_0 + [Z]_0 \right) \alpha + [E]_0 k_{14}' \beta \right\}$$

where $\alpha = k_6 \beta + k_8' k_9 k_{12}$ and $\beta = k_8' k_{10}' + k_{10}' k_{11} + k_8' k_{12}$.

<u>Target product is P_2:</u>

Overall contribution to P_2 is found using transposition of variables:

$[E]_0 \Leftrightarrow [Z]_0$
$k_1' \Leftrightarrow k_3'$
$k_2 \Leftrightarrow k_4$
$k_5 \Leftrightarrow k_6$
$k_7 \Leftrightarrow k_9$
$k_8' \Leftrightarrow k_{10}'$
$k_{11} \Leftrightarrow k_{12}$
$k_{13}' \Leftrightarrow k_{14}'$
$k_{15}' \Leftrightarrow k_{16}'$

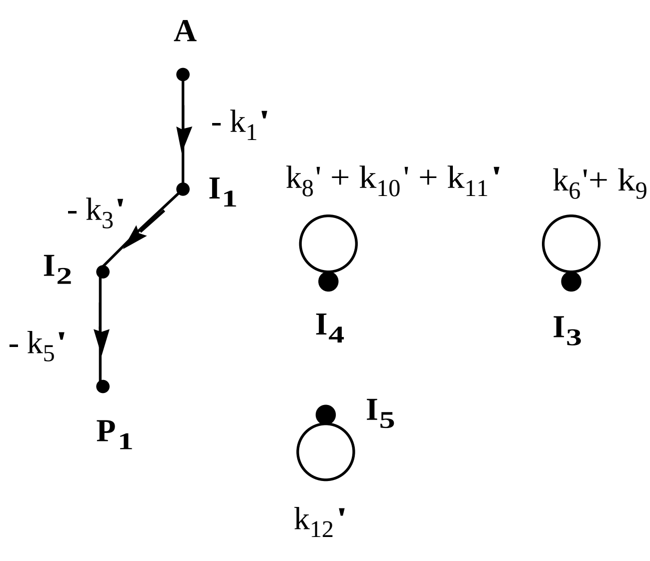
$$[P_2]_\infty \to k_1' k_3' k_{14}' k_{15}' k_{16}' \left\{ \left([E]_0 + [Z]_0 \right) \alpha^* + [Z]_0 k_{13}' \beta \right\}$$

where $\alpha = k_5 \beta + k_7 k_{10}' k_{11}$ and $\beta = k_8' k_{10}' + k_{10}' k_{11} + k_8' k_{12}$.

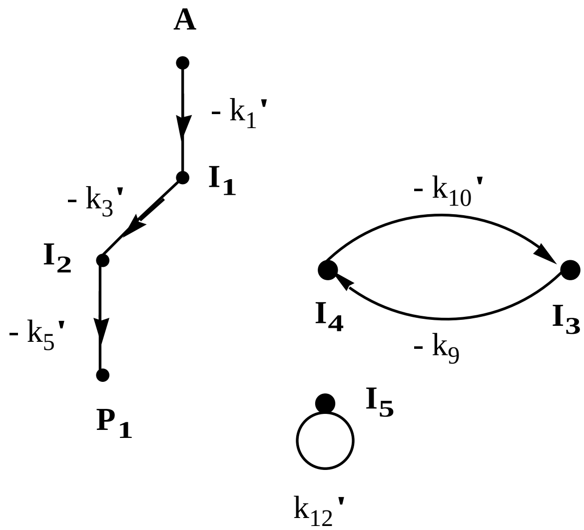
Dividing the contributions to P_1 and P_2 leads to eq. [39] for the final product ratio.

8. Subgraphs of digraph in Fig. 14.

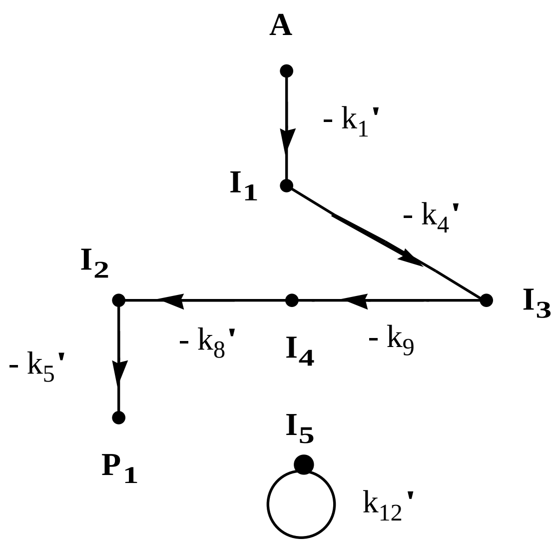
Target product is P_1:



$$[A]_0 (-1)^{7+3+1} \left(-k_1' k_3' k_5' k_{12}' \right) \left(k_6' + k_9 \right) \left(k_8' + k_{10}' + k_{11}' \right)$$
$$= [A]_0 k_1' k_3' k_5' k_{12}' \left(k_6' + k_9 \right) \left(k_8' + k_{10}' + k_{11}' \right)$$



$$[A]_0(-1)^{7+2+1}(-k_1'\,k_3'\,k_5'\,k_9 k_{10}'\,k_{12}')$$
$$= -[A]_0 k_1'\,k_3'\,k_5'\,k_9 k_{10}'\,k_{12}'$$



$$[A]_0(-1)^{7+1+1}(-k_1'\,k_4'\,k_5'\,k_8'\,k_9 k_{12}')$$
$$= [A]_0\, k_1'\,k_4'\,k_5'\,k_8'\,k_9 k_{12}'$$

Overall contribution to P_1 from A is found by summing above individual contributions:

$$[P_1]_\infty \rightarrow [A]_0 k_1'\,k_5'\,k_{12}'\left\{k_3'\,k_6'\left(k_8' + k_{10}' + k_{11}'\right) + k_9\left(k_3'\,k_8' + k_3'\,k_{11}' + k_4'\,k_8'\right)\right\}$$

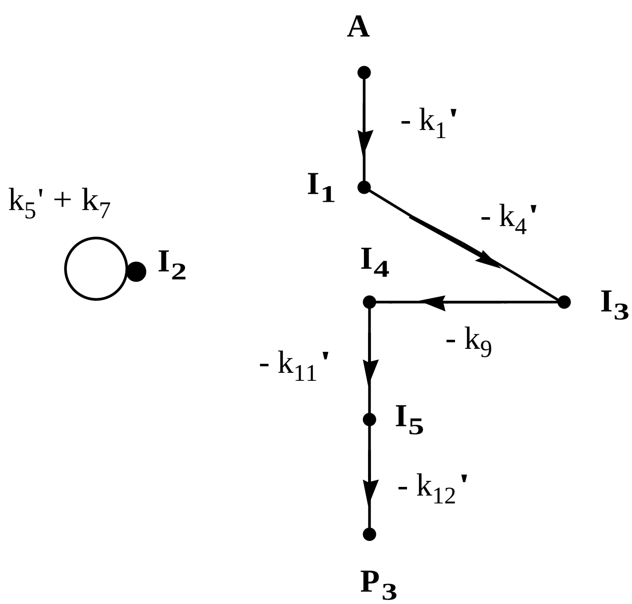
<u>Target product is P_2:</u>

Overall contribution to P_2 is found using transposition of variables:

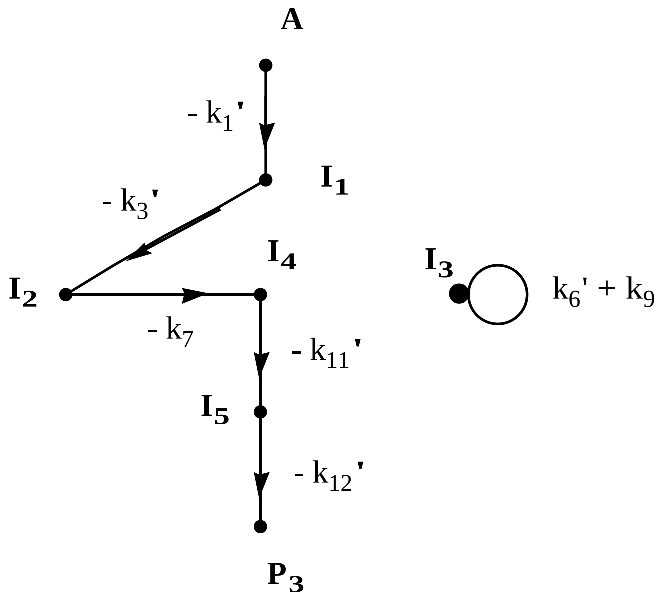
$k_3' \Leftrightarrow k_4'$
$k_5' \Leftrightarrow k_6'$
$k_7 \Leftrightarrow k_9$
$k_8' \Leftrightarrow k_{10}'$

$$[P_2]_\infty \to [A]_0 k_1' k_6' k_{12}' \{k_4' k_5' (k_8' + k_{10}' + k_{11}') + k_7 (k_4' k_{10}' + k_4' k_{11}' + k_3' k_{10}')\}$$

<u>Target product is P3:</u>



$$[A]_0 (-1)^{7+1+1} (-k_1' k_4' k_9 k_{11}' k_{12}')(k_5' + k_7)$$
$$= [A]_0 k_1' k_4' k_9 k_{11}' k_{12}' (k_5' + k_7)$$



$$[A]_0(-1)^{7+1+1}(-k_1' k_3' k_7 k_{11}' k_{12}')(k_6' + k_9)$$
$$= [A]_0 k_1' k_3' k_7 k_{11}' k_{12}' (k_6' + k_9)$$

Overall contribution to P_3 from A is found by summing above individual contributions:

$$[P_3]_\infty \rightarrow [A]_0 k_1' k_{11}' k_{12}' \{k_3' k_7 (k_6' + k_9) + k_4' k_9 (k_5' + k_7)\}$$

Dividing the contributions to P_1, P_2, and P_3 leads to eq. [48] for the final product ratio.