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SetDirectory[NotebookDirectory[]]
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D:\Github\SOHR\projects\catalytic_cycle\theory\SSA
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$$S \underset{k_{-S}}{\overset{k_S}{\rightleftharpoons}} A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} D \xrightarrow{k_D} P$$

Solve differential equation like

$$(\text{eq }1)\quad \frac{d[S]}{dt} = -k_S[S] + k_{-S}[A]$$

$$(\text{eq }2)\quad \frac{d[A]}{dt} = k_S[S] + k_{-1}[B] - (k_1 + k_{-S})[A]$$

$$(\text{eq }3)\quad \frac{d[B]}{dt} = k_1[A] + k_{-2}[C] - (k_2 + k_{-1})[B]$$

$$(\text{eq }4)\quad \frac{d[C]}{dt} = k_2[B] + k_{-3}[D] - (k_3 + k_{-2})[C]$$

$$(\text{eq }5)\quad \frac{d[D]}{dt} = k_3[C] - (k_{-3} + k_D)[D]$$

$$\begin{aligned}
&eq1 = -k_S * xS + k_{-S} * xA;\\
&eq2 = k_S * xS + k_{-1} * xB - (k_1 + k_{-S}) * xA;\\
&eq3 = k_1 * xA + k_{-2} * xC - (k_2 + k_{-1}) * xB;\\
&eq4 = k_2 * xB + k_{-3} * xD - (k_3 + k_{-2}) * xC;\\
&eq5 = k_3 * xC - (k_D + k_{-3}) * xD;\\
&eqz = xZ - (xA + xB + xC + xD);
\end{aligned}$$

Make a Steady State Approximation (SSA), let (eq 2) = 0 and (eq 3) = 0

```
soln = Solve[eq2 == 0 && eq3 == 0 && eq4 == 0 && eq5 == 0 && eqz == 0, {xS, xA, xB, xC, xD}] // Simplify
```

$$\Big\{\Big\{xS \to \frac{xZ\,\big(k_1 k_2 k_3 k_D + \big(k_{-3} k_{-2} k_{-1} + \big(k_{-2} k_{-1} + (k_{-1} + k_2)\,k_3\big)\,k_D\big)\,k_{-S}\big)}{\big(k_{-3}\,\big(k_{-2}\,(k_{-1} + k_1) + k_1 k_2\big) + \big(k_{-2} k_{-1} + (k_{-1} + k_2)\,k_3\big)\,k_D + k_1\,\big((k_{-2} + k_3)\,k_D + k_2\,(k_3 + k_D)\big)\big)\,k_S},$$

$$xA \to \frac{xZ\,\big(k_{-3} k_{-2} k_{-1} + \big(k_{-2} k_{-1} + (k_{-1} + k_2)\,k_3\big)\,k_D\big)}{k_{-3}\,\big(k_{-2}\,(k_{-1} + k_1) + k_1 k_2\big) + \big(k_{-2} k_{-1} + (k_{-1} + k_2)\,k_3\big)\,k_D + k_1\,\big((k_{-2} + k_3)\,k_D + k_2\,(k_3 + k_D)\big)},$$

$$xB \to \frac{xZ\,k_1\,\big(k_{-3} k_{-2} + (k_{-2} + k_3)\,k_D\big)}{k_{-3}\,\big(k_{-2}\,(k_{-1} + k_1) + k_1 k_2\big) + \big(k_{-2} k_{-1} + (k_{-1} + k_2)\,k_3\big)\,k_D + k_1\,\big((k_{-2} + k_3)\,k_D + k_2\,(k_3 + k_D)\big)},$$

$$xC \to \frac{xZ\,k_1 k_2\,(k_{-3} + k_D)}{k_{-3}\,\big(k_{-2}\,(k_{-1} + k_1) + k_1 k_2\big) + \big(k_{-2} k_{-1} + (k_{-1} + k_2)\,k_3\big)\,k_D + k_1\,\big((k_{-2} + k_3)\,k_D + k_2\,(k_3 + k_D)\big)},$$

$$xD \to \frac{xZ\,k_1 k_2 k_3}{k_{-3}\,\big(k_{-2}\,(k_{-1} + k_1) + k_1 k_2\big) + \big(k_{-2} k_{-1} + (k_{-1} + k_2)\,k_3\big)\,k_D + k_1\,\big((k_{-2} + k_3)\,k_D + k_2\,(k_3 + k_D)\big)}\Big\}\Big\}$$

```
xA = xA /. soln[[1, 2]];
xB = xB /. soln[[1, 3]];
xC = xC /. soln[[1, 4]];
xD = xD /. soln[[1, 5]];
```

Rate Constant of Z

$(k_{-S} * xA + k_D * xD) / xZ$ // Simplify

$$\left(k_1\, k_2\, k_3\, k_D + \left(k_{-3}\, k_{-2}\, k_{-1} + \left(k_{-2}\, k_{-1} + \left(k_{-1} + k_2\right) k_3\right) k_D\right) k_{-S}\right) / \left(k_{-3}\left(k_{-2}\left(k_{-1} + k_1\right) + k_1\, k_2\right) + \left(k_{-2}\, k_{-1} + \left(k_{-1} + k_2\right) k_3\right) k_D + k_1\left(\left(k_{-2} + k_3\right) k_D + k_2\left(k_3 + k_D\right)\right)\right)$$

Branching Ratios

Γ_A = Numerator[xA] $* k_{-S} /$ xZ // Simplify

$$\left(k_{-3}\, k_{-2}\, k_{-1} + \left(k_{-2}\, k_{-1} + \left(k_{-1} + k_2\right) k_3\right) k_D\right) k_{-S}$$

Γ_P = Numerator[xD] $* k_D /$ xZ // Simplify

$$k_1\, k_2\, k_3\, k_D$$

$\Gamma_A / (\Gamma_A + \Gamma_P)$

$$\left(\left(k_{-3}\, k_{-2}\, k_{-1} + \left(k_{-2}\, k_{-1} + \left(k_{-1} + k_2\right) k_3\right) k_D\right) k_{-S}\right) / \left(k_1\, k_2\, k_3\, k_D + \left(k_{-3}\, k_{-2}\, k_{-1} + \left(k_{-2}\, k_{-1} + \left(k_{-1} + k_2\right) k_3\right) k_D\right) k_{-S}\right)$$

$\Gamma_P / (\Gamma_A + \Gamma_P)$

$$\left(k_1\, k_2\, k_3\, k_D\right) / \left(k_1\, k_2\, k_3\, k_D + \left(k_{-3}\, k_{-2}\, k_{-1} + \left(k_{-2}\, k_{-1} + \left(k_{-1} + k_2\right) k_3\right) k_D\right) k_{-S}\right)$$