```
SetDirectory[NotebookDirectory[]]
D:\VS_workspace\CPlusPlus\SOHR\projects\catalytic_cycle\theory\SSA
```

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} D \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} E \xrightarrow{k_E} P$$

Solve differential equation like

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

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

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

$$(eq\ 4)\ \frac{d[D]}{dt} = k_3[C] + k_{-4}[E] - (k_4 + k_{-3})[D]$$

$$(eq\ 5)\ \frac{d[E]}{dt} = k_4[D] - (k_5 + k_{-4})[E]$$

$$\begin{aligned}
&eq1 = -k_1 * xA + k_{-1} * xB;\\
&eq2 = k_1 * xA + k_{-2} * xC - (k_2 + k_{-1}) * xB;\\
&eq3 = k_2 * xB + k_{-3} * xD - (k_3 + k_{-2}) * xC;\\
&eq4 = k_3 * xC + k_{-4} * xE - (k_4 + k_{-3}) * xD;\\
&eq5 = k_4 * xD - (k_E + k_{-4}) * xE;
\end{aligned}$$

$$A \underset{k_{-1}^{eff}}{\overset{k_1}{\rightleftharpoons}} Z \xrightarrow{k_3^{eff}} P$$

```
eqz = xZ - (xB + xC + xD + xE);
```

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

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

$$\Big\{\Big\{xA \to \frac{xZ\,(k_{-4}\,k_{-3}\,k_{-2}\,k_{-1} + (k_{-3}\,k_{-2}\,k_{-1} + (k_{-2}\,k_{-1} + (k_{-1} + k_2)\,k_3)\,k_4)\,k_e)}{k_1\,(k_{-4}\,(k_{-3}\,(k_{-2} + k_2) + k_2\,k_3) + (k_{-3}\,k_{-2} + (k_{-2} + k_3)\,k_4)\,k_e + k_2\,((k_{-3} + k_4)\,k_e + k_3\,(k_4 + k_e)))},$$

$$xB \to \frac{xZ\,(k_{-4}\,k_{-3}\,k_{-2} + (k_{-3}\,k_{-2} + (k_{-2} + k_3)\,k_4)\,k_e)}{k_{-4}\,(k_{-3}\,(k_{-2} + k_2) + k_2\,k_3) + (k_{-3}\,k_{-2} + (k_{-2} + k_3)\,k_4)\,k_e + k_2\,((k_{-3} + k_4)\,k_e + k_3\,(k_4 + k_e))},$$

$$xC \to \frac{xZ\,k_2\,(k_{-4}\,k_{-3} + (k_{-3} + k_4)\,k_e)}{k_{-4}\,(k_{-3}\,(k_{-2} + k_2) + k_2\,k_3) + (k_{-3}\,k_{-2} + (k_{-2} + k_3)\,k_4)\,k_e + k_2\,((k_{-3} + k_4)\,k_e + k_3\,(k_4 + k_e))},$$

$$xD \to \frac{xZ\,k_2\,k_3\,(k_{-4} + k_e)}{k_{-4}\,(k_{-3}\,(k_{-2} + k_2) + k_2\,k_3) + (k_{-3}\,k_{-2} + (k_{-2} + k_3)\,k_4)\,k_e + k_2\,((k_{-3} + k_4)\,k_e + k_3\,(k_4 + k_e))},$$

$$xE \to \frac{xZ\,k_2\,k_3\,k_4}{k_{-4}\,(k_{-3}\,(k_{-2} + k_2) + k_2\,k_3) + (k_{-3}\,k_{-2} + (k_{-2} + k_3)\,k_4)\,k_e + k_2\,((k_{-3} + k_4)\,k_e + k_3\,(k_4 + k_e))}\Big\}\Big\}$$

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

$$(xZ\,k_2\,k_3\,k_4) \Big/ (k_{-4}\,(k_{-3}\,(k_{-2} + k_2) + k_2\,k_3) + (k_{-3}\,k_{-2} + (k_{-2} + k_3)\,k_4)\,k_e + k_2\,((k_{-3} + k_4)\,k_e + k_3\,(k_4 + k_e)))$$

$$(xZ\,(k_{-4}\,k_{-3}\,k_{-2} + (k_{-3}\,k_{-2} + (k_{-2} + k_3)\,k_4)\,k_e)) \Big/ (k_{-4}\,(k_{-3}\,(k_{-2} + k_2) + k_2\,k_3) + (k_{-3}\,k_{-2} + (k_{-2} + k_3)\,k_4)\,k_e + k_2\,((k_{-3} + k_4)\,k_e + k_3\,(k_4 + k_e)))$$

$$(xZ\,k_2\,(k_{-4}\,k_{-3} + (k_{-3} + k_4)\,k_e)) \Big/ (k_{-4}\,(k_{-3}\,(k_{-2} + k_2) + k_2\,k_3) + (k_{-3}\,k_{-2} + (k_{-2} + k_3)\,k_4)\,k_e + k_2\,((k_{-3} + k_4)\,k_e + k_3\,(k_4 + k_e)))$$

$$(xZ\,k_2\,k_3\,(k_{-4} + k_e)) \Big/ (k_{-4}\,(k_{-3}\,(k_{-2} + k_2) + k_2\,k_3) + (k_{-3}\,k_{-2} + (k_{-2} + k_3)\,k_4)\,k_e + k_2\,((k_{-3} + k_4)\,k_e + k_3\,(k_4 + k_e)))$$

$$(xZ\,k_2\,k_3\,k_4) \Big/ (k_{-4}\,(k_{-3}\,(k_{-2} + k_2) + k_2\,k_3) + (k_{-3}\,k_{-2} + (k_{-2} + k_3)\,k_4)\,k_e + k_2\,((k_{-3} + k_4)\,k_e + k_3\,(k_4 + k_e)))$$

Rate Constant of Z

$$(k_{-1} * xB + k_E * xE) \Big/ xZ \text{ // Simplify}$$

$$(k_{-4}\,k_{-3}\,k_{-2}\,k_{-1} + (k_{-3}\,k_{-2}\,k_{-1} + (k_{-2}\,k_{-1} + (k_{-1} + k_2)\,k_3)\,k_4)\,k_e) \Big/ (k_{-4}\,(k_{-3}\,(k_{-2} + k_2) + k_2\,k_3) + (k_{-3}\,k_{-2} + (k_{-2} + k_3)\,k_4)\,k_e + k_2\,((k_{-3} + k_4)\,k_e + k_3\,(k_4 + k_e)))$$

Branching Ratios

Γ_A = Numerator[xB] * k_{-1} / xZ // Simplify

$$k_{-1} \left(k_{-4}\, k_{-3}\, k_{-2} + \left(k_{-3}\, k_{-2} + \left(k_{-2} + k_3\right) k_4\right) k_e\right)$$

Γ_P = Numerator[xE] * k_E / xZ // Simplify

$$k_2\, k_3\, k_4\, k_e$$

Γ_A / (Γ_A + Γ_P)

$$\left(k_{-1} \left(k_{-4}\, k_{-3}\, k_{-2} + \left(k_{-3}\, k_{-2} + \left(k_{-2} + k_3\right) k_4\right) k_e\right)\right) \Big/ \left(k_2\, k_3\, k_4\, k_e + k_{-1} \left(k_{-4}\, k_{-3}\, k_{-2} + \left(k_{-3}\, k_{-2} + \left(k_{-2} + k_3\right) k_4\right) k_e\right)\right)$$

Γ_P / (Γ_A + Γ_P)

$$\left(k_2\, k_3\, k_4\, k_e\right) \Big/ \left(k_2\, k_3\, k_4\, k_e + k_{-1} \left(k_{-4}\, k_{-3}\, k_{-2} + \left(k_{-3}\, k_{-2} + \left(k_{-2} + k_3\right) k_4\right) k_e\right)\right)$$