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

Solve differential equation like

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

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

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

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

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

```
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);
```

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
```

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

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

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

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

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

```
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
```

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

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
```

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

```
Γ_A / (Γ_A + Γ_P)
```

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

```
Γ_P / (Γ_A + Γ_P)
```

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