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

$$A \xrightarrow{k_A} P_A$$

$$B \xrightarrow{k_B} P_B$$

$$C \xrightarrow{k_C} P_C$$

$$D \xrightarrow{k_D} P_D$$

Solve differential equations like

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

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

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

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

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

```
eq1 = -k_S * xS + k_-S * xA;
eq2 = k_S * xS + k_-1 * xB - (k_1 + k_-S + k_A) * xA;
eq3 = k_1 * xA + k_-2 * xC - (k_-1 + k_2 + k_B) * xB;
eq4 = k_2 * xB + k_-3 * xD - (k_-2 + k_3 + k_C) * xC;
eq5 = k_3 * xC - (k_-3 + k_D) * xD;
eqz = xZ - (xA + xB + xC + xD);
```

Make a Steady State Approximation (SSA), let (eq 2) = 0 , (eq 3) = 0, (eq 4) = 0, (eq 5) = 0 and (eq z) = 0

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

$$\{\{xS \to (xZ\,(k_D\,(k_1\,(k_2\,(k_3+k_C)+k_B\,(k_{-2}+k_3+k_C))+(k_{-2}\,(k_{-1}+k_B)+(k_{-1}+k_2+k_B)\,(k_3+k_C))\,(k_A+k_{-S}))+k_{-3}\,(k_C\,(k_1\,(k_2+k_B)+(k_{-1}+k_2+k_B)\,(k_A+k_{-S}))+k_{-2}\,(k_{-1}\,(k_A+k_{-S})+k_B\,(k_1+k_A+k_{-S})))))/((k_{-3}\,(k_{-2}\,(k_{-1}+k_1+k_B)+(k_{-1}+k_2+k_B)\,k_C+k_1\,(k_2+k_C))+(k_{-2}\,(k_{-1}+k_B)+(k_{-1}+k_2+k_B)\,(k_3+k_C))\,k_D+k_1\,((k_{-2}+k_3+k_C)\,k_D+k_2\,(k_3+k_D)))\,k_S),$$
$$xA \to (xZ\,(k_{-3}\,(k_{-2}\,(k_{-1}+k_B)+(k_{-1}+k_2+k_B)\,k_C)+(k_{-2}\,(k_{-1}+k_B)+(k_{-1}+k_2+k_B)\,(k_3+k_C))\,k_D))/(k_{-3}\,(k_{-2}\,(k_{-1}+k_1+k_B)+(k_{-1}+k_2+k_B)\,k_C+k_1\,(k_2+k_C))+(k_{-2}\,(k_{-1}+k_B)+(k_{-1}+k_2+k_B)\,(k_3+k_C))\,k_D+k_1\,((k_{-2}+k_3+k_C)\,k_D+k_2\,(k_3+k_D))),$$
$$xB \to (xZ\,k_1\,(k_{-3}\,(k_{-2}+k_C)+(k_{-2}+k_3+k_C)\,k_D))/(k_{-3}\,(k_{-2}\,(k_{-1}+k_1+k_B)+(k_{-1}+k_2+k_B)\,k_C+k_1\,(k_2+k_C))+(k_{-2}\,(k_{-1}+k_B)+(k_{-1}+k_2+k_B)\,(k_3+k_C))\,k_D+k_1\,((k_{-2}+k_3+k_C)\,k_D+k_2\,(k_3+k_D))),$$
$$xC \to (xZ\,k_1\,k_2\,(-k_{-3}-k_D))/(-k_3\,(k_1\,k_2-k_{-3}\,(k_{-1}+k_1+k_2+k_B))+((-k_{-2}+k_1)\,k_2+(k_{-1}+k_1+k_2+k_B)\,(k_{-2}+k_3+k_C))\,(-k_{-3}-k_D)),$$
$$xD \to (xZ\,k_1\,k_2\,k_3)/(k_{-3}\,(k_{-2}\,(k_{-1}+k_1+k_B)+(k_{-1}+k_2+k_B)\,k_C+k_1\,(k_2+k_C))+(k_{-2}\,(k_{-1}+k_B)+(k_{-1}+k_2+k_B)\,(k_3+k_C))\,k_D+k_1\,((k_{-2}+k_3+k_C)\,k_D+k_2\,(k_3+k_D)))\}\}$$

```
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 + k_A) * xA + k_B * xB + k_C * xC + k_D * xD) / xZ // Simplify
```

$$(k_D\,(k_1\,(k_2\,(k_3+k_C)+k_B\,(k_{-2}+k_3+k_C))+(k_{-2}\,(k_{-1}+k_B)+(k_{-1}+k_2+k_B)\,(k_3+k_C))\,(k_A+k_{-S}))+k_{-3}\,(k_C\,(k_1\,(k_2+k_B)+(k_{-1}+k_2+k_B)\,(k_A+k_{-S}))+k_{-2}\,(k_{-1}\,(k_A+k_{-S})+k_B\,(k_1+k_A+k_{-S}))))/(k_{-3}\,(k_{-2}\,(k_{-1}+k_1+k_B)+(k_{-1}+k_2+k_B)\,k_C+k_1\,(k_2+k_C))+(k_{-2}\,(k_{-1}+k_B)+(k_{-1}+k_2+k_B)\,(k_3+k_C))\,k_D+k_1\,((k_{-2}+k_3+k_C)\,k_D+k_2\,(k_3+k_D)))$$

Branching Ratios

```
Γ_A = Numerator[xA] * (k_-S + k_A) / xZ // Simplify
```

$$(k_{-3}\,(k_{-2}\,(k_{-1}+k_B)+(k_{-1}+k_2+k_B)\,k_C)+(k_{-2}\,(k_{-1}+k_B)+(k_{-1}+k_2+k_B)\,(k_3+k_C))\,k_D)\,(k_A+k_{-S})$$

```
Γ_B = Numerator[xB] * k_B / xZ // Simplify
```

$$k_1\,k_B\,(k_{-3}\,(k_{-2}+k_C)+(k_{-2}+k_3+k_C)\,k_D)$$

```
Γ_C = Numerator[xC] * k_C / xZ // Simplify
```

$$-k_1\,k_2\,k_C\,(k_{-3}+k_D)$$

Γ_D = Numerator[xD] * k_D / xZ // Simplify

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

Γ_A / (Γ_A + Γ_B + Γ_C + Γ_D)

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

Γ_B / (Γ_A + Γ_B + Γ_C + Γ_D)

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

Γ_C / (Γ_A + Γ_B + Γ_C + Γ_D)

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

Γ_D / (Γ_A + Γ_B + Γ_C + Γ_D)

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