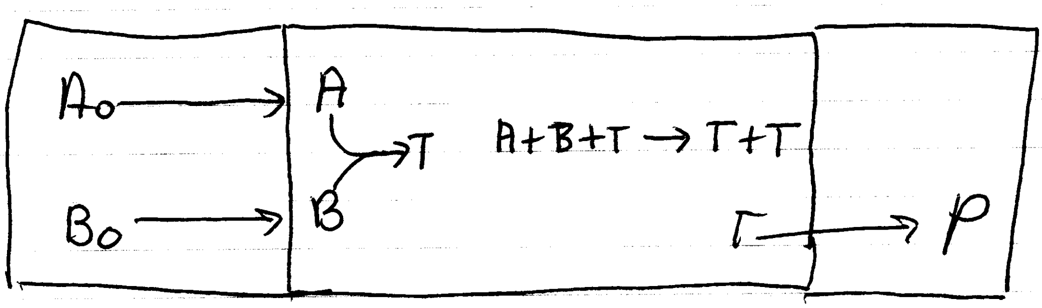
OPEN SYSTEM $\Rightarrow$ Non equilibrium (Thermodynamic) Steady State



$$A_0 + B_0 \longrightarrow P \quad \text{Overall rxn}$$

A_0, B_0 and P cannot oscillate $\rightarrow$ 2nd Law Thermo

$[A_0]$ $[B_0]$ $\downarrow$

$[P]$ $\uparrow$

Intermediates can oscillate.

SELF-REPLICATION

$$A + B \xrightarrow{k_u} T$$

$$A + B + T \xrightarrow{k_T} T + T$$

$$\frac{d[A]}{dt} = -k_u[A][B] - k_t[A][B][T]$$

$$\frac{d[B]}{dt} = -k_u[A][B] - k_t[A][B][T]$$

$$\frac{d[T]}{dt} = k_u[A][B] + k_t[A][B][T]$$

$$x = \frac{[A]+[B]}{2} \qquad [A] = x + y$$

$$y = \frac{[A]-[B]}{2} \qquad [B] = x - y$$

$$\frac{dx}{dt} = -k_u(x+y)(x-y) - k_t(x^2-y^2)[T]$$

$$\frac{dy}{dt} = 0$$

$$\frac{d[T]}{dt} = k_u(x^2-y^2) + k_t(x^2-y^2)[T]$$

$$y(t) = y_0 = 0 = \frac{[A]_0 - [B]_0}{2}$$

$$\frac{dX}{dt} = -k_u X^2 - k_t X^2 [T]$$

$$\frac{d[T]}{dt} = k_u X^2 + k_t X^2 [T]$$

$$\frac{dx}{dt} = r_0 - k_t x^2 [T] - k_u x^2$$

$$\frac{d[T]}{dt} = k_u x^2 + k_t x^2 [T] - \frac{V[T]}{K_M + [T]}$$

$$\left.\begin{aligned} u &\equiv \frac{x}{m} \\ v &\equiv \frac{[T]}{m} \\ \tau &= \frac{t}{s} \end{aligned}\right\}$$ dimensionless

$$\boxed{\begin{aligned} \frac{du}{d\tau} &= r - k\cancel{u}^2 - \cancel{u}^2 v \\ \frac{dv}{d\tau} &= ku^2 + u^2 v - \frac{v}{K+v} \end{aligned}}$$

DIMENSIONLES TEMPLATOR

<u>CONSIDER FIRST</u>

$$\frac{du}{d\tau} = r - u^2 v \equiv F(u,v)$$

$$\frac{dv}{d\tau} = u^2 v - \frac{v}{K+v} \equiv G(u,v)$$

$\underline{\underline{SS}}$ $$r - \bar{u}^2\bar{v} = 0$$

$$\bar{u}^2\bar{v} - \frac{\bar{v}}{K+\bar{v}} = 0$$

$\underline{\underline{SS}}$ $$r = \frac{\bar{v}}{K+\bar{v}} = \bar{u}^2\bar{v}$$

$$rK + r\bar{v} = \bar{v}$$

$$rK = (1-r)\bar{v}$$

$$\boxed{\bar{v} = \frac{rK}{1-r}} \qquad r < 1$$

$$\bar{u}^2 = \frac{r}{\bar{v}} = \frac{1-r}{K}$$

$$\boxed{\bar{u} = \sqrt{\frac{1-r}{K}}}$$

$$J_{11} = -2\bar{u}\bar{v} \qquad J_{12} = -\bar{u}^2$$

$$J_{21} = 2\bar{u}\bar{v} \qquad J_{22} = \underbrace{\bar{u}^2 - \frac{1}{K+\bar{v}}}_{0} + \frac{\bar{v}}{(K+\bar{v})^2} = \frac{r^2}{\bar{v}}$$

$$\det\begin{vmatrix} -2\bar{u}\bar{v} - \lambda & -\bar{u}^2 \\ 2\bar{u}\bar{v} & \frac{r^2}{\bar{v}} - \lambda \end{vmatrix} = 0$$

$$0 = +(\lambda + 2\bar{u}\bar{v})(\lambda - \frac{r^2}{\bar{v}}) + 2\bar{u}^3\bar{v}$$

$$\lambda^2 - \left(\frac{r^2}{\bar{v}} - 2\bar{u}\bar{v}\right) + 2(\bar{u}^3\bar{v} - 2\bar{u}r^2) = 0$$

$$\lambda^2 - \mathrm{tr}J + \det J = 0 \quad !$$

$$a\lambda^2 + b\lambda + c = 0$$

$$\lambda_\pm = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$a = 1$

$$\lambda_\pm = \frac{-b \pm \sqrt{b^2 - 4c}}{2}$$

Sign of $Re(\lambda_\pm)$

In our case $c = 2\bar{u}(\bar{u}^2\bar{v} - r^2) = 2\bar{u}r(1-r) > 0$

a) $b^2 > 4c$ $\quad \lambda_\pm \in \mathbb{R}$ $\quad \mathrm{Sign}(\lambda_\pm) = \mathrm{Sign}(-b)$

$Re(\lambda) < 0$ IF $\mathrm{sign}(b) > 0$ STABLE

$Re(\lambda) > 0$ IF $\mathrm{sign}(b) < 0$ UNSTABLE

$$b = -\mathrm{tr}\bar{J} \Rightarrow \boxed{\begin{array}{ll} \text{STABLE} & \mathrm{tr}J < 0 \\ \text{UNSTABLE} & \mathrm{tr}J > 0 \end{array}}$$

$$\mathrm{tr}J = \frac{r^2}{\bar{v}} - 2\frac{\bar{u}\bar{v}^2}{\bar{v}} = \frac{\bar{u}^4\bar{v}^2 - 2\bar{u}\bar{v}^2}{\bar{v}}$$

$$b = 2\bar{u}\bar{v} - \frac{r^2}{\bar{v}} = 2\bar{u}\bar{v}^2 - r^2$$

$$= 2\bar{u}\bar{v}^2 - \bar{u}^4\bar{v}^2 = \bar{u}\bar{v}^2(2-\bar{u}^3)$$

$2-\bar{u}^3 > 0$ STABLE

$2-\bar{u}^3 < 0$ UNSTABLE

$2 < \bar{u}^3$ UNSTABLE

$$2 < \frac{(1-r)^{3/2}}{K^{3/2}}$$

$$2^{\frac{2}{3}} < \frac{(1-r)}{K}$$

$$\boxed{K < \frac{1}{2^{2/3}}(1-r) \quad \text{UNSTABLE}}$$