BT209

Bioreaction Engineering

06/04/2023

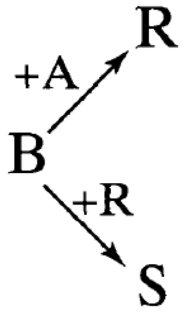
Deign for Multiple reactions:

- **Quantitative analysis of Two-Step Irreversible Series-Parallel Reactions**
- **Denbigh reaction scheme**

Quantitative analysis: Two-Step Irreversible Series-Parallel Reactions

Kinetics

$$\left.\begin{aligned} A + B &\xrightarrow{k_1} R \\ R + B &\xrightarrow{k_2} S \end{aligned}\right\}$$



or

$$A \xrightarrow{+B} R \xrightarrow{+B} S$$

$$r_A = \frac{dC_A}{dt} = -k_1 C_A C_B$$

$$r_B = \frac{dC_B}{dt} = -k_1 C_A C_B - k_2 C_R C_B$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A C_B - k_2 C_R C_B$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R C_B$$

What is the product distribution in a batch/PFR and CSTR ?

Product Distribution: in batch or PFR

$$\left.\begin{aligned} A + B &\xrightarrow{k_1} R \\ R + B &\xrightarrow{k_2} S \end{aligned}\right\}$$

Kinetics

$$r_A = \frac{dC_A}{dt} = -k_1 C_A C_B$$

$$r_B = \frac{dC_B}{dt} = -k_1 C_A C_B - k_2 C_R C_B$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A C_B - k_2 C_R C_B$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R C_B$$

$$\frac{dC_R}{dC_A} = -1 + \frac{k_2}{k_1}\frac{C_R}{C_A}$$

Use $C_R = uC_A$

$$\frac{dC_R}{dC_A} = \frac{du}{dC_A} C_A + u$$

=> $\frac{du}{dC_A} C_A + u = \frac{k_2}{k_1} u - 1$

=> $\frac{du}{u(k_2 - k_1) - k_1} = \frac{1}{k_1}\frac{dC_A}{C_A}$

=> $\int_0^{\frac{C_R}{C_A}} \frac{du}{u(k_2 - k_1) - k_1} = \frac{1}{k_1}\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A}$

When $C_A = C_{A0}$, $C_R = C_{R0} = 0$

=> $\frac{C_R}{C_{A0}} = \frac{1}{1 - k_2/k_1}\left[\left(\frac{C_A}{C_{A0}}\right)^{k_2/k_1} - \frac{C_A}{C_{A0}}\right]$

When $k_1 \neq k_2$

When $k_1 = k_2$ $\frac{du}{dC_A} C_A = -1$

$$\frac{C_R}{C_{A0}} = \frac{C_A}{C_{A0}} \ln \frac{C_{A0}}{C_A}$$

Cont..

$$\left.\begin{aligned} A + B &\xrightarrow{k_1} R \\ R + B &\xrightarrow{k_2} S \end{aligned}\right\}$$

$$\frac{C_R}{C_{A0}} = \frac{1}{1 - k_2/k_1}\left[\left(\frac{C_A}{C_{A0}}\right)^{k_2/k_1} - \frac{C_A}{C_{A0}}\right], \qquad \frac{k_2}{k_1} \neq 1$$

$$\frac{C_R}{C_{A0}} = \frac{C_A}{C_{A0}} \ln \frac{C_{A0}}{C_A}, \qquad \frac{k_2}{k_1} = 1$$

For C_R^{max}

Put $dC_R/dC_A = 0$

$$\frac{C_{R,max}}{C_{A0}} = \left(\frac{k_1}{k_2}\right)^{k_2/(k_2-k_1)}, \qquad \frac{k_2}{k_1} \neq 1$$

$$\frac{C_{R,max}}{C_{A0}} = \frac{1}{e} = 0.368 \qquad \frac{k_2}{k_1} = 1$$

Cont..

$$\left.\begin{aligned} A + B &\xrightarrow{k_1} R \\ R + B &\xrightarrow{k_2} S \end{aligned}\right\}$$

C_S=?

C_B=?

$$r_A = \frac{dC_A}{dt} = -k_1 C_A C_B$$

$$r_B = \frac{dC_B}{dt} = -k_1 C_A C_B - k_2 C_R C_B$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A C_B - k_2 C_R C_B$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R C_B$$

$$\boxed{\frac{dC_B}{dt} - \frac{dC_R}{dt} - 2\frac{dC_A}{dt} = 0}$$

$$\boxed{\frac{dC_A}{dt} + \frac{dC_R}{dt} + \frac{dC_s}{dt} = 0}$$

$$\Delta C_A + \Delta C_R + \Delta C_S = 0$$

$$C_{A0} + C_{R0} + C_{S0} = C_A + C_R + C_S$$

For pure feed of A and B, C_{R0}=C_{S0}=0

C_S can be calculated from the above equation using expression of R and known A

$$\boxed{\frac{dC_B}{dt} + \frac{dC_R}{dt} + 2\frac{dC_s}{dt} = 0}$$

$$\Delta C_B + \Delta C_R + 2\Delta C_S = 0$$

C_B can be calculated from the above equation

Product Distribution: in CSTR

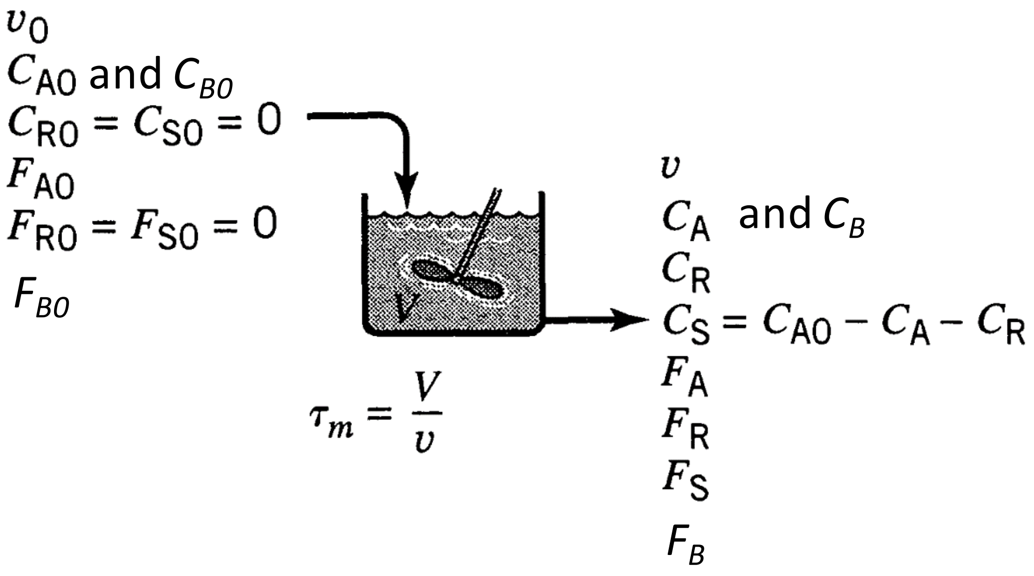
$$\left.\begin{aligned} A + B &\xrightarrow{k_1} R \\ R + B &\xrightarrow{k_2} S \end{aligned}\right\}$$

$$r_A = \frac{dC_A}{dt} = -k_1 C_A C_B$$

$$r_B = \frac{dC_B}{dt} = -k_1 C_A C_B - k_2 C_R C_B$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A C_B - k_2 C_R C_B$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R C_B$$



For A: $$\frac{V}{F_{A0}} = \frac{\tau_m}{C_{A0}} = \frac{X_A}{-r_A}$$

For R: $$\frac{V}{F_{R0}} = \frac{\tau_m}{C_{R0}} = \frac{X_R}{-r_R}$$

$$X_A = \frac{C_{A0} - C_A}{C_{A0}}$$

$$X_R = \frac{C_{R0} - C_R}{C_{R0}}$$

$$\boxed{\tau_m = \frac{C_{A0} - C_A}{-r_A} = \frac{-C_R}{-r_R}}$$

Cont..

=> $$\tau_m = \frac{C_{A0} - C_A}{k_1 C_A C_B} = \frac{-C_R}{k_2 C_R C_B - k_1 C_A C_B}$$

=> $$\frac{-C_R}{C_{A0} - C_A} = -1 + \frac{k_2 C_R}{k_1 C_A}$$

=> $$\boxed{C_R = \frac{C_A(C_{A0} - C_A)}{C_A + (k_2/k_1)(C_{A0} - C_A)}}$$

For C_R^{max}

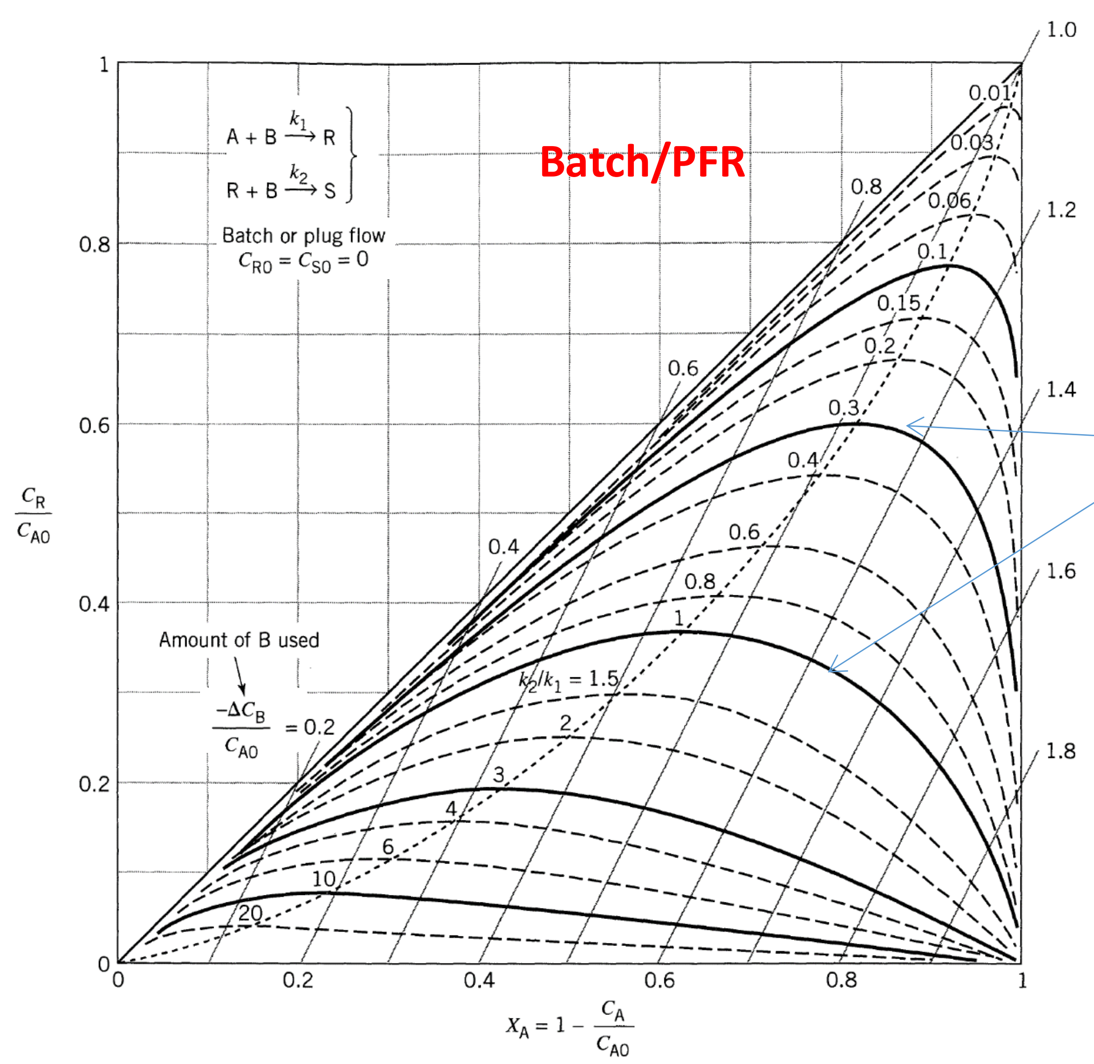
Put $dC_R/dC_A = 0$

$$\boxed{\frac{C_{R,\max}}{C_{A0}} = \frac{1}{[1 + (k_2/k_1)^{1/2}]^2}}$$

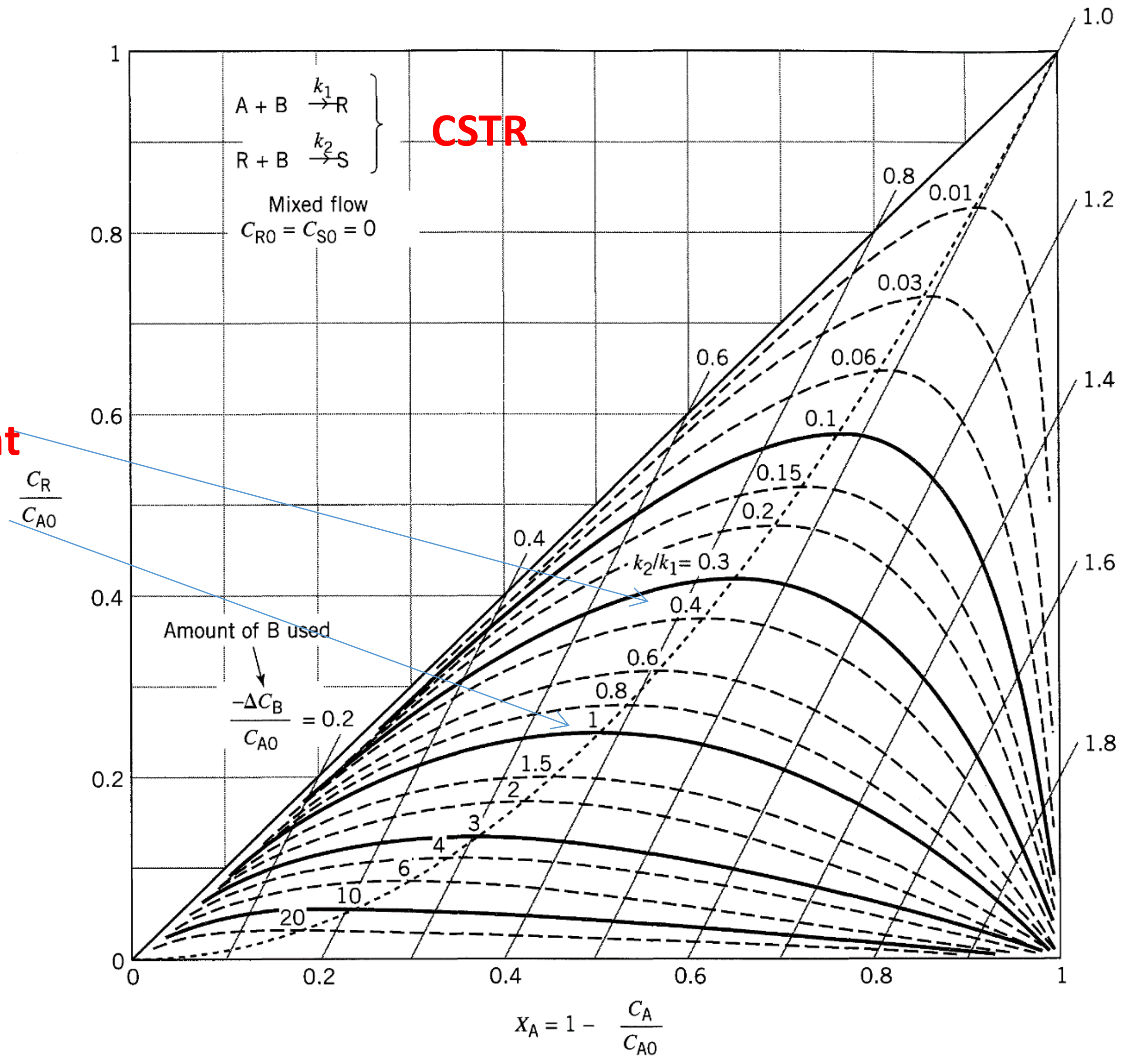
$$\frac{C_{R,max}}{C_{A0}} = 0.25 \ \ for\ k_1 = k_2$$

- ❑ Rate equations (kinetics) and Material balances about A and B in plug flow, hold equally well for mixed flow
- ❑ Product distribution (S and B) in this reactor can be calculated same way as in PFR

Product Distribution comparison Batch/PFR and CSTR



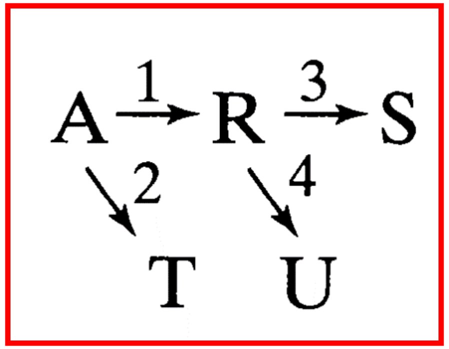
R at different k2/k1



- Plug flow again giving a higher concentration of intermediate than mixed flow.

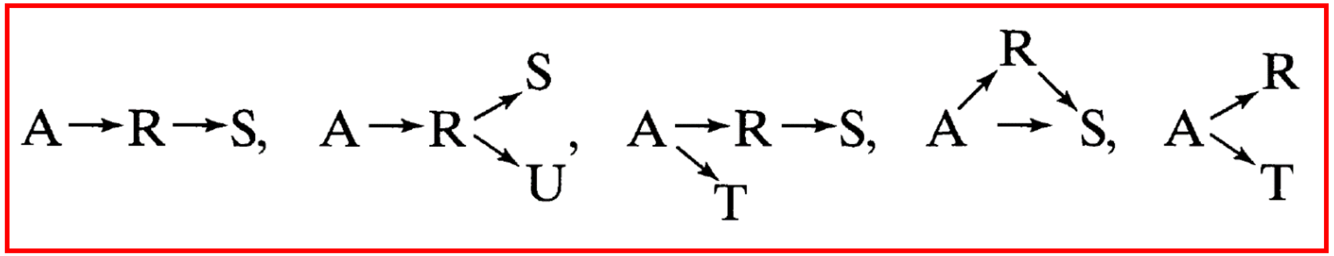
Denbigh reactions scheme

- Denbigh analyzed the general reaction scheme



Denbigh reaction scheme

Denbigh reaction scheme can reduce directly to all the different special cases



$$-r_A = -\frac{dC_A}{dt} = k_1 C_A + k_2 C_A = k_{12} C_A$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_3 C_R - k_4 C_R = k_1 C_A - k_{34} C_R$$

$$r_S = \frac{dC_S}{dt} = k_3 C_R$$

$$r_T = \frac{dC_T}{dt} = k_2 C_A$$

$$r_U = \frac{dC_U}{dt} = k_4 C_R$$

$$\boxed{\begin{aligned} k_{12} &= k_1 + k_2 \\ k_{34} &= k_3 + k_4 \end{aligned}}$$

$$r_A + r_R + r_S + r_T + r_U = 0$$

$$\frac{dC_A}{dt} + \frac{dC_R}{dt} + \frac{dC_S}{dt} + \frac{dC_T}{dt} + \frac{dC_U}{dt} = 0$$

$$C_A + C_R + C_S + C_T + C_U = constant$$

$$At, t = 0, C_{A0} + C_{R0} + C_{s0} + C_{U0} + C_{T0} = \text{constant}$$

$$\boxed{C_{A0} + C_{R0} + C_{S0} + C_{T0} + C_{U0} = C_A + C_R + C_S + C_T + C_U}$$

Product distribution of the Denbigh reaction scheme in Batch/PFR

$$\begin{array}{ccccc} A & \xrightarrow{1} & R & \xrightarrow{3} & S \\ \searrow{\scriptstyle 2} & & \searrow{\scriptstyle 4} & & \\ T & & U & & \end{array}$$

Product distribution ?

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A + k_2 C_A = k_{12} C_A$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_3 C_R - k_4 C_R = k_1 C_A - k_{34} C_R$$

$$r_S = \frac{dC_S}{dt} = k_3 C_R$$

$$\boxed{\begin{aligned} k_{12} &= k_1 + k_2 \\ k_{34} &= k_3 + k_4 \end{aligned}}$$

$$r_T = \frac{dC_T}{dt} = k_2 C_A$$

$$r_U = \frac{dC_U}{dt} = k_4 C_R$$

$$\frac{C_A}{C_{A0}} = \exp(-k_{12}t)$$

$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_{34} - k_{12}}[\exp(-k_{12}t) - \exp(-k_{34}t)] + \frac{C_{R0}}{C_{A0}}\exp(-k_{34}t)$$

$$\frac{C_S}{C_{A0}} = \frac{k_1 k_3}{k_{34} - k_{12}}\left[\frac{\exp(-k_{34}t)}{k_{34}} - \frac{\exp(-k_{12}t)}{k_{12}}\right] + \frac{k_1 k_3}{k_{12} k_{34}}$$

$$+ \frac{C_{R0}}{C_{A0}}\frac{k_3}{k_{34}}[1 - \exp(-k_{34}t)] + \frac{C_{S0}}{C_{A0}}$$

$$\frac{C_T}{C_{A0}} = \frac{k_2}{k_{12}}[1 - \exp(-k_{12}t)] + \frac{C_{T0}}{C_{A0}}$$

$\frac{C_U}{C_{A0}}$ . . . same as $\frac{C_S}{C_{A0}}$ but with $k_3 \leftrightarrow k_4$ and $C_{S0} \leftrightarrow C_{U0}$

For PFR t will be replaced by τ

Cont..

Special case: pure feed of A

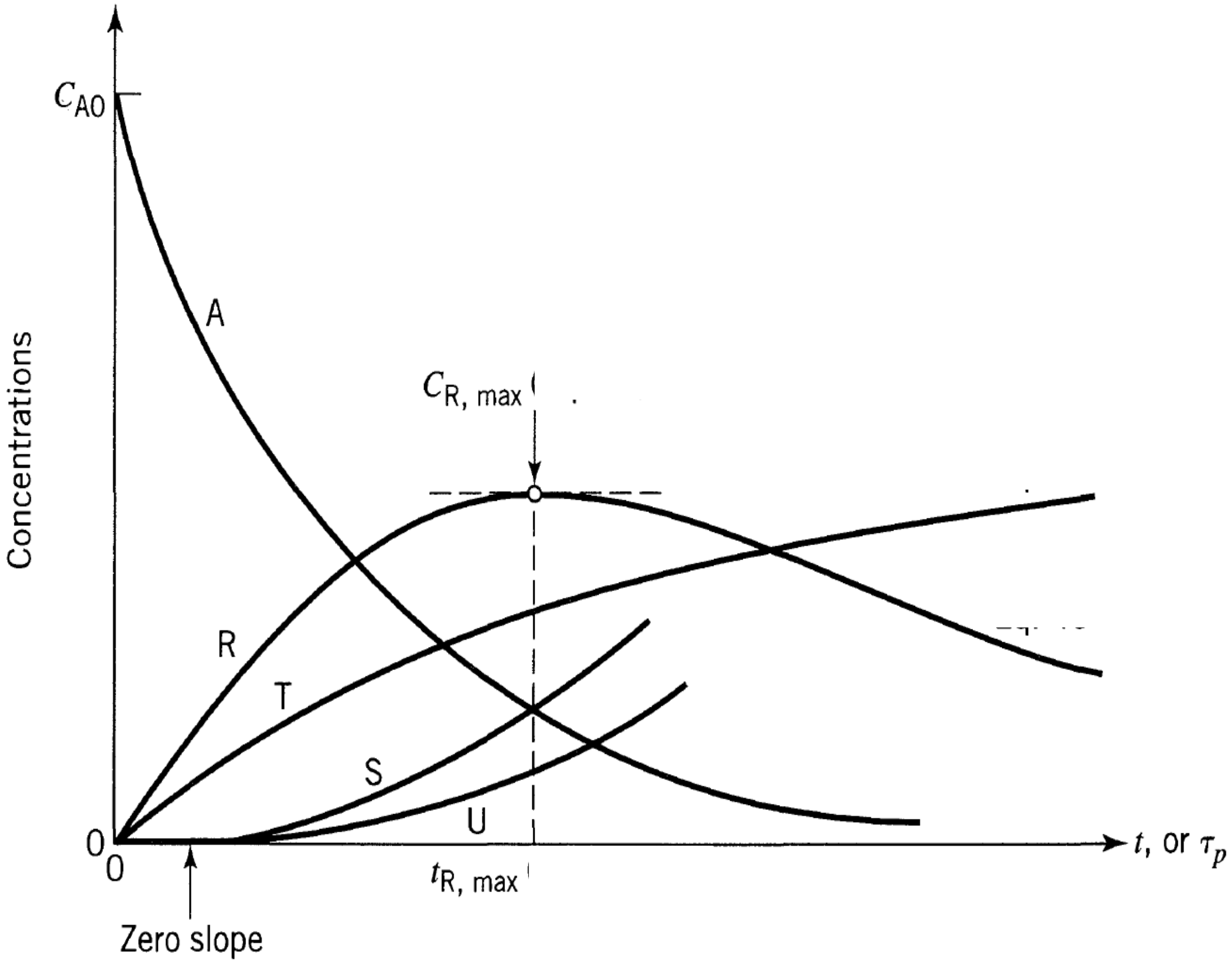
$$C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$$

$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_{34} - k_{12}} [\exp(-k_{12}t) - \exp(-k_{34}t)]$$

For C_R^{max} , Put $dC_R/dt = 0$

$$\frac{C_{R,max}}{C_{A0}} = \frac{k_1}{k_{12}} \left(\frac{k_{12}}{k_{34}}\right)^{k_{34}/(k_{34}-k_{12})}$$

$$t_{max} = \frac{\ln(k_{34}/k_{12})}{k_{34} - k_{12}}$$



$$C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$$

Product distribution of the Denbigh reaction scheme in CSTR

For A: $$\frac{\tau_m}{C_{A0}} = \frac{X_A}{-r_A}$$

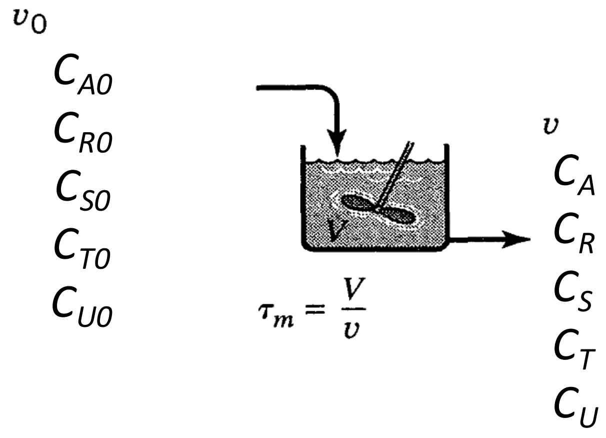
For R: $$\frac{\tau_m}{C_{R0}} = \frac{X_R}{-r_R}$$

For S: $$\frac{\tau_m}{C_{S0}} = \frac{X_S}{-r_S}$$

For T: $$\frac{\tau_m}{C_{T0}} = \frac{X_T}{-r_T}$$

For U: $$\frac{\tau_m}{C_{U0}} = \frac{X_U}{-r_U}$$

$$X_A = \frac{C_{A0} - C_A}{C_{A0}}$$
$$X_R = \frac{C_{R0} - C_R}{C_{R0}}$$
$$X_S = \frac{C_{S0} - C_S}{C_{S0}}$$
$$X_T = \frac{C_{T0} - C_T}{C_{T0}}$$
$$X_U = \frac{C_{U0} - C_U}{C_{U0}}$$



For liquid
$v = v_0$

$$\frac{C_A}{C_{A0}} = \frac{1}{(1 + k_{12}\tau_m)}$$

$$\frac{C_R}{C_{A0}} = \frac{k_1\tau_m}{(1 + k_{12}\tau_m)(1 + k_{34}\tau_m)} + \frac{C_{R0}}{C_{A0}}\frac{1}{(1 + k_{34}\tau_m)}$$

$$\frac{C_S}{C_{A0}} = \frac{k_1 k_3\tau_m^2}{(1 + k_{12}\tau_m)(1 + k_{34}\tau_m)} + \frac{C_{R0}}{C_{A0}}\frac{k_3\tau_m}{(1 + k_{34}\tau_m)} + \frac{C_{S0}}{C_{A0}}$$

$$\frac{C_T}{C_{A0}} = \frac{k_2\tau_m}{(1 + k_{12}\tau_m)} + \frac{C_{T0}}{C_{A0}}$$

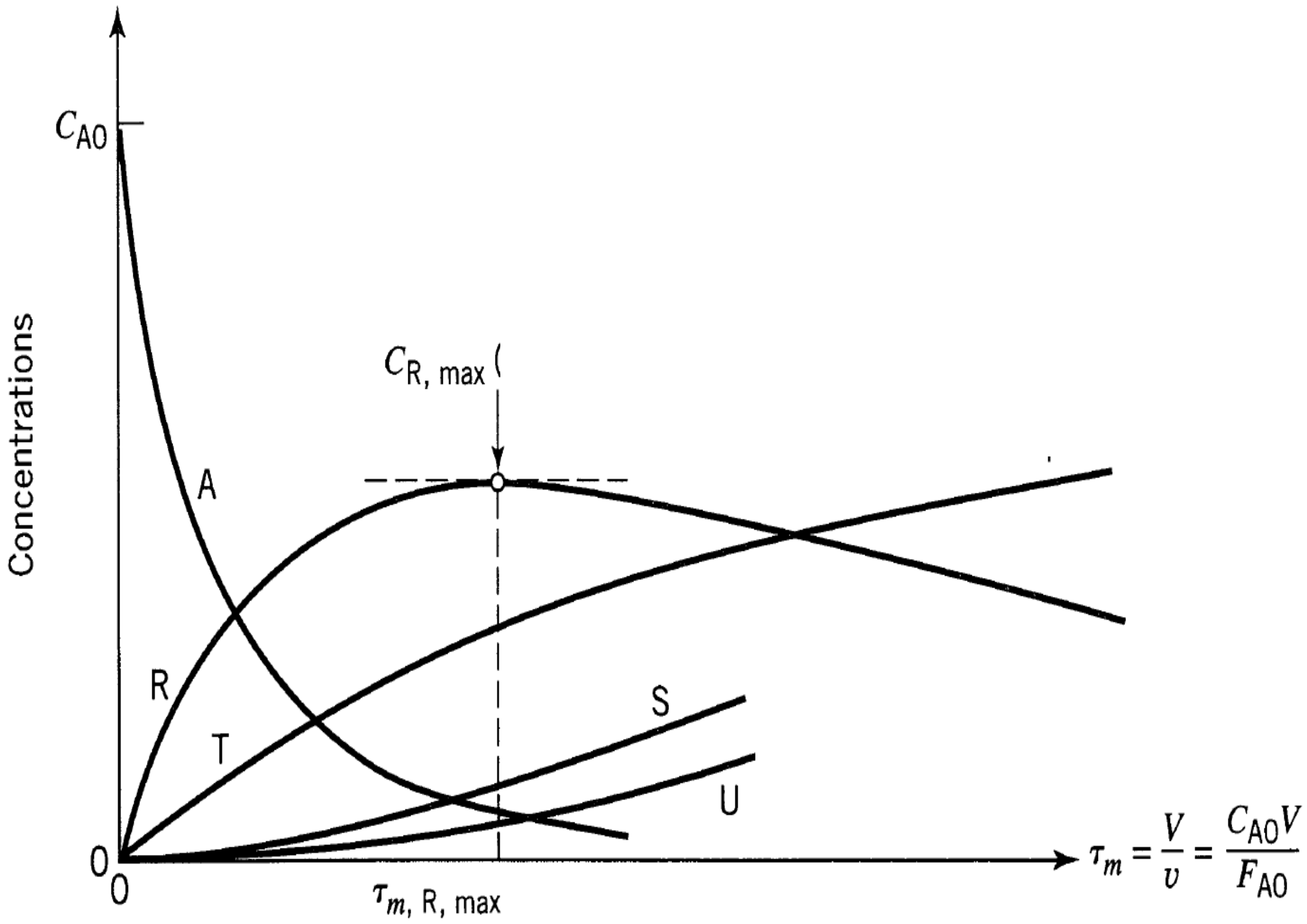
$\frac{C_U}{C_{A0}} \cdots$ same as $\frac{C_S}{C_{A0}}$ but with $k_3 \leftrightarrow k_4$ and $C_{S0} \leftrightarrow C_{U0}$

Cont..

For C_R^{max} , Put $dC_R/d\tau_m = 0$

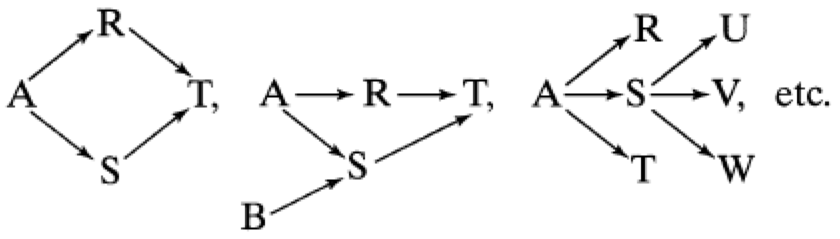
$$\frac{C_{\mathrm{Rmax}}}{C_{\mathrm{A0}}} = \left(\frac{k_1}{k_{12}}\right) \cdot \frac{1}{[(k_{34}/k_{12})^{1/2} + 1]^2}$$

$$\tau_{m,\mathrm{Rmax}} = \frac{1}{(k_{12}/k_{34})^{1/2}}$$



Some general comments

- **The reactions can be extended to different form of other reaction schemes, such as**



- If the two steps of first-order reactions in series have very different values for their rate constants, we can approximate the overall behavior as follows:

$$A \xrightarrow{k_1=100} R \xrightarrow{k_2=1} S \Rightarrow A \xrightarrow{k} S, \qquad \text{where } k = \frac{1}{\dfrac{1}{k_1} + \dfrac{1}{k_2}} = 0.99$$

- The key to optimum design for multiple reactions is proper contacting and proper flow pattern of fluids within the reactor. These requirements are determined by the stoichiometry and observed kinetics.