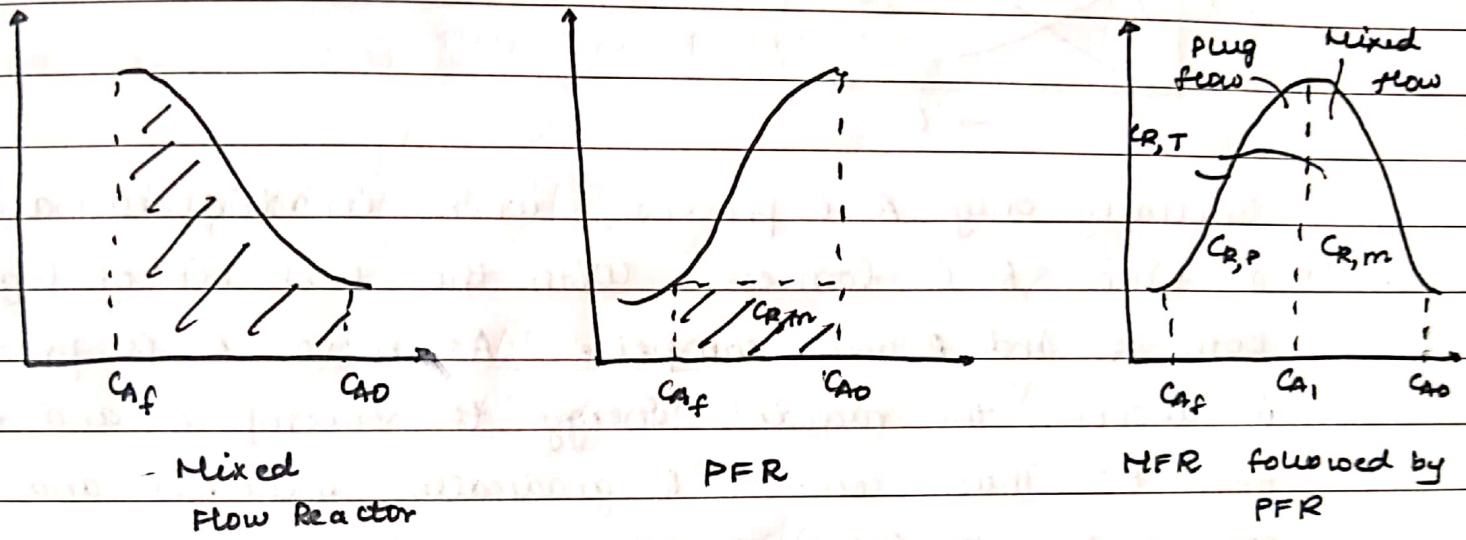


## Selection of type of reactor

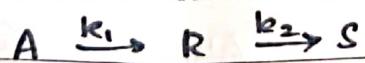
In case of single or multiple mixed flow reactors, selection of best outlet conc. of A is desired, to maximize  $C_A$ . Max. area of rectangle from plots will give max. formation of prod. R in mixed flow reactor. shape of  $Q$  vs  $C_A$  gives tk which type of reactor gives best pdt. distn.



In general form,  $\phi = M/N$ ,  $M \rightarrow$  inst. fractional yield of H based on consumption or formation of N

## Qualitative Analysis for Series Rns

For easy visualization consider,



proceed only in the presence of light, the rate eqn's are given by

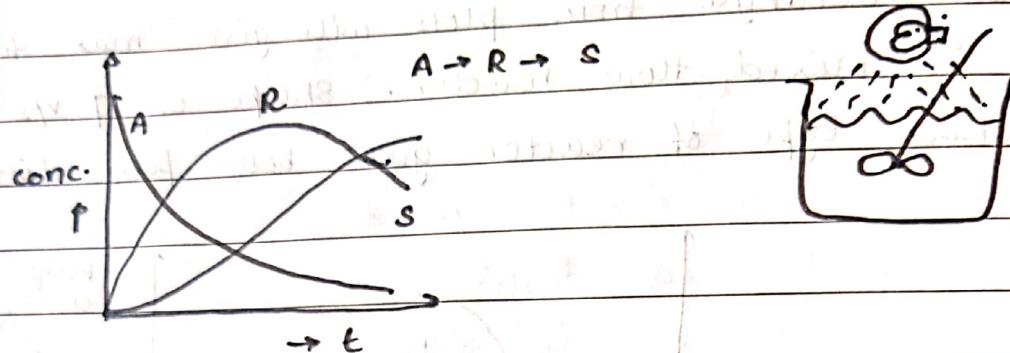
$$r_A = -k_1 C_A$$

$$r_R = k_1 C_A - k_2 C_R$$

$$r_S = k_2 C_R$$

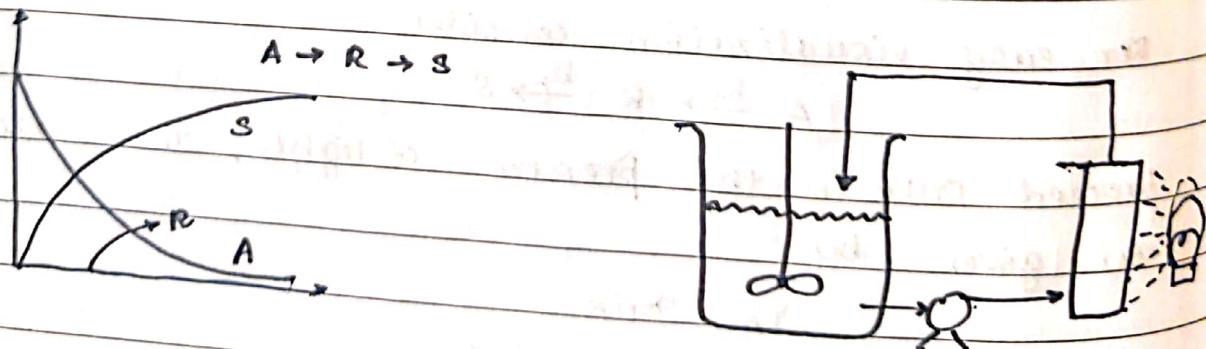
In a photochemical reaction, we can consider two ways to treat the reactant A in beaker

a) Contents of beaker are irradiated at all times



Initially only A is present, when irradiated all at a time R is formed. With the next bit of light both A and R will compete. As more A is present, it absorbs the radiant energy to decompose and form more R. Thus, conc. of R gradually increases and conc. of A will fall. In this way R gradually increases reaches a max. Both R and A will compete for light energy  $A \rightarrow R \rightarrow S$  and the conc. of R drops.

b) A portion of stream is withdrawn from the beaker and irradiated outside by light and returned to beaker



A portion A is removed from the beaker and irradiated in a sep. vessel. However total absorption rate & const. The reaction is essentially

## Quantitative treatment in batch or plug flow reactor

For first order series m:,  $A \xrightarrow{k_1} R \xrightarrow{k_2} S$

$$-r_A = -\frac{dc_A}{dt} = k_1 c_A$$

Rate eqn's,  $r_R = \frac{dc_R}{dt} = k_1 c_A - k_2 c_R$        $r_S = \frac{dc_S}{dt} = k_2 c_R$

The conc. of R varies as,

$$\frac{c_R}{c_{AO}} = \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

The conc. of A varies as,  $\frac{c_A}{c_{AO}} = e^{-k_1 t}$

using,  $c_S = c_{AO} - c_A - c_R$

$$\frac{c_S}{c_{AO}} = \left( 1 + \frac{k_2}{k_1 - k_2} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right)$$

PFR with series m:

$$\frac{c_A}{c_{AO}} = e^{-k_1 \tau_P}$$

$$\frac{c_R}{c_{AO}} = \frac{k_1}{k_2 - k_1} (e^{-k_1 \tau_P} - e^{-k_2 \tau_P})$$

The conc. of R varies with time as

$$\frac{c_R}{c_{AO}} = \left( 1 + \frac{k_2}{k_1 - k_2} e^{-k_1 \tau_P} + \frac{k_1}{k_2 - k_1} e^{-k_2 \tau_P} \right)$$

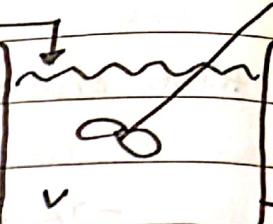
$$\frac{c_{R,\max.}}{c_{AO}} = \left( \frac{k_1}{k_2} \right)^{\frac{k_2}{k_1 - k_2}} \quad \tau_{P,\text{opt}} = \frac{1}{k_{\text{avg mean}}} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$

## Quantitative Treatment, Mixed Flow Reactor

$$t_m, \text{opt} = \frac{1}{\sqrt{k_1 k_2}}$$

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

$$\begin{aligned} u_0 \\ C_{AO} \\ C_{RO} = C_{AO} - 0 \\ F_{AO} \\ F_{RO} = F_{AO} = 0 \end{aligned}$$



$$t_m = V/u$$

- Except when  $k_1 = k_2$ , plug flow reactor requires a smaller time than mixed flow reactor to achieve  $C_{R,\max}$ . However, in PFR  $C_{R,\max}$  is higher.

CSTR  
For PFR,

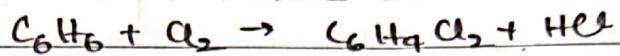
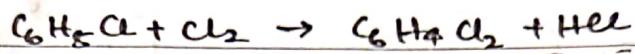
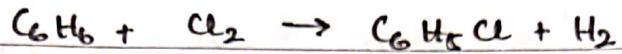
$$\frac{C_{R,\max}}{C_{AO}} = \frac{1}{((k_2/k_1)^{1/2} + 1)^2}$$

$$\text{For PFR, } \frac{C_{R,\max}}{C_{AO}} = \left(\frac{k_1}{k_2}\right)^{k_2/(k_2-k_1)}$$

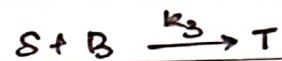
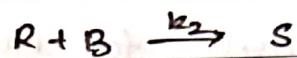
The fractional yield of R is higher for PFR.

- If  $k_2/k_1 < 1$ , then we need to recycle the unused A.
- If  $k_2/k_1 \geq 1$ , the fractional yield drops rapidly even at low conversion.

## Series parallel combination



General form,



A series type,  $A \xrightarrow{+B, k_1} R \xrightarrow{+B, k_2} S \xrightarrow{+B, k_3} T$

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

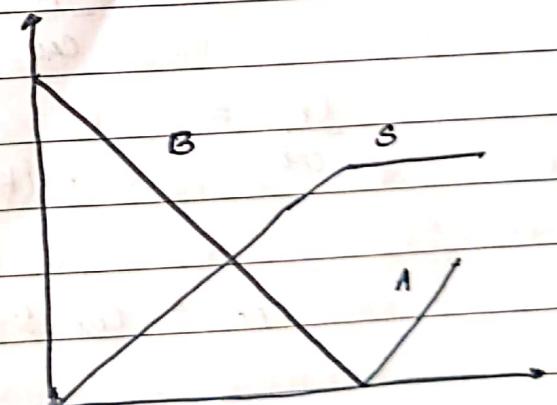
$$r_B = \frac{dC_B}{dt} = -k_1 C_A C_B - k_2 C_R C_B \quad r_S = \frac{dC_S}{dt} = k_2 C_R C_B$$

A is added slowly to B

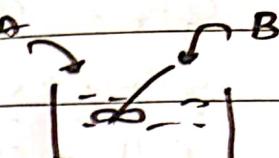
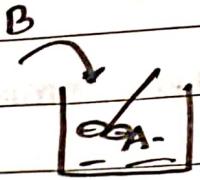
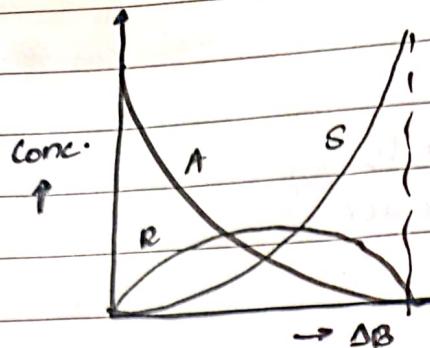
A is added in little amounts into beaker containing B.

In each addn. of A, a bit of R is formed. This R finds excess B and reacts to form S. B

reduce gradually. Finally mixture doesn't contain any R. S will be the

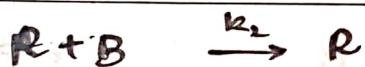
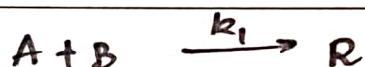


B is added slowly to A. They react to get R. When B is added, both A and R react completely with B. A reacts more with B (as it is more in quantity). R forms and conc. of R increases gradually (A & B). S forms slowly. R gradually reaches max.



Quantitative treatment for batch and PFR.

For the same series - parallel m.s



$$\frac{r_R}{r_A} = \frac{\frac{dC_R}{dt}}{\frac{dC_A}{dt}} = -1 + \frac{k_2 C_B}{k_1 C_A}$$

$$\frac{C_R}{C_{AO}} = \frac{C_A}{C_{AO}} \left( \frac{C_{AO}}{C_{AO}} - \ln \frac{C_A}{C_{AO}} \right) \quad \frac{k_2}{k_1} = 1$$

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

$$C_{AO} + C_{B0} + C_{R0} = C_A + C_B + C_R$$

## Non-Ideal Behaviour

Deviation from ideality depends on,

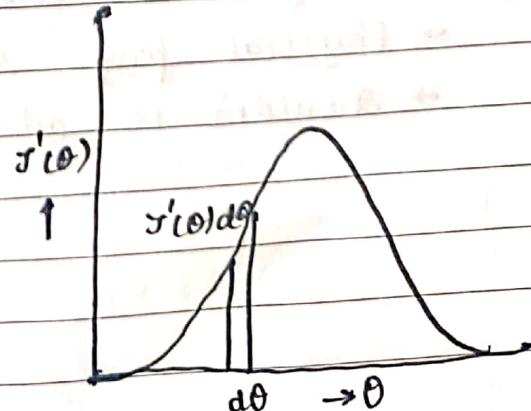
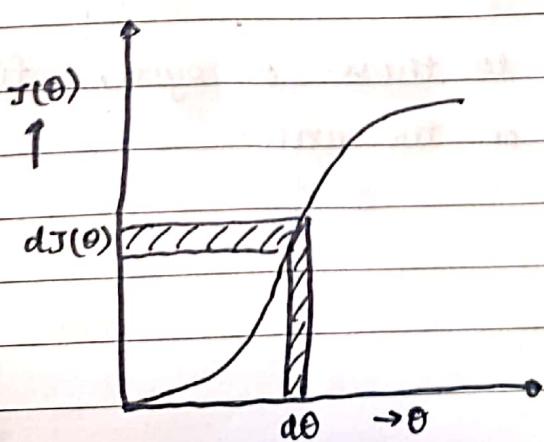
- Creation of stagnant region in the vessel or dead zones or partially segregated as they move.
- Micro-mixing in direction of flow or dispersion.
- Elements of fluid may move at diff. velocities causing channelling.
- Formation of vortices, turbulence near inlet

<sup>idence</sup> Resistance Time: Time req. to pass a molecule through a reactor is called residence time. The detail velocity profile in a reactor should be known to predict the behavior of the vessel. knowing the RTD, the conversion in the reactor can be predicted.

For RTD Analysis,

- a) Steady State Flow
- b) No rn' in the vessel
- c) Const. P
- d) A single fluid

Let us assume a fluid is flowing through a vessel and no rn' in the fluid. let  $J(\theta)$  fract. of effluent stream has a residence less than  $\theta$  min, at  $\theta = 0$ ;  $J(\theta) = 0$  and  $dJ(\theta)$  is vol. fraction of element has a residence time between  $\theta$  and  $\theta + d\theta$



Mean Residence Time

$$\bar{\theta} = V/Q, \frac{dJ(\theta)}{d\theta} = J'(\theta)$$

$$\bar{\theta} = \int_0^\infty \theta J'(\theta) d\theta$$

If  $\theta J'(\theta)$  or  $tE$  is plotted against residence time, the area under curve from 0 to  $\infty$  will give avg. or mean residence time  $\bar{\theta}$

$$\bar{\theta} = \int_0^\infty \theta J'(\theta) d\theta = \int_0^\infty tE dt$$

If  $E_i$  is the exit age distn. at  $t_i$  and  $e_i$  is measured at equal time interval  $\Delta t_i$

$$\bar{t} = \sum t_i e_i \Delta t$$

$$\int_0^\infty E dt = 1 \quad \text{and}$$

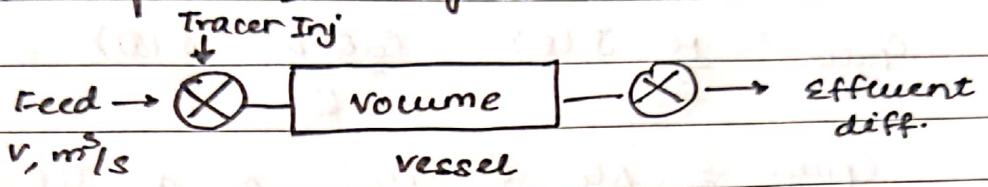
$$\int_{t_i}^\infty E dt = 1 - \int_0^{t_i} E dt$$

→ RTD is determined experimentally by usually an inert demand chemical called a tracer.

- Characteristic properties of the tracer:
- Non-reactive → Completely soluble in system fluid
  - Easily can be detected
  - Physical prop. similar to those of system fluid
  - Shouldn't be adsorbed on the wall.

## Stimulus - Response Technique

In order to determine 'E' curve. A tracer input is added at the inlet of reactor as stimulus. The outlet conc. of tracer is determined as a fn. of time. Various input fn. may be introduced at inlet.



### Step Input : F-Curve

Suppose a stream with conc.  $C_0$  flows through a reactor with volumetric flow rate  $Q$ .

At  $\theta = 0$  all molecules are marked to distinguish them from the molecules entered prior to  $\theta = 0$ . As total conc. remains same, so marked molecule conc. ' $J$ ' is measured at outlet by any suitable method at various time.

Then,  $\frac{C}{C_0} = J(\theta) = \text{fraction of molecules of residence less than } \theta$

Mass Balance:  $C_0 Q J(\theta) = C Q$

$$\text{so, } t = \frac{C}{C_0} = J(\theta)$$

$$dJ(\theta) = E dt = J'(\theta) d\theta$$

The relation b/w step and pulse response

$$J'(\theta)_{\text{step}} = \frac{d J(\theta)}{d \theta} = \frac{d (C/C_0)}{d \theta}$$

$$\text{For pulse } J'(\theta) = \frac{\text{pulse Q}}{V}$$

$$\text{Pulse } \frac{V}{Q} J'(\theta) = \frac{C_0 Q \Delta \theta}{V} J'(\theta)$$

$$\text{Pulse} = \frac{C_0}{Q} \Delta \theta \frac{d (C/C_0)}{d \theta} \propto \frac{d J(\theta)}{d \theta} \Big|_{\text{step}}$$

RTD of known mixing conditions : CSTR

$$C_0 Q \Delta \theta - C Q \Delta \theta = V \Delta C$$

$\Delta C \rightarrow$  Change in conc. inside the reactor in  $\Delta \theta$

$C_0 \rightarrow$  initial conc.  $C \rightarrow$  effluent conc.

$$\frac{dc}{d\theta} = \frac{Q}{V} (C_0 - c) = \frac{1}{\bar{\theta}} (C_0 - c)$$

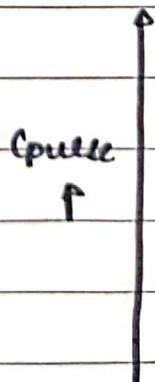
$$\left( \frac{c}{C_0} \right)_{\text{step}} = J(\theta) = 1 - e^{-\theta/\bar{\theta}}$$

$$\text{If } \theta = \bar{\theta}, J(\theta) = 1 - e^{-1} = 0.631$$

63.1% effluent stream has a residence time less than avg. residence time  $\bar{\theta}$ .

$$J'(\theta) = \frac{1}{\bar{\theta}} e^{-\theta/\bar{\theta}}$$

$$\text{Pulse } \frac{V}{Q} C_0 \Delta \theta \frac{1}{\bar{\theta}} e^{-\theta/\bar{\theta}}$$



Segregated Model: laminar flow in a tubular reactor

The velocity profile

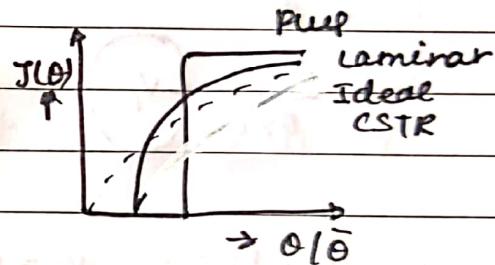
$$u(r) = \frac{2Q}{\pi R^2} \left[ 1 - \left( \frac{r}{R} \right)^2 \right]$$

$$\Theta = \frac{L}{u} = \frac{V/Q}{2 \left[ 1 - \left( \frac{r}{R} \right)^2 \right]}, \quad \frac{\Theta}{\bar{\Theta}} = \frac{1}{2 \left[ 1 - \left( \frac{r}{R} \right)^2 \right]}$$

$$dJ(\Theta) = \frac{4}{R^2} \left[ 1 - \left( \frac{r}{R} \right)^2 \right] r dr$$

$$\frac{dJ(\Theta)}{d\Theta} = J'(\Theta) = \frac{1}{2} \frac{\bar{\Theta}^2}{\Theta^3} \quad E\text{-curve}$$

$$\Theta_{min} = \frac{V}{2Q} = \frac{1}{2} \bar{\Theta}$$

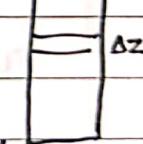


### Dispersion Model

In a tubular flow assume axial velocity  $u$  and conc. are const. across the diameter

$$\frac{dc}{dz} = 0 \quad z=L$$

A step input  $c_0$  is introduced at  $\Theta=0$



$$\text{At } \Theta = 0, \quad c = c_0, \quad z = -\infty \quad \text{for } \Theta > 0$$

$$c^* = \frac{c}{c_0}$$

$$\text{At } z = \infty, \quad c = 0 \quad \text{for } \Theta > 0$$

$$\alpha = \frac{z - u\Theta}{\sqrt{4D_L \Theta}}$$

$$\frac{d^2 c^*}{d\alpha^2} + 2\alpha \frac{dc^*}{d\alpha} = 0$$

$$c^* = 1, \quad \alpha = -\infty$$

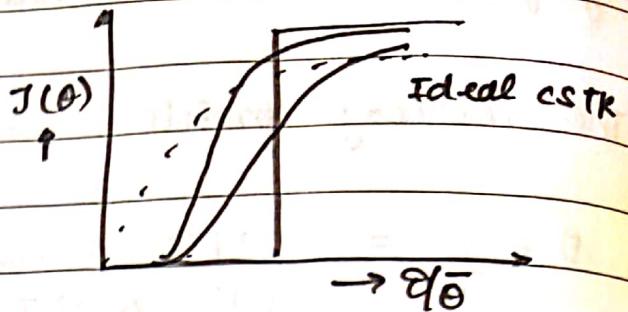
$$c^* = 0, \quad \alpha = \infty$$

$$J(\Theta) = \left( \frac{c}{c_0} \right)_{step} = \frac{1}{2} \left[ 1 - \operatorname{erf} \left( \frac{1}{2} \sqrt{\frac{uL}{D_L}} \frac{1 - \Theta/\bar{\Theta}}{\sqrt{\Theta/\bar{\Theta}}} \right) \right]$$

$D/uL$  is dispersion

$D/uL = 0$ , PFR

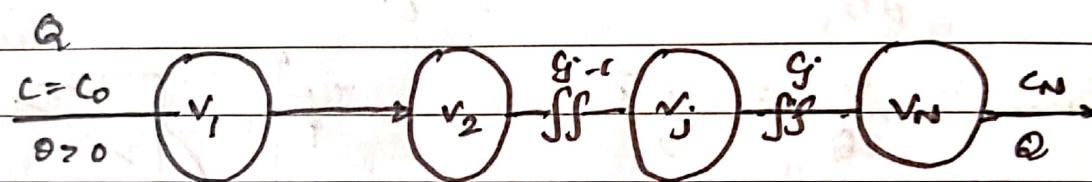
$D/uL = \infty$ , CSTR



### Series of Stirred Tanks

If  $N$  number of tanks are connected in series.

All tanks are of same size



$$V_1 = V_2 = \dots = V_j = V_N$$

$$C_{j-1}Q - C_jQ = V_j \frac{dC_j}{d\theta}$$

$$\bar{\theta}_t = \frac{N V_t}{Q} = \frac{V_t}{Q}$$

For 1<sup>st</sup> tank,  $(C_{j-1} - C_j) \frac{N}{\bar{\theta}_t} = \frac{dC_j}{d\theta} \rightarrow$  First order diff. eqn.

$$\text{The soln. is, } \frac{C_j}{C_0} = 1 - e^{-N\theta/\bar{\theta}_t}$$

$$\text{For 2<sup>nd</sup> tank, } \frac{C_j}{C_0} = 1 - e^{-N\theta/\bar{\theta}_t} \left( 1 + \frac{N\theta}{\bar{\theta}_t} \right)$$

$$\text{For } N^{\text{th}} \text{ tank, } \frac{C_N}{C_0} = 1 - e^{-N\theta/\bar{\theta}_t} \left( 1 + \frac{N\theta}{\bar{\theta}_t} + \frac{1}{2!} \left( \frac{N\theta}{\bar{\theta}_t} \right)^2 + \dots \right)$$

$$\left( 1 - \frac{C_N}{C_0} \right) = X_N = 1 - \frac{1}{\left( 1 + \frac{k\bar{\theta}_t}{N} \right)^N}$$

$J(\theta) = cn/c_0$  can be plotted with diff. N to get various F-plots.

### Experimental RTD

If pulse input is added and response from exit is measured. we get c-plot. From c-plot, E-plot is determined

$$E = \frac{c}{\int_0^\infty c dt}, \text{ where } \int_0^\infty c dt = \sum c \Delta t$$

For discrete  $\Delta t$ ,  $E = \frac{c}{\sum c \Delta t}$

$E$  vs  $t$  is called RTD,

$$\bar{t} = \frac{\int_0^\infty t c dt}{\int_0^\infty c dt} \approx \sum t_i E_i \Delta t$$

Conversion calculation from tracer information

$$\bar{C}_A = \int_0^\infty C_{A,\text{elem}} E dt$$

For irrev first order m: with constant density, the conc. in any element changes with time as

$$\ln \frac{C_A, \text{elem}}{C_{AO}} = -kt \quad \text{or} \quad C_A, \text{elem} = C_{AO} e^{-kt}$$

$$\frac{C_A}{C_{AO}} = \sum e^{-kt} E \Delta t$$

For rev. first order  $r_n$  with no pdt in feed

$$\bar{C}_A = C_{AO} \int_0^\infty [1 - x_{Ae} + x_{Ae} e^{-kt/x_{Ae}}] E dt$$

for successive first order  $r_n$  with R as int. pdt

$$\bar{C}_R = \frac{C_{AO} k_1}{k_2 - k_1} \int_0^\infty [e^{-k_1 t} - e^{-k_2 t}] E dt$$

$$\begin{aligned} \text{Spread of distrn: } (\sigma^2) &= \frac{\int_0^\infty t^2 c dt}{\int_0^\infty c dt} - \bar{t}^2 \\ &= \sum t_i^2 E_i \Delta t - \bar{t}^2 \end{aligned}$$

For closed vessel Disp. no. is calculated as  $\Theta^2 = \sigma^2 / \bar{t}^2$

$$\sigma^2 = \frac{2D}{UL} - 2 \left( \frac{D}{UL} \right)^2 (1 - e^{-UL/D})$$

$$N \approx 1/\Theta^2$$

Conversion by dispersion model

$$\frac{C_A}{C_{AO}} = 1 - X_A = \frac{a \exp(-\frac{1}{2} \frac{UL}{D})}{(1+a^2) \exp(\frac{a}{2} \frac{UL}{D}) - (1-a)^2 \exp(-\frac{a}{2} \frac{UL}{D})}$$

$$a = \sqrt{1 + 4k_e(D/UL)}$$

For small deviation from plug flow  $D/UL$

$$\frac{C_A}{C_{AO}} = \exp \left[ -k_e + (k_e)^2 \frac{D}{UL} \right]$$

$$= \exp \left[ -k_e + \frac{k^2 \sigma^2}{2} \right]$$