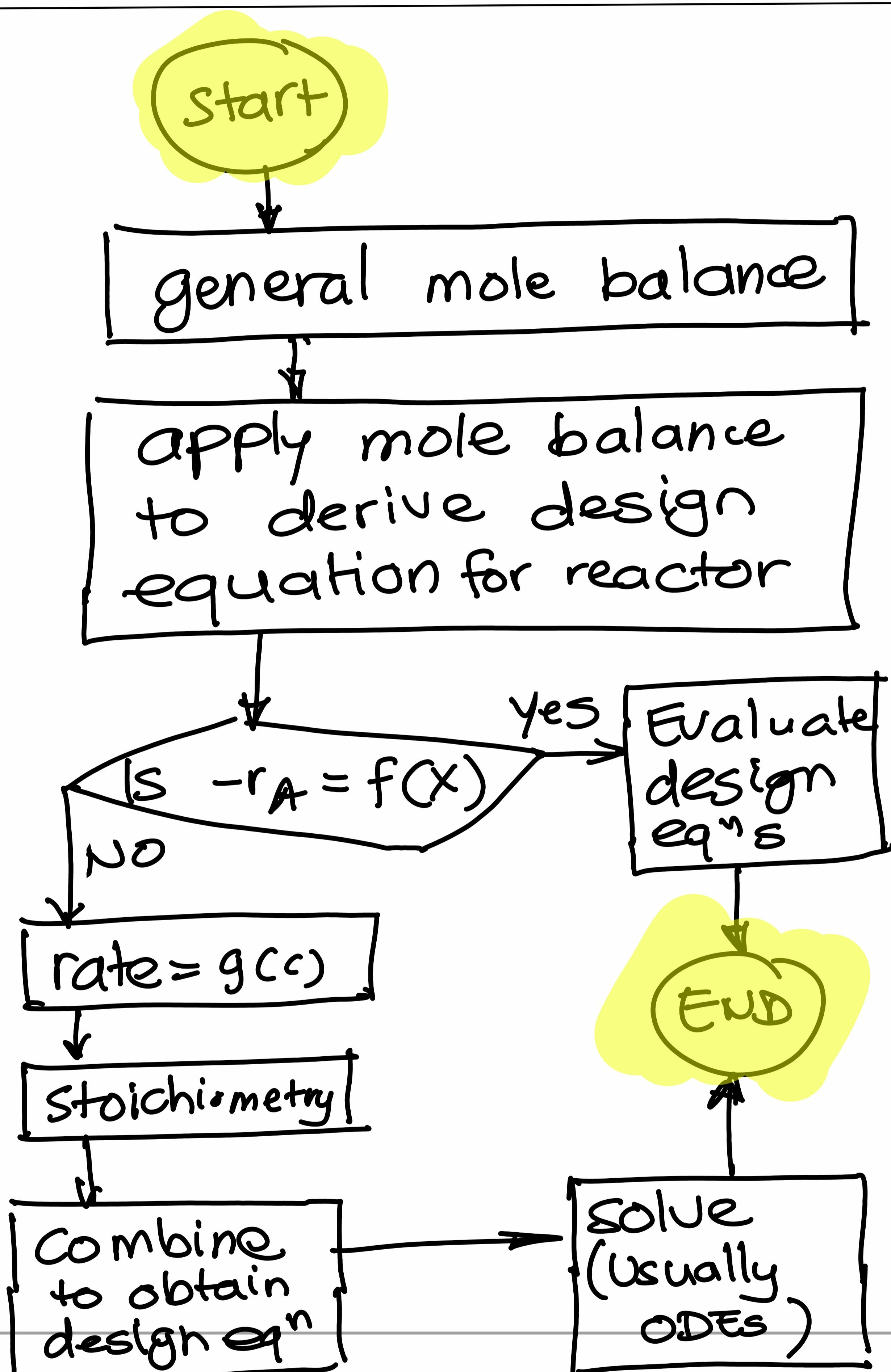


Notes on chemical Reaction Engineering

Design Structure of isothermal reactors

Chapter 5 Isothermal reactor design



⇒ Use algorithm rather than memorizing equations

The algorithm

- ① Mole balance
- ② rate law
- ③ stoichiometry
- ④ combine
- ⑤ evaluate

① Mole balance

$$F_{AO} - F_A + \int_V r_A dV = \frac{dN_A}{dt}$$

↳ apply this to the specific reactor in question

In terms of X

- Batch reactor (ODE)

$$N_{AO} \frac{dx}{dt} = -r_A V$$

- CSTR (algebraic equation)

$$V = \frac{F_{AO} X}{-r_A}$$

- PFR (ODE)

$$F_{AO} \frac{dx}{dv} = -r_A$$

- PBR (ODE)

$$F_{AO} \frac{dx}{dw} = -r'_A$$

② Rate law

If $-r_A$ is given as $f(X)$
 we can directly solve the
 design equations otherwise
 we need to convert
 the rate expression and
 make it a function of X

③ Stoichio- metry

IF $-r_A \neq f(X)$
 say $-r_A = g(C)$ then
 we need to use stoichiometry
 and write the rate law
 in terms of X

Liquid phase :

$$C_A = C_{A0}(1-X)$$

$$C_B = C_{B0}\left(\theta_B - \frac{b}{a}X\right)$$

Gas phase :

$$C_A = C_{A0} \frac{(1-X)}{(1+\epsilon X)} \frac{P}{P_0} \quad (\text{const } T)$$

For PBRs : We also need to consider
 pressure drop along the length

$$\frac{dP}{dx} = \frac{\alpha}{2P} (1-\epsilon X), \quad p = \frac{P}{P_0}$$

④ Combine

Gathering all the equations

- mole balance
- rate law
- stoichiometry
- other eqⁿ: (like pressure drop)

gives us a system of equations we must solve to obtain reactor volume.

⑤ Evaluate/ solve

The system of equations obtained by combining can be solved

- analytically
- graphically
- numerically
- using software.

**French Menu
Analogy**

Choices



1. MOLE BALANCES

$$\text{PFR} \quad \frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

$$\text{CSTR} \quad V = \frac{F_{A0}X}{-r_A}$$

$$\text{BATCH} \quad \frac{dX}{dt} = \frac{-r_A V}{N_{A0}}$$

2. RATE LAWS

$$-r_A = k C_A$$

$$-r_A = \frac{k C_A}{1 + K_A C_A}$$

$$-r_A = k \left[C_A - \frac{C_B C_C}{K_e} \right]$$

3. STOICHIOMETRY

$$\text{FLOW} \quad C_A = \frac{F_A}{V}$$

$$\text{BATCH} \quad C_A = \frac{N_A}{V}$$

$$F_A = F_{A0} (1 - X)$$

$$N_A = N_{A0} (1 - X)$$

LIQUID
Constant flow rate

IDEAL GAS
Variable flow rate

IDEAL GAS
Variable volume

LIQUID OR GAS
Constant volume

$$v = v_0$$

$$v = v_0 (1 + \varepsilon X) \frac{P_0 T}{P T_0}$$

$$V = V_0 (1 + \varepsilon X) \frac{P_0 T}{P T_0}$$

$$V = V_0$$

$$C_A = C_{A0} (1 - X)$$

$$C_A = \frac{C_{A0} (1 - X)}{(1 + \varepsilon X)} \frac{P T_0}{P_0 T}$$

$$C_A = \frac{C_{A0} (1 - X)}{(1 + \varepsilon X)} \frac{P T_0}{P_0 T}$$

$$C_A = C_{A0} (1 - X)$$

4. COMBINE (First-Order Gas-Phase Reaction in a PFR)

From mole balance

From rate law

From stoichiometry

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$$

$$\frac{k C_A}{F_{A0}}$$

$$= \frac{k}{F_{A0}} \left(C_{A0} \frac{(1 - X)}{(1 + \varepsilon X)} \right) \frac{P T_0}{P_0 T}$$

$$\frac{dX}{dV} = \frac{k}{v_0} \frac{(1 - X)}{(1 + \varepsilon X)} p \frac{T_0}{T}, \text{ where } p = \frac{P}{P_0} \quad (\text{A})$$

5. EVALUATE

Integrating for the case of constant temperature ($T = T_0$) and constant pressure ($p = 1$) gives

$$V = \frac{v_0}{k} \left[(1 + \varepsilon) \ln \left(\frac{1}{1 - X} \right) - \varepsilon X \right] \quad (\text{B})$$

Figure 5-2 Algorithm for isothermal reactors.

Batch Reactor

⇒ Usually we are interested in calculating batch reaction time for a given X or X for a given batch reaction time.

$-r_A$ is now in terms of X

Consider rxn: $2A \rightarrow B+C$

Algorithm :

① Mole balance (const. $V=V_0$)

$$N_{AO} \frac{dX}{dt} = -r_A V_0$$

$$C_{AO} = \frac{N_{AO}}{V_0}$$

$$\therefore \frac{dx}{dt} = \frac{-r_A}{C_{AO}}$$

② rate law

$$-r_A = k_2 C_A^2$$

③ Stoichiometry

$$C_A = C_{AO} (1-X)$$

$$\therefore -r_A = k_2 C_{AO}^2 (1-X)^2$$

④ Combine

$$\frac{dx}{dt} = k_2 C_{AO} (1-X)^2$$

$$\text{Evaluate } \Rightarrow t = \frac{1}{k_2 C_{AO}} \int_0^X \frac{dx}{(1-X)^2}$$

For 2nd order reaction

$$t = \frac{1}{k_2 C_{AO}} \frac{x}{1-x}$$

Similarly for 1st order reaction
we can show that

$$t = \frac{1}{k_1} \ln \left(\frac{1}{1-x} \right)$$

Batch reactor times

First order $k_1 t \left(\frac{1}{s}\right)$	2^{nd} order $k_2 C_{A0} \left(\frac{1}{s}\right)$	Reaction time (t_R)
10^{-4}	10^{-3}	Hours
10^{-2}	10^{-1}	Minutes
1	10	Seconds
1000	10000	milliseconds

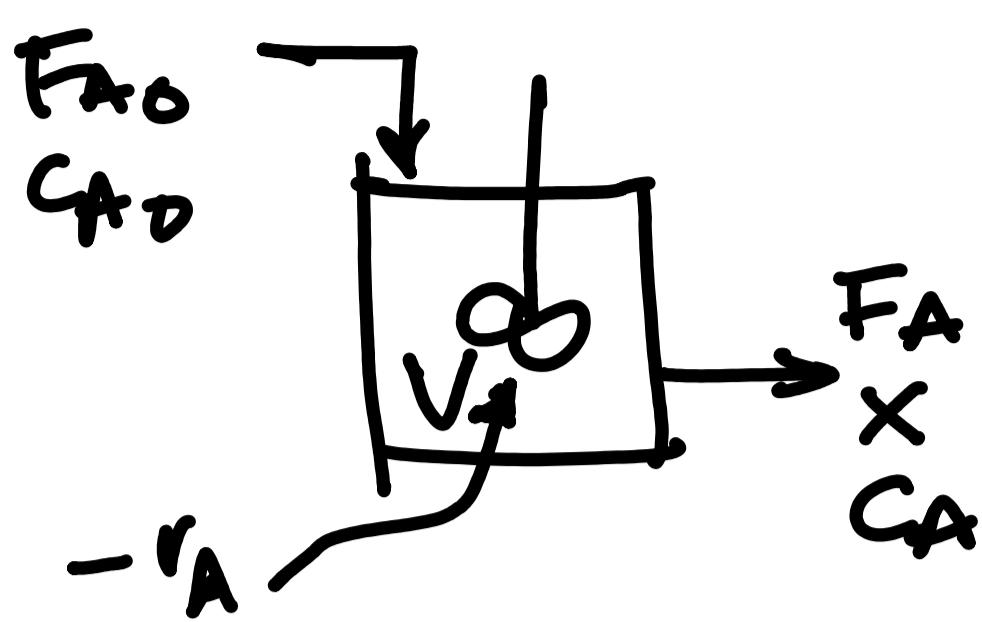
Batch cycle times

→ Time between batches

Activity	Time (h)
1. charge feed t_f	0.5 - 2
2. heat to rxn temp t_e	0.5 - 2
3. reaction t_R	varies
4. Empty and clean reactor t_c	1.5 - 3.0
Total $\Rightarrow (2.5 \text{ h to } 7.0 \text{ h}) + t_R$	

Batch reaction time is just one component in batch cycle time.

CSTR



Mole balance

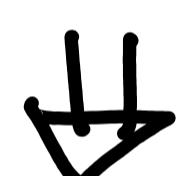
$$V = \frac{F_{A0} X}{-r_A|_{\text{exit}}}$$

⇒ Concentration everywhere in the reactor is same as the exit concentration.

∴ rate everywhere $= -r_A|_{\text{exit}}$
in the reactor

Space time

$$\tau = \frac{V}{V_0}$$



time necessary to process one reactor volume of fluid based on inlet conditions.

$$F_{A0} = C_{A0} V_0$$

$$\therefore \frac{V}{V_0} = \tau = \frac{C_{A0} X}{-r_A|_{\text{exit}}}$$

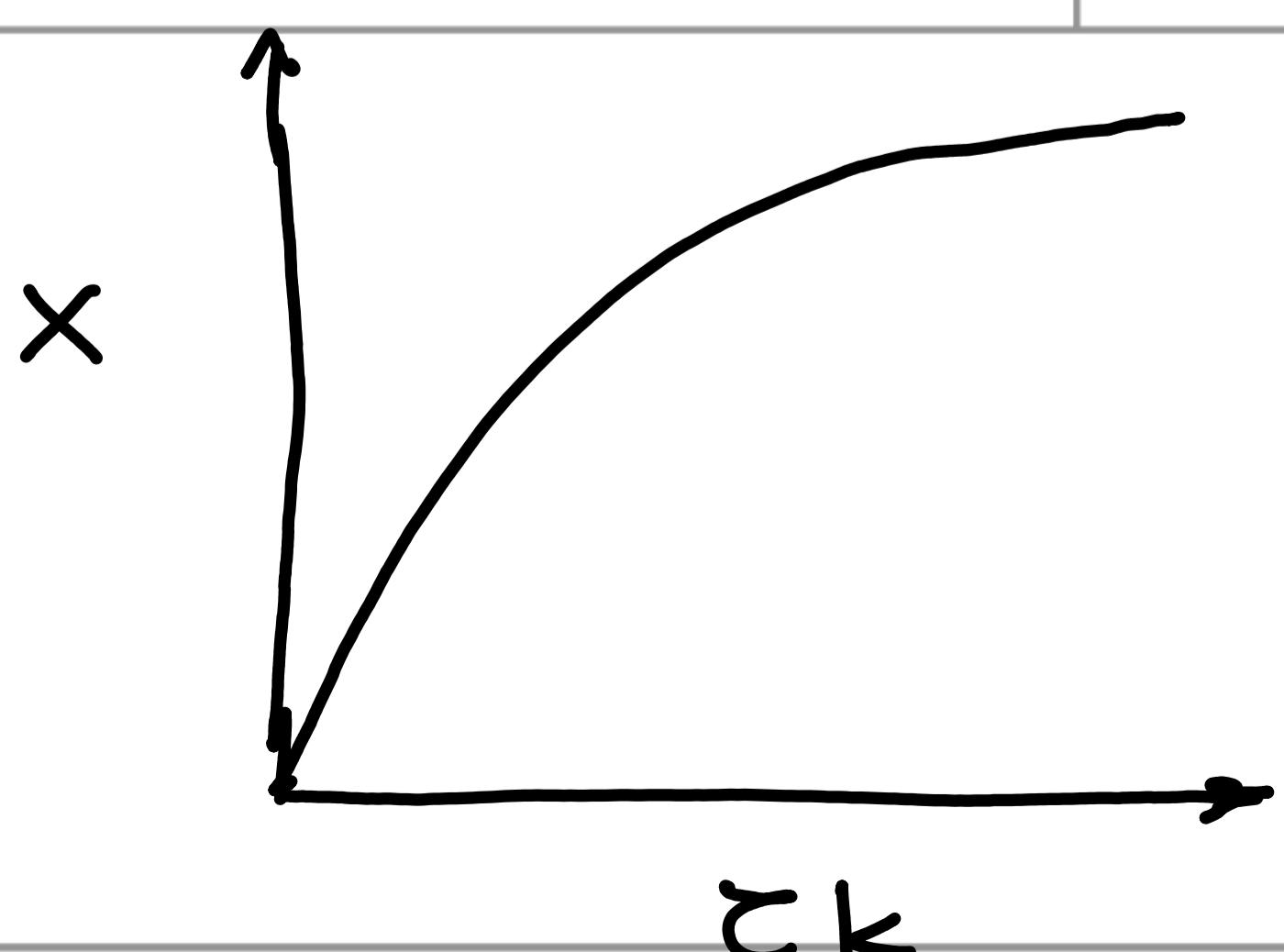
First order reaction :

$$-r_A = k C_A ; C_A = C_{A0}(1-X)$$

$$\tau = \frac{1}{k} \frac{X}{1-X}$$

or

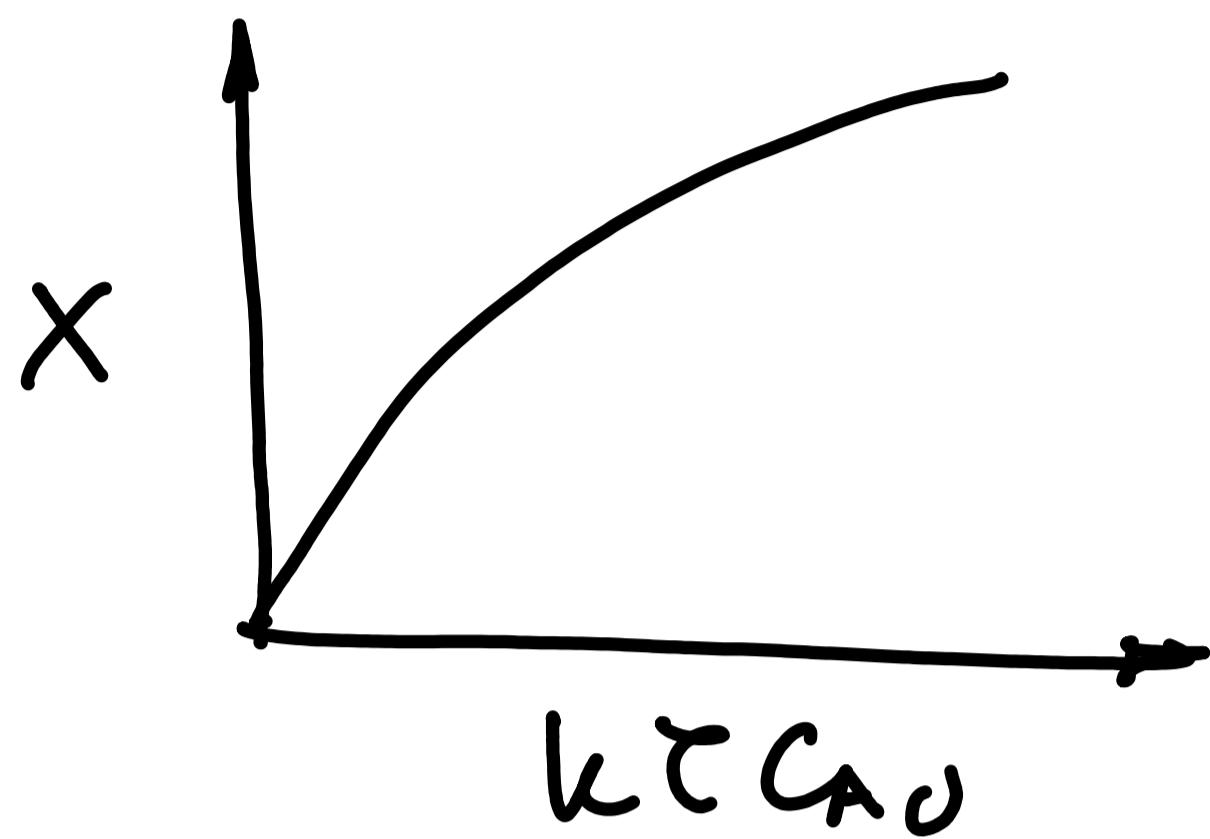
$$X = \frac{\tau k}{1 + \tau k}$$



⇒ Increasing τk increases X

- ↳ Increase temperature (k)
- ↳ Increase space time (τ)
 - ↳ Increase volume
 - ↳ decrease V_0

2nd order rxn
in CSTR



$$V = \frac{F_{A_0} X}{k C_A^2} = \frac{r_0 C_{A_0} X}{k C_{A_0}^2 (1-X)^2}$$

$$\tau = \frac{X}{k C_{A_0} (1-X)^2}$$

or

$$X = \frac{(1 + 2k\tau C_{A_0}) - \sqrt{1 + 4k\tau C_{A_0}}}{2k\tau C_{A_0}}$$

Damköhler No

$$Da = \frac{-r_{AO} V}{F_{AO}}$$

Da gives quick estimate of degree of conversion that can be obtained in continuous flow reactors.

$$Da = \frac{\text{rate of reaction at entry}}{\text{Entering flow rate of A}}$$

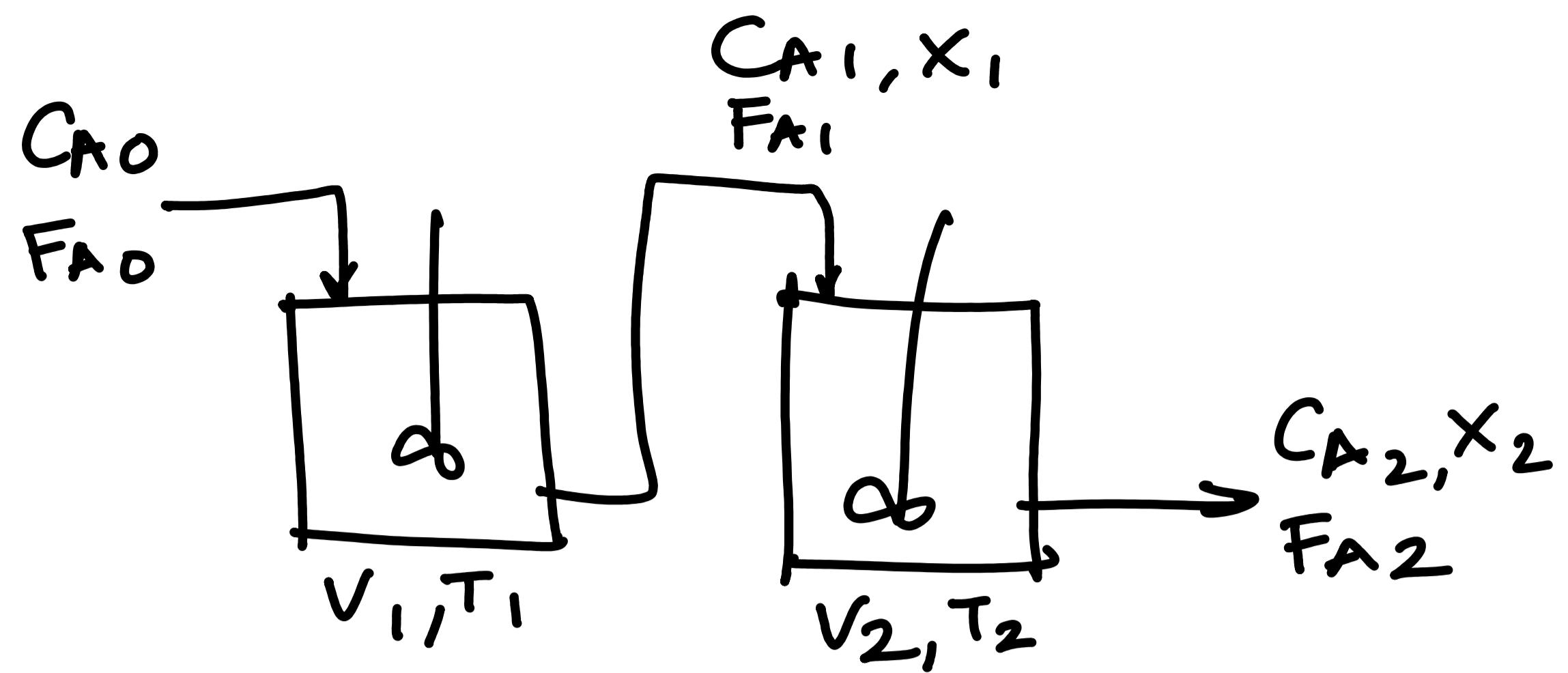
1st and 2nd order Da

$$Da_1 = \tau k ; \quad Da_2 = \tau k C_{A_0}$$

If $Da < 1$, then $X < 0.1$

If $Da > 10$, then $X > 0.9$

CSTR in Series



First order reaction

$$X = 1 - \frac{1}{(1 + Da_1)^n}$$

For 1st order reaction

$$X_1 = \frac{C_{A1}}{C_{A0}} = \frac{1}{1 + \tau_1 k_1} \Rightarrow C_{A1} = \frac{C_{A0}}{1 + \tau_1 k_1}$$

For 2nd reactor

$$V_2 = \frac{F_{A1} - F_{A2}}{-r_{A2}} = \frac{\tau_0 (C_{A1} - C_{A2})}{k_2 C_{A2}}$$

$$C_{A2} = \frac{C_{A1}}{1 + \tau_2 k_2}$$

$$\Rightarrow C_{A2} = \frac{C_{A0}}{(1 + \tau_2 k_2)(1 + \tau_1 k_1)}$$

If the reactors are equal sized and operate at same T

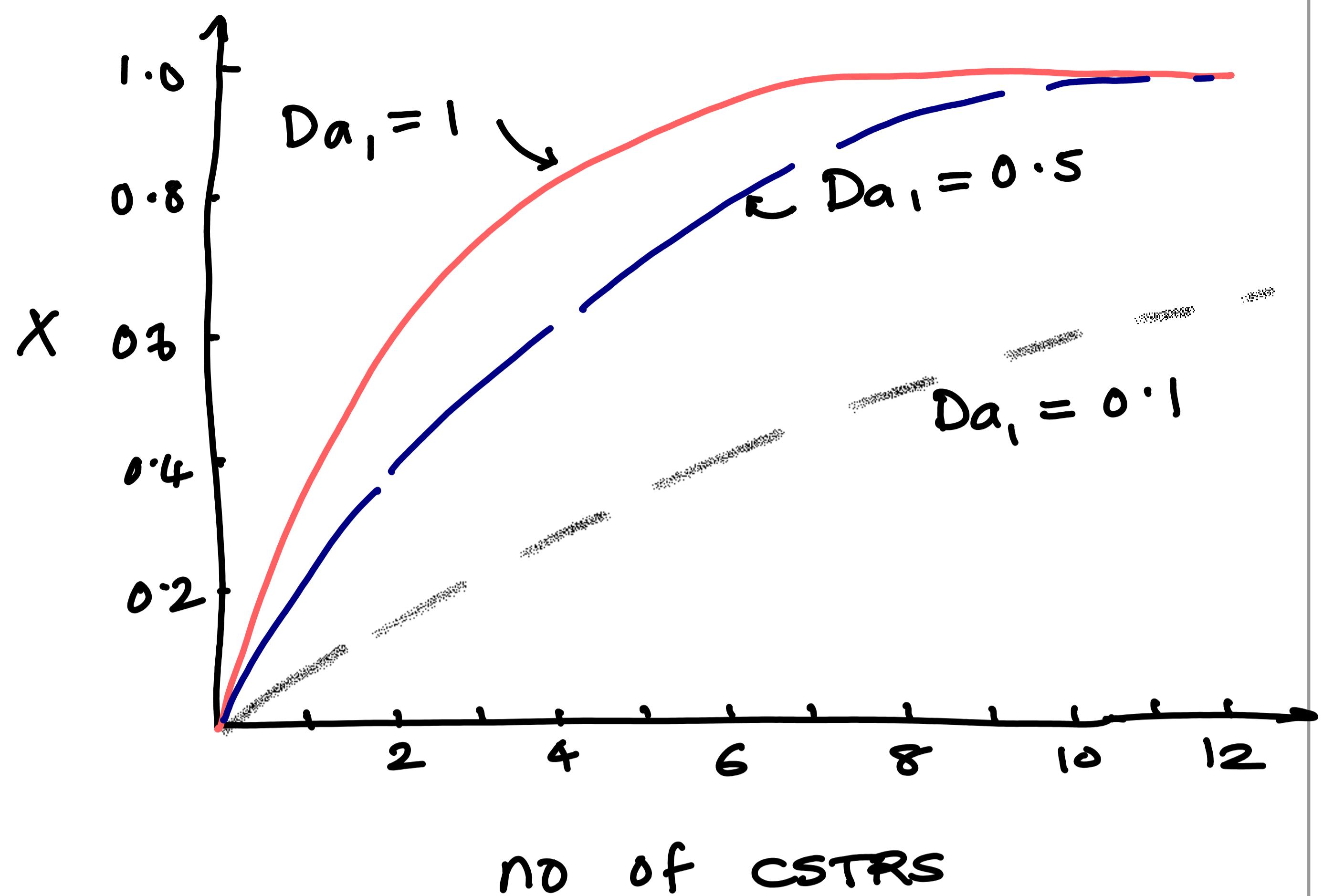
$$C_{A2} = \frac{C_{A0}}{(1 + \tau k)^2} = \frac{C_{A0}}{(1 + Da_1)^2}$$

For n reactors in series

$$X = 1 - \frac{1}{(1 + Da_1)^n}$$

For large D_{A_1}
 ⇒ Small no. of reactors are sufficient to achieve high conversion

For small D_{A_1}
 ⇒ increasing no. of reactors increases conversion significantly.



Plug flow reactors

Must use the differential form if there is significant pressure drop.

Mole balance

$$F_{A_0} \frac{dX}{dV} = -r_A$$

$$V = F_{A_0} \int_0^X \frac{dx}{-r_A} \dots \left. \right\} \text{No pressure drop}$$

2nd order reaction

$2A \rightarrow \text{products}$

$$-r_A = k C_A^2$$

Liquid phase PFR $\tau = \tau_0$

$$\frac{dx}{dV} = \frac{k C_A^2}{F_{AO}}$$

$$C_A = C_{AO} (1-x)$$

$$F_{AO} = C_{AO} \tau_0$$

$$\therefore V = \frac{\tau_0}{k C_{AO}} \int_0^x \frac{dx}{(1-x)^2}$$

$$V = \frac{\tau_0}{k C_{AO}} \left(\frac{x}{1-x} \right)$$

$$x = \frac{\tau k C_{AO}}{1 + \tau k C_{AO}} = \frac{Da_2}{1 + Da_2}$$

gas phase:
→ consider changes in
moles,
pressure,
temperature

Gas phase PFR

$$\tau = \tau_0 (1 + \epsilon x) \left(\frac{T}{T_0} \right) \left(\frac{P_0}{P} \right)$$

Change in moles

Temp

pressure

For const P & T

$$\tau = \tau_0 (1 + \epsilon x)$$

$$C_A = \frac{F_A}{\varsigma} = \frac{F_{A0}(1-X)}{\varsigma_0(1+\epsilon X)}$$

$$C_A = C_{A0} \frac{(1-X)}{(1+\epsilon X)}$$

Combining

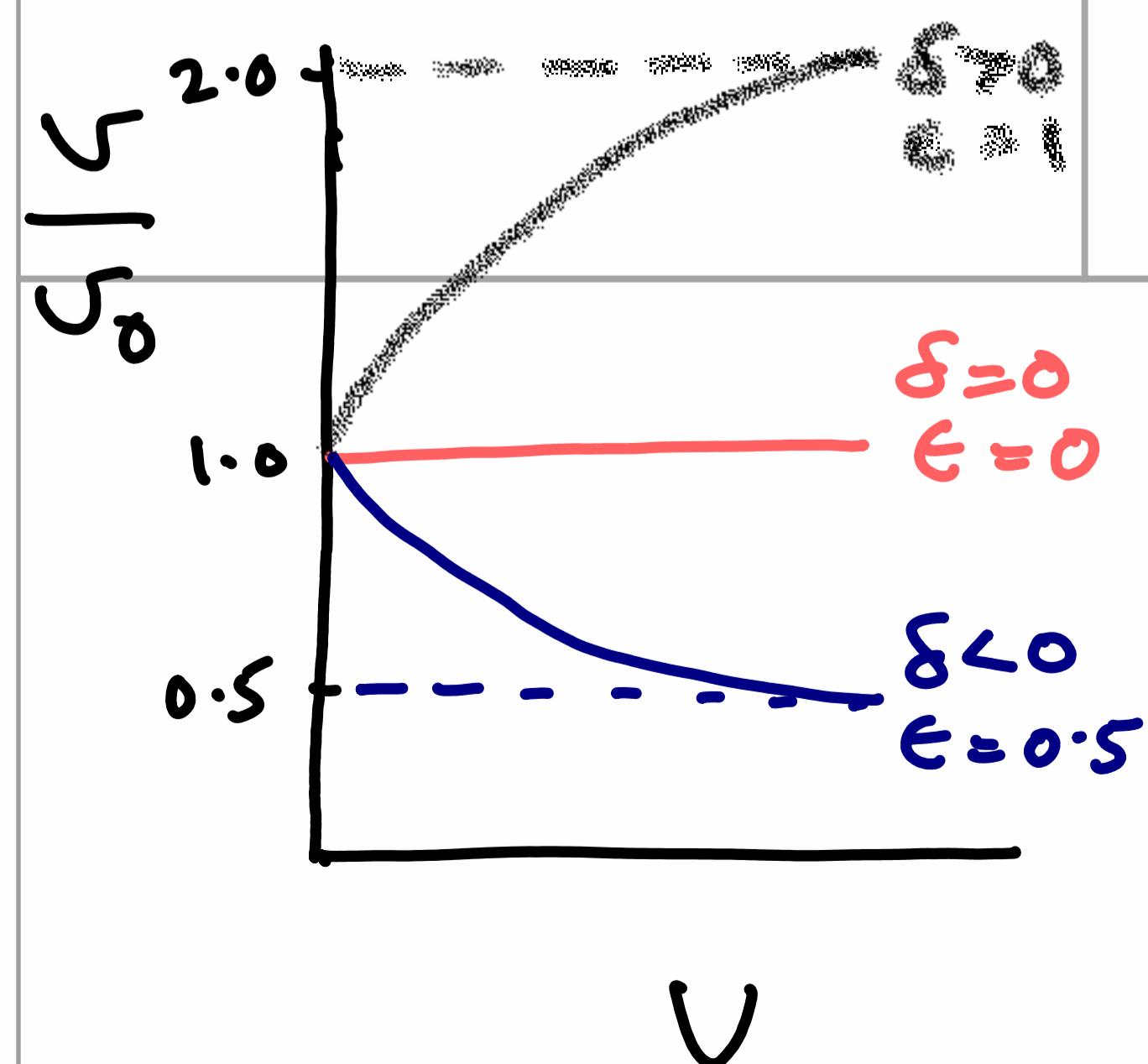
$$V = F_{A0} \int_0^X \frac{(1+\epsilon X)^2}{k C_{A0}^2 (1-X)^2} dX$$

$$V = \frac{\varsigma_0}{k C_{A0}} \int_0^X \frac{(1+\epsilon X)^2}{(1-X)^2} dX$$

Evaluate

$$V = \frac{\varsigma_0}{k C_{A0}} \left[2\epsilon(1+\epsilon) \ln(1-X) + \epsilon^2 X + \frac{(1+\epsilon)^2 X}{1-X} \right]$$

Effect of ϵ on X



No change in no. of moles \Rightarrow Fluid moves at const. ς as X increases

$\underline{\epsilon < 0}$: decrease in no. of moles
 $\Rightarrow \varsigma$ decreases as X increases
 \Rightarrow longer τ / smaller V for same X

$\underline{\epsilon > 0}$: increase in no. of moles
 $\Rightarrow \varsigma$ increases as X increases
 \Rightarrow smaller τ / $X < X$ at $\varsigma = \varsigma_0$

Pressure drop in reactors

liquid phase
 ⇒ ignore effect
 of pressure
 as Conc. not
 affected by P

For gas phase reactions
 $C \propto P \Rightarrow$ must account
 for pressure drop.

Consider reaction in a PBR



Mole balance:

$$F_{AO} \frac{dx}{dw} = -r'_A$$

Rate law:

$$-r'_A = k C_A^2$$

Stoichiometry:

$$C_A = \frac{C_{AO}(1-x)}{(1+\epsilon x)} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

combine:

$$\frac{dx}{dw} = \frac{k C_{AO}}{\epsilon S_0} \left(\frac{1-x}{1+\epsilon x} \right)^2 \left(\frac{P}{P_0} \right)^2$$

$$\Rightarrow \frac{dx}{dw} = f(x, P)$$

Need equation for P

isothermal
 reactor $T=T_0$

Flow through
Packed bed

Only gas
density varies
with pressure

Ergun Equation

$$\frac{dP}{dz} = \frac{-G}{\rho g_c D_p} \left(\frac{1-\phi}{\phi^3} \right) \left[\underbrace{\frac{150(1-\phi)\mu}{D_p}}_{\text{Term 1}} + \underbrace{1.75G}_{\text{Term 2}} \right]$$

P : pressure (kPa)

ϕ : porosity = $\frac{\text{vol. of void}}{\text{bed volume}}$

$g_c = 1$

D_p : particle diameter (m)

μ : viscosity (kg/m-s)

G : superficial mass velocity
(kg/m²s)

$$= \rho u$$

ρ : density of gas (kg/m³)

u : superficial velocity (m/s)
volumetric flow rate/(c/s area)

z : length of packed bed (m)

Various forms
of Ergun
equation:

Packed bed reactors

→ Mass flow rate is constant

$$\dot{m}_0 = \dot{m} \Rightarrow P_0 V_0 = \rho V$$

$\beta_0 \rightarrow$ constant
depends on the
properties of
packed bed

$$\frac{dP}{dz} = -\beta_0 \left(\frac{P_0}{P}\right) \left(\frac{T}{T_0}\right) \frac{F_T}{F_{T_0}}$$

In terms of weight of
catalyst

$$\frac{dP}{dw} = -\frac{\alpha}{2} \left(\frac{P_0}{P}\right) \left(\frac{T}{T_0}\right) \left(\frac{F_T}{F_{T_0}}\right)$$

$$\frac{dP}{dw} = -\frac{\alpha}{2\rho} \left(\frac{T}{T_0}\right) \left(\frac{F_T}{F_{T_0}}\right)$$

Use for
multiple
reactions

$$\alpha = \frac{2\beta_0}{A_c P_c (1-\phi) P_0} \quad (\text{unit } \frac{1}{\text{kg}})$$

$$P = P/P_0$$

For single
reaction

$$\frac{F_T}{F_{T_0}} = 1 + \epsilon X$$

$$\frac{dP}{dw} = -\frac{\alpha}{2\rho} \left(\frac{T}{T_0}\right) (1 + \epsilon X)$$

⇒ Solve mole balance and the
pressure drop equation simultaneously.