Chapter 1:

→ Chemical reaction Engineering [CRE]: is the field that studies the rates & mechanisims of chemical reactions & the design of the reactor in which they take place.

Pillars of CRE:

1- Mole Balance
2- Rate Laws
3- Stiochiometry
4- Energy Balances
5- Diffusion
6- Contacting

* CRE Algorithim

Mole Balance + Rate Laws + Stiochiometry + Energy Balance + Combine → Solution [isothermal system]

→ Mole Balances:-

→ Four most common types of industrial reactors

1- Batch Reactor
2- Continous - Stirred tank Reactor (CSTR)
3- Tubular Reactor or Plug flow Reactor (PFR)
4- Packed bed Reactor (PBR)

* The selection of a reaction system that operates in the safest & most efficient manner can be the key to the economic success or failure of a chemical plant.

→ if a reaction system produces a large amount of undesirable product, subsequent purification & seperation of the desired product could make the entire process economically unfeasible.

Rate of Reaction ($-r_A$)

Rate of Reaction: how fast a number of moles of one chemical species are being consumed to form another chemical species

⇓

Chemical species: any chemical component or element with a given identity

⇓

Identity of chemical species: atoms, Number of atoms, configuration

→ A chemical reaction has taken place when a detectable number of molecules of one or more species have lost their identity ; change in kind or number of atoms &/or change in structure or configuration.

→ Total mass is neither created nor destroyed ←

Conservation of mass principle

→ Three ways for a species to loose it's identity

1- Decomposition
2- Combination
3- isomerization

→ The rate of reaction is the number of moles of species A loosing their chemical identity per unit time per unit volume

→ Rate of Disappearance of reactant : $-r_A$

→ Rate of formation (Generation) of a product : r_P

$$A \rightarrow B$$

$-r_A$: rate of disappearance of A

r_A : rate of formation of A

r_B : rate of formation of B

* consider species j

- if species j is a reactant $r_j = -4 \text{ mol} / \text{dm}^3/\text{s}$
- if species j is a product $r_j = 4 \text{mol} / \text{dm}^3/\text{s}$ example.

- r_j is a function of temperature, pressure, & Type of catalyst.

- r_j is independent of the type of reaction system

- r_j is an algebric equation, not a differential equation → independent of time

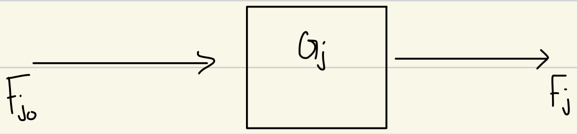
$\frac{dC_A}{dt}$ is not the rate of reaction

⇒ r_A'

- Heterogenous reactions involve more than one phase, the rate of reaction is usually expressed in measures other than volume [reaction surface area, catalyst weight]
- For gas-solid catalytic reaction, the gas molecules must interact with the solid catalyst surface for the reaction to take place.

r_A' : number of moles A reacting per unit time per unit mass of catalyst

General Mole Balance Equation



Molar flow rate of species j in − Molar flow rate of species j out + Molar Generation of species j = Molar rate Accumulation of species j

$$F_{jo} - F_j + \underset{\substack{+\text{ Generation} \\ -\text{ consumption}}}{G_j} = \frac{dN_j}{dt}$$

→ number of moles inside system

- if the system is uniform throught its entire volume ⇒ spatially uniform

$$G_j = r_j V$$

↳ rate of reaction

$$\left(\frac{\text{mol}}{\text{time} \cdot \cancel{\text{volume}}} \right) \quad \cancel{\text{Volume}} \quad = \quad G_j \left[\frac{\text{mole}}{\text{time}} \right]$$

r_j product (+) ⇒ $+G$ generation

r_j reactant (−) ⇒ $-G$ consumption

→ if not spatially uniform

$$G_j = \sum r_{ji} \Delta V_i \quad = \int r_j \, dV$$

species j at element i ↲

↳ elemental volumes

$$F_{A0} - F_A + \int r_A \, dV = \frac{dN}{dt}$$

1- Batch Reactor

- Reactants are placed in the reactor, & the reaction is allowed to proceed for some time
- closed system: no addition of reactants or removal of products during the reaction.
- Unsteady state conditions: changes in composition with time. (↓ reactant, ↑ product)

→ Ideal Batch Reactor: Perfect mixing

- Spatially constant temperature & concentration, but not constant in time.

closed sys.

→ Mole Balance: $\cancel{\text{In}} - \cancel{\text{out}} + \text{Generation} = \text{Accumulation}$

$$\boxed{\int r_j \, dV = \frac{dN_j}{dt}}$$

Batch Reactor Design Equation

- if the reactor is perfectly mixed, spatially constant temperature & concentration :-

$$\boxed{\frac{dN_A}{dt} = r_A V}$$

ideal Batch Reactor Design Equation

$$dt = \frac{dN_A}{r_A V} \Rightarrow t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A V}$$

↳ time necessary to reduce the number of moles A from N_{A0} to N_A

2- Continous Stirred Tank Reactor [CSTR]

- Continously add reactants & remove products (open system)
- Inlet stream instantanously mixes with bulk of reactor volume.

→ Ideal CSTR: Assume perfect mixing occurs in vessel

- Spatially constant temperature & concentration
- Composition of the exit stream is the same as that inside reactor ($C_{A,outlet} = C_{A,tank}$)
- Steady state conditions. Reaction Rate is the same at every point & doesnot change with time

→ Mole Balance: In − Out + Generation = $\cancel{\text{Accumulation}}$ steady state

$$\boxed{F_{j0} - F_j + \int r_j \, dV = 0}$$ Steady state CSTR Design Equation

- Perfectly mixed, spatially constant CSTR:

$$F_{j0} - F_j + r_j V = 0$$

$$\boxed{V = \frac{F_{j0} - F_j}{-r_j}}$$ Ideal Steady state CSTR Design Equation

r_j is measured at the exit ($C_{j\,exit} = C_{j\,tank}$)

↳ Reactor Volume required to reduce the entering flow rate of species j from F_{j0} to F_j at the outlet

Molar flow Rate = Concentration j x volumetric flow Rate

$$\left[\frac{\text{moles } j}{\text{time}}\right] = \left[\frac{\text{moles } j}{\text{volume}}\right] \times \left[\frac{\text{volume}}{\text{time}}\right]$$

$$F_j = C_j \times v$$

$$\therefore \quad V = \frac{C_{j0} v - C_j v}{-r_j}$$

3- Plug Flow Reactor [PFR]

- Cylindrical pipe with openings at both ends
- steady movement of material down the length of the reactor
- Reactants are consumed as they flow down the length of the reactor.
- Steady State operation
- No radial variation in temperature, concentration, & reaction rate
- All fluids /gas elements have the same residance time

→ Mole Balance

- the composition of the fluid varies from point to point along a flow path. Consequently the material balance for a reaction component must be made for a differential element of volume ΔV

$$F_A\big|_V - F_A\big|_{V+\Delta V} + r_A \Delta V = 0$$

$$\lim_{V \to 0} \frac{F_A\big|_{V+\Delta V} - F_A\big|_V}{\Delta V} = r_A \quad \rightarrow \quad \frac{dF_A}{dV} = r_A$$

$$\boxed{V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}}$$

Ideal Steady State PFR Design Equation.

Volume necessary to reduce the entering molar flow rate from F_{A0} to F_A

→ Degree of completion of ideal PFR is not affected by PFR shape, only volume.

4- Packed bed Reactor [PBR]

- Cylindrical shell, vertically oriented [gravity driven flow]
- Heterogenous reaction : fixed bed of catalyst inside
- Concentration gradient of reactant & product down the length of reactor
- Reaction occurs on the surface of the catalyst pellets
- Reaction Rate is based on the mass of solid catalyst [W], not reactor volume [V]

→ Mole Balance

$$F_{j0} - F_j + r_j \, dV = 0$$

$$r_j = \frac{dF_j}{dV}$$ → similar to PFR, but expressed in catalyst weight

* Units for the rate of homogenous rxn (r_j) $= \frac{mol}{s.m^3}$

* Units for the rate of heterogenous rxn (r_j') $= \frac{mol}{s.Kg\ catalyst}$

$$\boxed{\frac{dF_j}{dW} = r_j'}$$

Reactors Mole Balances Summary

Reactor	Differential	Algebric	Integral	comments
Batch	$\frac{dN_A}{dt} = r_A V$		$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A V}$	spatially constant unsteady state
CSTR		$V = \frac{F_{A0} - F_A}{-r_A}$		spatially constant steady state
PFR	$\frac{dF_A}{dV} = r_A$		$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$	steady state
PBR	$\frac{dF_j}{dW} = r_A'$		$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A'}$	steady state

* CSTR → Algebric due to constant concentration

only volume changes (residence time)

Selection of Reactors:-

Batch:
- small scale
- production of expensive products (pharmacy)
- high labour costs per batch
- difficult for large scale production

CSTR:
- most homogenous liquid-phase flow reactor
- when intense agitation is required
- easy to maintain good temperature control
- the conversion per volume of reactor is the smallest of the flow reactors

PFR:
- most homogenous gas-phase flow reactor
- relatively easy to maintain
- usually produces the highest conversion per reactor volume
- Difficult to control temperature
- hot spots can occur

Chapter 2: Conversion & Reactor Sizing

Defenition of conversion

$$aA + bB \rightarrow cC + dD$$

→ choose Limiting reactant A as a basis of calculation

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

⇒ Conversion X_A: the number of moles of A that have reacted per mole of A fed to the system

$$X_A = \frac{\text{moles A racted}}{\text{moles A fed}}$$

- for Batch system: moles A fed is the amount of A at the start of the reactor at $(t=0)$
- for flow System: moles A fed is the amount of A entering the reactor

Expressing other Components Conversion in Terms of X_A

$$\underset{\text{Basis "Limiting reactant"}}{A} + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

$$X_A = \frac{\text{moles A reacted}}{\text{moles A fed}}$$

↳ "Stiochiometric coefficient"

- Batch system: Longer reactant is in the reactor, more reactant is converted into product (until reactant is consumed or the reaction reaches equilibruim [reversible reaction])

Conversion (X_j) is a function of time (t) in the batch reactor

$$N_A = N_{A0} - [N_{A0}][X_A]$$

Moles A in Reactor at time = t = Moles A fed − moles A consumed (reacted)

$$* \; X_A = \frac{\text{moles A reacted}}{\text{moles A fed}}$$

$$N_{A_{\text{consumed}}} = N_{A0} \cdot X_A$$

$$\rightarrow N_A = N_{A0}(1 - X_A)$$

for B: $N_B = N_{B0} \overset{\text{reactant}}{\overset{\downarrow}{-}} \frac{b}{a}[N_{A0}][X_A]$

* $\uparrow t \quad \uparrow X \quad \uparrow N_A \quad \downarrow N_{A0}$

for C : $N_C = N_{C0} \overset{\text{product}}{\overset{\downarrow}{+}} \frac{c}{a}[N_{A0}][X_A]$

for D : $N_D = N_{D0} + \frac{d}{a}[N_{A0}][X_A]$

for inert : $N_i = N_{i0}$ [no rxn]

Batch Reactor :

Moles A remaining = Moles A initially − moles A reacted

$$N_A = N_{A0} - (N_{A0} \cdot X_A)$$

* Batch Reactor Mole Balance

$$\frac{dN_A}{dt} = r_A V$$

$$dN_A = 0 - N_{A0}\, dX$$

$$\frac{dN_A}{dt} = -N_{A0}\frac{dX}{dt} = r_A V$$

$$\hookrightarrow \frac{dX}{dt} = \frac{r_A V}{-N_{A0}}$$

$t=0 \quad X=0$

$t=t \quad X=X$

$$= t = N_{A0}\int_0^X \frac{dX}{-r_A V}$$

⇒ t necessary to achive conversion X

CSTR

- At steady state $\frac{dN_A}{dt} = 0$

- well mixed $\int r_A \, dV = r_A V$

$$V = \frac{F_{A0} - F_A}{-r_A}$$ * CSTR Mole Balance

Moles A leaving = Moles A entering − Moles A reacted

$$F_A = F_{A0} - [F_{A0} X_A]$$

$$V = \frac{F_{A0} - F_A}{-r_A} \Longrightarrow V = \frac{F_{A0} - [F_{A0} - (F_{A0} X_A)]}{-r_A}$$

$$\boxed{V = \frac{F_{A0} X_A}{-r_A}}$$ CSTR volume necessary to achive conversion X

PFR

- At steady state $\frac{dF_A}{dV} = r_A$

Moles A leaving = Moles A entering − Moles A Reacted

$$F_A = F_{A0} - (F_{A0} X_A)$$

$$dF_A = 0 - F_{A0} \, dX_A$$

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

$X=0 \quad V=0$

$X=X \quad V=V$

$$V = \int_0^X \frac{F_{A0}}{-r_A} dX$$ PFR volume necessary to achive conversion X

Reactors Mole Balance Summary in terms of conversion X

Reactor	Differential	Algebric	Integral
Batch	$N_{A0} \frac{dX}{dt} = -r_A V$		$t = N_{A0} \int_0^X \frac{dX}{-r_A V}$
CSTR		$V = \frac{F_{A0} X}{-r_A}$	
PFR	$F_{A0} \frac{dX}{dV} = -r_A$		$V = \int_0^X \frac{F_{A0}}{-r_A} dX$
PBR	$F_{A0} \frac{dX}{dW} = -r'_A$		$W = \int_0^X \frac{F_{A0}}{-r'_A} dX$

Applications of the Design Equations for Continous Flow Reactors

- Levenspiel plots

↬ $-r_A$ as a function of conversion

$$-r_A = f(X)$$

↬ Levenspiel plot, either $(F_{A0}/-r_A)$ or $(-1/r_A)$ as a function of X

↬ shaded area in Levenspiel plot → volume of CSTR & PFR

$$\frac{F_{A0}}{-r_A} = g(X)$$

→ For all irreversible reactions of order > zero, as complete conversion is approached, all the limiting reactant is used up

As $X \to 1$

$-r_A \to 0$, $\frac{1}{-r_A} \to \infty$

$\therefore V \to \infty$

→ For reversible reactions, the maximum conversion is the equilibrium conversion X_e

[At equilibrium the reaction rate is zero]

As $X \to X_e$

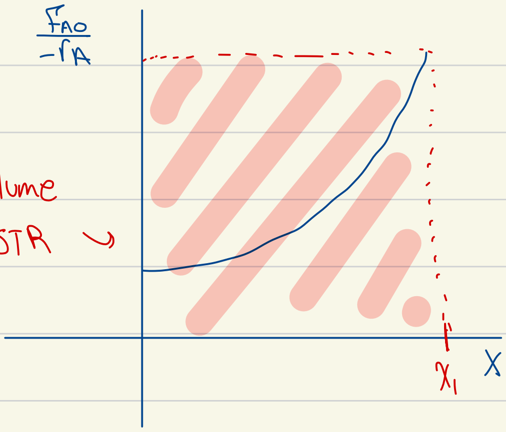
$-r_A \to 0$ $\frac{1}{-r_A} \to \infty$

$\therefore V \to \infty$

CSTR:

$$V = \frac{F_{A0}\,X}{-r_A} \rightarrow V = \left[\frac{F_{A0}}{-r_A}\right]_{X_1} X_1$$

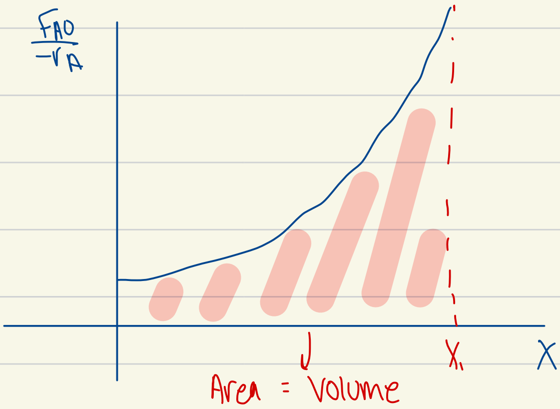
Area = volume of CSTR ↪



PFR

$$V = \int_0^X \frac{F_{A0}\, dX}{-r_A}$$

$$V = \int_0^{X_1} \left[\frac{F_{A0}}{-r_A} \right] dX$$



Area = Volume of PFR

* CSTR volume > PFR volume for reactions above zero order due to CSTR operating at lowest possible reaction rate, whereas PFR starts with highest & decrease gradually

$$\frac{1}{-r_A} \propto V$$

Reactors in Series.

- Given $-r_A$ as a function of conversion, one can also design any sequence of reactors in series by defining X_i

$$X_1 = \frac{\text{total moles of A reacted upto point } i}{\text{moles of A fed to first reactor}}$$

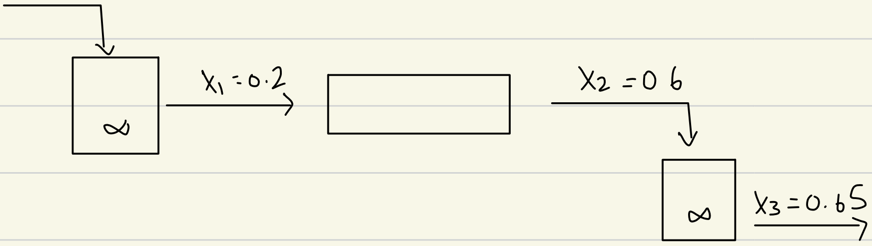
*moles into first reactor → reference.

*only valid if there are no side streams

→ Molar flow rate of species A at point i

$$F_{Ai} = F_{A0} - F_{A0} X_i$$

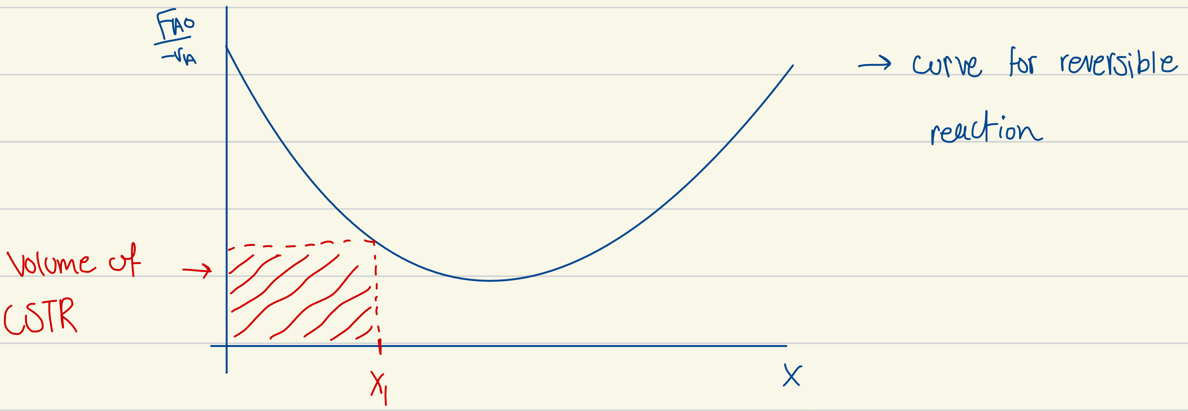
→ Reactors in series.



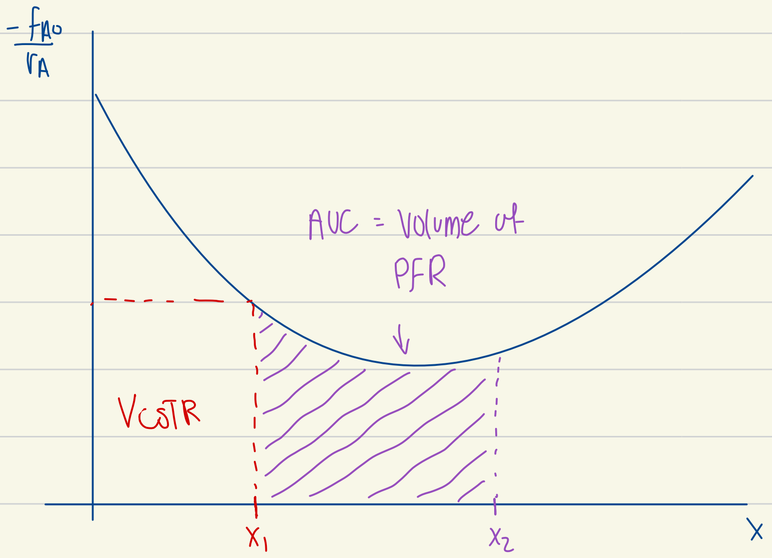
Reactor 1 : $F_A = F_{A0} - F_{A0} X_1$

CSTR

$$V_1 = \frac{F_{A0} - F_A}{-r_{A_1}} = \frac{F_{A0} - (F_{A0} - F_{A0}X_1)}{-r_{A_1}} = \frac{F_{A0}X_1}{-r_{A_1}}$$



Reactor 2. $V_2 = \int_{X_1}^{X_2} \frac{F_{A0}}{-r_A} dX$

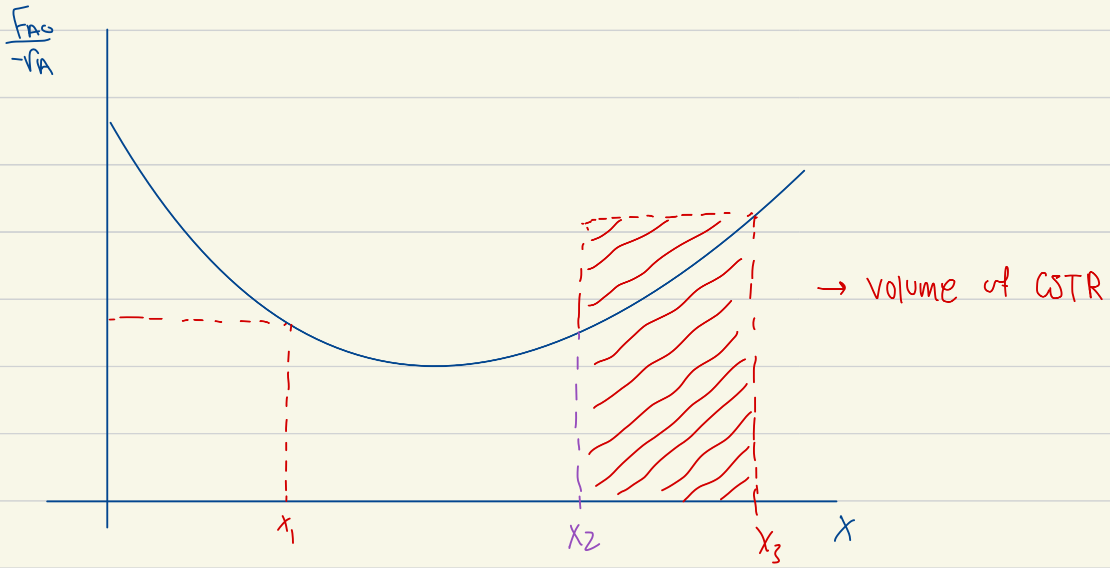


Reactor 3:

$$F_{A2} - F_{A3} + r_3 V_3 = 0$$

$$(F_{A0} - F_{A0} X_2) - (F_{A0} - F_{A0} X_3) + r_3 V_3 = 0$$

$$V_3 = \frac{F_{A0} (X_3 - X_2)}{-r_{A3}}$$



Space Time, τ

→ space time, τ is the time necessary to process one reactor volume of fluid at enterance conditions.

$$\tau = \frac{V}{v_0} = \frac{\text{Volume of reactor}}{\text{Volumetric flow rate}}$$

* liq → incompressible ∴ $v_{in} = v_{out}$
* Gas → compressible ∴ $v_{in} \neq v_{out}$
] due to density effects

→ for CSTR $\tau = \frac{V}{v_0} = \frac{C_{A0} X}{-r_A}$

→ for PFR $\tau = \frac{V}{v_0} = C_{A0} \int_0^X \frac{dX}{-r_A}$

Space velocity

$SV = \frac{v_0}{V}$ $SV = \frac{1}{\tau}$

→ liquid hourly space velocity $LHSV = \frac{v_{0\,liq}}{V}$

→ Gas hourly space velocity $GHSV = \frac{v_{0\,STP}}{V}$

* Two CSTR's in series → less volume needed than one CSTR (more efficient)

→ This case doesn't hold true for two PFR reactors in series. [the total reactor volume needed to achieve the same conversion will be the same]

Chapter 3 : Rate Laws

Types of Reactions:

- Homogenous Reaction : involves only one phase
- Heterogenous Reaction : involves more than one phase , reaction on the interface
- Irreversible Reaction : proceeds in only one direction & continues in that direction until the reactants are exhausted [complete reaction ex. Acid - base reactions]
- Reversible Reaction : proceeds in either direction , depending on concentrations till equilibrium

Molecularity of Reaction

- Molecularity of Reaction → number of atoms , ions or molecules involved in a reaction step

→ Most common unimolecular reaction:

$$U \longrightarrow Th + He \qquad -r_U = K C_U$$

→ The true bimolecular reactions that exist are reactions involving free radical.

$$Br\bullet + C_2H_6 \longrightarrow HBr + C_2H_5\bullet \qquad -r_{Br\bullet} = K C_{Br\bullet} C_{C_2H_6}$$

→ Probability of teramolecular reaction occuring is almost nonexistant [reaction pathway follows a series of bimolecular reactions]

$$2NO + O_2 \longrightarrow 2NO_2$$

→ Rate Law

- Rate Law [kinetic expression] → Algebric equation that relates $-r_A$ to the species concentrations.

Power Law Model

$$-r_A = K C_A^{\alpha} C_B^{\beta}$$

α = order in A

β = order in B

overall reaction order = $\alpha + \beta$

- A reaction follows an elementary rate law if the reaction order agrees with the stiochiometric coefficients

Ex: $2A + B \rightarrow 3C$

→ if reaction follows elementary rate law

$$-r_A = K\ C_A^2\ C_B$$

* Rate Laws are determined by experimental observation

Relative Rates of Reaction

$$aA + bB \rightarrow cC + dD$$

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}$$

Ex: $2A + B \rightarrow 3C$

$-r_A = 10\ \text{mol}/\text{dm}^3.s$

$$\frac{r_A}{-2} = \frac{r_B}{-1} = \frac{r_C}{3}$$

$$-r_B = \frac{10}{-2} = -5\ \text{mol}/\text{dm}^3.s$$

$$\frac{r_C}{3} = \frac{-5}{-1} = 15\ \text{mol}/\text{dm}^3.s$$

→ Reversible Elementary Reaction

$$2A + B \underset{K_{-A}}{\overset{K_A}{\rightleftharpoons}} 3C$$

$$-r_A = K\ C_A^2 C_B - K_{-A}\ C_C^3 = K_A\left[C_A^2 C_B - \frac{C_C^3}{K_A/K_{-A}}\right]$$

$$-r_A = K_A\left[C_A^2\ C_B - \frac{C_C^3}{K_e}\right]$$

↳ K at equilibrium

The Reaction Rate Constant

- k → specific reaction rate or the reaction rate constant
- not truly a constant → independent of the concentrations of the species involved
- Strongly dependent on temperature.
- depends on whether or not a catalyst is present, & in gas phase reactions it may be a function of total pressure
- In liq system it can be a function of other parameters, such as ionic strength & choice of solvent
  → Those variables have much less effect than temperature does with the exception of supercritical solvents.

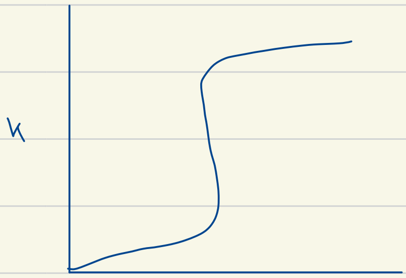
Arrhenius Equation

$$k = A e^{-E/RT}$$

$T \to \infty \quad k \to A$

$T \to 0 \quad k \to 0$

$A \cong 10^{13}$



E = Activation Energy [cal/mol]

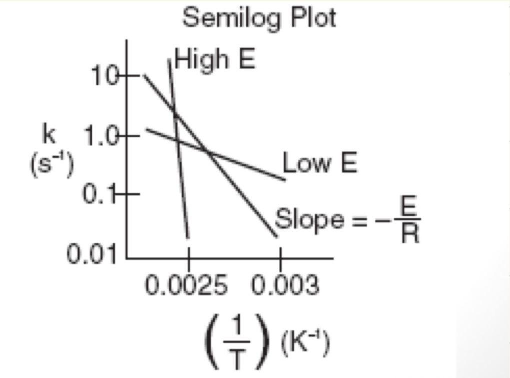
R = Gas Constant [cal/mol·k]

T = Temperature [k]

A = frequancy factor [units of A & K depend on overall reaction order]

* ↑k ↑T till a specific temp [increasing exponentially]

$$\ln k_A = \underbrace{\boxed{\ln A}}_{\text{Intercept}} - \underbrace{\boxed{\frac{E}{R}}}_{\text{Slope}}\left(\frac{1}{T}\right)$$



* The Activation Energy can be thought of as a barrier to energy transfer [from KE to PE]

Reaction coordinates denote the energy of the system as a function of progress along the reaction path [reactants → Intermediate → products]

→ for a reaction to occur the reactants must overcome an energy barrier [Activation Energy]

1. molecules need energy to disort or stretch their bonds [break & form new bonds]
2. overcome stearic & electron repulsion forces.

→ Collision Theory: By increasing the temp, kinetic energy increases ⟶ transferred into Internal Energy to increase the stretching & bending of bonds → reach Activated state.

* ↑ Temp, ↑ rate of reaction, ↑ Activation Energy (E)

Chapter 4. Stiochiometry

→ Stiochiometric tables to express the concentration as a function of conversion

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

*A is the limiting reactant

$$N_A = N_{A0} - N_{A0}X$$

→ for every mole of A that reacts, $\frac{b}{a}$ moles of B react

→ Moles of B remaining

$$N_B = N_{B0} - \frac{b}{a}N_{A0}X = N_{A0}\left[\frac{N_{B0}}{N_{A0}} - \frac{b}{a}X\right]$$

let $\Theta_B = \frac{N_{B0}}{N_{A0}}$

$$N_B = N_{A0}\left[\Theta_B - \frac{b}{a}X\right]$$

& for Product C

$$N_C = N_{C0} + \frac{c}{a}N_{A0}X = N_{A0}\left[\Theta_C + \frac{c}{a}X\right]$$

Batch System Stoichiometry Table

Species	Initial	Change	Remaining
A	N_{A0}	$-N_{A0}X$	$N_A = N_{A0}(1-X)$
B	$N_{B0} = N_{A0}\Theta_B$	$-\frac{b}{a}N_{A0}X$	$N_B = N_{A0}\left(\Theta_b - \frac{b}{a}X\right)$
C	$N_{C0} = N_{A0}\Theta_C$	$\frac{c}{a}N_{A0}X$	$N_C = N_{A0}\left(\Theta_C + \frac{c}{a}X\right)$
D	$N_{D0} = N_{A0}\Theta_D$	$\frac{d}{a}N_{A0}X$	$N_D = N_{A0}\left(\Theta_C + \frac{d}{a}X\right)$
inert	$N_{I0} = N_{A0}\Theta_I$	no change	$N_I = N_{A0}\Theta_I$
	$\Sigma = N_{T0}$		$N_T = N_{T0} + \delta N_{A0}X$

$$\Theta_I = \frac{N_{I0}}{N_{A0}} = \frac{C_{I0}\cancel{\nu_0'}}{C_{A0}\cancel{\nu_0'}} = \frac{C_{I0}}{C_{A0}} = \frac{y_{I0}}{y_{A0}}$$

δ = change in total number of mol per mol A reacted [product - reactant]

$$\delta = \frac{c}{a} + \frac{d}{a} - \frac{b}{a}\boxed{-1}$$

↳ constant $\frac{a}{a} = 1$

* if the reaction occurs in the liquid phase [uncompressible], or gas phase reaction in a rigid [constant volume] batch reactor $V = V_0$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)$$

$$C_B = \frac{N_B}{V} = \frac{N_{A0}\left(\Theta_B - \frac{b}{a}X\right)}{V_0} = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

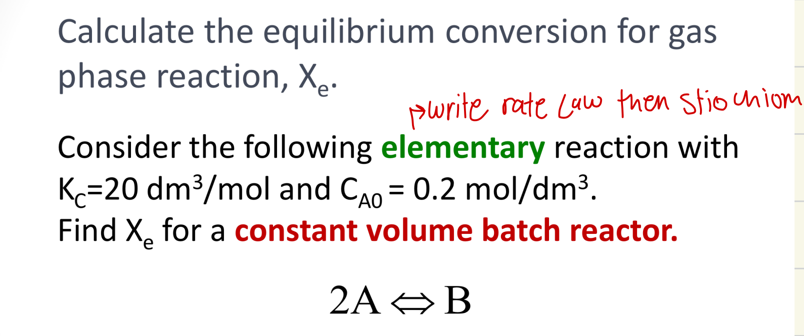
* Suppose $-r_A = kC_A^2 C_B$

→ Batch $V = V_0$

$$\therefore \; -r_A = k\, C_{A0}^2 (1-X)^2 \cdot C_{A0}\left(\theta_B - \frac{b}{a}X\right)$$

$$-r_A = k\, C_{A0}^3 (1-X)^2 \left(\theta_B - \frac{b}{a}X\right)$$

- for equimolar feed $\theta_B = 1$ $\left[\theta_B = \frac{N_{B0}}{N_{A0}} = \frac{0.5}{0.5} = 1\right]$
- stoichiometric feed $\theta_B = \frac{b}{a}$



Calculate the equilibrium conversion for gas phase reaction, X_e.

Consider the following **elementary** reaction with K_C=20 dm³/mol and C_{A0} = 0.2 mol/dm³.
Find X_e for a **constant volume batch reactor.**

$$2A \Leftrightarrow B$$

→write rate law then stoichiometry

$K_C = 20\ \text{dm}^3/\text{mol}$

$C_{A0} = 0.2\ \text{mol}/\text{dm}^3$

1. rate law : $-r_A = k_A\left[C_A^2 - \frac{C_B}{K_C}\right]$ $\quad K_C = \frac{k_A}{k_B}$

2. mole Balance [constant volume Batch reactor]:

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

3. Stoichiometry $\quad A \rightleftharpoons \frac{1}{2} B$

	Initial	Change	remaining
A	N_{A0}	$-N_{A0}X$	$N_A = N_{A0}(1-X)$
B	0	$\frac{1}{2}N_{A0}X$	$N_B = N_{A0}(\cancel{\theta_B}^{\,0} + \frac{1}{2}X)$

$\theta_B = 0$

$N_T = N_{A0}$ $\quad N_T = N_{A0} - \frac{1}{2}N_{A0}X$ $\quad \delta = \frac{1}{2} - 1 = -\frac{1}{2}$

* at equilibrium $-r_A = 0$ $\quad$ $0 = C_{A_e}^2 - \frac{C_{Be}}{K_C}$

$$C_{Ae} = \frac{N_{Ae}}{V} = \frac{N_{A0}(1-X_e)}{V_0} = C_{A0}(1-X_e)$$

$$C_{Be} = \frac{N_{Be}}{V} = \frac{\frac{1}{2} N_{A0} X_e}{V_0} = C_{A0}\left(\tfrac{1}{2} X_e\right)$$

4. Combine [substitute concentrations into rate law eq]

$$0 = C_{A_e}^2 - \frac{C_{Be}}{K_e}$$

$$C_{A0}^2 (1-X_e)^2 - \frac{C_{A0}\left(\frac{1}{2} X_e\right)}{K_e} = 0$$

$$C_{A0}^2 (1-X)^2 = \frac{C_{A0}\left(\frac{1}{2} X_e\right)}{K_e}$$

$$K_e \, C_{A0}^2 (1-X_e)^2 = C_{A0}\left(\tfrac{1}{2} X_e\right)$$

$$K_e = \frac{C_{A0}\left(\frac{1}{2} X_e\right)}{C_{A0}^2 (1-X_e)^2} = \frac{X_e}{2\,C_{A0}(1-X_e)^2}$$

$$20 = \frac{X_e}{2(0.2)(1-X_e)^2}$$

$X_e = 0.703$ ⇒ max conversion under these conditions

Flow System Stoichiometry Table

	Reactor feed	Change	Reactor effluent
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	$F_{B0} = F_{A0}\Theta_B$	$-\frac{b}{a}F_{A0}X$	$F_B = F_{A0}\left[\Theta_B - \frac{b}{a}X\right]$
C	$F_{C0} = F_{A0}\Theta_C$	$\frac{c}{a}F_{A0}X$	$F_C = F_{A0}(\Theta_C + \frac{c}{a}X)$
D	$F_D = F_{A0}\Theta_D$	$\frac{d}{a}F_{A0}X$	$F_D = F_{A0}(\Theta_D + \frac{d}{a}X)$
Inert	$F_i = F_{A0}\Theta_i$	no change	$F_i = F_{A0}\Theta_i$
	F_{T0}		$F_T = F_{T0} + \delta F_{A0}X$

$$\Theta = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}v_0}{C_{A0}v_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$$

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

$$\boxed{C_A = \frac{F_A}{v}}$$

→ Concentration for flow system $C_A = \frac{F_A}{v}$

→ liq phase flow system $v = v_0$ [constant volume]

- $C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0} = C_{A0}(1-X)$
- $C_B = \frac{F_B}{v} = \frac{F_{A0}(\Theta_B - \frac{b}{a}X)}{v_0} = C_{A0}(\Theta_B - \frac{b}{a}X)$

- if the rate of reaction was: $-r_A = k C_A C_B$

↳ then: $-r_A = k C_{A0}(1-X) C_{A0}(\theta_B - \frac{b}{a}X)$

$$-r_A = k C_{A0}^2 (1-X)(\theta_B - \frac{b}{a}X)$$

→ Gas Flow Systems

Ex: $N_2 + 3H_2 \rightleftharpoons 2NH_3$

4mol of reactants give 2 mols of product

* The molar flow rate will be changing as the reaction progresses

* Because equal number of moles occupy equal volumes in the gas phase at the same temperature & pressure

→ The volumetric flow rate will also change $[v \neq v_0]$

→ Combine the compressibility factor equation of state $Z = Z_0$ (to generalize, not only ideal gases)

$$C_T = \frac{P}{ZRT} \qquad F_T = C_T v$$

$$C_{T0} = \frac{P_0}{Z_0 R T_0} \qquad F_{T0} = C_{T0} v_0$$

$$v = v_0 \frac{F_T}{F_{T0}} \frac{T}{T_0} \frac{P_0}{P}$$

→ volumetric flow rate in gases is affected by T & P

* when T & P & no. of mols doesn't change $v = v_0$

→ Stoichiometry

$$C_A = \frac{F_A}{v} = \frac{F_A}{v_0\left(\frac{F_T}{F_{T0}} \frac{T}{T_0} \frac{P_0}{P}\right)} = \frac{F_{T0}}{v_0} \frac{F_A}{F_T} \frac{T_0}{T} \frac{P}{P_0} = C_{T0} \frac{F_A}{F_T} \frac{T_0}{T} \frac{P}{P_0}$$

$$C_B = C_{T0} \frac{F_B}{F_T} \frac{T_0}{T} \frac{P}{P_0}$$

→ Total molar flow Rate $F_T = F_{T0} + \delta X F_{A0}$

↳ Substituting F_T in $v = v_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0}$

$$v = v_0 \frac{(F_{T0} + \delta F_{A0} X)}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0}$$

$$\boxed{v = v_0 \left(1 + \frac{F_{A0}}{F_{T0}} \delta X\right) \frac{P_0}{P} \frac{T}{T_0}}$$ where $\varepsilon = y_{A0}\delta$ $\left(y_{A0} = \frac{F_{A0}}{F_{T0}}\right)$

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

- $C_A = \frac{F_A}{v} = C_{A0} \frac{(1-X)}{(1+\varepsilon X)} \frac{P}{P_0} \frac{T_0}{T}$
- $C_B = \frac{F_B}{v} = C_{A0} \frac{(\Theta_B - \frac{b}{a}X)}{(1+\varepsilon X)} \frac{P}{P_0} \frac{T_0}{T}$

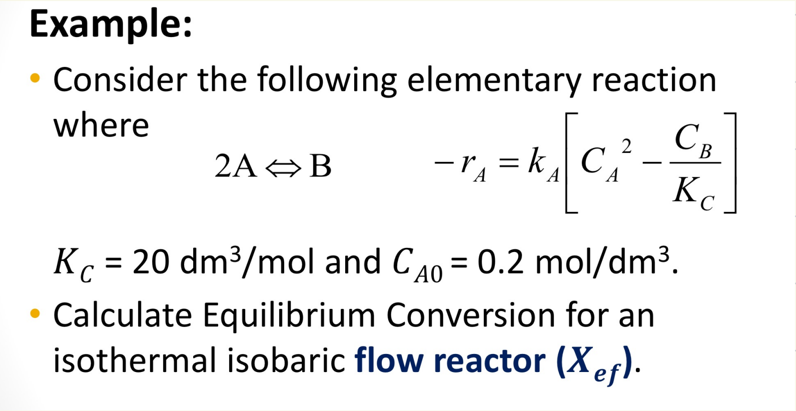
⇒ if $-r_A = k C_A C_B$

$$-r_A = k \left[C_{A0}^2 \frac{(1-X)}{(1+\varepsilon X)} \frac{(\Theta_B - \frac{b}{a} X)}{(1+\varepsilon X)} \left(\frac{P}{P_0} \frac{T_0}{T} \right)^2 \right]$$

$$\delta = \frac{\text{Change in total number of moles}}{\text{moles of A reacted}}$$

$$\varepsilon = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) \frac{F_{A0}}{F_{T0}} \quad = \delta y_{A0}$$

$$\varepsilon = \frac{\text{change in total number of moles for complete conversion}}{\text{total number of moles fed to the reactor}}$$



Example:

- Consider the following elementary reaction where

$$2A \Leftrightarrow B \qquad -r_A = k_A\left[C_A^2 - \frac{C_B}{K_C}\right]$$

K_C = 20 dm³/mol and C_{A0} = 0.2 mol/dm³.

- Calculate Equilibrium Conversion for an isothermal isobaric **flow reactor (X_{ef})**.

$C_{A0} = 0.2$ mol / dm³

$K_C = 20$ dm³/mol

1. Rate law $\quad -r_A = k_A \left[C_A^2 - \frac{C_B}{K_C} \right]$

2. Stoichiometry $\quad A \rightarrow \frac{1}{2} B$

	Feed	change	Remaining
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	0	$F_{A0}(\frac{1}{2}X)$	$F_B = F_{A0}(\theta_B + \frac{1}{2}X)$

$\theta_B = 0$

$F_{T_0} = F_{A0}$

$F_T = F_{T_0} + \delta F_{A0} X$

$F_T = F_{A0} - \frac{1}{2} F_{A0} X$

$\delta = \frac{1}{2} - 1 = -\frac{1}{2}$

$F_T = F_{A0}\left(1 - \frac{1}{2}X\right)$

→ Isothermal $\quad T = T_0$

→ Isobaric $\quad P = P_0$

$$v = v_0 (1 + \varepsilon X)$$

$$C_A = \frac{F_A}{v} = C_{A0}\,\frac{(1-X)}{(1+\varepsilon X)}$$

$$C_B = \frac{F_B}{v} = C_{A0}\,\frac{(\Theta_B + \frac{1}{2}X)}{(1+\varepsilon X)} = \frac{C_{A0}\,X}{2(1+\varepsilon X)}$$

→ Subtitute in rate Law:

$$-r_A = k\left[\left(C_{A0}\,\frac{(1-X)}{(1+\varepsilon X)}\right)^2 - \frac{C_{A0}\,X}{2(1+\varepsilon X)K_C}\right]$$

$\varepsilon = y_{A0}\,\delta$ ⇒ pure A in feed $y_{A0} = 1$

$\delta = -\frac{1}{2}$

$\varepsilon = -\frac{1}{2}$

→ At equilibrium $-r_A = 0$

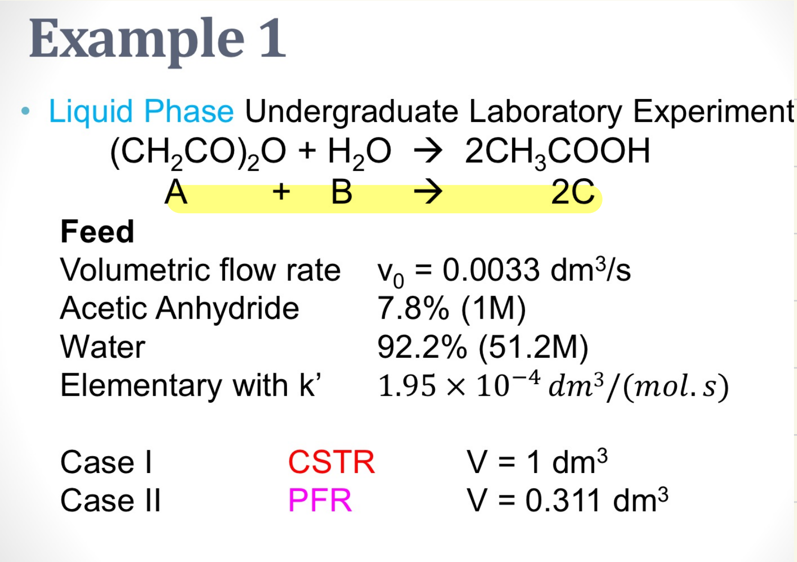
$$0 = \left(C_{A0}\,\frac{(1-X)}{(1+\varepsilon X)}\right)^2 - \frac{C_{A0}\,X}{2(1+\varepsilon X)\,K_C}$$

$$\frac{2K_C}{C_{A0}} \times \left(\frac{C_{A0}(1-X)}{(1+\varepsilon X)}\right)^2 = \frac{C_{A0}\,X}{2(1+\varepsilon X)K_C} \times \frac{2K_C}{C_{A0}}$$

$$2\,K_C \cdot C_{A0} \cdot \frac{(1-x)^2}{(1+\varepsilon x)^2} = \frac{x}{(1+\varepsilon X)}$$

$$2K_C\,C_{A0} = \frac{X_e\,(1+\varepsilon X)}{(1-x)^2}$$

$$2(20)(0.2) = \frac{X_e\,(1-\frac{1}{2}X_e)}{(1-X_e)^2} \qquad X_e = 0.757$$



Example 1

- Liquid Phase Undergraduate Laboratory Experiment

$(CH_2CO)_2O + H_2O \rightarrow 2CH_3COOH$

$A + B \rightarrow 2C$

Feed

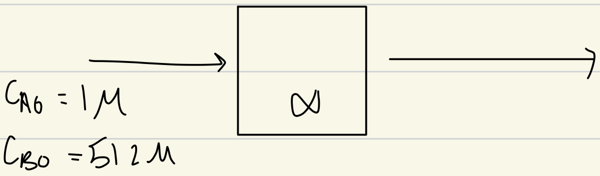
Volumetric flow rate	$v_0 = 0.0033\ dm^3/s$
Acetic Anhydride	7.8% (1M)
Water	92.2% (51.2M)
Elementary with k’	$1.95 \times 10^{-4}\ dm^3/(mol.s)$

Case I	CSTR	$V = 1\ dm^3$
Case II	PFR	$V = 0.311\ dm^3$

Case 1 CSTR

$V = 1\ dm^3$ (liq $v_0 = v$)

$v_0 = 0.0033\ dm^3/s$



1. mole Balance CSTR

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

2. Elementary Rate law

$$-r_A = kC_AC_B$$

3. Stoichiometry

$$C_A = \frac{F_{A0}}{v_0} = \frac{F_{A0}(1-X)}{v_0} = C_{A0}(1-X)$$

$$C_B = \frac{F_{B0}}{v} = \frac{F_{A0}(\theta_B - X)}{v_0} = C_{A0}(\theta_B - X)$$

$$\theta_B = \frac{51.2}{1} = 51.2$$

$$\therefore C_B = C_{A0}(51.2 - X) \approx C_{A0}(51.2) \approx C_{B0}$$

	Entering	Change	Remaining
A	F_{A0}	$-F_{A0} X$	$F_A = F_{A0}(1-X)$
B	$F_{B0}\ \theta_B$	$-F_{A0} X$	$F_B = F_{A0}(\theta_B - X)$
C	0	$2F_{A0} X$	$F_C = F_{A0}(\theta_C + 2X)$

4. Combine

$$-r_A = \underbrace{k' C_{B0}}_{k}\ C_{A0}(1-X)$$

$$-r_A = k\, C_{A0}(1-X)$$

→ into mole Balance

$$V = \frac{F_{A0}\ X}{k\, C_{A0}(1-X)}$$

$F_{A0} = v_0 C_{A0}$

$$V = \frac{v_0\ \cancel{C_{A0}}\ X}{k\ \cancel{C_{A0}}(1-X)}$$

$$\frac{V}{v_0} = \frac{X}{k(1-X)}$$

$$\tau = \frac{V}{v_0} = \frac{1\ dm^3}{0.0033\ dm^3/s} = 303.03 = \frac{X}{1.94\times10^{-4}(51.2)(1-X)}$$

$$X = 0.75$$

Case 2: PFR

1. Mole Balance

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

2. Rate Law

$$-r_A = k C_A C_B$$

3. Stoichiometry

	Entering	Change	Remaining
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	$F_{A0}\Theta_B$	$-F_{A0}X$	$F_B = F_{A0}(51.2 - X)$
C	0	$2F_{A0}X$	$F_C = F_{A0}(\Theta_C - 2X)$

$$C_A = \frac{F_A}{v_0} = \frac{F_{A0}(1-X)}{v_0} = C_{A0}(1-X)$$

$$C_B = \frac{F_B}{v_0} = \frac{F_{A0}(51.2 - X)}{v_0} \approx C_{A0}(51.2) \approx C_{B0}$$

4. Combine

$$-r_A = \underbrace{k' C_{B0}}_{\Rightarrow k} C_{A0}(1-X)$$

$$\frac{dX}{dV} = \frac{k \cancel{C_{A0}}(1-X)}{\cancel{C_{A0}} v_0}$$

$$\frac{dX}{dV} = \frac{k(1-X)}{v_0}$$

$$dV\, k(1-X) = dX\, v_0$$

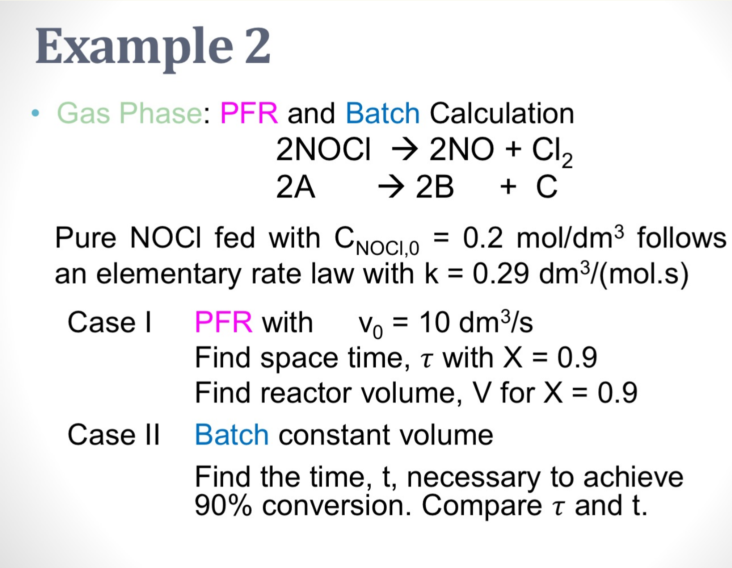
$$\frac{k}{v_0}\, dV = \frac{1}{(1-X)}\, dX$$

Integrate →

$$k\,\frac{V}{v_0} = -\ln(1-X)$$

$$k\tau = -\ln(1-X)$$

$$51.2 \times 1.94\times10^{-4} \times \frac{0.311}{0.0033} = -\ln(1-X) \qquad X = 0.61$$



Example 2

- Gas Phase: PFR and Batch Calculation

$$2NOCl \rightarrow 2NO + Cl_2$$
$$2A \rightarrow 2B + C$$

Pure NOCl fed with $C_{NOCl,0} = 0.2$ mol/dm^3 follows an elementary rate law with $k = 0.29$ dm^3/(mol.s)

Case I PFR with $v_0 = 10$ dm^3/s
Find space time, τ with $X = 0.9$
Find reactor volume, V for $X = 0.9$

Case II Batch constant volume
Find the time, t, necessary to achieve 90% conversion. Compare τ and t.

$v_0 = 10\ dm^3/s$ $C_{A0} = 0.2\ mol/dm^3$

$k = 0.29\ dm^3/mol.s$

$T = T_0$ $P = P_0$ $V = ?$ $X = 0.9$

Case 1. PFR

1 mole Balance

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

2. Rate law [Elementary]

$$-r_A = k C_A^2$$

3. Stoichiometry

$$2A \rightarrow 2B + C$$
$$A \rightarrow B + \tfrac{1}{2}C$$

$$v = v_0 \left(\frac{F_T}{F_{T0}} \cancel{\frac{P_0}{P}} \cancel{\frac{T}{T_0}} \right)$$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}$$

4 Combine

$$-r_A = k \left[C_{A0}^2 \frac{(1-X)^2}{(1+\varepsilon X)^2} \right]$$

$$\frac{dX}{dV} = \frac{k\, C_{A0}^2 (1-X)^2}{F_{A0}(1+\varepsilon X)^2}$$

$F_{A0} = C_{A0} v_0$

$$\frac{dX}{dV} = k\,\frac{C_{A0}^{\cancel{2}}\,(1-X)^2}{\cancel{C_{A0}}\,v_0\,(1+\varepsilon X)^2}$$

$$k\,C_{A0}\,(1-X)^2\,dV = v_0\,(1+\varepsilon X)^2\,dX$$

$$\frac{k\,C_{A0}}{v_0}\,dV = \frac{(1+\varepsilon X)^2}{(1-X)^2}\,dX \qquad \Rightarrow \text{Integrate}$$

$$\frac{k\,C_{A0}\,V}{v_0} = 2\varepsilon\,(1+\varepsilon X)\ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon)^2 X}{1-X}$$

$\varepsilon = y_{A0}\,\delta \qquad = 1(1/2) = 1/2$

$\delta = 1/2 + 1 - 1 \quad = 1/2$

$$k\,C_{A0}\,\tau = 2(\tfrac{1}{2})(1+\tfrac{1}{2}\cdot 0.9)\ln(1-0.9) + (\tfrac{1}{2})^2 0.9 + \frac{(1+\tfrac{1}{2})^2 0.9}{1-0.9}$$

$$k\,C_{A0}\,\tau = 17.14$$

$$\tau = 295\ \text{s} \qquad = \frac{V}{v_0}$$

$$V = 2954\ \text{dm}^3$$

Case 2: Batch $v = v_0$

1. Mole Balance $\quad \dfrac{dX}{dt} = \dfrac{-r_A V}{N_A} \qquad C_{A0} = \dfrac{N_{A0}}{V_0}$

$$\frac{dX}{dt} = \frac{-r_A}{C_{A0}}$$

2. Rate Law $\quad -r_A = kC_A^2$

3. Stoichiometry

$V = V_0$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)$$

4. Combine

$$-r_A = k\, C_{A0}^2 (1-x)^2$$

$$\frac{dX}{dt} = \frac{k\, C_{A0}^{\cancel{2}} (1-X)^2}{\cancel{C_{A0}}}$$

$$dX = k\, C_{A0} (1-X)^2\, dt$$

$$\frac{1}{(1-X)^2}\, dX = k\, C_{A0}\, dt$$

$$\frac{X}{(1-X)} = k\, C_{A0}\, t$$

$$\frac{0.9}{(1-0.9)} = 0.29(0.2)\, t$$

$t = 155\,s$

Chapter 5: Isothermal Reactor Design

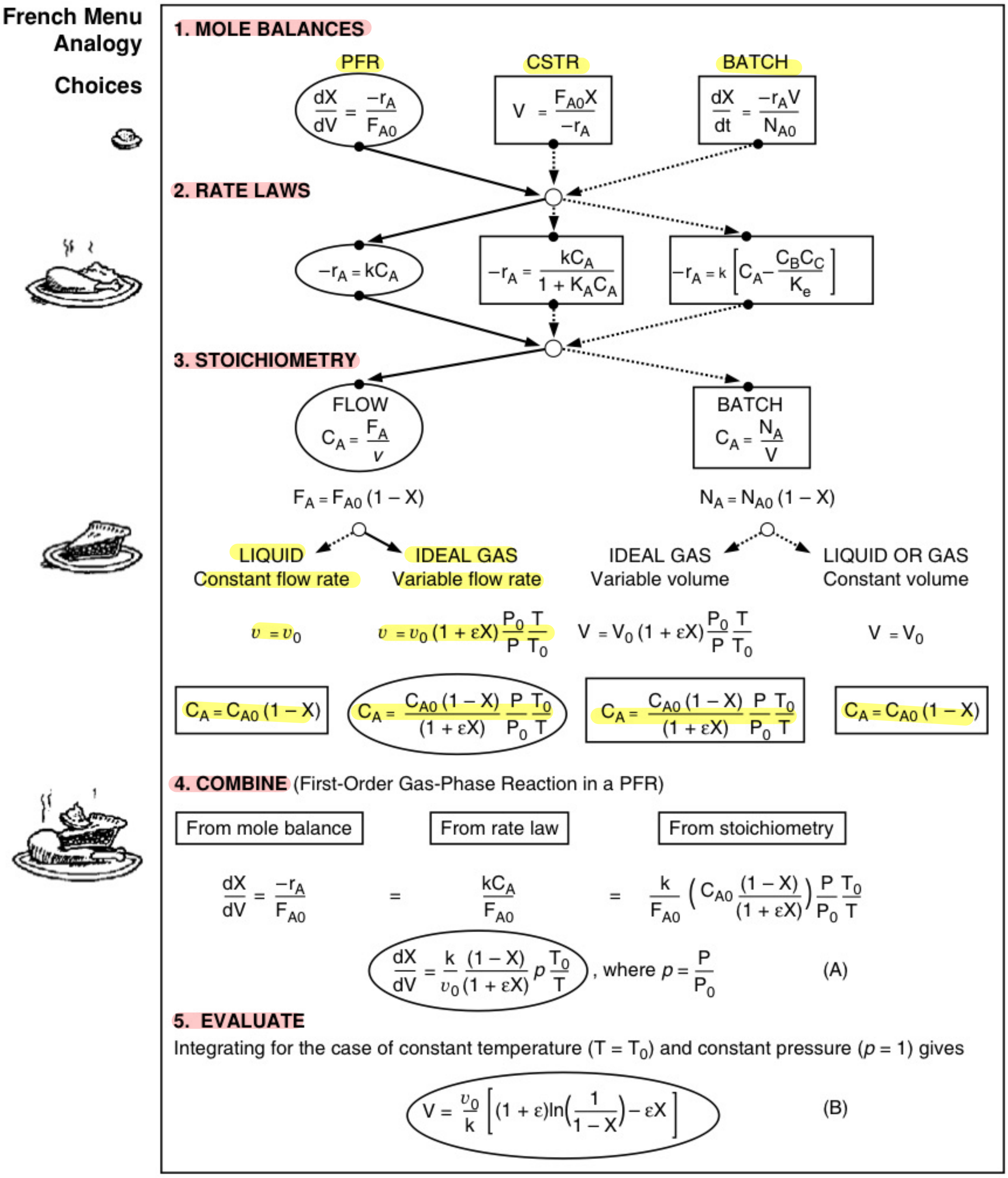


Figure 5-2 Algorithm for isothermal reactors.

1- Batch Reactors: [Liquid]

- no inflow or outflow
- perfect mixing
- incompressible ⇒ Constant volume $V = V_0$

$$2A \longrightarrow B + C$$

Algorithim:

1- Mole Balance $\frac{dX}{dt} = \frac{-r_{A0} V_0}{N_{A0}}$ $C_{A0} = \frac{N_{A0}}{V_0}$

$$\frac{dX}{dt} = \frac{-r_{A0}}{C_{A0}}$$

2. Rate Law $-r_A = K C_A^2$

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

4. Combine $-r_A = K C_{A0}^2 (1-X)^2$

$$\frac{dX}{dt} = \frac{K C_{A0}^2 (1-X)^2}{C_{A0}} \Rightarrow \frac{dX}{dt} = k C_{A0} (1-X)^2$$

5. Evaluate $dX = k C_{A0} (1-X)^2 dt$

$$\frac{dX}{(1-X)^2} = K C_{A0} dt$$

$$\frac{X}{1-X} = K C_{A0} t \qquad t = \frac{X}{(1-X) K C_{A0}}$$

CSTR

1. mole Balance $V = \frac{F_{A0} X}{-r_A}$ $\quad F_{A0} = C_{A0} v_0$

$$V = \frac{C_{A0} X v_0}{-r_A} \qquad \tau = \frac{C_{A0} X}{-r_A}$$

2. Rate law $-r_A = k C_A$

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

4. combine $-r_A = k C_{A0}(1-X)$

$$\tau = \frac{C_{A0} X}{k C_{A0}(1-X)} = \frac{X}{k(1-X)}$$

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

→ to increase τk . 1. increase T to increase K ⇒ ↑X

2. increase τ by increasing Volume $\uparrow \tau = \frac{\uparrow V}{v_0}$ ⇒ ↑X

3. decreasing volumetric flow rate $\uparrow \tau = \frac{V}{\downarrow v_0}$ ⇒ ↑X

→ Second order Reaction in CSTR

Rate law $-r_A = k C_A^2$

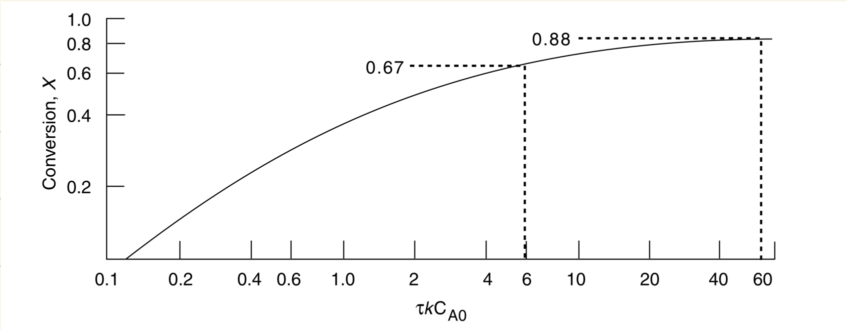
Stoichiometry $C_A = C_{A0}(1-X)$

combine $V = \frac{C_{A0} v_0 X}{k C_{A0}^2 (1-X)^2} \qquad \tau = \frac{X}{C_{A0}(1-X)^2}$

$$X = \frac{(1+2\tau k C_{A0}) - \sqrt{1+4\tau k C_{A0}}}{2\tau k C_{A0}}$$

Damkohler number $Da = \tau k C_{A0}$

$$\therefore \quad X = \frac{(1+2Da) - \sqrt{1+4Da}}{2Da}$$



→ At high conv (67%), Increase in reactor Volume will only increase conversion upto (88%)

→ CSTR operates under the condition of the lowest reactant concentration

The Damkohler number gives a quick estimate of the degree of conversion that can be achieved in continous flow reactor

$$Da = \frac{-r_{A0} V}{F_{A0}} = \frac{\text{Rate of reaction at enterance}}{\text{Entering flow rate of A}}$$

→ first order reaction $Da = \tau k$

→ second order reaction $Da = \tau k C_{A0}$

if $Da < 0.1$ $X < 0.1$

if $Da > 10$ $X > 0.9$

CSTR's in Series $[\,v = v_0\,]$

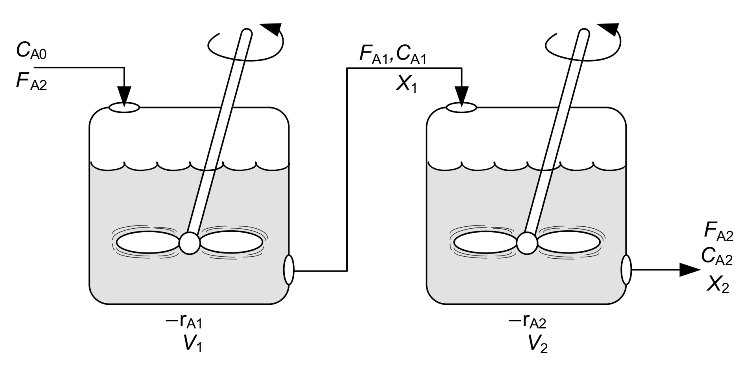


Figure 5-5 Two CSTRs in series.

→ effluent from first reactor

$$C_{A1} = \frac{C_{A0}}{1+\tau k}$$

→ mole Balance on reactor 2

$$V = \frac{F_{A1} - F_{A2}}{-r_{A2}} = \frac{v_0\,(C_{A1} - C_{A2})}{-r_{A2}}$$

→ Concentration of second reactor

$$C_{A2} = \frac{C_{A1}}{1+\tau k} = \frac{C_{A0}}{(1+\tau k)(1+\tau k)}$$

* same size $\tau_1 = \tau_2 = \tau_3$

same temp $k_1 = k_2 = k_3$

→ n CSTR's in Series

$$C_{An} = \frac{C_{A0}}{(1+\tau k)^n} = \frac{C_{A0}}{(1+Da)^n}$$

→ The rate of disapperance of A

$$-r_A = k\,C_{An} = k\,\frac{C_{A0}}{(1+Da)^n}$$

** when entering molar flow rate is divided into two CSTR's in parallel ⇒ overall conversion is same as single CSTR , for two CSTR's in series ⇒ conversion is greater than single CSTR

True for isothermal reactions with power rate law with reaction orders > zero.

Tubular Reactors

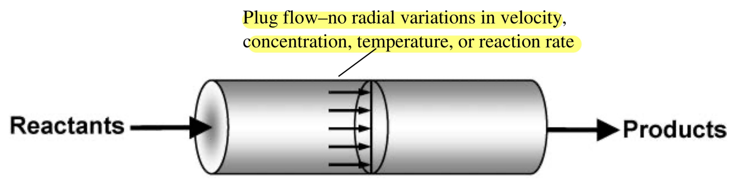


Figure 1-9 (Revisited) tubular reactor.

→ $\frac{dX}{dV} F_{A0} = -r_A$: must be used for pressure drop

$V = \int_0^X \frac{F_{A0}}{-r_A} dX$: if no pressure drop

Ex: liq phase no pressure drop PFR reaction [Algorithim]

$2A \rightarrow B$

1. Mole Balance $V = \int_0^X \frac{F_{A0}}{-r_A} dX$

2. Rate law $-r_A = k C_A^2$

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

4. Combine $-r_A = k C_{A0}^2 (1-X)^2$

$$V = \int_0^X \frac{v_0 C_{A0}}{k C_{A0}^2 (1-X)^2} dX \Rightarrow \frac{v_0}{k C_{A0}} \int_0^X \frac{dX}{(1-X)^2}$$

$$\boxed{V = \frac{v_0}{k C_{A0}} \left[\frac{X}{1-X} \right]}$$

* k is outside the integral ⇒ isothermal

$$\tau = \frac{V}{v_0} = \frac{X}{k C_{A0}(1-X)}$$

$$\boxed{X = \frac{\tau k C_{A0}}{1 + \tau k C_{A0}}} = \frac{Da_2}{1 + Da_2}$$

Ex: gas phase no pressure drop PFR reaction [Algorithm]

1. mole Balance:

$$V = \int_0^X \frac{F_{A0}\, dX}{-r_A}$$

2. Rate Law $-r_A = k C_A^2$

3. Stoichiometry $v = v_0(1+\varepsilon X)\left(\cancel{\frac{T}{T_0}}\right)\left(\cancel{\frac{P_0}{P}}\right)$ isothermal, isobaric

$$C_A = \frac{F_A}{v} = \frac{F_A}{v_0(1+\varepsilon X)} = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = \frac{C_{A0} v_0 (1-X)}{v_0(1+\varepsilon X)} = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}$$

→ $\varepsilon = y_{A0}\,\delta$

4. combine $-r_A = k \dfrac{C_{A0}^2 (1-X)^2}{(1+\varepsilon X)^2}$

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

$$\boxed{V = \frac{v_0}{k C_{A0}}\left[2\varepsilon(1+\varepsilon)\ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon X)^2 X}{1-X}\right]}$$

Effect of ε on conversion

→ The effect of change in the total number of moles in the gas phase on the relationship between conversion & volume. [for constant T & P]

$$v = v_0 (1 + \varepsilon X)$$

Case 1: $\varepsilon = 0$ $\delta = 0$

→ no change in number of moles in the reaction ex: $A \rightarrow B$ $\delta = 1 - 1 = 0$

$\varepsilon = y_{A0}\delta = 0$

→ The fluid moves through the reactor at constant volumetric flow rate

$v = v_0$, as the conversion increases.

case 2: $\varepsilon < 0$ $\delta < 0$

→ Decrease in the number of moles in the gas phase

$$2A \rightarrow B$$

take A as Basis

$$A \rightarrow \tfrac{1}{2}B$$

$\delta = \frac{1}{2} - 1 = -\frac{1}{2}$

$\varepsilon = 1(-\frac{1}{2}) = -\frac{1}{2}$

$$v = v_0 (1 - 0.5X) \quad \downarrow v_0$$

→ The volumetric gas flow rate decreases & the conversion increases

→ Gas molecules will have longer residence time resulting in higher conversion

$$\boxed{\frac{V}{\downarrow v_0} = \uparrow \tau}$$

[higher residence time, ↑X]

Case 3: $\varepsilon > 0$ $\delta > 0$

→ Increase in the total number of moles in the gas phase

$$A \rightarrow 2B$$

$\delta = 2 - 1 = 1$

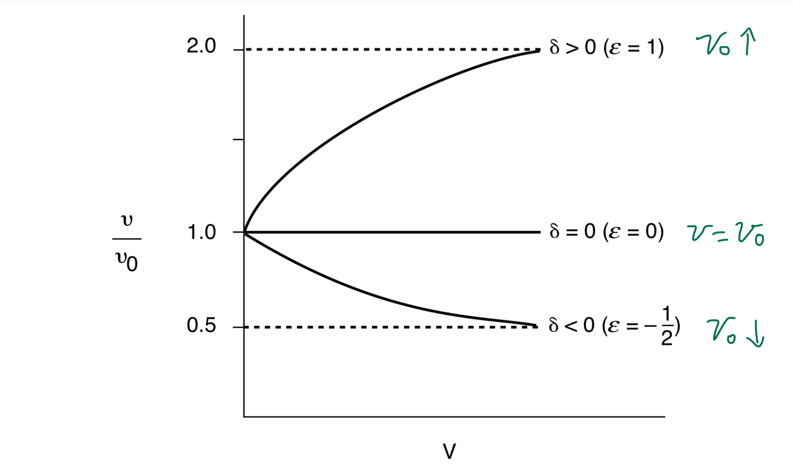
$\varepsilon = 1(1) = 1$

$$v = v_0 (1 + X) \quad \uparrow v_0$$

→ The volumetric flow rate will increase as the conversion increases

→ The molecules would spend less time in the reactor, resulting in smaller residence time → less conversion

$$\boxed{\downarrow \tau = \frac{V}{v_0 \uparrow}}$$ [lower residence time, ↓ X]



Pressure Drop in Reactors

→ The effect of pressure drop on the rate of reaction when sizing a liq reactor → negligable (incompressible)

→ In gas phase, the concentration of the reacting species is proportional to the total pressure.

Pressure Drop & the rate law

$$C_i = C_{A0}\left[\frac{\theta_i + \nu_i X}{1 + \varepsilon X}\right]\frac{T_0}{T}\,\frac{P}{P_0}$$

$\theta_i = \frac{F_{i0}}{F_{A0}}$ $\varepsilon = \delta y_{A0}$ ν_i = stoichiometric coefficient

Ex: $2A \longrightarrow B$

1. mole Balance $F_{A0}\frac{dX}{dW} = -r_A'$ [Differential form of mole Balance]

2. Rate Law $\quad -r_A' = k C_A^2$

3. Stoichiometry

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

4. Combine & assume isothermal

$$-r_A' = k\, C_{A0}^2 \frac{(1-X)^2}{(1+\varepsilon X)^2}\left(\frac{P}{P_0}\right)^2$$

$$\frac{dX}{dW} = \frac{k\, C_{A0}^2}{F_{A0}}\frac{(1-X)^2}{(1+\varepsilon X)^2}\left(\frac{P}{P_0}\right)^2$$

* We now need to relate the pressure drop to the catalyst weight in order to determine the conversion as a function of the catalyst weight.

* The majority of gas phase reactions are catalyzed by passing the reactant through a packed bed of catalyst particles

Eurgen Equation

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

ϕ = Porosity $= \dfrac{\text{Volume of Void}}{\text{Tot bed volume}}$

D_p = Diameter of particle in bed

μ = Viscosity of gas passing through the bed

ρ = gas density

$G = \rho u$ = superficial mass velocity

$(1-\phi)$ = fraction of solids

→ The only parameter that varies with pressure is the gas density ρ.

→ PBR operates at steady state :

$$\dot{m}_0 = \dot{m}$$

$$\rho_0 v_0 = \rho v$$

→ $v = v_0 \frac{T}{T_0} \frac{P_0}{P} \frac{F_T}{F_{T0}}$

→ $\rho = \rho_0 \frac{v_0}{v} = \rho_0 \frac{T_0}{T} \frac{P}{P_0} \frac{F_{T0}}{F_T}$

→ combine:

$$\frac{dP}{dz} = \underbrace{\frac{-G}{g_c D_p \rho_0} \left(\frac{1-\phi}{\phi^3}\right) \left[\frac{150(1-\phi)\mu}{D_p} + 1.75 G\right]}_{\beta_0} \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

β_0 → constant that depends only on the properties of the packed bed (atm/ft) or (Pa/m)

$$\frac{dP}{dz} = \beta_0 \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

→ The catalyst weight up to a distance z down the reactor :

$$W = z A_c \rho_c = \underbrace{z A_c (1-\phi)}_{\text{Volume of solids}} \rho_c$$ → density of solid catalyst

$$\rho_b = (1-\phi)\rho_c$$ → bulk density

→ Rewrite in terms of catalyst weight

$$\frac{dP}{dW} = \frac{-\beta_0}{A_c(1-\phi)\rho_c} \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

→ let $\boxed{\alpha = \frac{2\beta_0}{A_c(1-\phi)\rho_c} \frac{1}{P_0}}$ → & $p = \frac{P}{P_0}$

$$\frac{dy}{dw} = -\frac{\alpha}{2y} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

$$\Rightarrow \boxed{\frac{d(P/P_0)}{dw} = -\frac{\alpha}{2} \frac{1}{(P/P_0)} \frac{T}{T_0} (1+\varepsilon X)}$$ for single reactions

* when ε is negative ΔP will be less [higher pressure] than that for $\varepsilon = 0$

* When ε is positive ΔP will be greater [lower pressure] than that for $\varepsilon = 0$

→ for isothermal reactions:

$$\frac{d(P/P_0)}{dw} = -\frac{\alpha}{2} \frac{1}{P/P_0} (1+\varepsilon X)$$

For $\varepsilon = 0$

$$\frac{dy}{dw} = \frac{-\alpha}{2y} (1+\varepsilon X)$$

→ when $W=0$ & $y=1$

$$dy^2 = -\alpha \, dW$$

$$y^2 = 1 - \alpha W$$

$$y = (1-\alpha W)^{\frac{1}{2}}$$

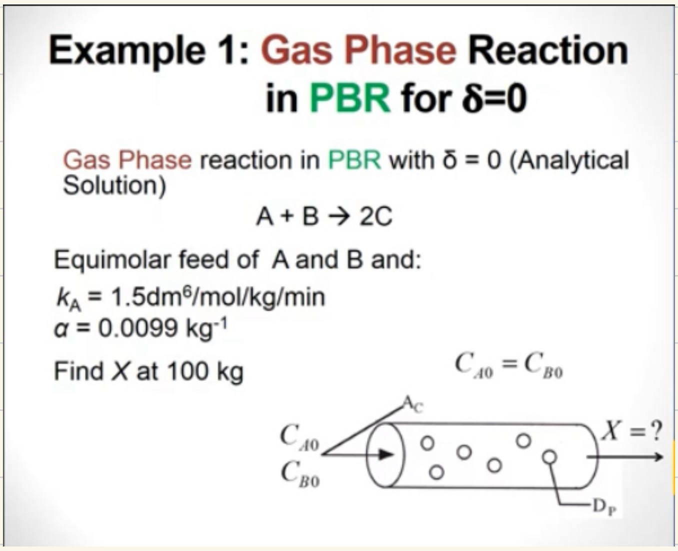
* isothermal $\varepsilon = 0$

$$p = \frac{P}{P_0} = y = (1-\alpha W)^{\frac{1}{2}}$$

* Conversion when no ΔP higher than conversion with ΔP

* Concentration when no ΔP < concentration with ΔP

* when P decreases, volumetric flow rate increases, less residence time ⇒ less conversion



Example 1: Gas Phase Reaction in PBR for δ=0

Gas Phase reaction in PBR with δ = 0 (Analytical Solution)

A + B → 2C

Equimolar feed of A and B and:

$k_A = 1.5 dm^6/mol/kg/min$

$\alpha = 0.0099\ kg^{-1}$

Find X at 100 kg

$C_{A0} = C_{B0}$

Equimolar $F_{A0} = 0.5$

1. mole Balance $\quad \dfrac{dX}{dW} = \dfrac{-r_A'}{F_{A0}}$

2. Rate Law $\quad -r_A' = k C_A C_B$

3. Stoichiometry

$$C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)} \frac{P}{P_0} \qquad \varepsilon = y\delta = 0$$

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

$$C_B = C_{A0}\left(\frac{\theta_B + \nu_i X}{1+\varepsilon X}\right)\frac{P}{P_0} \qquad \theta_B = 1 \quad \nu_i = -1$$

$\varepsilon = 0$

$$C_B = C_{A0}(1-X)\,y$$

4. y & w relationship

$$\frac{dy}{dW} = -\frac{\alpha}{2y} \Rightarrow 2y\,dy = -\alpha\,dW$$

Integrate

$$y^2 = (1-\alpha W)$$

$$W = 0 \quad y = 1 \Rightarrow \boxed{y = (1-\alpha W)^{1/2}}$$

↳ only when $\delta = 0$

$\varepsilon = 0$

5.combine $-r_A' = kC_{A0}^2(1-x)^2y^2 \rightarrow kC_{A0}^2(1-X)^2(1-\alpha W)$

$$\frac{dX}{dW} = \frac{kC_{A0}^2(1-X)^2(1-\alpha W)}{F_{A0}}$$

seperate & Integrate

$$F_{A0}\,dX = kC_{A0}^2(1-X)^2(1-\alpha W)\,dW$$

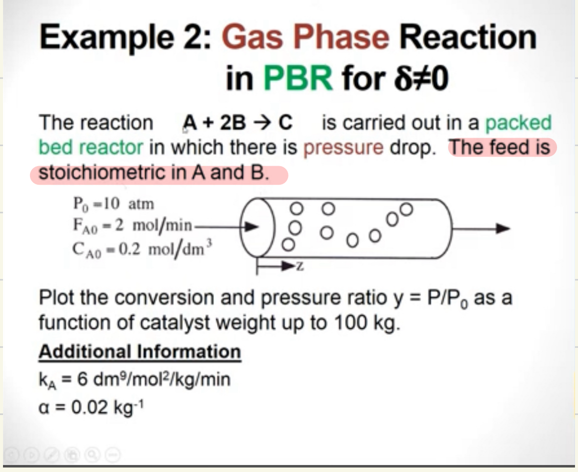
$$\frac{dX}{(1-X)^2} = \frac{kC_{A0}^2}{F_{A0}}\left[1-\alpha W\,dW\right]$$

$$\frac{X}{1-X} = \frac{kC_{A0}^2}{F_{A0}}\left(W-\frac{\alpha W^2}{2}\right)$$

Boundary conditions: $W=0$ $X=0$, $W=W$ $X=X$

$$\frac{X}{1-X} = \frac{1.5(0.1)^2}{0.5}\left(100-\frac{0.0099(100)^2}{2}\right)$$

$X=0.6$



Example 2: Gas Phase Reaction in PBR for δ≠0

The reaction $A + 2B \rightarrow C$ is carried out in a packed bed reactor in which there is pressure drop. The feed is stoichiometric in A and B.

Plot the conversion and pressure ratio $y = P/P_0$ as a function of catalyst weight up to 100 kg.

Additional Information

$k_A = 6$ dm^9/mol^2/kg/min

$\alpha = 0.02$ kg^{-1}

$$\frac{C_{A0}}{C_{B0}} = \frac{1}{2}$$

1. mole Balance $\frac{dX}{dW} = \frac{-r_A'}{F_{A0}}$

2 Rate Law $-r_A' = k C_A C_B^2$

3. Stoichiometry $C_A = C_{A0} \frac{(1-X)}{(1+\varepsilon X)} y$

$C_B = C_{A0} \frac{(\theta_B - 2X)}{(1+\varepsilon X)} y$ $\theta_B = 2$

4 Relationship $\frac{dy}{dW} = -\frac{\alpha}{2y} (1+\varepsilon X)$

$f = \frac{v}{v_0} = \frac{(1+\varepsilon X)}{y}$

$\varepsilon = y_{A0} \delta = \frac{1}{2+1} [1-2-1] = \left[\frac{1}{3}\right] -2 = -\frac{2}{3}$

Boundary conditions: $W=0$ $X=0$ $y=1$, $W=100$

→ Solve in polymath ($\varepsilon \neq 0$)

→ what if we decrease the catalyst size by a factor of 4 & increase the entering pressure by a factor of 3

$$\alpha = \frac{2}{A_c(1-\phi)\rho_c P_0} \qquad \beta_0 = \frac{2}{A_c(1-\phi)\rho_c P_0}\left[\frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3}\left[\underbrace{\frac{150(1-\phi)\mu}{D_p}}_{\text{Laminar}} + \underbrace{1.75G}_{\text{Turbulent}}\right]\right]$$

→ Using Avg molecular weight of gas & Ideal gas Law

$$\rho_0 = \frac{1}{MW}\,\frac{P_0}{RT_0}$$

→ Substitute:

$$\alpha = \frac{2\,R\,T\,MW}{A_c\,\rho_c\,g_c\,P_0^2\,D_p\,\phi^3}\,G\left[\frac{150(1-\phi)\mu}{D_p} + 1.75G\right]$$

1) If Laminar flow is dominant

* we only consider change in G, D_p, A_c, P_0, T_0

$$\alpha = \frac{G\,T_0}{A_c\,D_p^2\,P_0^2}$$

$$\frac{\text{Case 1}}{\text{case 2}} \qquad \alpha_2 = \alpha_1\left(\frac{G_2}{G_1}\right)\left(\frac{T_{02}}{T_{01}}\right)\left(\frac{A_{c1}}{A_{c2}}\right)\left(\frac{D_{p1}}{D_{p2}}\right)^2\left(\frac{P_{01}}{P_{02}}\right)^2$$

2) If Turbulent flow is dominent

$$\alpha = \frac{G^2\,T_0}{A_c\,P_0^2\,D_p}$$

$$\frac{\text{case 1}}{\text{case 2}} \qquad \alpha_2 = \alpha_1\left(\frac{G_2}{G_1}\right)^2\left(\frac{T_{02}}{T_{01}}\right)\left(\frac{A_{c1}}{A_{c2}}\right)\left(\frac{P_{01}}{P_{02}}\right)^2\left(\frac{D_{p1}}{D_{p2}}\right)$$

→ if the mass flow rate $\dot{m}$ is the same for two cases $G = \frac{\dot{m}}{A_C}$

$$\alpha_2 = \alpha_1 \left(\frac{A_{C1}}{A_{C2}}\right)^3 \left(\frac{T_{02}}{T_{01}}\right)\left(\frac{P_{01}}{P_{02}}\right)^2 \left(\frac{D_{P1}}{D_{P2}}\right)$$

Ex: Increase P_0 by factor of 3 & Decrease D_P by factor of 4

$P_{02} = 3P_{01}$ $D_{P2} = \frac{1}{4} D_{P1}$

① Laminar

$$\alpha = \frac{G\, T_0}{A_c\, P_0^2\, D_P^2}$$

$$\alpha_2 = \alpha_1 \left(\frac{P_{01}}{3P_{01}}\right)^2 \left(\frac{4D_{P1}}{D_{P1}}\right)^2 = \frac{16}{9}\alpha_1$$

② Turbulent

$$\alpha = \frac{G\, T_0}{A_c\, P_0^2\, D_P}$$

$$\alpha_2 = \alpha_1 \left(\frac{P_{01}}{3P_{01}}\right)^2 \left(\frac{4D_{P1}}{D_{P1}}\right) = \frac{4}{9}\alpha_1$$

Chapter 6 : Isothermal reactor Design : [Moles & Molar flow rates]

The molar flow rate Balance Algorithim

→ Membrane reactors & multiple reactions taking place in the gas phase ⇒ necessary to use molar flow rates instead of conversion

→ Modify the algorithim by using Concentrations for liquids & molar flow rates for gases as dependent variables

* In molar Flow rate & concentration Algorithim → mole Balance on each & every species

Algorithim

1. Mole Balance on all species present
2. Rate Law
3. Relative rates of reaction
4. Combine

* Liquid phase

→ No change in either volume V or volumetric flow rate v_0 ⇒ Concentration is the preferred design variable

$$aA + bB \longrightarrow cC + dD$$

Relative rates of Reaction $\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}$ * used to couple the mole Balances

$$A + 2B \rightleftharpoons C$$

1. Mole Balance on each species: $\frac{dF_A}{\partial V} = r_A$ $\quad \frac{dF_B}{\partial V} = r_B$ $\quad \frac{dF_C}{\partial V} = r_C$

2. Rate Law $\quad -r_A = k\left[C_A C_B^2 - \frac{C_C}{K_C}\right]$

3. Rates of reaction $\quad \frac{r_A}{-1} = \frac{r_B}{-2} = \frac{r_C}{1}$

$$r_B = 2r_A \qquad r_C = -r_A$$

4. Stoichiometry [conc. in terms of molar flow rates]

→ Gas phase: $\quad C_A = C_{T0} \frac{F_A}{F_T} \frac{T_0}{T} \frac{P}{P_0}$

$$C_B = C_{T0} \frac{F_B}{F_T} \frac{T_0}{T} \frac{P}{P_0}$$

→ liquid phase $\quad$ Use concentrations C_A, C_B

5. Gas phase pressure Drop $\quad \frac{dP}{dW} = -\frac{\alpha}{2p}\left(\frac{T}{T_0}\right)\left(\frac{P_0}{P}\right) \qquad p = \frac{P}{P_0}$

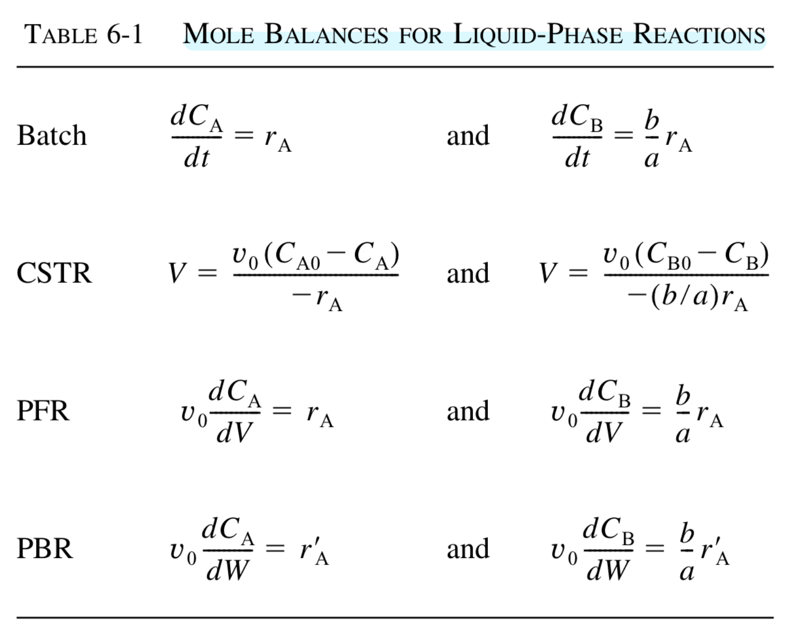


TABLE 6-1 MOLE BALANCES FOR LIQUID-PHASE REACTIONS

Batch	$\frac{dC_A}{dt} = r_A$	and	$\frac{dC_B}{dt} = \frac{b}{a} r_A$
CSTR	$V = \frac{v_0(C_{A0} - C_A)}{-r_A}$	and	$V = \frac{v_0(C_{B0} - C_B)}{-(b/a) r_A}$
PFR	$v_0 \frac{dC_A}{dV} = r_A$	and	$v_0 \frac{dC_B}{dV} = \frac{b}{a} r_A$
PBR	$v_0 \frac{dC_A}{dW} = r'_A$	and	$v_0 \frac{dC_B}{dW} = \frac{b}{a} r'_A$

Gas phase:

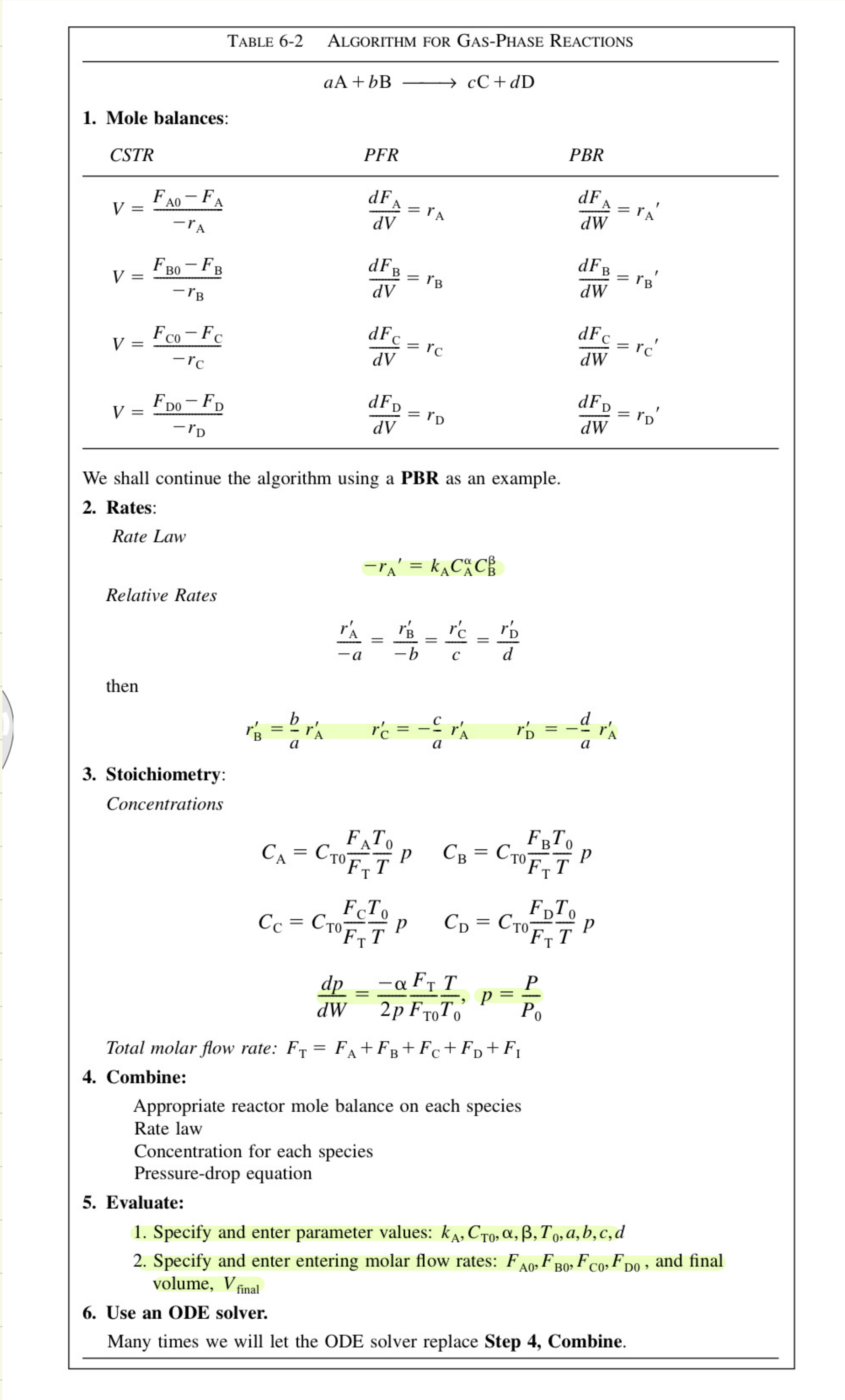


Table 6-2 Algorithm for Gas-Phase Reactions

$$aA + bB \longrightarrow cC + dD$$

1. Mole balances:

CSTR	*PFR*	*PBR*
$V = \dfrac{F_{A0} - F_A}{-r_A}$	$\dfrac{dF_A}{dV} = r_A$	$\dfrac{dF_A}{dW} = r_A{}'$
$V = \dfrac{F_{B0} - F_B}{-r_B}$	$\dfrac{dF_B}{dV} = r_B$	$\dfrac{dF_B}{dW} = r_B{}'$
$V = \dfrac{F_{C0} - F_C}{-r_C}$	$\dfrac{dF_C}{dV} = r_C$	$\dfrac{dF_C}{dW} = r_C{}'$
$V = \dfrac{F_{D0} - F_D}{-r_D}$	$\dfrac{dF_D}{dV} = r_D$	$\dfrac{dF_D}{dW} = r_D{}'$

We shall continue the algorithm using a **PBR** as an example.

2. Rates:

Rate Law

$$-r_A{}' = k_A C_A^{\alpha} C_B^{\beta}$$

Relative Rates

$$\frac{r'_A}{-a} = \frac{r'_B}{-b} = \frac{r'_C}{c} = \frac{r'_D}{d}$$

then

$$r'_B = \frac{b}{a} r'_A \qquad r'_C = -\frac{c}{a} r'_A \qquad r'_D = -\frac{d}{a} r'_A$$

3. Stoichiometry:

Concentrations

$$C_A = C_{T0} \frac{F_A}{F_T} \frac{T_0}{T} p \qquad C_B = C_{T0} \frac{F_B}{F_T} \frac{T_0}{T} p$$

$$C_C = C_{T0} \frac{F_C}{F_T} \frac{T_0}{T} p \qquad C_D = C_{T0} \frac{F_D}{F_T} \frac{T_0}{T} p$$

$$\frac{dp}{dW} = \frac{-\alpha}{2p} \frac{F_T}{F_{T0}} \frac{T}{T_0}, \quad p = \frac{P}{P_0}$$

Total molar flow rate: $F_T = F_A + F_B + F_C + F_D + F_I$

4. Combine:

Appropriate reactor mole balance on each species
Rate law
Concentration for each species
Pressure-drop equation

5. Evaluate:

1. Specify and enter parameter values: $k_A, C_{T0}, \alpha, \beta, T_0, a, b, c, d$
2. Specify and enter entering molar flow rates: $F_{A0}, F_{B0}, F_{C0}, F_{D0}$, and final volume, V_{final}

6. Use an ODE solver.

Many times we will let the ODE solver replace **Step 4, Combine**.

Algorithim to a microreactor

Micro reactors are charactarized by their high surface area to volume ratios [tubes or channels]

↓

Reduces or eleminates heat & mass transfer resistences

surface catalyzed reactions can be greatly facilitated

- hot spots in highly exothermic reactions can be minimized
- highly exothermic reactions can be carried out isothermally

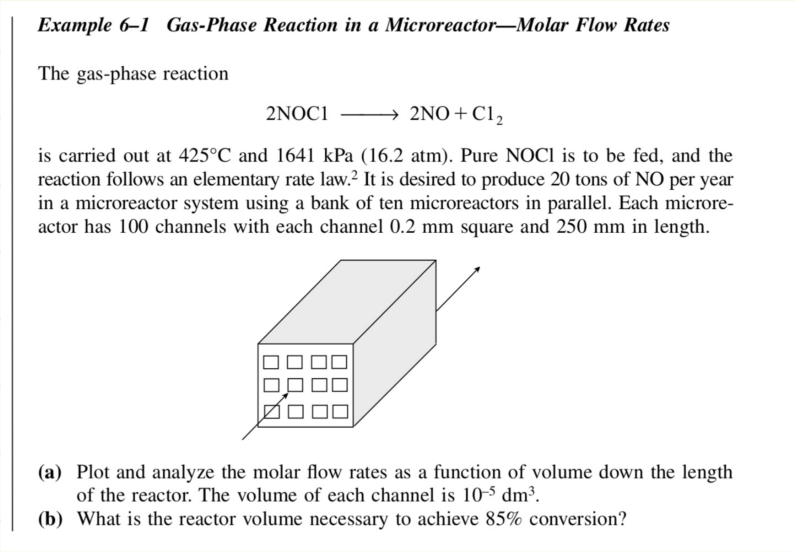
* Used in production of toxic or explosive materials

* Include shorter Residence time.

* Heat $\dot{Q}$, can be added or taken away by the fluid flowing perpindicular to the reaction channels.

In modeling Assume in plug flow

$$\frac{dF_A}{\partial V} = r_A$$



Example 6–1 Gas-Phase Reaction in a Microreactor—Molar Flow Rates

The gas-phase reaction

$$2NOCl \longrightarrow 2NO + Cl_2$$

is carried out at 425°C and 1641 kPa (16.2 atm). Pure NOCl is to be fed, and the reaction follows an elementary rate law.[2] It is desired to produce 20 tons of NO per year in a microreactor system using a bank of ten microreactors in parallel. Each microreactor has 100 channels with each channel 0.2 mm square and 250 mm in length.

(a) Plot and analyze the molar flow rates as a function of volume down the length of the reactor. The volume of each channel is 10^{-5} dm^3.

(b) What is the reactor volume necessary to achieve 85% conversion?

$A \rightarrow B + \frac{1}{2} C$

$T = 425°C$ $P = 16.2$ atm

elementary Rate Law

$F_B = 20$ tons/year

$X = 0.85$

$F_{A0} = 0.0226$ mol/s

$K = 0.29$ dm^3/mol·s

1. mole Balance

$$\frac{dF_A}{\partial V} = r_A$$

$$\frac{dF_B}{\partial V} = r_B$$

$$\frac{dF_C}{\partial V} = r_C$$

Differential Equations into Polymath

2. Rate Law $-r_A = k C_A^2$

3. Relative Rates

$$\frac{r_A}{-1} = \frac{r_B}{1} = 2 r_C$$

$$r_B = -r_A \qquad r_C = -\tfrac{1}{2} r_A$$

4. Stoichiometry [Gas phase]

$$C_A = C_{T0} \frac{F_A}{F_T}$$

$$C_B = C_{T0} \frac{F_B}{F_T}$$

$$C_C = C_{T0} \frac{F_C}{F_T}$$

5. Combine

$$-r_A = k \, C_{T0}^2 \left(\frac{F_A}{F_T}\right)^2$$

$$\left.\begin{aligned} \frac{dF_A}{dV} &= k \, C_{T0}^2 \left(\frac{F_A}{F_T}\right)^2 \\ \frac{dF_B}{dV} &= -k \, C_{T0}^2 \left(\frac{F_A}{F_T}\right)^2 \\ \frac{dF_C}{dV} &= \tfrac{1}{2} k \, C_{T0}^2 \left(\frac{F_A}{F_T}\right)^2 \end{aligned}\right) \text{Differential Equations [combined]}$$

$$\rightarrow C_{T0} = \frac{P_0}{R T_0} = \frac{16.2 \text{ atm}}{0.08206 \text{ atm} \cdot \text{dm}^3} \left| \frac{\text{mol} \cdot \text{K}}{698} \right. = 0.282 \text{ mol}/\text{dm}^3$$

$$F_T = F_A + F_B + F_C$$

* Explicit Equations into polymath

Membrane Reactors

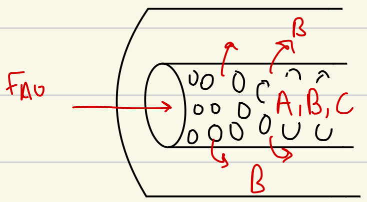
* Used to increase conversion when the reaction is thermodinamically limited, & to increase the selectivity when multiple reactions occur.

→ These higher conversions are the result of le Chatelier's principle, you can remove reaction products & drive the reaction to the right.

* To accomplish this a membrane that is permeable to the reaction product, but impermeable to all other species is placed around the reacting mixture.

- **Inert membrane reactor with catalyst pellets on the feed side (IMRCF)**. membrane is inert & serves as a barrier to the reactanst & some of the products.
- **Catalytic membrane reactor (CMR)**: The catalyst is deposited directly on the membrane, & only specific reaction products are able to exit the permeate side

$A \rightleftharpoons 3B + C$



$W = \rho_b V$ → solids weight

$\rho_b = (1-\phi)\rho_c$ → bulk solid density

ρ_c → density of solids

A & C stay behind, B goes through the membrane

Mole Balances

$$In - out + Generation = 0$$

$$F_{A0} - F_A + r_A \Delta V = 0$$

PFR:

$$\left.\begin{aligned} \frac{dF_A}{dV} &= r_A \\ \frac{dF_C}{dV} &= r_C \end{aligned}\right) \text{within the reactor}$$

→ Mole Balance on species B

$$\text{In} - \text{Out} - \text{out membrane} + \text{Generation} = 0$$

$$F_{B0} - F_B - R_B \Delta V + r_B \Delta V = 0$$

$$\frac{dF_B}{dV} = (r_B - R_B)$$

$$R_B = \frac{\text{moles B leaving through the sides}}{\text{Volume of Reactor}}$$

* The rate of Transport B out through the membrane (R_B), is the product of the molar flux of B normal to the membrane (W_B), & the surface area per unit volume of reactor.

$$R_B = W_B \, a$$

$$W_B = \underset{\text{overall mass transfer coefficient}}{k_c'}(C_B - \overset{\text{Conc. of B in swept gas channel}}{C_{BS}}) = \frac{\text{molar flow rate through membrane}}{\text{Surface area of membrane}} \left[\frac{\text{mol}}{m^2 \cdot s}\right]$$

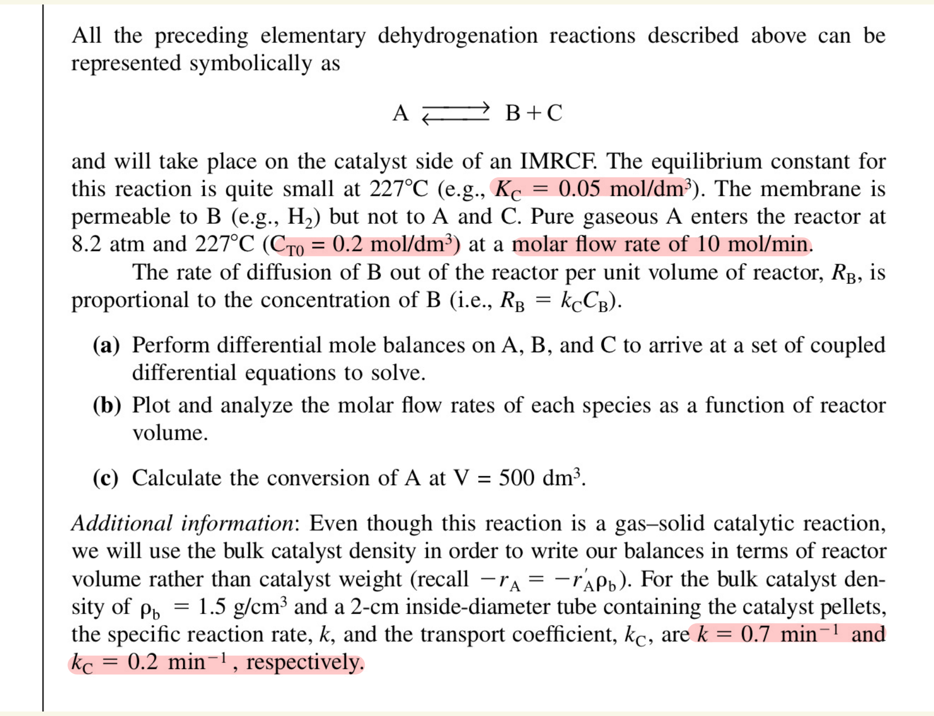
$$a = \frac{\text{membrane surface Area}}{\text{Reactor volume}} = \frac{\pi D L}{\frac{\pi D^2}{4} L} = \frac{4}{D} \left[\frac{m^2}{m^3}\right]$$

$$R_B = k_c'(C_B - C_{BS})\, a$$

Let $k_c = k_c' a$

& $C_{BS} \cong 0$

$$\boxed{R_B = k_c C_B \quad \left[\frac{\text{mol}}{m^3 \cdot s}\right]}$$



All the preceding elementary dehydrogenation reactions described above can be represented symbolically as

$$A \rightleftarrows B + C$$

and will take place on the catalyst side of an IMRCF. The equilibrium constant for this reaction is quite small at 227°C (e.g., $K_C = 0.05\ \text{mol/dm}^3$). The membrane is permeable to B (e.g., H_2) but not to A and C. Pure gaseous A enters the reactor at 8.2 atm and 227°C ($C_{T0} = 0.2\ \text{mol/dm}^3$) at a molar flow rate of 10 mol/min.

The rate of diffusion of B out of the reactor per unit volume of reactor, R_B, is proportional to the concentration of B (i.e., $R_B = k_C C_B$).

(a) Perform differential mole balances on A, B, and C to arrive at a set of coupled differential equations to solve.

(b) Plot and analyze the molar flow rates of each species as a function of reactor volume.

(c) Calculate the conversion of A at V = 500 dm^3.

Additional information: Even though this reaction is a gas–solid catalytic reaction, we will use the bulk catalyst density in order to write our balances in terms of reactor volume rather than catalyst weight (recall $-r_A = -r'_A \rho_b$). For the bulk catalyst density of $\rho_b = 1.5\ \text{g/cm}^3$ and a 2-cm inside-diameter tube containing the catalyst pellets, the specific reaction rate, k, and the transport coefficient, k_C, are $k = 0.7\ \text{min}^{-1}$ and $k_C = 0.2\ \text{min}^{-1}$, respectively.

1. Mole Balances

$$\frac{dF_A}{dV} = r_A$$

$$\frac{dF_B}{dV} = r_B - R_B$$

$$\frac{dF_C}{dV} = r_C$$

2. Rate law

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

$k = 0.7\ \text{min}^{-1}$

3. Relative Rates

$$\frac{r_A}{-1} = \frac{r_B}{1} = \frac{r_C}{1}$$

$r_B = -r_A$ $\quad$ $r_C = -r_A$

4. Transport law

$R_B = k_C C_B$

$k_C = 0.2\ \text{min}^{-1}$

5. Stoichiometry

$$C_A = C_{T0}\frac{F_A}{F_T}$$

$$C_B = C_{T0}\frac{F_B}{F_T}$$

$$C_C = C_{T0}\frac{F_C}{F_T}$$

$$F_T = F_A + F_B + F_C$$

6 combine

$$-r_A = k\, C_{T0}\left[\frac{F_A}{F_T} - \frac{C_{T0}}{K_C}\,\frac{F_B}{F_T}\,\frac{F_C}{F_T}\right]$$

$$\frac{dF_A}{dV} = r_A$$

$$\frac{dF_B}{dV} = -r_A - k_C\, C_{T0}\,\frac{F_B}{F_T}$$

$$\frac{dF_C}{dV} = -r_A$$

Ex: Isothermal membrane Reaction with no ΔP, membrane only permeable to C [PBR]

$$A \rightleftharpoons B + 3C$$

1. Mole Balances

$$\frac{dF_A}{dW} = r_A'$$

$$\frac{dF_B}{dW} = r_B'$$

$$\frac{dF_C}{dW} = r_C' - R_C \qquad R_C = k_c C_c$$

$$\frac{dF_C}{dW} = r_c' - k_C C_c \qquad k_C = 0.5$$

2. Rate Law

$$-r_A = k_A\left[C_A - \frac{C_B C_C^3}{K_C}\right] \qquad K_C = 200 \qquad k_A = 10$$

3. Relative Rates

$$\frac{r_A'}{-1} = \frac{r_B'}{1} = \frac{r_C'}{3} \qquad r_B' = -r_A'$$

$$r_C' = -3r_A'$$

4. Stachiometry

$$C_A = C_{T0} \frac{F_A}{F_T}$$

$$C_B = C_{T0} \frac{F_B}{F_T} \qquad F_T = F_A + F_B + F_C$$

$$C_C = C_{T0} \frac{F_C}{F_T}$$

→ Combine in polymath with givens:

$C_{T0} = 0.2$ $\qquad F_{A0} = 10$

$k_A = 10$ $\qquad k_C = 0.5$

$K_C = 200$

Semi batch Reactors

Semi batch reactors can be very effective in maximizing selectivity in liquid phase reactions.

$A + B \xrightarrow{k_D} D$ [Desired] $r_D = k C_A^2 C_B$

$A + B \xrightarrow{k_U} U$ [undesired] $r_U = k C_A C_B^2$

$$\text{Selectivity}_{D/U} = \frac{r_D}{r_U} = \frac{k_D C_A^2 C_B}{k_U C_A C_B^2} = \frac{k_D}{k_U} \frac{C_A}{C_B}$$

$\uparrow C_A \quad \downarrow C_B \Rightarrow \uparrow S_{D/U}$

Mole Balances

$A + B \rightarrow C$ * A in vat, B added in slowly

→ Mole Balance on A

In - out + Gen = Accumulation

$$0 - 0 + r_A V(t) = \frac{dN}{dt}$$

$$r_A V = \frac{dN}{dt} = \frac{d(C_A V)}{dt} = V \frac{dC_A}{dt} + C_A \frac{dV}{dt}$$

* The volume V varies with time, volume at any time ⇒ overall mass balance

mass in - mass out + Gen = Acc

$$\dot{m}_0 - 0 + 0 = \frac{dm}{dt}$$

$$\rho v_0 = \frac{d\rho V}{dt}$$

→ for constant $\rho = \rho_0$ [liq]

$$\frac{dV}{dt} = v_0$$

at $V = V_0$ & $t = 0$

$$\boxed{V = V_0 + v_0 t}$$

$$\therefore \quad -v_0 C_A + V r_A = V \frac{dC_A}{dt}$$

Mole Balance on species A

$$\text{In} - \text{out} + \text{Gen} = \text{Acc}$$

$$0 - 0 + r_A V = \frac{dN_A}{dt}$$

$$\frac{dN_A}{dt} = V \frac{dC_A}{dt} + C_A \frac{dV}{dt} \qquad \frac{dV}{dt} = v_0$$

$$\boxed{\frac{dC_A}{dt} = r_A - \frac{v_0 C_A}{V}}$$

Mole Balance on species B

$$\text{In} - \text{out} + \text{Gen} = \text{Acc}$$

$$F_{B0} - 0 + r_B V = \frac{dN_B}{dt}$$

$$\frac{dN_B}{dt} = V \frac{dC_A}{dt} + C_A \frac{dV}{dt}$$

$$F_{B0} = C_{B0} v_0 \qquad \frac{dV}{dt} = v_0$$

$$\boxed{\frac{dC_B}{dt} = r_B + \frac{(C_{B0} - C_B) v_0}{V}}$$

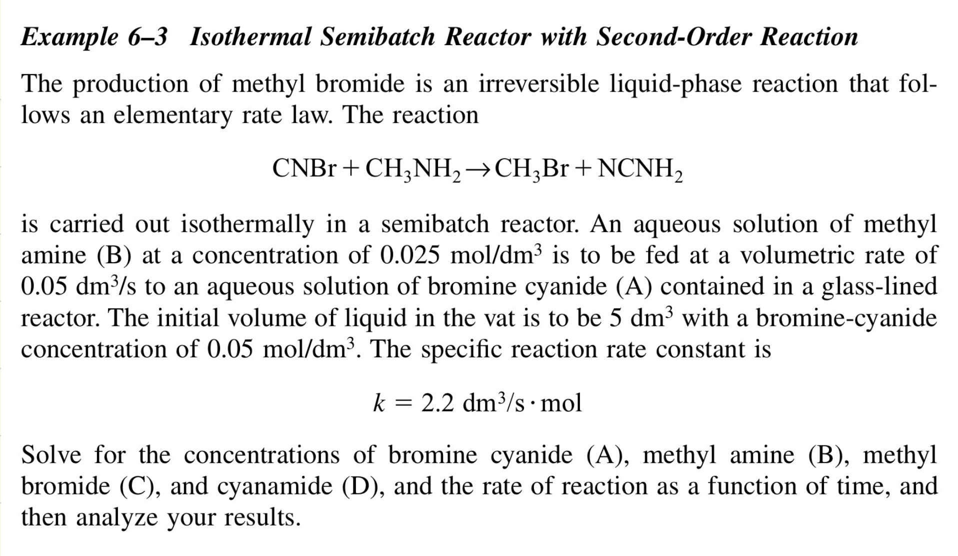
Mole Balance for C & D ...

$$\frac{dC_C}{dt} = r_C - \frac{C_C v_0}{V}$$

$$\frac{dC_D}{dt} = r_D - \frac{C_D v_0}{V}$$

* if the reaction order is other than zero or first order, or non-isothermall

⇒ Numerical techniques.



Example 6–3 Isothermal Semibatch Reactor with Second-Order Reaction

The production of methyl bromide is an irreversible liquid-phase reaction that follows an elementary rate law. The reaction

$$CNBr + CH_3NH_2 \rightarrow CH_3Br + NCNH_2$$

is carried out isothermally in a semibatch reactor. An aqueous solution of methyl amine (B) at a concentration of 0.025 mol/dm^3 is to be fed at a volumetric rate of 0.05 dm^3/s to an aqueous solution of bromine cyanide (A) contained in a glass-lined reactor. The initial volume of liquid in the vat is to be 5 dm^3 with a bromine-cyanide concentration of 0.05 mol/dm^3. The specific reaction rate constant is

$$k = 2.2 \text{ dm}^3/\text{s}\cdot\text{mol}$$

Solve for the concentrations of bromine cyanide (A), methyl amine (B), methyl bromide (C), and cyanamide (D), and the rate of reaction as a function of time, and then analyze your results.

$A + B \rightarrow C + D$

$C_{B0} = 0.025 \text{ mol}/\text{dm}^3$

$v_0 = 0.05 \text{ dm}^3/\text{s}$

$V_0 = 5 \text{ dm}^3$

$C_{A0} = 0.05 \text{ mol}/\text{dm}^3$

1 mole Balances

$$\frac{dC_A}{dt} = r_A - \frac{v_0 C_A}{V}$$

$$\frac{dC_B}{dt} = \frac{v_0 (C_{B0} - C_B)}{V} + r_B$$

$$\frac{dC_C}{dt} = r_C - \frac{v_0 C_C}{V}$$

$$\frac{dC_D}{dt} = r_D - \frac{v_0 C_D}{V}$$

2. Elementary Rate law

$$-r_A = K C_A C_B$$

3. Relative Rates

$$\frac{r_A}{-1} = \frac{r_B}{-1} = \frac{r_C}{1} = r_D$$

4 combine

$$\frac{dC_A}{dt} = -K C_A C_B - \frac{v_0 C_A}{V}$$

$$\frac{dC_B}{dt} = \frac{v_0 (C_{B0} - C_B)}{V} - K C_A C_B$$

$$\frac{dC_C}{dt} = K C_A C_B - \frac{v_0 C_C}{V}$$

$$\frac{dC_D}{dt} = K C_A C_B - \frac{v_0 C_D}{V}$$

5. Stoichiometry $V = V_0 + v_0 t$

$$X = \frac{N_{A0} - N_A}{N_{A0}}$$

6. Evaluate in polymath.

Equilibrium Conversion in semibatch Reactors with reversible Reactions.

$$A + B \rightleftharpoons C + D$$

→ Rate Law $-r_A = k\left[C_A C_B - \frac{C_C C_D}{K_C}\right]$

→ $C_A = \frac{N_{A0}(1-X)}{V}$

$C_B = \frac{(F_{B0}t - N_{A0}X)}{V}$

$C_C = C_D = \frac{N_{A0}X}{V}$

* At equilibrium $-r_A = 0$

$$K_C = \frac{C_{Ce}\, C_{De}}{C_{Be}\, C_{Ae}} = \frac{N_{Ce}\, N_{De}}{N_{Ae}\, N_{Be}} = \frac{N_{A0}\, X_e^2}{(1-X_e)(F_{B0}t - N_{A0}X_e)}$$

Three forms of Mole Balance

1. Molar Basis $$\frac{\partial N_A}{\partial t} = r_A V$$

$$\frac{\partial N_B}{\partial t} = F_{B0} + r_B V$$

2. Concentration Basis $$\frac{dC_A}{dt} = r_A - \frac{v_0 C_A}{V}$$

$$\frac{dC_B}{dt} = r_B + \frac{(C_{B0} - C_B) v_0}{V}$$

3. Conversion Basis $$\frac{dX}{dt} = \frac{-r_A V}{N_{A0}}$$

Chapter 8: Multiple Reactions

Types of Reactions

1. Parallel reactions (competing reactions): Reactions where the reactant is consumed by two different reaction pathways to form different products

$$A \rightarrow D$$
$$A \rightarrow U$$

2. Series Reaction (consecutive reactions): Reactions where the reactant forms an Intermediate product, which reacts further to form another product

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

3. Independent Reactions: occur at the same time but neither the products nor the reactants react with themselves or one another

$$A \rightarrow B$$
$$C \rightarrow D$$

4. Complex Reactions: Multiple Reactions that involve combinations of series & independent parallel reactions.

$$A + B \rightarrow C + D$$
$$A + C \rightarrow E$$

* with multiple reactors either molar flow rate or number of moles must be used [not conversion]

Selectivity

→ Desired & Undesired Reactions

In parallel sequance form:

$$A \xrightarrow{k_D} D$$
$$A \xrightarrow{k_U} U$$

* D → Desired

* U → Undesired

In series sequance $A \xrightarrow{k_D} D \xrightarrow{k_U} U$

→ We want to minimize the formation of U & maximize the formation of D

Selectivity tells how one product is favored over the other (in multiple reactions)

Instantaneous selectivity of D with respect to U is the ratio of the rate of formation of D to the rate of formation of U

- Instantaneous Selectivity $S_{D/U} = \frac{r_D}{r_U}$
- Overall selectivity $\tilde{S}_{D/U} = \frac{F_D}{F_U} = \frac{\text{Exit molar flow rate of desired product}}{\text{Exit molar flow rate of undesired product}}$
- overall selectivity for Batch Reactor $\tilde{S}_{DU} = \frac{N_D}{N_U}$ (Number of moles at the end of Reaction time)

Yield

Reaction yield based on the ratio of reaction rates

→ Yield at a point can be defined as the ratio of the reaction rate of a given product to the reaction rate of the key reactant (Basis of calculations A)

- Instantaneous yield $Y_D = \frac{r_D}{-r_A}$

Reaction yield based on the ratio of molar flow rates

→ Ratio of moles of product formed at the end of a reaction to the number of moles of key reactant A, that have been consumed.

- overall yield for Batch system $\tilde{Y}_D = \frac{N_D}{N_{A0} - N_A}$

- overall yield for flow system $\tilde{Y}_D = \frac{F_D}{F_{A0} - F_A}$

Ex: $A + B \xrightarrow{k_1} D$ $r_D = k_1 C_A^2 C_B$

$A + B \xrightarrow{k_2} U$ $r_U = k_2 C_A C_B$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1 C_A^2 C_B}{k_2 C_A C_B} = \frac{k_1}{k_2} C_A$$

To maximize selectivity of D, use high conc of A & PFR reactor.

Algorithm for multiple reactions

1) Mole Balance

Flow	Batch
$\frac{dF_A}{dV} = r_A$	$\frac{dN_A}{dt} = r_A V$
$\frac{dF_B}{dV} = r_B$	$\frac{dN_B}{dt} = r_B V$

for each & every species

2) Rates

→ Rate law for each reaction $-r_{1A} = k_{1A} C_A C_B$

$-r_{2A} = k_{2A} C_C C_A$

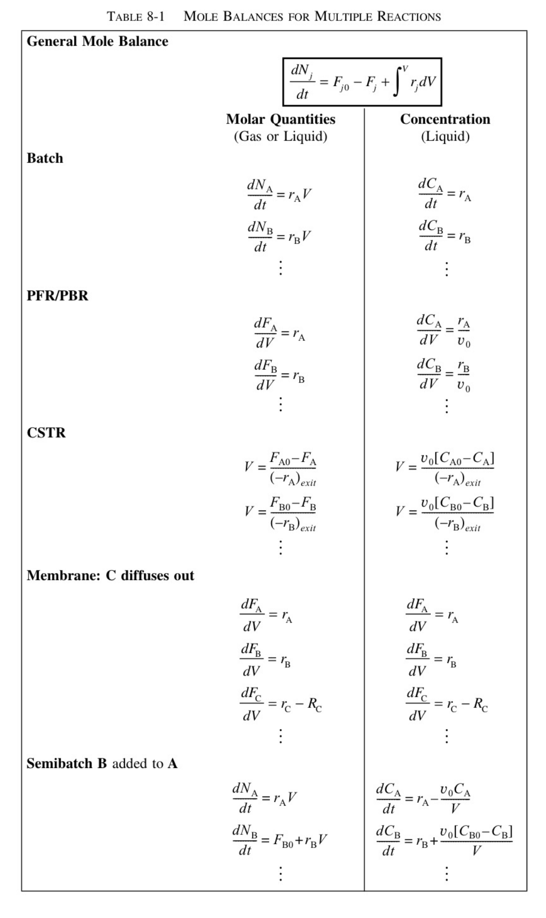


TABLE 8-1 MOLE BALANCES FOR MULTIPLE REACTIONS

General Mole Balance

$$\boxed{\frac{dN_j}{dt} = F_{j0} - F_j + \int^V r_j dV}$$

	Molar Quantities (Gas or Liquid)	Concentration (Liquid)
Batch	$\frac{dN_A}{dt} = r_A V$ $\frac{dN_B}{dt} = r_B V$ ⋮	$\frac{dC_A}{dt} = r_A$ $\frac{dC_B}{dt} = r_B$ ⋮
PFR/PBR	$\frac{dF_A}{dV} = r_A$ $\frac{dF_B}{dV} = r_B$ ⋮	$\frac{dC_A}{dV} = \frac{r_A}{v_0}$ $\frac{dC_B}{dV} = \frac{r_B}{v_0}$ ⋮
CSTR	$V = \frac{F_{A0} - F_A}{(-r_A)_{exit}}$ $V = \frac{F_{B0} - F_B}{(-r_B)_{exit}}$ ⋮	$V = \frac{v_0[C_{A0} - C_A]}{(-r_A)_{exit}}$ $V = \frac{v_0[C_{B0} - C_B]}{(-r_B)_{exit}}$ ⋮
Membrane: C diffuses out	$\frac{dF_A}{dV} = r_A$ $\frac{dF_B}{dV} = r_B$ $\frac{dF_C}{dV} = r_C - R_C$ ⋮	$\frac{dF_A}{dV} = r_A$ $\frac{dF_B}{dV} = r_B$ $\frac{dF_C}{dV} = r_C - R_C$ ⋮
Semibatch B added to **A**	$\frac{dN_A}{dt} = r_A V$ $\frac{dN_B}{dt} = F_{B0} + r_B V$ ⋮	$\frac{dC_A}{dt} = r_A - \frac{v_0 C_A}{V}$ $\frac{dC_B}{dt} = r_B + \frac{v_0[C_{B0} - C_B]}{V}$ ⋮

→ Net Rates $r_A = \sum r_{iA} = r_{1A} + r_{2A} + \cdots$

→ Relative Rates $\frac{r_{iA}}{a_1} = \frac{r_{iB}}{b} = \frac{r_{iC}}{c} = \frac{r_{iD}}{d}$

3) Stiochiometry

→ Gas $C_A = C_{T0} \frac{F_A}{F_T} \left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$

→ liquid $C_A = \frac{F_A}{v_0}$

Parallel Reactions

$A \xrightarrow{k_D} D$ $r_D = k_D C_A^{\alpha_1}$

$A \xrightarrow{k_U} U$ $r_U = k_U C_A^{\alpha_2}$

→ Net Rate $-r_A = r_D + r_U = k_D C_A^{\alpha_1} + k_U C_A^{\alpha_2}$

→ Instantaneous Selectivity $S_{D/U} = \frac{r_D}{r_U} = \frac{k_D C_A^{\alpha_1}}{k_U C_A^{\alpha_2}} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$

Maximizing the Desired Product In Parallel Reactions

$A + B \xrightarrow{k_D} D$ $r_D = k_D C_A^{\alpha_1} C_B^{\beta_1}$ $\longrightarrow$ $r_D = A_D e^{-E/RT} C_A^{\alpha_1} C_B^{\beta_1}$

$A + B \xrightarrow{k_U} U$ $r_U = k_U C_A^{\alpha_2} C_B^{\beta_2}$ $r_U = A_U e^{-E/RT} C_A^{\alpha_2} C_B^{\beta_2}$

$$k(T) = A e^{-E/RT}$$

→ Net Rate of disappearance A $-r_A = r_D + r_U$

$$-r_A = A_D e^{-E/RT} C_A^{\alpha_1} C_B^{\beta_1} + A_U e^{-E/RT} C_A^{\alpha_2} C_B^{\beta_2}$$

→ Instantaneous Selectivity $S_{DU} = \frac{r_D}{r_U} = \frac{A_D e^{-E/RT} C_A^{\alpha_1} C_B^{\beta_1}}{A_U e^{-E/RT} C_A^{\alpha_2} C_B^{\beta_2}}$

$$S_{D/U} = \frac{A_D}{A_U} e^{\frac{-(E_D - E_U)}{RT}} C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2}$$

↳ Maximize $S_{D/U}$ to maximize Desired product production.

① Temperature [affects k]

1. if $E_D > E_U$

↑ $E_D - E_U$ ⇒ ↓e   Specific rate of desired reaction k_D increases more rapidly with increasing T

[Use higher T for more D]

2. if $E_U > E_D$

↓ $E_D - E_U$ ⇒ ↑e   specific rate of desired k_D increases less rapidly with increasing T

[Use lower T for desired, not so low]

② Concentrations

1. $\alpha_1 > \alpha_2 \rightarrow \alpha_1 - \alpha_2 > 0$ large C_A (PFR, Batch)

2. $\alpha_2 > \alpha_1 \rightarrow \alpha_1 - \alpha_2 < 0$ Small C_A (CSTR)

3. $\beta_1 > \beta_2 \rightarrow \beta_1 - \beta_2 > 0$ large C_B (PFR, Batch)

4. $\beta_2 > \beta_1 \rightarrow \beta_1 - \beta_2 < 0$ Small C_B (CSTR)

Concentration Requirements & Reactor Selection

1. PBR or PFR : concentration is high at the inlet & progressively drops to outlet conc.
2. CSTR : concentration is always at its lowest value [exit conc.]
3. Batch : concentration is high at $t=0$ & progressively drops with increasing time
4. Semi batch: concentration of one reactant is high at $t=0$ & progressively drops with time , conc of other reactant can be kept low at all times

	$\alpha_1 > \alpha_2$ ($\uparrow C_A$)	$\alpha_1 < \alpha_2$ ($\downarrow C_A$)
$\beta_1 > \beta_2$ ($\uparrow C_B$)	Batch reactor / PFR & PBR (no inert, high P no diluent)	PFR or PBR → side streams for $\downarrow C_A$ Semibatch → slowly feed A to high B CSTR's in series
$\beta_1 < \beta_2$ ($\downarrow C_B$)	PFR / PBR → side streams for $\downarrow C_B$ Semibatch → slowly add C_B to high C_A CSTR's in series	CSTR PFR or PBR with high recycle → dilute feed with inert low P

Ex: Conditions to maximize selectivity

$$A + C \xrightarrow{k_D} D \qquad r_D = 800\, e^{-\frac{2000}{T}}\, C_A^{0.5}\, C_C$$

$$A + C \xrightarrow{k_U} U \qquad r_U = 10\, e^{-\frac{300}{T}}\, C_A\, C_C$$

1. Temp $E_D - E_U$ ($E_D > E_U$)

$2000 - 300$ → ↑e → highest possible T

2. Conc $\alpha_1 - \alpha_2$ ($\alpha_2 > \alpha_1$)

$0.5 - 1 = -0.5$ → lowest C_A possible

$$S_{D/U} = \frac{800\, e^{-\frac{2000}{T}}\, C_A^{0.5}\, C_C}{10\, e^{-\frac{300}{T}}\, C_A\, C_C} = 80\, e^{\frac{-1700}{T}}\, C_A^{-0.5}$$

→ k_D increases faster than k_U as the temp increases [operate at high temp]

→ C_A low to maximize C_D with respect to C_U

→ Changing C_C doesnot influence selectivity ⇒ high C_C will increase the reaction rate & offset the slow reaction that is caused by low C_A

Use: PFR / PBR with C_A in side streams

Semi batch feeding C_A slowly

Ex2: $A + C \xrightarrow{k_D} D$ $\qquad r_D : 800\, e^{-\frac{2000}{T}}\, C_A^{0.5}\, C_C$

$A + C \xrightarrow{k_{U_1}} U_1$ $\qquad r_{U_1} : 10\, e^{-\frac{300}{T}}\, C_A\, C_C$

$D + C \xrightarrow{k_{U_2}} U_2$ $\qquad r_{U_2} : 10^6\, e^{-\frac{8000}{T}}\, C_C\, C_D$

→ Maximize S_{D/U_1} & S_{D/U_2}

↳ previous ex

$$S_{D/U_2} = \frac{800\, e^{-\frac{2000}{T}}\, C_A^{0.5}\, C_C}{10^6\, e^{-\frac{8000}{T}}\, C_C\, C_D}$$

→ $E_D > E_U$ → low T conflict with S_{D/U_1}

→ $\alpha_D > \alpha_{U_2}$ → keep C_A high conflict with S_{D/U_1}

→ high C_C will offset the rate decrease due to low C_A

→ low C_D reduses the production of U_2 conflict with S_{D/U_1}

* Consider relative magnitude of S_{D/U_1} & S_{D/U_2} as a function of position in PFR

→ PFR with side streams feeding low C_A

- High T, C_C is initially high, C_A is low

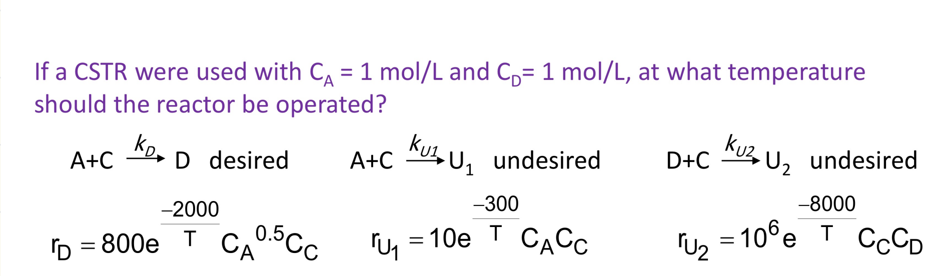
- Initially $C_C = 0$ → $r_{U2} = 0$ Both gradually increase down the reactor

→ high S_{D/U_1}

→ Initially high S_{D/U_2} [C_D is low] → gradually decreases down the reactor.

when significant amount of D have formed S_{D/U_2} becomes significant with respect to S_{D/U_1}

At this point → low T, high C_A, & low C_C



If a CSTR were used with C_A = 1 mol/L and C_D= 1 mol/L, at what temperature should the reactor be operated?

$A+C \xrightarrow{k_D} D$ desired $A+C \xrightarrow{k_{U1}} U_1$ undesired $D+C \xrightarrow{k_{U2}} U_2$ undesired

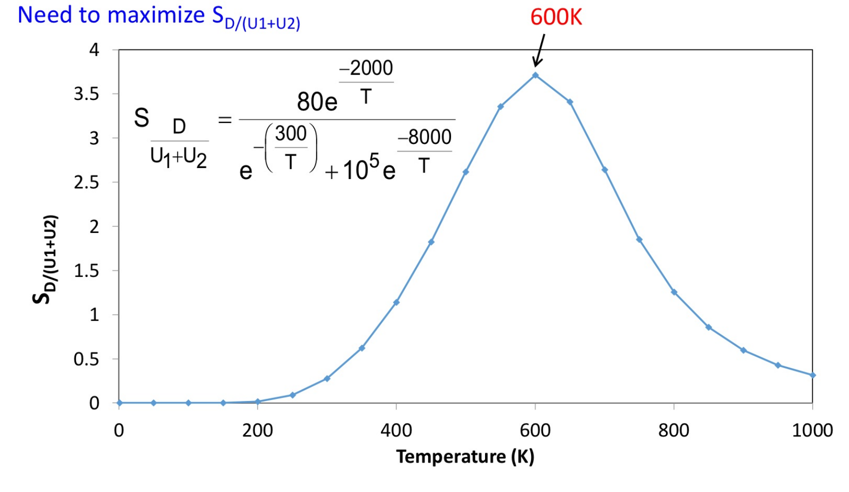
$r_D = 800 e^{\frac{-2000}{T}} C_A^{0.5} C_C$ $r_{U_1} = 10 e^{\frac{-300}{T}} C_A C_C$ $r_{U_2} = 10^6 e^{\frac{-8000}{T}} C_C C_D$

$$S_{D/U_1+U_2} = \frac{800\, e^{-\frac{2000}{T}}\, C_A^{0.5}\, \cancel{C_C}}{10\, e^{-\frac{300}{T}}\, C_A\, \cancel{C_C} + 10^6\, e^{-\frac{8000}{T}}\, \cancel{C_C}\, C_D}$$

$$S_{D/U_1+U_2} = \frac{800\, e^{-\frac{2000}{T}}\, (1)^{0.5}}{10\, e^{-\frac{300}{T}}\, (1) + 10^6\, e^{-\frac{8000}{T}}\, (1)}$$

$$S_{D/U_1+U_2} = \frac{80\, e^{-\frac{2000}{T}}}{e^{-300/T} + 10^5\, e^{-8000/T}}$$

Plot T vs S_{D/U_1+U_2} to find T that maximizes S_{D/U_1+U_2}



Need to maximize $S_{D/(U1+U2)}$

600K

$$S_{\frac{D}{U_1+U_2}} = \frac{80e^{\frac{-2000}{T}}}{e^{-\left(\frac{300}{T}\right)} + 10^5 e^{\frac{-8000}{T}}}$$

Calculate the yield of forming B in a **CSTR** and PFR when the conversion of A is 90% and C_{A0} = 4 mol/L. The following reactions occur in the reactor:

$$A \xrightarrow{k_B} B \quad r_B = k_B = 2\frac{\text{mol}}{\text{L}\cdot\text{min}} \qquad A \xrightarrow{k_C} C \quad r_C = k_C C_A \quad k_C = 1\ \text{min}^{-1}$$

What is the expression for the yield of B for a CSTR?

$$\tilde{Y}_B = \frac{F_B}{F_{A0} - F_A}$$

$$\tilde{Y}_B = \frac{C_B v_0}{C_{A0} v_0 - C_A v_0} \rightarrow \tilde{Y}_B = \frac{C_B}{C_{A0} - C_A}$$

We know C_{A0} and C_A when X_A=0.9. How do we get C_B?

$$\cancelto{0}{In} - \text{out} + \text{Gen} = \cancelto{0}{Acc}$$

$$-F_B + r_B V = 0 \longrightarrow -C_B v_0 + r_B V = 0$$

$$r_B = \frac{C_B v_0}{V} = \frac{C_B}{\tau}$$

$$2 = \frac{C_B}{\tau} \rightarrow C_B = 2\tau$$

Use the mole balance on A to find τ (at 90% conversion)

$$F_{A0} - F_A + r_A V = 0$$

$$C_{A0} v_0 - C_A v_0 + r_A V = 0$$

$$C_{A0} v_0 - C_A v_0 = -r_A V$$

$$-r_A \frac{V}{v_0} = C_{A0} - C_A$$

$$-r_A \tau = C_{A0} - C_A \longrightarrow \tau = \frac{C_{A0} - C_A}{-r_A}$$

Calculate the yield of forming B in a **CSTR** and PFR when the conversion of A is 90% and C_{A0} = 4 mol/L. The following reactions occur in the reactor:

$A \xrightarrow{k_B} B \quad r_B = k_B = 2\,\frac{\text{mol}}{\text{L}\cdot\text{min}}$ $\qquad A \xrightarrow{k_C} C \quad r_C = k_C C_A \quad k_C = 1\ \text{min}^{-1}$

$$\tilde{Y}_B = \frac{C_B}{C_{A0} - C_A}$$

→ to find C_B

$$0 - F_B + r_B V = 0$$

$$-C_B \nu_0 + r_B V = 0$$

$$-C_B \nu_0 = r_B V$$

$$C_B = r_B \tau \qquad\qquad r_B = 2 = \frac{C_B}{\tau}$$

→ to find τ

$$\frac{C_{A0} - C_A}{-r_A} = \tau \qquad\qquad -r_A = r_B + r_C$$

$$-r_A = 2 + k_C C_A$$

$$-r_A = 2 + C_A$$

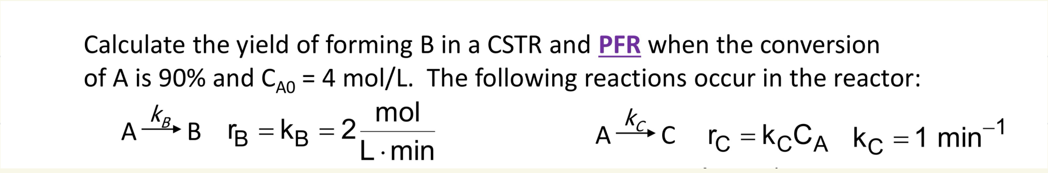
$$\tau = \frac{4 - C_A}{2 + C_A} \qquad\qquad C_A = C_{A0}(1 - X)$$

$$4(1 - 0.9) = 0.4$$

$$\tau = \frac{4 - 0.4}{2 + 0.4} = 1.5\ \text{min}$$

$$\frac{C_B}{\tau} = 2 \qquad \frac{C_B}{1.5} = 2 \qquad C_B = 3$$

$$\tilde{Y}_B = \frac{3}{4 - 0.4} = 0.83$$



Calculate the yield of forming B in a CSTR and PFR when the conversion of A is 90% and C_{A0} = 4 mol/L. The following reactions occur in the reactor:

$A \xrightarrow{k_B} B \quad r_B = k_B = 2 \frac{mol}{L \cdot min}$ $\qquad A \xrightarrow{k_C} C \quad r_C = k_C C_A \quad k_C = 1\ min^{-1}$

$$\tilde{Y}_B = \frac{F_B}{F_{A0} - F_A} = \frac{C_B v_0}{C_{A0} v_0 - C_A v_0} = \frac{C_B}{C_{A0} - C_A}$$

→ mole Balance $\quad \frac{\partial F_B}{\partial V} = r_B \rightarrow \frac{\partial C_B v_0}{\partial V} = r_B$

$$\frac{\partial C_B}{\partial \tau} = 2$$

$$dC_B = 2\, d\tilde{\tau}$$

$$C_B = 2\tau$$

$\frac{dC_A}{d\tau} = r_A \qquad r_A = r_B + r_C$

$\qquad\qquad\qquad r_A = 2 + C_A$

$$\frac{dC_A}{d\tau} = -(2 + C_A)$$

$$\frac{dC_A}{-2 - C_A} = d\tau \rightarrow \ln \frac{-2 - C_{A0}}{-2 - C_A} = \tau$$

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

$\quad 4(1 - 0.9)$

$C_A = 0.4$

$$\ln \frac{-2 - 4}{-2 - 0.4} = \tau$$

$$\tau = 0.92$$

$$C_B = 2(0.92) = 1.83$$

$$\tilde{Y}_B = \frac{1.83}{4 - 0.4} = 0.51$$

Reactions In series

for series (consecutive reactions) , the most important variable is time [τ for flow reactor & real time for batch reactor]

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Ex: Batch Series reaction:

$$A \rightarrow B \rightarrow C$$

$$A \rightarrow B \qquad k_1$$

$$B \rightarrow C \qquad k_2$$

1) Mole Balances

$$\frac{dN_A}{dt} = r_A V \qquad V = V_0 \qquad \frac{dC_A}{dt} = r_A$$

$$\frac{dN_B}{dt} = r_B V \qquad \frac{dC_B}{dt} = r_B$$

$$\frac{dN_c}{dt} = r_C V \qquad \frac{dN_C}{dt} = r_C$$

2) Rate

Rate laws: $-r_{1A} = k_1 C_{A1}$

$-r_{2B} = k_2 C_{B2}$

Relative Rates $\frac{r_{A1}}{-1} = \frac{r_{B1}}{1}$ $\qquad r_{B1} = -r_{A1}$

$\frac{r_{B2}}{-1} = \frac{r_{C2}}{1}$

Net Rates $-r_A = k_1 C_{A1}$

$r_B = r_{B1} + r_{B2}$

$r_B = k_1 C_{A1} - k_2 C_{B2}$

3) Combine $\frac{dC_A}{dt} = -k_1 C_{A1}$

$$\frac{dC_A}{dt} = -k_1 C_{A0} e^{-k_1 t} \xrightarrow[\text{Integrate}]{\text{Seperate \&}} C_{A1} = C_{A0} e^{-k_1 t}$$

$$\frac{dC_B}{dt} = k_1 C_{A1} - k_2 C_{B2}$$

$$\frac{dC_B}{dt} + k_2 C_{B2} = k_1 C_{A0} e^{-kt}$$

Integrating factor [Appendix A.1]

$$IF = \exp\int k_2 \, dt = e^{k_2 t}$$

$$\frac{d(C_B e^{2kt})}{dt} = e^{k_2 t} k_1 e^{-k_1 t} C_{A0} = k_1 e^{(k_2 - k_1)t} C_{A0}$$

at $C_B = 0$ $t = 0$ → $C_B = \frac{k_1 C_{A0}}{k_2 - k_1}\left[e^{-k_1 t} + e^{-k_2 t}\right]$

$$C_C = C_{A0} - C_A - C_B$$

$$C_C = \frac{C_{A0}}{k_2 - k_1}\left[k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t})\right]$$

Ex: CSTR series Example

$$A \rightarrow B \rightarrow C$$

1) Mole Balances

$$C_{A0} v_0 - C_A v_0 + r_A V = 0$$

$$C_{A0} - C_A + r_A \tau = 0$$

$$0 - C_B v_0 + r_B V = 0$$

$$-C_B + r_B \tau = 0$$

2) Rates

Rate laws

$$-r_{A1} = k_1 C_{A1}$$

$$-r_{B2} = k_2 C_{B2}$$

Relative Rates

$$\frac{r_{A1}}{-1} = \frac{r_{B1}}{1} \qquad r_{B1} = -r_{A1}$$

$$\frac{r_{B2}}{-1} = \frac{r_{C2}}{1}$$

Net Rates

$$r_A = -k_1 C_{A1}$$

$$r_B = r_{1B} + r_{2B} = k_1 C_{A1} - k_2 C_{B2}$$

3) Combine

$$C_{A0} - C_A + k_1 C_A \tau = 0$$

$$C_A = \frac{C_{A0} - C_A}{k_1 C_A \tau} \rightarrow C_A = \frac{C_{A0}}{1 + k_1 \tau}$$

$$-C_B + (k_1 C_A - k_2 C_{B2})\tau = 0$$

$$C_B = \frac{k_1 C_A \tau}{1 + k_2 \tau}$$

$$C_B = \frac{k_1 \; C_{A0} \; \tau}{(1+k_1\tau)\,(1+k_2\tau)}$$

$1 + k_2\tau + k_1\tau + k_1k_2\tau^2$

→maximum τ gives max C_B

$$\frac{dC_B}{d\tau} = 0 = \frac{k_1 C_{A0}\left[1 + k_2\tau + k_1\tau + k_1k_2\tau^2\right) - k_1 C_{A0}\tau\left(k_2 + k_1 + 2k_1k_2\tau\right)}{\left[(1+k_1\tau)(1+k_2\tau)\right]^2}$$

$$k_1C_{A0} + \cancel{k_1k_2C_{A0}}\tau + \cancel{k_1^2C_{A0}}\tau + k_1^2k_2C_{A0}\tau^2 - \cancel{k_1k_2C_{A0}}\tau + \cancel{k_1^2C_{A0}}\tau + 2k_1^2k_2C_{A0}\tau^2 = 0$$

$$k_1C_{A0} - k_1^2k_2C_{A0}\tau^2 = 0$$

$$k_1C_{A0} = k_1^2k_2C_{A0}\tau^2$$

$$\tau^2 = \frac{\cancel{k_1}\,\cancel{C_{A0}}}{k_1^{\cancel{2}}\,k_2\,\cancel{C_{A0}}} \qquad \tau_{max} = \frac{1}{\sqrt{k_1k_2}}$$

Complex Reactions

$A + 2B \rightarrow C$

$2A + 3C \rightarrow D$

Algorithim:

1) Number Every Reaction
2) Mole Balance on every species
3) Rate law
   - → Net Rates of Reaction for every species

$$r_A = \sum r_{iA}$$

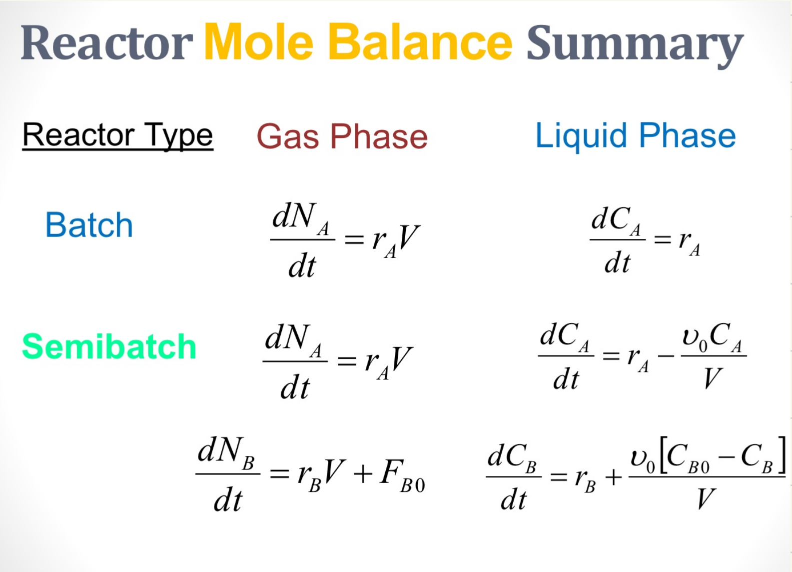
   - → Rate laws for every reaction

$$-r_{1A} = k_1 C_A C_B^2$$

$$-r_{2A} = k_2 C_A^2 C_C^3$$

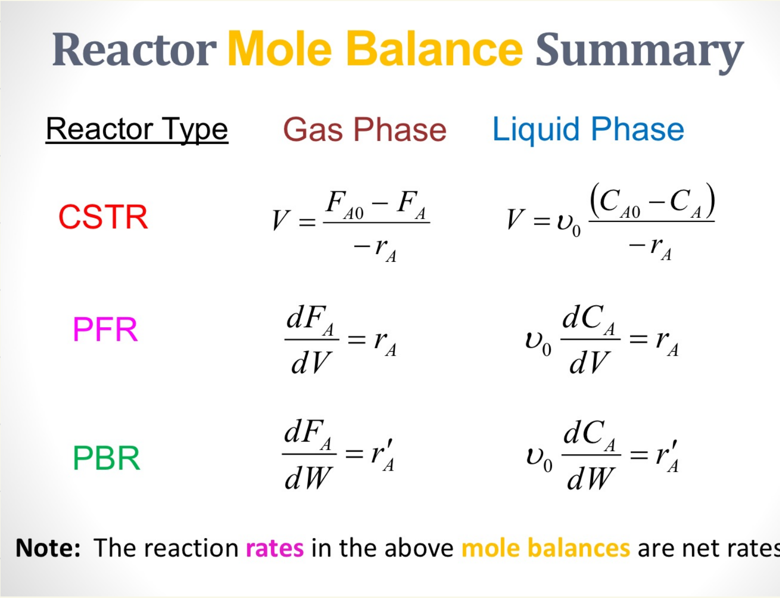
   - → Relative rates of reaction for every reaction

$$\frac{r_{1A}}{-a} = \frac{r_{1B}}{-b} = \frac{r_{1C}}{c} = \frac{r_{1D}}{d}$$



Reactor Mole Balance Summary

Reactor Type	Gas Phase	Liquid Phase
Batch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A$
Semibatch	$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A - \frac{\upsilon_0 C_A}{V}$
	$\frac{dN_B}{dt} = r_B V + F_{B0}$	$\frac{dC_B}{dt} = r_B + \frac{\upsilon_0 [C_{B0} - C_B]}{V}$



Reactor Mole Balance Summary

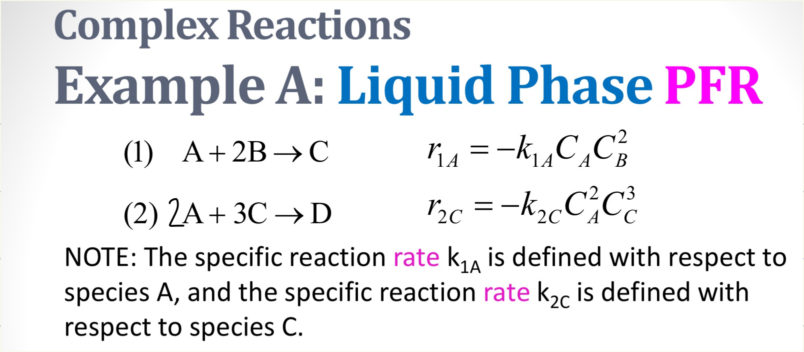
Reactor Type	Gas Phase	Liquid Phase
CSTR	$V = \frac{F_{A0} - F_A}{-r_A}$	$V = \upsilon_0 \frac{(C_{A0} - C_A)}{-r_A}$
PFR	$\frac{dF_A}{dV} = r_A$	$\upsilon_0 \frac{dC_A}{dV} = r_A$
PBR	$\frac{dF_A}{dW} = r_A'$	$\upsilon_0 \frac{dC_A}{dW} = r_A'$

Note: The reaction rates in the above mole balances are net rates

4) Stoichiometry

Concentration of Gas : $C_A = C_{T0} \frac{F_A}{F_T} \frac{P}{P_0} \frac{T_0}{T}$ $\quad F_T = F_A + F_B + F_C + F_D$

Concentration of Liquids $C_A = \frac{F_A}{V_0}$ $\quad C_A = \frac{N_A}{V_0}$



Complex Reactions

Example A: Liquid Phase PFR

(1) $A + 2B \rightarrow C$ $\quad r_{1A} = -k_{1A} C_A C_B^2$

(2) $2A + 3C \rightarrow D$ $\quad r_{2C} = -k_{2C} C_A^2 C_C^3$

NOTE: The specific reaction rate k_{1A} is defined with respect to species A, and the specific reaction rate k_{2C} is defined with respect to species C.

1) Mole Balances

$$\frac{dF_A}{dV} = r_A$$

$$\frac{dF_B}{dV} = r_B$$

$$\frac{dF_C}{dV} = r_C$$

$$\frac{dF_D}{dV} = r_D$$

2) Rates

Rate laws

$$r_{1A} = -k_{1A} C_A C_B^2$$

$$r_{2C} = -k_{2C} C_A^2 C_C^3$$

Relative Rates

$$\frac{r_{1A}}{-1} = \frac{r_{1B}}{-2} = \frac{r_{1C}}{1} \qquad r_{1B} = 2r_{1A} \qquad r_{1C} = -r_{1A}$$

$$\frac{r_{2A}}{-2} = \frac{r_{2C}}{-3} = \frac{r_{2D}}{1} \qquad r_{2A} = \frac{2}{3} r_{2C} \qquad r_{2D} = \frac{1}{-3} r_{2C}$$

Net Rates

$$r_A = r_{1A} + r_{2A}$$

$$r_{1A} = -k_{1A} C_A C_B^2 - \frac{3}{2}\left[k_{2C} C_A^2 C_C^3\right]$$

$$r_B = r_{1B}$$

$$r_B = -2k_{1A} C_A C_B^2$$

$$r_C = r_{1C} + r_{2C}$$

$$r_C = k_1 C_A C_B^2 - k_2 C_A^2 C_C^3$$

$r_D : r_{2D}$

$$r_D = \frac{1}{3} k_{2C} C_A^2 C_C^3$$

3) Stoichiometry (liquid)

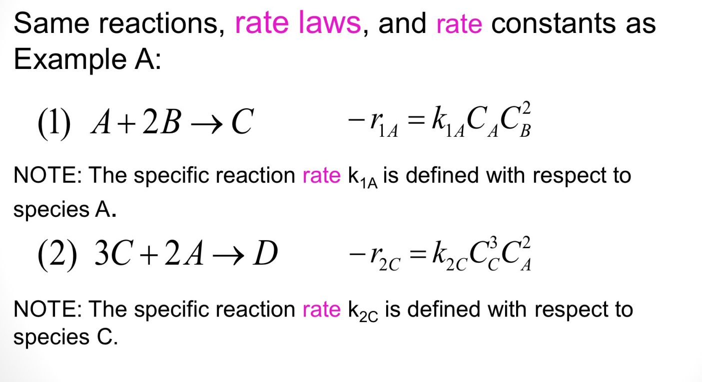
$$C_A = \frac{F_A}{v_0} \qquad C_C = \frac{F_C}{v_0}$$

$$C_B = \frac{F_B}{v_0} \qquad C_D = \frac{F_D}{v_0}$$

$$\tilde{S}_{C/D} = \frac{F_C}{F_D}$$ only if $V > 0.0001$ [else 0]

→ Define parameters for softwares.

Complex Reactions in Semibatch



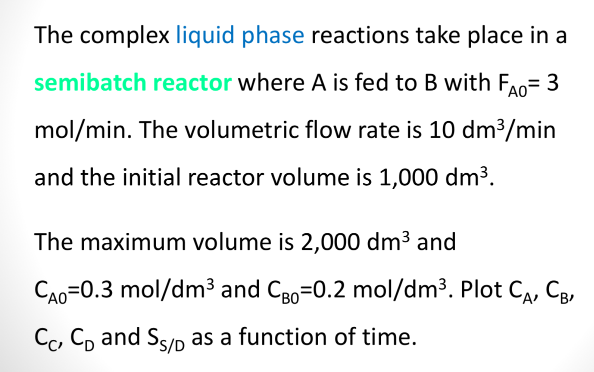
Same reactions, rate laws, and rate constants as Example A:

$$(1)\quad A + 2B \rightarrow C \qquad -r_{1A} = k_{1A} C_A C_B^2$$

NOTE: The specific reaction rate k_{1A} is defined with respect to species A.

$$(2)\quad 3C + 2A \rightarrow D \qquad -r_{2C} = k_{2C} C_C^3 C_A^2$$

NOTE: The specific reaction rate k_{2C} is defined with respect to species C.



The complex liquid phase reactions take place in a semibatch reactor where A is fed to B with F_{A0}= 3 mol/min. The volumetric flow rate is 10 dm³/min and the initial reactor volume is 1,000 dm³.

The maximum volume is 2,000 dm³ and C_{A0}=0.3 mol/dm³ and C_{B0}=0.2 mol/dm³. Plot C_A, C_B, C_C, C_D and $S_{S/D}$ as a function of time.

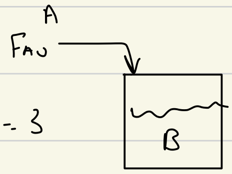
1) Mole Balances

$$\frac{dN_A}{dt} = r_A V + F_{A0}$$

$$\frac{dN_B}{dt} = r_B V$$

$$\frac{dN_C}{dt} = r_C V$$

$$\frac{dN_D}{dt} = r_D V$$



$F_{A0} = 3$

$v_0 = 10$

$N_{A0} = 0$

$N_{B0} = C_{B0} v_0$

$0.2(10) = 2$

$N_{C0} = 0$

$N_{D0} = 0$

2) Rate

Rate Laws $r_{1A} = -k_{1A} C_A C_B^2$

$r_{2C} = -k_{2C} C_A^2 C_C^3$

Relative Rates $\frac{r_{1A}}{-1} = \frac{r_{1B}}{-2} = \frac{r_{1C}}{1}$ $r_{1B} = 2r_{1A}$ $r_{1C} = -r_{1A}$

$\frac{r_{2A}}{-2} = \frac{r_{2C}}{-3} = \frac{r_{2D}}{1}$ $r_{2A} = \frac{2}{3} r_{2C}$ $r_{2D} = \frac{1}{-3} r_{2C}$

Net Rates $r_A = r_{1A} + r_{2A}$

$r_{1A} = -k_{1A} C_A C_B^2 - \frac{3}{2}\left[k_{2C} C_A^2 C_C^3 \right]$

$r_B = r_{1B}$

$r_B = -2k_{1A} C_A C_B^2$

$r_C = r_{1C} + r_{2C}$

$r_C = k_1 C_A C_B^2 - k_2 C_A^2 C_C^3$

$r_D = r_{2D}$

$r_D = \frac{1}{3} k_{2C} C_A^2 C_C^3$

⇒ Same as previous Example

3) Stoichiometry $V = V + v_0 t$

$C_A = \frac{N_A}{V}$ $C_C = \frac{N_C}{V}$

$C_B = \frac{N_B}{V}$ $C_D = \frac{N_C}{V}$

Selectivity $= \frac{N_C}{N_D}$

Ch. 11 Steady State Non-isothermal Reactor Design

Energy Balance, Rationale & overview

1. Mole Balance [PFR]

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

2. Rate Law

$$r_A = -k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] C_A$$

3. Stoichiometry

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

4. Combine

$$\frac{dX}{dV} = \frac{k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]}{F_{A0}} C_{A0}(1-X)$$

↳ to solve this equation X has to be a function of either V or T

⇒ Energy Balance

1. Adiabatic CSTR, PFR, Batch or PBR

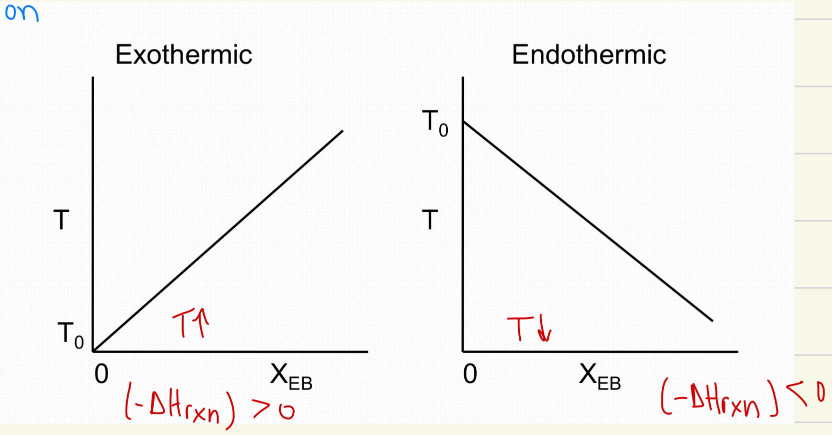
$\dot{W}_S = 0$ $\Delta C_p = 0$

↳ Heat Capacity

$$X_{EB} = \frac{\sum \Theta_i C_{p_i} (T - T_0)}{-\Delta H_{rxn}}$$

$$T = T_0 + \frac{(-\Delta H_{rxn})X}{\sum \Theta_i C_{P_i}}$$

heat of reaction ↵

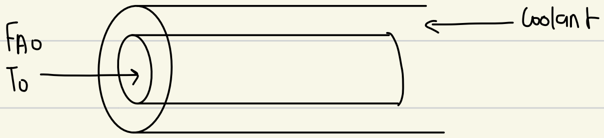


2. CSTR with heat exchange

$$Q = \underbrace{U}_{\text{overall heat transfer coefficient}}\overset{\text{CSTR heat exchange Area.}}{A}\,(\overset{\text{ambient temp}}{T_a} - T) \quad \& \text{ large coolant flow rate}$$

$$X_{EB} = \frac{\left(\frac{UA}{F_{A0}}(T - T_a)\right) + \Sigma\theta_i C_{p_i}(T - T_0)}{-\Delta H_{rxn}}$$

3 PFR / PBR with heat exchange



$$\frac{dT}{dV} = \frac{(\text{Heat gen} - \text{heat removed})}{\Sigma F_i C_{p_i}}$$

$$\frac{dT}{dV} = \frac{Q_g - Q_R}{\Sigma F_i C_{p_i}}$$

↳ 3.A PFR in terms of conversion

$$\frac{dT}{dV} = \frac{\overset{Q_g}{r_A \Delta H_{rxn}(T)} - \overset{Q_R}{Ua(T - T_a)}}{F_{A0}(\Sigma\theta_i C_{p_i} + \Delta C_p X)} = \frac{Q_g - Q_R}{F_{A0}(\Sigma\theta_i C_{p_i} + \Delta C_p X)}$$

↳ 3.B PBR in terms of Conversion

$$\frac{dT}{dW} = \frac{r_A' \Delta H_{rxn}(T) - \frac{Ua}{\rho}(T - T_a)}{F_{A0}(\Sigma\theta_i C_{p_i} + \Delta C_p X)}$$

↳ 3.C PFR in terms of Molar Flow rates

$$\frac{dT}{dV} = \frac{r_A \, \Delta H_{rxn}(T) - Ua(T - T_a)}{\sum F_i C_{pi}}$$

↳ 3.D PBR in terms of Molar Flow rates

$$\frac{dT}{dW} = \frac{r_A' \, \Delta H_{rxn}(T) - \frac{Ua}{\rho}(T - T_a)}{\sum F_i C_{pi}}$$

4. Batch Reactor

$$\frac{dT}{dt} = \frac{(r_A V)(\Delta H_{rxn}) - UA(T - T_a)}{\sum N_i C_{pi}}$$

5 Semibatch or unsteady CSTR

$$\frac{dT}{dt} = \frac{\dot{Q} - W_s - \sum F_{i0}\left[C_{pi}(T - T_{i0}) + \left(-\Delta H_{rxn}(T)\right)(-r_A V) \right]}{\sum N_i C_{pi}}$$

6. Multiple Reactions in a PFR

↱ summation (reactions)

$$\frac{dT}{dV} = \frac{\sum r_{ij} \, \Delta H_{rxn,ij} - Ua(T - T_a)}{\sum F_i C_{pi}}$$

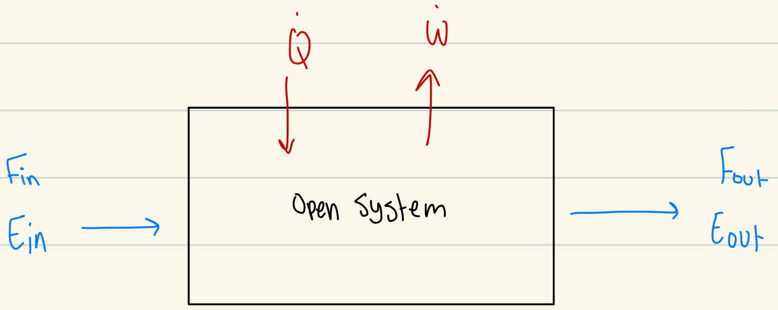
↳ summation (species)

Convection

- → Heat added (+)
- → Heat removed (−)
- → work done by sys (+)
- → work done on the sys (−)

Energy Balance

→ Reactor with no spatial variations



Rate of Acc. of E within the system = heat to system from surr − work done by sys on surr + Energy into sys by mass − Energy out sys by mass

for one species: $$\frac{dE}{dt} = \dot{Q} - \dot{W} + F_{in}E_{in} - E_{out}F_{out}$$

for multiple species $$\frac{dE}{dt} = \dot{Q} - \dot{W} + \sum^{n} FE\Big|_{in} - \sum^{n} FE\Big|_{out}$$

- ↳ Replace U by $U_i = H_i - PV_i$
- ↳ Express H in terms of heat capacities
- ↳ Express F_i in terms of conversion or rates of reaction
- ↳ Define ΔH_{rxn}
- ↳ Define ΔC_p

Intro to Heat Effects

Assumptions

$$E_i = U_i + \cancelto{0}{PE_i} + \cancelto{0}{KE_i}$$

→ other energies (Potenial & kinetic) are small compared to internal Energy

↱ produced by stirrer in CSTR or turbine in PFR

W = Flow work + Shaft work

work necessary to get ↲ the mass into & out of the system

Flow work = $-\sum F_{io} P_o \tilde{V}_{io} + \sum F_i P \tilde{V}_i$

$\tilde{V} = m^3/mol$

Pressure ↲ ↳ specific molar volume

→ Substitute in Energy Balance Equation

$$\frac{dE}{dt} = \sum F_0 U_0 - \sum F U + \dot{Q} - \left[- \sum F_{i0} P_0 \tilde{V}_{i0} + \sum F_i P \tilde{V}_i + \dot{W}_s \right]$$

$$\frac{dE}{dt} = \sum F_0 \left[\overset{H_0}{U_0 + P V_0} \right] - \sum F \left[\overset{H}{U + PV} \right] + \dot{Q} - \dot{W}_s$$

$$\frac{dE}{dt} = \sum F_0 H_0 - \sum F H + \dot{Q} - \dot{W}_s$$

General Energy Balance

Steady state: $0 = \sum F_0 H_0 - \sum F H + \dot{Q} - \dot{W}_s$

Intro to Heat Effects

$$\sum F_{i0} H_{i0} = F_{A0} \sum \Theta_i H_{i0}$$

$\Theta_i = \frac{F_{i0}}{F_{A0}}$

ΔH_{rxn} - Heat of Reaction

$$\sum F_i H_i = F_{A0} \sum (\Theta_i + \nu_i X) H_i = F_{A0} \sum \Theta_i H_i + F_{A0} X \sum \nu_i H_i$$

Stoichiometric ↲ coeff.

$$\dot{Q} - \dot{W}_s + F_{A0} \left(\sum \Theta_i (H_{i0} - H_i) + F_{A0} X \Delta H_{Rxn} \right) = 0$$

↳ phase change

→ For no phase changes

$$H_i(T) = H_i^0 (T_R) + \int_{T_R}^{T} C_{p_i} \, dT$$

↳ Enthalpy of formation at T_R

* heat of formation of all elements (ex: H_2, N_2, ...) at $T = 25°C$

$H_i^0 = 0$

$$\dot{Q} - W_s - F_{A0} \sum \Theta_i C_{P_i} [T_i - T_{i0}] - \Delta H_{rxn}(T) \, F_{A0} X = 0$$

⇒ Constant Heat Capacities

$$H_i(T) = H_i^\circ(T_R) + C_{P_i}(T - T_R)$$

$$H_{i0} - H_i = C_{P_i}(T - T_0)$$

$$\sum \nu_i H_i = \sum \nu_i H_i^\circ + \sum \nu_i C_{P_i}(T - T_R)$$

↳ Heat of reaction at Temp T

$$\Delta H_R(T) = \Delta H_R^\circ(T_R) + \Delta \hat{C}_p (T - T_R)$$

$$\sum \nu_i \hat{C}_p = \Delta \hat{C}_p = \frac{d}{a}\hat{C}_{p_D} + \frac{c}{a}\hat{C}_{p_C} - \frac{b}{a}\hat{C}_{p_B} - \hat{C}_{p_A}$$

$$Q - W_s - F_{A0}X\left[\Delta H_R^\circ(T_R) + \Delta\hat{C}_p(T - T_R)\right] - F_{A0}\sum \Theta_i \tilde{C}_{p_i}(T - T_{i0}) = 0$$

→ Unless the reaction is carried out adiabatically, the equation is still difficult to evaluate, because in Non-adiabatic Reactors the heat added to or removed from the system varies along the length of the Reactor

Adiabatic Energy Balance

→ Adiabatic $Q = 0$ & $\dot{W} = 0$

$$T = T_0 - \frac{X\left[\Delta H_R^\circ(T_R) + \Delta C_p(T - T_R)\right]}{\sum \Theta_i \tilde{C}_{p_i} + X \Delta\hat{C}_p} = T_0 - \frac{X\left[\Delta H_R(T)\right]}{\sum \Theta_i \tilde{C}_{p_i} + \Delta\hat{C}_p X}$$

Example: Adiabatic PFR

$$A \longleftrightarrow B$$

1) Mole Balance $\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$

2) Rate law $-r_A = K\left[C_A - \frac{C_B}{K_e}\right]$

$$k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

$$k_e = k_{e1} \exp\left[\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

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

$C_B = C_{A0}X$

4) Energy Balance $T = T_0 + \frac{-\Delta H_x^o X}{\Sigma \Theta_i C_{P_i}}$

→ Calculate maximum conversion [adiabatic equilibrium conversion] (Temp that gives max conv)

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

$$0 = C_A - \frac{C_B}{k_e} \qquad C_A = \frac{C_B}{k_e}$$

$$C_{A0}(1-X) = \frac{C_{A0}X}{k_e}$$

$$1-X = \frac{X}{k_e}$$

$$X_e = \frac{k_e}{1+k_e}$$

1) set X

2) calculate T $\qquad T = T_0 + \frac{-\Delta H_x^\circ X}{\sum \theta_i C_{p_i}}$

$$T - T_0 = \frac{-\Delta H_x^\circ X}{\sum \theta_i C_{p_i}}$$

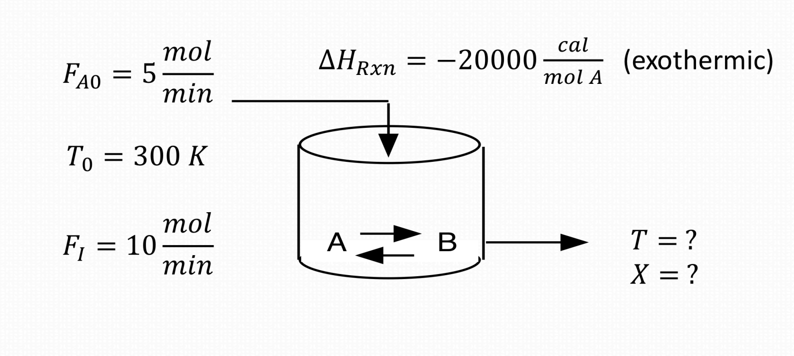
$$X = \frac{(T - T_0)\sum \theta_i C_{p_i}}{-\Delta H^\circ_x}$$ $\Rightarrow$ X at every T

3) solve for rate law

↳ $F_{A0}/-r_A$ use levenspiel plot

Ex: Adiabatic CSTR

$C_{A0} = 2$

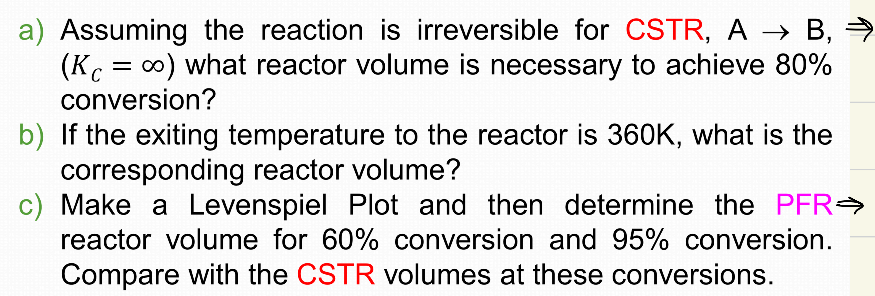


$C_{p_A} = 164$

$C_{p_I} = 18$

$K @ 298 = 0.1$

$E = 10{,}000$



a) Assuming the reaction is irreversible for CSTR, A → B, ($K_C = \infty$) what reactor volume is necessary to achieve 80% conversion? $\Rightarrow$ $A + 2I \rightarrow B$

b) If the exiting temperature to the reactor is 360K, what is the corresponding reactor volume?

c) Make a Levenspiel Plot and then determine the PFR $\Rightarrow$ AUC reactor volume for 60% conversion and 95% conversion. Compare with the CSTR volumes at these conversions.

1) Mole Balance $\qquad V = \frac{F_{A0} X}{-r_A}$

2) Rate Laws $\qquad -r_A = kC_A \qquad k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$

3) Stoichiometry $\qquad C_A = C_{A0}(1 - X)$

4) Energy Balance

Adiabatic $C_p = 0$

$$T = T_o + \frac{-\Delta H_{rxn} \; X}{\Sigma \theta_i C_{p_i}}$$

$$T = 300 + \frac{-(-20\,000) \; X}{\theta_A C_{P_A} + \theta_I \; C_{P_I}}$$

$$T = 300 + \frac{20{,}000 \; X}{1(164) + \frac{2}{1}(18)}$$

$$T = 300 + 100X$$

A) $T = 300 + 100(0.8) = 380$

$$k = k_1 \exp\left(\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$$

$$0.1 \exp\left[\frac{10{,}000}{1.989}\left(\frac{1}{298} - \frac{1}{380}\right)\right] = 3.81$$

$$V = \frac{F_{A0} X}{-r_A} = \frac{F_{A0} X}{k C_{A0}(1-X)} = \frac{5(0.8)}{3.81(2)(1-0.8)} = 2.62 \text{ dm}^3$$

B) $k = 0.1 \exp\left[\frac{10{,}000}{1.989}\left(\frac{1}{298} - \frac{1}{360}\right)\right] = 1.83$

$$T = 300 + 100X$$

$$360 = 300 + 100X \qquad X = 0.6$$

$$V = \frac{F_{A0} X}{-r_A} = \frac{5(0.6)}{1.83(2)(1-0.6)} = 2.05 \text{ dm}^3$$

c) $X \longrightarrow T \longrightarrow k \longrightarrow -r_A \longrightarrow \frac{F_{A0}}{-r_A}$

for $X=0$ $T = 300 + 100\,X$

$300 + 100\,(0) = 300$

$$k = 0\,1 \exp\left[\frac{10{,}000}{1.989}\left(\frac{1}{298} - \frac{1}{300}\right)\right] = 0.111$$

$$-r_A = 0.1119\,(2)(1-0) = 0.2238$$

$$\frac{F_{A0}}{-r_A} = \frac{5}{0.2238} = 22.3$$

$\downarrow$ repeat till $X = 1$

↳ max conv & plot $-F_{A0}/r_A$ vs X

d) Now assume the reaction is reversible, make a plot of the equilibrium conversion as a function of temperature between 290K and 400K.

1) Mole Balance $V = \frac{F_{A0} X}{-r_A}$

2) Rate law $-r_A = k\left[C_A - \frac{C_B}{K_C}\right]$ $k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$

$K_C = K_{C1} \exp\left[\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$

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

$C_B = C_{A0} X$

4) Energy Balance $T = 300 + 100X$

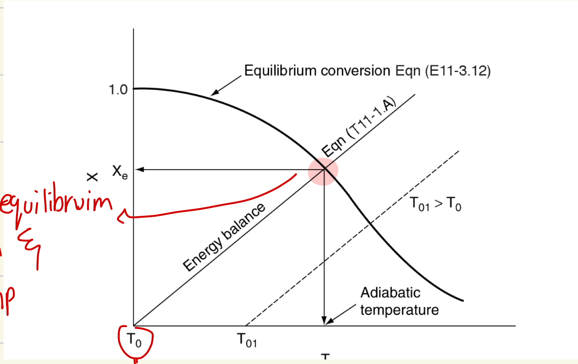
Adiabatic Conversion

The highest conversion that can be achived in reversible reactions

Endothermic equilibrium conversion ↑ with ↑T
Exothermic equilibrium conversion ↓ with ↑T

In Exothermic Reactions, to determine the maximum conversion that can be achieved, Find the intersection of the equilibrium conversion as a function of T

* if the inlet temp is increased from T_0 to T_{01} ⇒ the adiabatic equilibrium conversion decreases

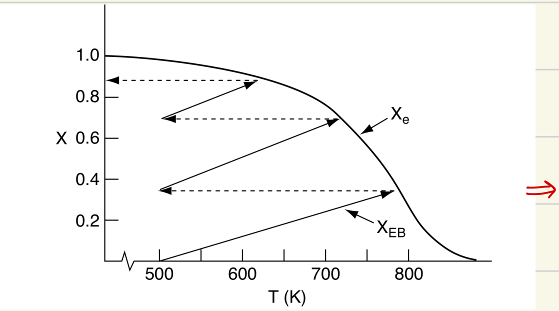


Adiabatic equilibruim conversion & Temp

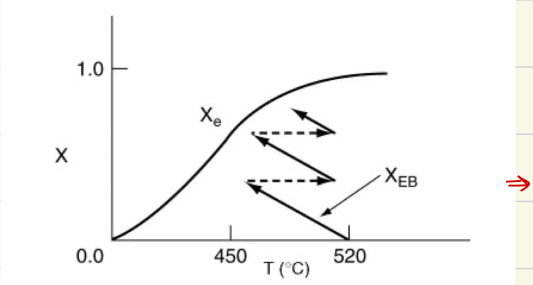
entering temp

Reactor Staging

higher conversion can be achieved for adiabatic operations by connecting reactors in series with interstaged cooling



⇒ Exothermic Reactions ↑T ↓X_e

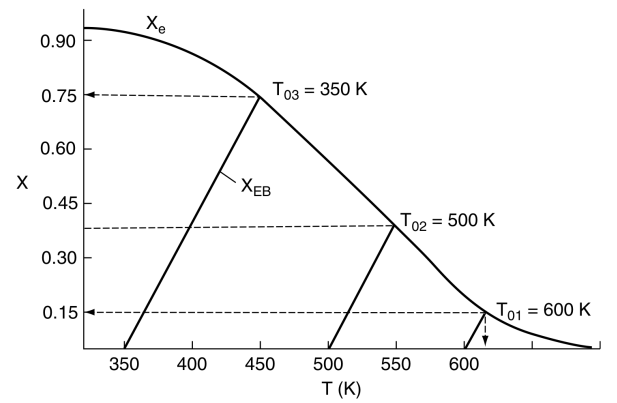


⇒ Endothermic Reactions ↑T ↑X_e

Optimum feed Temperature

→ Using very high feed temp , the specific reaction rate will be high & reaction will proceed rapidly but equilibrium conversion will be close to zero ⇒ very little product will be formed

→ Using very low feed temp , very little product will be formed because the reaction rate is so low.



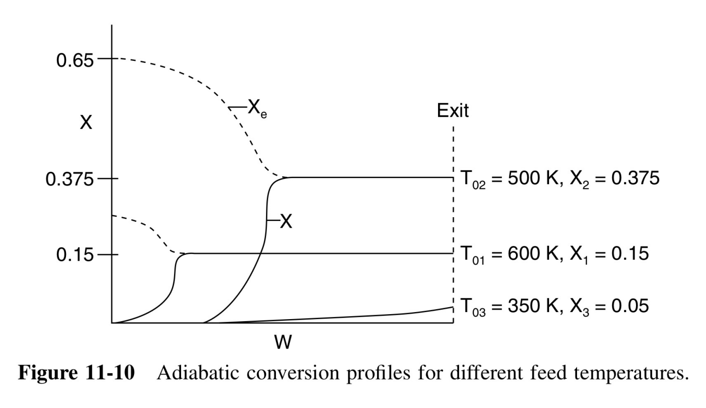
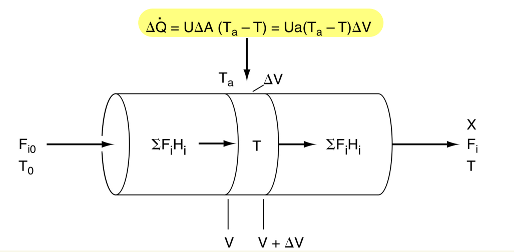


Figure 11-10 Adiabatic conversion profiles for different feed temperatures.

Chapter 12: Steady state - Nonisothermal Reactor Design [Reactors with heat exchange]

Steady state Tubular Reactor with heat exchange
[PFR]



Tubular reactor with heat either added or Removed

No Radial gradient in the reactor

→ Energy Balance on Volume ΔV

$$\sum F_iH_i\Big|_V - \sum F_iH_i\Big|_{V+\Delta V} + Ua(T_a - T)\Delta V = 0$$

a: heat exchange area per unit volume of Reactor

$$a = \frac{\pi D L}{\frac{\pi}{4} D^2 L} = \frac{4}{D}$$

→ Dividing by ΔV & taking limit ΔV → ∞

$$\frac{-d\sum F_iH_i}{dV} + Ua(T_a - T) = 0$$

$$\frac{-d\sum F_iH_i}{dV} = -\left[\sum F_i \frac{dH_i}{dV} + \sum H_i \frac{dF_i}{dV}\right]$$

→ Mole Balance on Species i

$$\frac{dF_i}{dV} = r_i = \nu_i(-r_A)$$

→ $H_i = H_i^{\circ} + Cp_i\,(T - T_R)$

$$\frac{dH_i}{dV} = Cp_i \frac{dT}{dV}$$

→ Combine

$$-\frac{d\sum F_iH_i}{dV} = -\left[\sum F_i\, C_{p_i}\frac{dT}{dV} + \sum H_i\, \nu_i(-r_A)\right]$$

$\sum H_i \nu_i = \Delta H_{rxn}$

→ Back into Energy Balance

$$-\left[\sum F_i\, C_{p_i}\frac{dT}{dV} + \Delta H_{rxn}(-r_A)\right] + Ua(T_a - T) = 0$$

$$\sum F_i C_{p_i}\frac{dT}{dV} = \Delta H_{rxn}(r_A) - Ua(T - T_a)$$

$$\frac{dT}{dV} = \frac{\underbrace{\Delta H_{rxn}(r_A)}_{\text{Heat gen}} - \underbrace{Ua(T - T_a)}_{\text{Heat removed}}}{\sum F_i C_{p_i}}$$

* For exothermic reactions (Q gen) will be a positive number

$Q_g > Q_r$ ⇒ Temperature will increase down the reactor

$Q_r > Q_g$ ⇒ Temperature will decrease down the reactor

* For endothermic reactions (Qgen & Qr) will be negative numbers ⇒ $T_a > T$

$-Q_g > -Q_r$ ⇒ Temp will decrease

$-Q_r > -Q_g$ ⇒ Temp will increase

$$\rightarrow \sum F_i C_{p_i} = F_{A0}\left[\sum \Theta_i C_{p_i} + \Delta C_p X\right]$$

if $C_p = 0$ then

$$\frac{dT}{dV} = \frac{(-r_A)(-\Delta H_{rxn}) - Ua(T - T_a)}{F_{A0}\sum \Theta_i C_{p_i}}$$

User friendly Energy Balance for [PBR]

$$\int_0^W \frac{Ua}{\rho_B}(T_a - T)\,dW + \sum F_{i0} H_{i0} - \sum F_i H_i = 0$$

→ Differentiating with respect to W

$$\frac{Ua}{\rho_B}(T_a - T) + 0 - \sum \frac{dF_i}{dW} H_i - \sum \frac{dH_i}{dW} F_i = 0$$

→ Mole Balance on species i

$$\frac{dF_i}{dW} = r_i = \nu_i(-r_A')$$

→ Enthalpy for species i

$$H_i = H_i^\circ(T_R) + \int_{T_R}^{T} C_{p_i}\,dT$$

$$\frac{dH_i}{dW} = 0 + C_{p_i}\frac{dT}{dW}$$

→ combine

$$\frac{Ua}{\rho_B}(T_a - T) + r_A' \underbrace{\sum \nu_i H_i}_{\Delta H_{rxn}} - \sum \underbrace{F_i}_{} C_{p_i}\frac{dT}{dW} = 0$$

$\hookrightarrow F_i = F_{A0}(\Theta_i + \nu_i X)$

→ Back into Energy Balance [Terms of conv]

$$\frac{dT}{dW} = \frac{\frac{Ua}{\rho_B}(T_a - T) + r_A' \Delta H_{rxn}}{F_{A0}\left[\sum \Theta_i C_{p_i} + \Delta C_p X\right]} = f(X,T)$$

→ Back into Energy Balance [Terms of Molar Flow Rate]

$$\frac{dT}{dW} = \frac{\frac{Ua}{\rho_B}(T_a - T) + r_A' \Delta H_{rxn}}{F_i C_{p_i}}$$

$$\frac{dX}{dW} = \frac{-r_A'}{F_{A0}} \quad g(X,T)$$

User Friendly Equations Cases:

1. Constant T_a

2. Variable T_a [Co-current]

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}\, C_{P_{cool}}} \qquad V = 0 \qquad \therefore\ T_a = T_{a0}$$

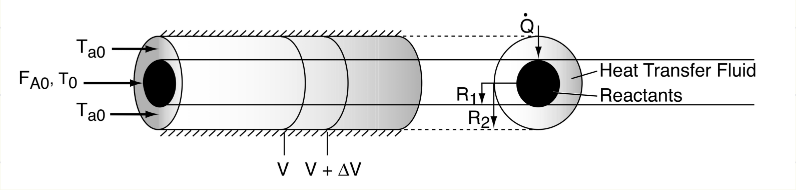
3. Variable T_a [Counter-current]

$$\frac{dT_a}{dV} = \frac{Ua(T_a - T)}{\dot{m}\, C_{P_{cool}}} \qquad V = 0 \qquad \therefore\ T_a = ?$$

↳ Guess T_a at $V=0$ to match $T_{a0} = T_{a0}$ at exit

Variable Ta [Co-current]

* The heat transfer fluid will be a coolant for exothermic reactions & heating meduim for endothermic



coolant between R_1 & R_2 [annulus]

$\dot{Q}$ = heat added to the system

Reactant & coolant flow in the same direction

1. Energy Balance on the coolant

In − out + Heat added = 0

$$\dot{m}_c H_c \Big|_V - \dot{m}_c H_c \Big|_{V+\Delta V} + Ua(T - T_a) = 0$$

↳ Temp of heat Transfer fluid

2. Divide by ΔV & taking lim $V \rightarrow 0$

$$-\dot{m}_c \frac{\partial H}{\partial V} + U_a (T - T_a) = 0$$

3. Coolant Enthalpy

$$H_c = H_c^o + C_{p_c} (T_a - T_r)$$

$$\frac{dH_c}{dV} = C_{p_c} \frac{dT_a}{dV}$$

4. Combine

$$\boxed{\frac{dT_a}{dV} = \frac{U_a (T - T_a)}{\dot{m}_c C_{p_c}}} \qquad V = 0 \quad T_a = T_{a0}$$

↳ The variation of coolant temperature down the length of Reactor

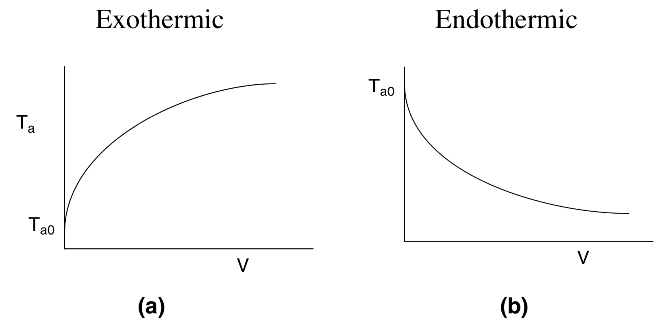
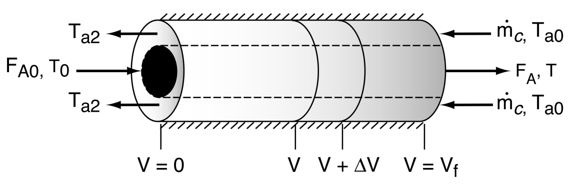


Figure 12-3 Heat-transfer fluid temperature profiles for co-current heat exchanger. **(a)** Coolant. **(b)** Heating medium.

Variable T_a [counter - current]



Reacting mixture & heat transfer fluid flow in opposite direction

At reactor enterance $V = 0$ Reactants T_0 , Coolant T_{a2}
↓ in ↳ out

At the end of the reactor Reactants T , coolant T_{a0}
↓ out ↳ in

Energy Balance on the coolant

In - out + heat added = 0

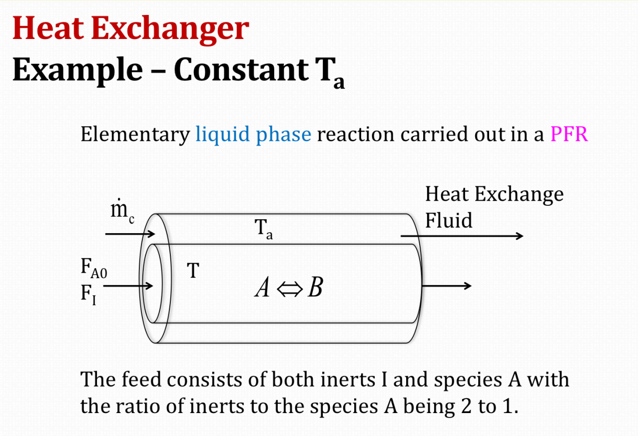
$$\dot{m}_c H_c \Big|_{V} - \dot{m}_c H_c \Big|_{V+\Delta V} + Ua(T - T_a) = 0$$

$$\dot{m}_c \frac{dH_c}{dV} + Ua(T - T_a) = 0$$

$$\boxed{\frac{dT_a}{dV} = \frac{Ua(T_a - T)}{\dot{m}_c C_{pc}}}$$

- At the enterance $V = 0$, $X = 0$, $T_a = T_{a2}$
- At the exit $V = V_f$, $T = T_{a0}$

↳ Solution to counter-current : Trial & error [exit conversion & temperature]



Heat Exchanger

Example – Constant T_a

Elementary liquid phase reaction carried out in a PFR

The feed consists of both inerts I and species A with the ratio of inerts to the species A being 2 to 1.

1. Mole Balance $\quad \frac{dX}{dV} = \frac{-r_A}{F_{A0}}$

2. Rate laws $\quad -r_A = k\left[C_A - \frac{C_B}{K_C}\right]$

$$k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

$$K_C = K_{C1} \exp\left[\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

3. Stoichiometry $\quad C_A = C_{A0}(1-X)$

$$C_B = C_{A0}X$$

4. Heat effects $\quad \frac{dT}{dV} = \frac{(-\Delta H_{rxn})(-r_A) - Ua(T-T_a)}{F_{A0}\sum \Theta_i C_{pi}}$ $\quad \Delta C_p = 0$

$$X_{eq} = \frac{K_C}{1+K_C}$$

$$\sum \Theta_i C_{pi} = (1)C_{pA} + \Theta_I C_{pI}$$

→needed parameters: ΔH_{rxn}, E, R, T_1, T_2, T_a, k_1, K_{C1}, Ua, F_{A0}, C_{A0}, C_{pA}, C_{pI}, Θ_I, $-r_A$

Ex: Adiabatic PFR Algorithim

1. Mole Balance $\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$

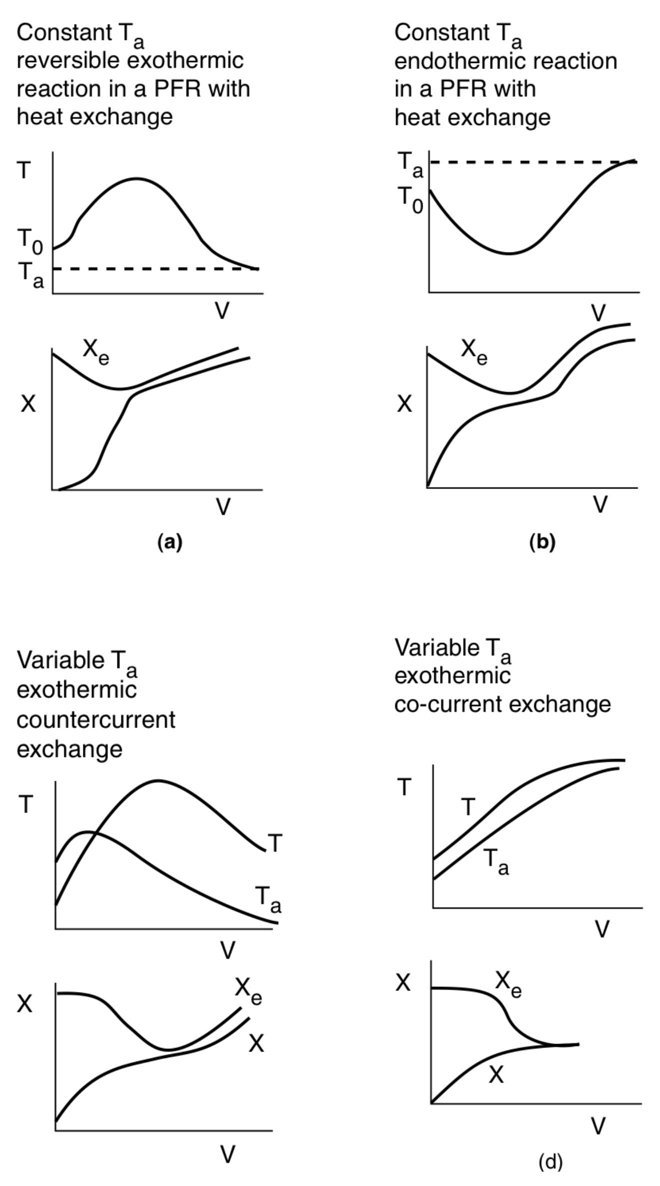
2. Energy Balance

Adiabatic $\Delta C_p = 0$ $Ua = 0$

$$T = T_0 + \frac{(-\Delta H_{rxn})X}{\sum \Theta_i C_{p_i}}$$

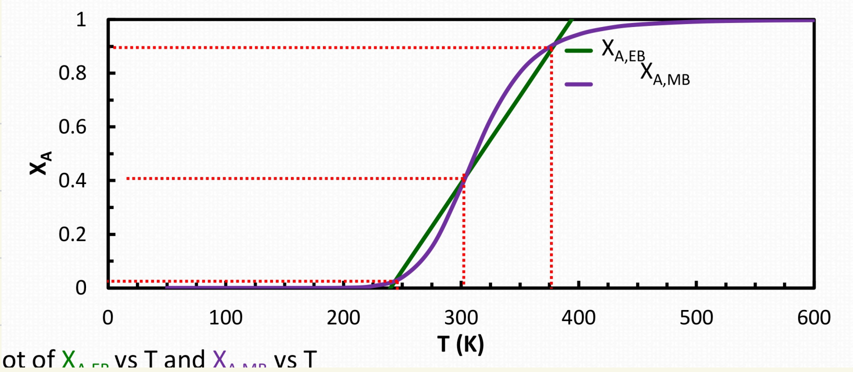
$$\sum \Theta_i C_{p_i} = C_{pA} + \Theta_I C_{pI}$$

PBR & PFR Design with Heat Effects



Study Example 12.1 & 12.2

CSTR with Heat Effects [Multiple Steady States in CSTR]



ot of $X_{A,EB}$ vs T and $X_{A,MB}$ vs T

Plot of X_{MB} & X_{EB} vs T

→ Intersections of T & X_A satisfy both the Mole Balance & Energy Balance ⇒ Steady states

→ Reaction must operate near one of these steady states

→ Steady state Energy Balance on CSTR

Considering a jacketed CSTR, with constant heat capacity, negligable shaft work, $\Delta C_p = 0$, first order kinetics, $T_{i0} = T_0$, constant T_a in jacket

$$Q = UA(T_a - T)$$

→ Energy Balance : $(-\Delta H_{rxn}) F_{A0} X - F_{A0} \sum \theta_i C_{p_i} (T - T_0) - UA(T_a - T) = 0$

$$\underbrace{\sum \theta_i C_{p_i} [T - T_{i0}] - \frac{UA(T_a - T)}{F_{A0}}}_{\text{Heat Removed } R(T)} = \underbrace{-\Delta H^\circ_{rxn}(T_R)\, X}_{\text{Heat Generated } G(T)}$$

$G(T) - R(T) = 0$ ⇒ Steady state

$$\sum \Theta_i C_{P_i} [T - T_{i0}] - \frac{UA(T_a - T)}{F_{A0}} = -\Delta H_{rxn}^{\circ}(T_R) X$$

$C_{P0} = \sum \Theta_i C_{P_i}$

$V = \frac{F_{A0} X_A}{-r_A} \rightarrow X_A = \frac{V(-r_A)}{F_{A0}}$

→ Substitute:

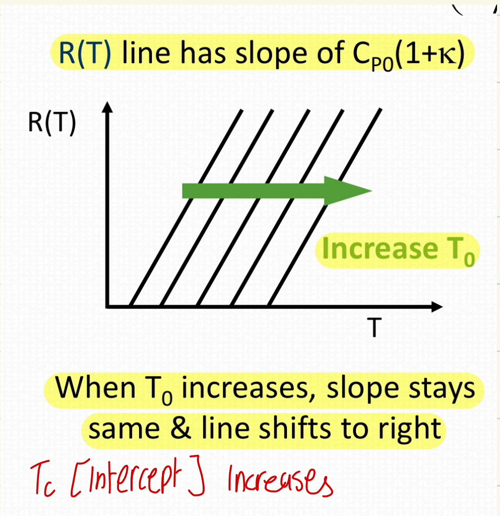
$$C_{P0}(T - T_{i0}) - \frac{UA(T_a - T)}{F_{A0}} = -\Delta H_{Rx}^{\circ}(T_R)\left[\frac{-r_A V}{F_{A0}}\right]$$

non-adiabatic parameter

$\kappa = \frac{UA}{C_{P0} F_{A0}} \rightarrow T_c = \frac{T_0 F_{A0} C_{P0} + UA\, T_a}{UA + C_{P0} F_{A0}}$ ∴ $T_c = \frac{\kappa T_a + T_0}{1 + \kappa}$

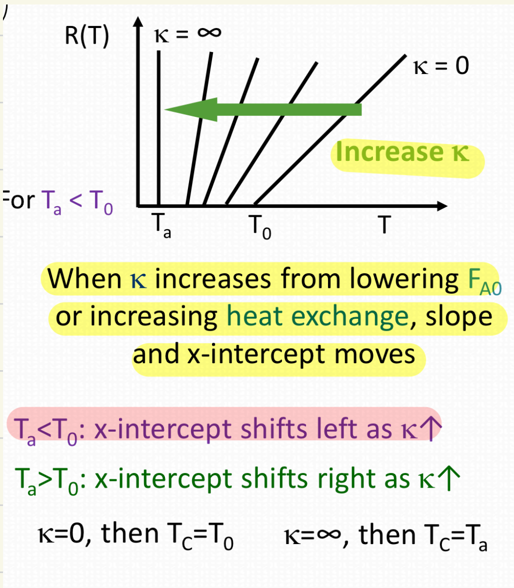
$$\Rightarrow \underbrace{C_{P0}(1+\kappa)(T - T_c)}_{\text{Heat removed } R(T)} = \underbrace{-\Delta H_{rxn}^{\circ}\left(\frac{-r_A V}{F_{A0}}\right)}_{\text{Heat Gen } G(T)}$$

Heat Removal Term R(T)


R(T) line has slope of $C_{P0}(1+\kappa)$

When T_0 increases, slope stays same & line shifts to right

T_c [Intercept] Increases



When κ increases from lowering F_{A0} or increasing heat exchange, slope and x-intercept moves

$T_a < T_0$: x-intercept shifts left as κ↑

$T_a > T_0$: x-intercept shifts right as κ↑

κ=0, then $T_c = T_0$ κ=∞, then $T_c = T_a$

$\kappa = \frac{UA}{C_{P0} F_{A0}}$ ↓F_{A0} ↑κ

* κ & T_c are used to simplify equations for non-adiabatic CSTR

Heat Generation Term G(T)

$$G(T) = -\Delta H^{\circ}_{rxn}(-r_A)$$

→ to obtain a plot of heat gen as a function of temperature ⇒ solve for X as a function of T

$$V = \frac{F_{A0}X}{-r_A} = \frac{C_{A0}v_0 X}{k C_{A0}(1-X)}$$

$$V = \frac{v_0 X}{k(1-X)} \qquad \tau = \frac{X}{k(1-X)}$$

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

→ substituting for X

$$G(T) = \frac{-\Delta H^{\circ}_{rxn}\tau k}{1+\tau k}$$

$$G(T) = \frac{-\Delta H^{\circ}_{rxn}\tau A e^{-E/RT}}{1+\tau A e^{-E/RT}}$$

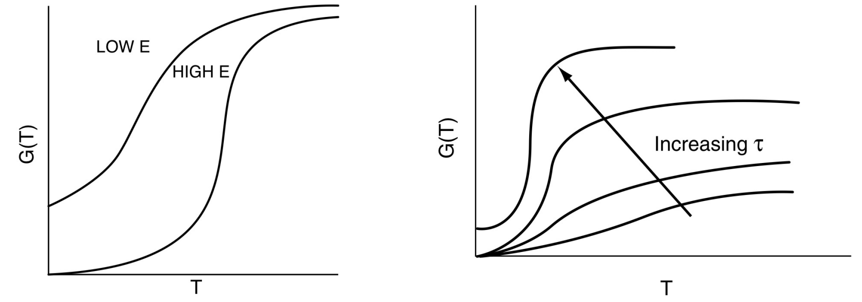
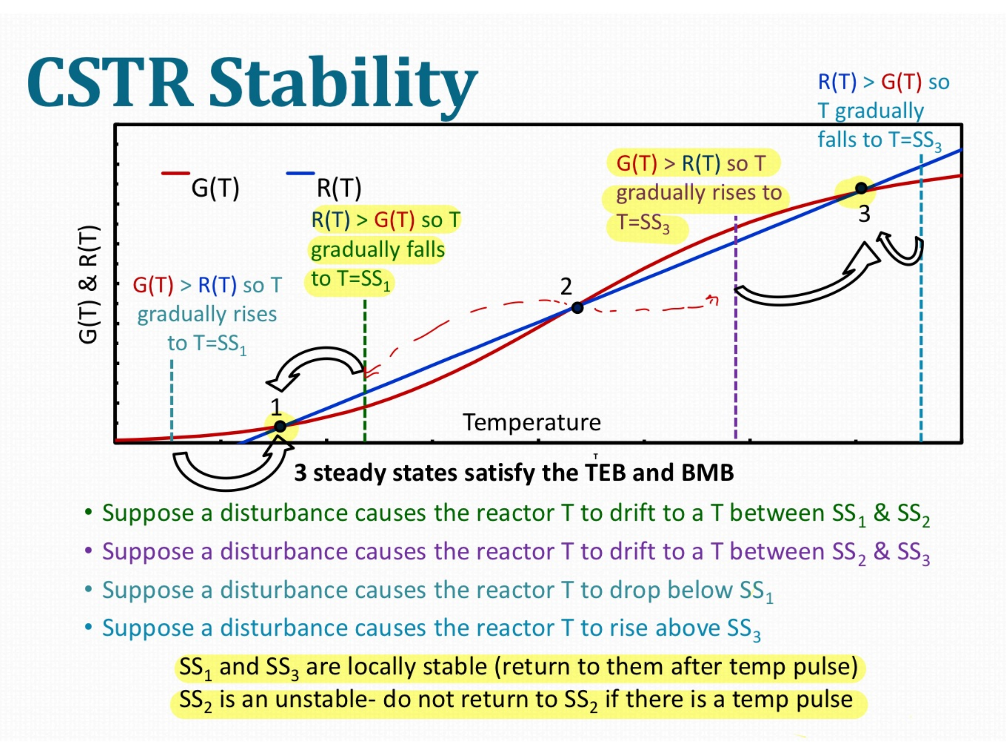


Figure 12-9 Variation of G(T) curve with activation energy.

Figure 12-10 Variation of G(T) curve with space time.



CSTR Stability

3 steady states satisfy the TEB and BMB

- Suppose a disturbance causes the reactor T to drift to a T between SS_1 & SS_2
- Suppose a disturbance causes the reactor T to drift to a T between SS_2 & SS_3
- Suppose a disturbance causes the reactor T to drop below SS_1
- Suppose a disturbance causes the reactor T to rise above SS_3

SS_1 and SS_3 are locally stable (return to them after temp pulse)

SS_2 is an unstable- do not return to SS_2 if there is a temp pulse

Ignition & Extinction Curves

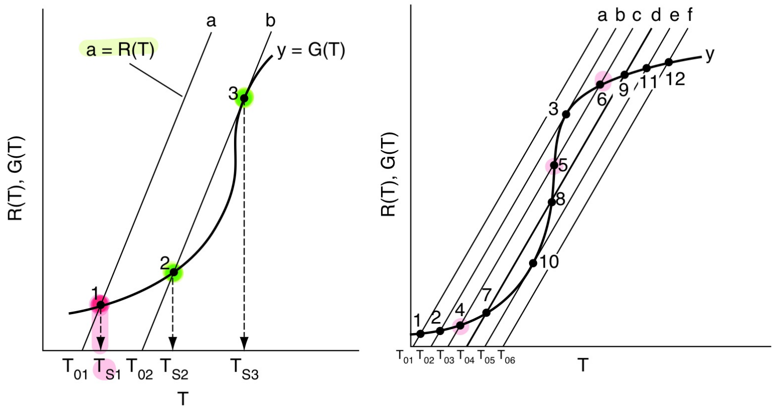


Figure 12-11 Finding multiple steady states with T_0 varied.

Figure 12-12 Finding multiple steady states with T_0 varied.

The points of intersection of G(T) & R(T), give us the temp at which the reactor can operate at a steady state

By increasing the inlet temp (T_0), the G(T) curve remains unchanged, but the R(T) line would move to the right

⇒ By plotting T_s vs. T_o [Temp Ignition - extinction curve]

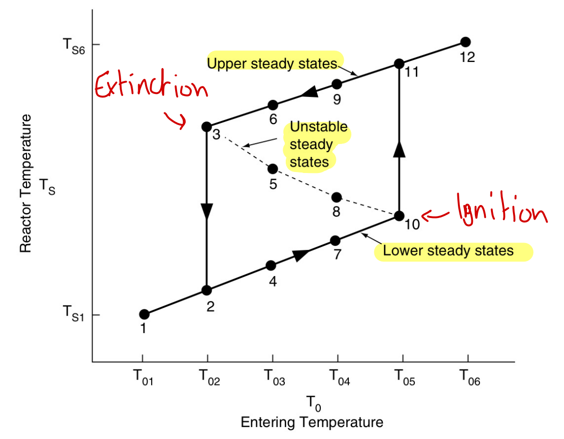
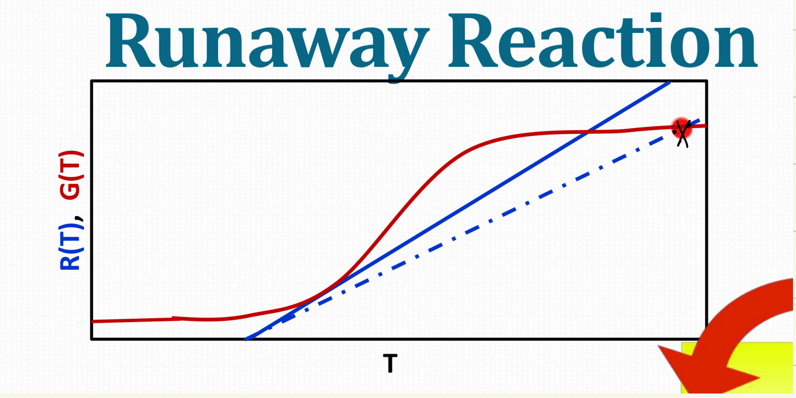


Figure 12-13 Temperature ignition-extinction curve.

- As T_o Increases, T_s increases
- Ignition temp : T where jump from $T_{s\,lower}$ to $T_{s\,upper}$ occurs
- Extinction temp: T where drop from $T_{s\,upper}$ to $T_{s\,lower}$ occurs.
- Points 5 & 8 ⇒ unstable steady states. (Avoid working on their corresponding temperatures)



when T_o exceeds $T_{ignition}$ ⇒ Transition to the upper steady state will occur

Undesirable & Dangerous

Runaway Reactions : R(T) only intersects with upper steady state