

Chemical Reaction Engineering

□ **Objective:-**

1- Technological

- Maximum possible product in minimum time
- Desired quantity in minimum time
- Maximum possible product in desired time

2- Economic

- Maximize profit

□ **Constraints**

1- Market

- Raw materials availability – quality and quantity
- Demand for the product

2- Society/Legislative

- Safety
- Pollution control

3- Technological

- Thermodynamics
- Stoichiometry
- Kinetics

□ **Type of reactor**

- Tubular, Fixed Bed, Stirred tank, Fluidized bed

□ **Mode**

- Mass Flow: Batch, Continuous, Semibatch
- Energy: Isothermal, Adiabatic, Co/counter current

□ **Process Intensification**

- Combining more than one type of unit operation

LECTURE ONE

This lecture covers: reaction stoichiometry, lumped stoichiometry in complex systems such as bioconversions and cell growth (yields), extent of reaction, independence of reactions, measures of concentrations, single reactions and reaction networks, and bioreaction pathways.

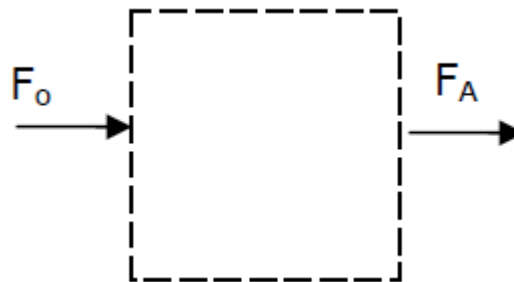


Figure 1. A schematic of a control volume with inflow of F_o and outflow of species A, F_A .

F = total molar flow rate (moles/sec)

F_o = total molar flow rate entering control volume

F_A = molar flow rate of species A

F_{Ao} = molar flow rate of species A entering control volume

N_A = Moles of species A

Mass balance: (change in “A” inside control volume)= (amount of “A” that entered)- (amount of “A” that exited) + (amount of “A” created inside the control volume) – (amount of “A” destroyed inside the control volume).

$$\frac{dN_A}{dt} = F_{Ao} - F_A + G_A$$

$$G_A [=] \frac{\text{moles}}{\text{sec}}$$

If homogeneous, $G_A = r_A V$

else, $G_A = \int r_A dV$

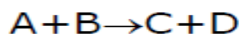
where V is volume and r_A is the rate of A created or destroyed (moles/sec/volume).

The mass balance can also be written as:

$$\frac{d\rho_A}{dt} = \overbrace{v\nabla\rho_A}^{\text{convection}} + \overbrace{D\nabla^2\rho_A}^{\text{diffusion}} + r_A$$

where v is velocity, D is the diffusion coefficient, and ρ_A is the molar density of A (moles/volume).

Example:



$$r_A = -k[A][B], \quad r_C = +k[A][B], \quad [A][B] = \frac{\text{mole A}}{\text{liter}}$$

where k is a measurable rate constant that changes with respect to T and P but remains constant with respect to changing concentrations.

If $r_1 = k[A][B]$, then

$$r_A = \overbrace{v_{A,1}}^{-1} r_1$$

where $v_{A,1}$ is the stoichiometric coefficient for species A in reaction 1. Likewise,

$$r_C = \overbrace{v_{C,1}}^{+1} r_1$$

If there are n reactions involving species “A” then

$$r_A = \sum_{i=1}^n v_{A,i} r_i$$

$$G_A(t) = \iiint_{Vol.} \underbrace{r_A(x, y, z, t)}_{-k(T(x,y,z,t))[A(x,y,z,t)][B(x,y,z,t)]} dx dy dz$$

$$\frac{d \overbrace{[A]}^{N_A/V}}{dt} = -k[A][B] \rightarrow \text{*only true if there are no flows!}$$

$$\frac{dN_A}{dt} = \int r_A dV \approx r_A V, \text{ assume } r_A \text{ is true throughout volume}$$

If the system is homogeneous and there are no flows:

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

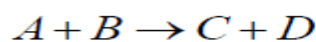
Therefore:

$$\frac{d}{dt} \left(\frac{N_A}{V} \right) = r_A \text{ iff homogeneous, no flow, constant V}$$

Extent of Reaction

$\xi [=]$ moles, extent of rxn.

$\dot{\xi} [=] \frac{\text{moles}}{\text{sec}}$, rate of extent of rxn.



$N_A = N_{A,\text{initially}} - \xi$, if there is one reaction involving A

$N_A = N_{A,\text{initially}} - \sum_n \nu_{A,n} \xi_n$, if there are several reactions

$\dot{\xi}_n = \int r_n dV$, n is the reaction number

$G_A = \int r_A dV$, A is the species

Conversion



$$X_A = \frac{N_{A,\text{initial}} - N_A}{N_{A,\text{initial}}} \text{ (dimensionless)}$$

$$X_C = \frac{N_C}{N_{A,\text{initial}}} \text{ (} \approx 1 \text{ since rxn is 1:1)}$$

$\left(\begin{array}{l} A + B \rightarrow C + D \\ A \rightarrow U \end{array} \right)$ Selectivity is good if $A \rightarrow C$, bad if $A \rightarrow U$.

*May worsen as rxn. goes on ($A \rightarrow C$ slows, $A \rightarrow U$ keeps going)

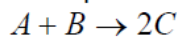
Lecture 2: The Reaction Rate & Reaction Mechanisms

The lecture covers: Definitions in terms of reacting compounds and reaction extent, rate laws, Arrhenius equation, elementary, reversible, non-elementary, catalytic reactions.

From previous lecture:

$$\frac{dN_A}{dt} = F_{Ao} - F_A + G_A, \quad G_A = \int r_A dV$$

Example:



*Reactions are reversible (often will neglect reverse)

$$X_A = \frac{N_{Ao} - N_A}{N_{Ao}} \quad X_A = \frac{F_{Ao} - F_A}{F_{Ao}} \quad X_C = \frac{F_C}{2F_{Ao}}$$

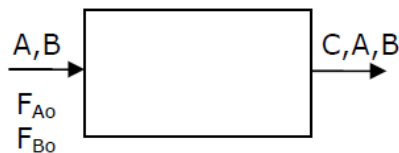


Figure 1. A reactor with reactants A and B constantly flowing in and product C and unused reactants A and B flowing out.

$$F_{Ao} = \frac{\text{moles A flowing in}}{\text{sec}} = [A]_{input} \frac{v_{in}}{\frac{\text{liters}}{\text{sec}}} = [A]_o v_o$$

$$F_A = \frac{\text{moles A flowing out}}{\text{sec}} = [A]_{output} v_{out}$$

$$X = 1 - \frac{[A]_{output} v_{out}}{[A]_{in} v_{in}}$$

Closed reactor, const. V

Detailed balance- all steps in equilibrium, total system

$$\frac{d[A]}{dt} = r_A = -k[A][B]$$

$$K_{eq} = \frac{[C]^2}{[A][B]}$$

when $[A][B] = \frac{[C]^2}{K_{eq}}$ the rxn. stops $\rightarrow r_A=0$

$$r_A = -k \left([A][B] - \frac{[C]^2}{K_{eq}} \right), \quad k_{rev} = \frac{k_{for}}{K_{eq}}$$

↙ same! ↗

forward-reverse in one expression

Catalysis

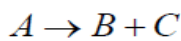
$$r_{A,forward} = k_{cat} [\text{catalyst}] [A] \underbrace{f([B])}_{\substack{\text{may be included} \\ \text{i.e. when B is} \\ \text{very small}}}$$

Rate limiting step determines the kinetics (slow step). The kinetics are insensitive to [B] because B is not part of this slow step.

$$r_{A,reverse} = r_{A,forward} \frac{[C]^2}{K_{eq} [A][B]}$$

$$r_{A,net} = -k_{cat} [\text{catalyst}] \left([A] - \frac{[C]^2}{K_{eq} [A][B]} \right)$$

$$K_{eq} = e^{-\Delta G/RT} \quad \Delta G = \Delta G_{f,products}^{\circ} - \Delta G_{f,reactants}^{\circ} \quad \leftarrow \text{Standard state}$$



$$K_{eq} = \frac{[B][C]}{[A]} [=] \frac{\text{moles}}{\text{liter}}$$

$$\downarrow$$

$$\rightarrow K_C$$

Partial Pressures

$$\frac{P_B P_C}{P_A P^{\circ}} = K_{eq} = \frac{[B][C]}{[A] \frac{P^{\circ}}{RT}}$$

$$\text{Ideal Gas: } pV = nRT \Rightarrow \frac{n}{V} = \frac{P}{RT}$$

P° is the standard state pressure (1 atm), this makes the units cancel. Using partial pressures is accurate within 10%, more error with liquids.

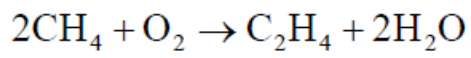
$$N_A = N_{A,initial} + \sum v_{A,i} \xi_i$$

↖ Stoichiometric coefficient
↙ Extent of rxn.

$$N_C = N_{C,initial} + \sum_{i=1}^{N_{rxn}} v_{C,i} \xi_i$$

Conservation Laws

Conserve atoms



$$\underbrace{C_A}_{\text{constant moles}} N_A + C_B N_B + C_C N_C = \text{const.}$$

$$\underline{C}: 1 \times N_{\text{CH}_4} + 2 \times N_{\text{C}_2\text{H}_4} = N_{\text{C},\text{initial}}$$

$$\underline{H}: 4 \times N_{\text{CH}_4} + 4 \times N_{\text{C}_2\text{H}_4} + 2 N_{\text{H}_2\text{O}} = N_{\text{H},\text{initial}}$$

Lecture 3: Continuous Stirred Tank Reactors (CSTRs)

This lecture covers: Reactions in a perfectly stirred tank. Steady State CSTR.

Continuous Stirred Tank Reactors (CSTRs)

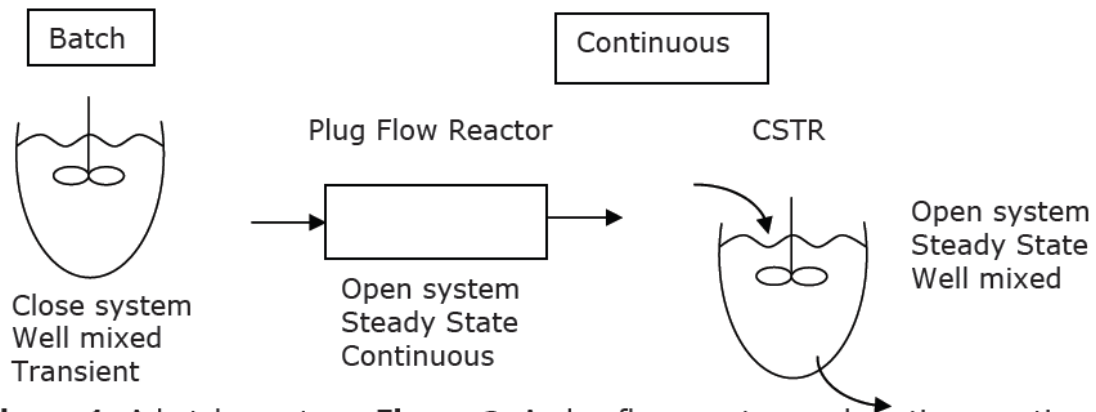


Figure 1. A batch reactor. **Figure 2.** A plug flow reactor, and continuous stirred tank reactor.

Mole Balance on Component A

In-Out+Production=Accumulation

$$F_{Ao} - F_A + r_A V = 0 \text{ (steady state)}$$

$$V = \frac{F_{Ao} - F_A}{-r_A} \quad F_A = F_{Ao} - X_A F_{Ao}$$

In terms of conversion, X_A ?

What volume do you need for a certain amount of conversion?

$$V = \frac{F_{Ao} X_A}{-r_A}$$

where r_A is evaluated at the reactor concentration. This is the same as the exit concentration because the system is well mixed.

For a liquid phase with constant P:

$$F_{Ao} = C_{Ao} v_0 \text{ (} v_0 = \text{volumetric flow rate)}$$

$$F_A = C_A v_0$$

$$\frac{V}{v_0} = \frac{C_{Ao} X_A}{-r_A}$$

$$v_0$$

$$\tau = \frac{V}{v_0} \leftarrow \text{average time a volume element of fluid stays in the reactor}$$

$$\tau = \frac{C_{A0} X_A}{-r_A}$$

Consider: 1st Order Reaction Kinetics

$-r_A = kC_A$ concentration or conversion?

→ convert rate law from C_A to X_A

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

$$-r_A = kC_{A0}(1 - X_A)$$

$$\tau = \frac{C_{A0} X_A}{kC_{A0}(1 - X_A)} = \frac{X_A}{k(1 - X_A)} \left. \vphantom{\tau} \right\} \text{ reactor size in terms of conversion and rate constant}$$

→ rearrange to find how much conversion for a given reactor size

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

$\tau \equiv$ average reactor residence time

$\frac{1}{k} \equiv$ average time until reaction for a given molecule

We can now define a "Damköhler number"

$$Da = \frac{\text{reaction rate}}{\text{flow}} = \frac{-r_{A0} V}{F_{A0}}, \quad r_{A0} \text{ is the reaction rate law at the feed conditions}$$

For a liquid at constant pressure with 1st order kinetics:

$$Da = k\tau$$

$$\Rightarrow X_A = \frac{Da}{1 + Da}$$

therefore:

As $Da \uparrow$, $X_A \rightarrow 1$

As $Da \downarrow$, $X_A \rightarrow 0$ (molecule probably leaves before it can react)

For a liquid at constant pressure with 2nd order kinetics:

$$-r_A = kC_A^2$$

$$= kC_{A0}^2 (1 - X_A)^2$$

$$\tau = \frac{C_{A0} X_A}{-r_A} = \frac{C_{A0} X_A}{kC_{A0}^2 (1 - X_A)^2} = \frac{X_A}{kC_{A0} (1 - X_A)^2}$$

solving for conversion:

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

$$Da = \frac{kC_{Ao} V}{C_{Ao} v_o} = \tau k C_{Ao}$$

Thus, conversion can be put in terms of Da.

$$X_A = \frac{(1 + 2Da) - \sqrt{1 + 4Da}}{2Da}$$

How long does it take for a CSTR to reach steady state?

In-Out+Production=Accumulation

$$F_{Ao} - F_A + r_A V = \frac{dN_A}{dt}$$

For a liquid at constant density this is:

$$C_{Ao} - C_A + r_A \tau = \tau \frac{dC_A}{dt}$$

→non-dimensionalize

$$\hat{C}_A = \frac{C_A}{C_{Ao}} \quad \hat{t} = \frac{t}{\tau}$$

$$C_{Ao} - C_{Ao} \hat{C}_A - k C_{Ao} \hat{C}_A \tau = \frac{\cancel{C_{Ao}}}{\cancel{C_{Ao}}} \frac{d\hat{C}_A}{d\hat{t}}$$

$$\frac{d\hat{C}_A}{d\hat{t}} + \left(1 + \frac{Da}{k\tau}\right) \hat{C}_A = 1$$

$$\frac{d\hat{C}_A}{d\hat{t}} + (1 + Da) \hat{C}_A = 1$$

with initial conditions:

$$\hat{C}_A = 0, \hat{t} = 0$$

we have the solution:

$$\hat{C}_A = \frac{1}{1 + Da} \left(1 - e^{-(1 + Da)\hat{t}}\right)$$

In nondimensional terms, it exponentially approaches a new steady state with a

characteristic time $\frac{\tau}{1 + Da}$.

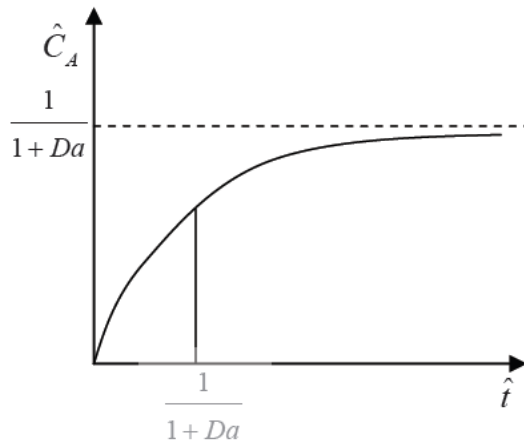


Figure 3. Approach to steady state in a continuous stirred tank reactor (CSTR).

The time at which 1/2 of the steady state concentration of C_A is achieved is the half

time: $\frac{\ln(2)}{1+Da} \tau$

CSTRs in Series

(Liquid and at constant pressure)

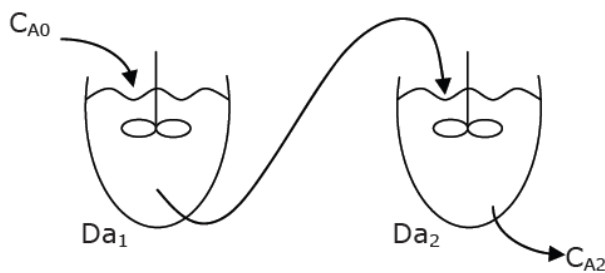


Figure 4. Two tanks in series. The output of the first tank is the input of the second tank.

1st order reaction kinetics

$$C_{A1} = \frac{C_{A0}}{1+Da_1}$$

For the second reactor → iterate

$$C_{A2} = \frac{C_{A0}}{(1+Da_1)(1+Da_2)}$$

If the CSTRs are identical,

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

→ many CSTRs in series looks like a plug flow reactor.

Lecture 4: Batch Reactors

This lecture covers batch reactor equations, reactor sizing for constant volume and variable volume processes.

Batch Reactors

Run at non-steady state conditions

Which to choose? Batch vs. CSTR?



Figure 1. Schematics of a batch reactor and a CSTR.

	Batch (small quantities)	CSTR (does not tie up equipment continuously)
Small Amount of Material		
Flexibility	+	-
Expensive Reactants	+	-
If product does not flow, Materials Handling (e.g. Polymers)	+	-
Do not have to shut down and clean, less down time	-	+
Capital costs? For size of reactor, for given conversion	+	-
	(concentration stays higher longer)	
Operability & Control (T, P, p4) e.g. Exothermic reaction	-	+
		(Manipulate only one setpoint, steady state. You can control additional variables. Such as flow rates.)

Material Balance

$$\cancel{0} \text{ In} - \cancel{0} \text{ Out} + \text{Product} = \text{Accumulation}$$

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

Constant V , $r_A = \frac{dC_A}{dt}$

In terms of conversion, $C_{A0} \frac{dX_A}{dt} = r_A$

Integrating, $t = \int_{C_{A0}}^{C_A} \frac{dC_A}{r_A}$ or $t = C_{A0} \int_0^{X_A} \frac{dX_A}{r_A}$

1st Order Reaction $A \xrightarrow{k} B$

$$-r_A = kC_A = kC_{A0}(1 - x_A)$$

$$t = C_{A0} \int_0^{x_A} \frac{dx_A}{-kC_{A0}(1 - x_A)} \quad \longrightarrow \quad t = \frac{1}{k} \ln \left(\frac{1}{1 - x_A} \right)$$

$$x_A = 1 - e^{-kt}$$

90% conversion $t_{90.0\%} = \frac{1}{k} \ln \left(\frac{1}{1 - 0.9} \right) = \frac{2.3}{k}$

(order of $\frac{1}{k}$)

2nd Order Reaction $A + A \xrightarrow{k} B$

$$-r_A = kC_A^2 = kC_{A0}^2(1 - X_A)^2$$

$$t = C_{A0} \int_0^{X_A} \frac{dX_A}{-kC_{A0}^2(1 - X_A)^2} = \frac{1}{-kC_{A0}} \int_0^{X_A} \frac{dX_A}{(1 - X_A)^2}$$

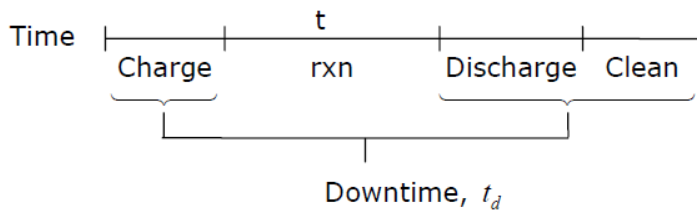
$$t = \frac{1}{kC_{A0}} \frac{X_A}{1 - X_A} \quad X_A = \frac{kC_{A0}t}{1 + kC_{A0}t}$$

If $k_{\text{first order}} = k_{\text{second order}} C_{A0}$, which is faster?

	1	2	3	
1 st order	0.63	0.86	0.95	} X_A
2 nd order	0.50	0.67	0.75	

For a given Damkohler number, 1st order is faster. The second order reaction has greater concentration dependence. Exponential approach (1st order) is faster.

Batch Cycle



How long should t be?

How high should X_A be?

Economic calculation: Compare economics of further conversion to a different use of equipment

Chemical consideration: Will product degrade? Assume product stable.

Product produced in one cycle = $X_A C_{A0} V$

$$P_r(\text{Rate of Production}) = \frac{X_A C_{A0} V}{t + t_d}$$

What value of t will maximize P_r ?

If there is a maximum of P_r vs. t, $\frac{dP_r}{dt} = 0$

Assume $t_d = \text{constant}$. $0 = \frac{dP_r}{dt} = C_{A0} V \frac{(t_{\text{optimum}} + t_d) \frac{dX_A}{dt} - X_A}{(t_{\text{optimum}} + t_d)^2}$

$$(t_{\text{optimum}} + t_d) \frac{dX_A}{dt} - X_A = 0$$

Now specify kinetics. There may be no optimum.

1st order $X_A = 1 - e^{-kt}$

$$\frac{dX_A}{dt} = ke^{-kt}$$

$$(t_{\text{optimum}} + t_d) ke^{-kt_{\text{optimum}}} - (1 - e^{-kt_{\text{optimum}}}) = 0$$

Can numerically solve for t_{optimum} .

Semi-batch Reactor

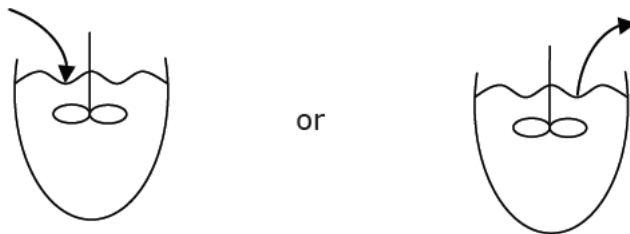


Figure 2. Schematics of two types of fed-batch reactors.

1) Why?

- To remove "poisonous" product
- Make room in reactor (expansion of product)
- If a reactant has a negative order effect on rate, add in small quantities
- Selectivity $A + B \rightarrow \text{Desired}$
(control) $A + A \rightarrow \text{Byproduct}$

Start with B, slowly feed A.

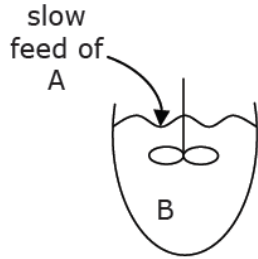


Figure 3. A fed-batch reactor with a slow feed of one reactant.

- To shift equilibrium, strip off product
- To control evolution of heat
- In biological cases
 - Fed-batch - Feed in carbon source slowly to avoid overflow metabolism
 - (glucose)
 - O₂ sparingly soluble, must feed.

2) Balances

A Balance

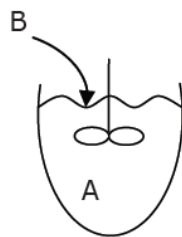


Figure 4. Fed-batch reactor with a feed of B.

In - Out + Product = Accumulation

$$r_A V(t) = \frac{d(r_A V)}{dt}$$

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

Liquid $V = V_0 + v_0 t$ ← flow

$$\frac{dC_A}{dt} = r_A - \underbrace{\frac{v_0}{V_0} C_A}_{\text{dilution}}$$

B Balance

$$\frac{dC_B}{dt} = r_B + \underbrace{\frac{v_0}{V_0} C_{B_0}}_{\text{Addition}} - \underbrace{\frac{v_0}{V_0} C_B}_{\text{Dilution}}$$

Lecture 5: The Plug Flow Reactor

$$r_A = -k[A]^2$$

$$X_A F_{Ao} = -r_A V$$

$$V_{CSTR} = \frac{X_A F_{Ao}}{k[A]_0^2 (1 - X_A)^2} \quad (2^{\text{nd}} \text{ order reaction})$$

$$t_{\text{react.}} = \frac{X_A}{k[A]_0 (1 - X_A)}$$

$$V_{\text{Batch}}([A]_0) = ?$$

$$F_{Ao} = \frac{\text{moles A}}{\text{time}} = \frac{V_{\text{Batch}} [A]_0}{t_{\text{react}} + t_d}$$

$$V_{\text{Batch}} = \frac{F_{Ao}}{[A]_0} \left[t_d + \frac{X_A}{k[A]_0 (1 - X_A)} \right]$$

Assume $X_A = 90\%$

If $t_{\text{react}} > t_d$ then

$$V_{\text{Batch}} = \frac{2F_{Ao} \cdot 0.9}{[A]_0 k [A]_0 (1 - 0.9)}$$

$$V_{\text{CSTR}} = \frac{0.9F_{Ao}}{k[A]_0^2} \leq \frac{1.8F_{Ao}}{k[A]_0^2}$$

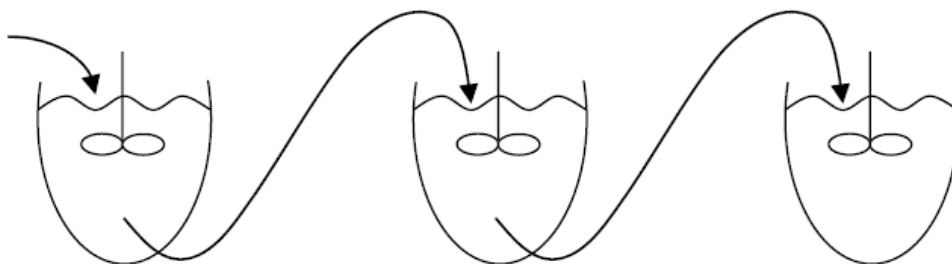


Figure 1. Three tanks in series.

$$[A]_{\text{CSTR}} = [A]_{\text{in}} + r_A \frac{V}{v_0}$$

If $r_A = -k[A]$

$$[A]_{\text{out}} = \frac{[A]_{\text{in}}}{1 + Da} = \frac{[A]_{\text{in}}}{1 + \frac{kV}{v_0}}$$

If n CSTRs are in series:

$$\text{each volume} = \frac{V}{n}$$

$$[A]_{out} = \frac{[A]_{in}}{1 + \left(\frac{kV}{nv_0}\right)^n}$$

→improves productivity:

concentration of A in 1st one is higher than would be in one large CSTR

$$[A]_{out}^{Batch} = [A]_0 e^{-\frac{kV}{v_0}}$$

$$\frac{kV}{v_0} = 3 \Rightarrow 95\% \text{ conversions}$$

$$[A]_{CSTR}^{out} = \frac{[A]_0}{\left(1 + \frac{3}{n}\right)^n}$$

N	X _A
1	.75
10	.93
100	.948

Plug Flow Reactor (behaves like an infinite number of infinitely small CSTRs)

$$F_{Ain} - F_{Aout} + r_A (\Delta V) = 0 \quad \text{CSTR}$$

$$\left(\frac{F_{Ain} - F_{Aout}}{\Delta V}\right) = -r_A$$

$$\frac{dF_A}{dV} = -r_A \quad \text{design equation for PFR}$$

$$\frac{dF_A}{dV} = r(C_A, C_B, \dots)$$

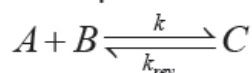
$$= -kC_A C_B \quad (\text{for example})$$

$$F_A = C_A v_0$$

$$\frac{dF_A}{dV} = -k \frac{F_A}{v_0} \frac{F_B}{v_0}$$

This can be expressed as: $\frac{dY}{dt} = F(t, Y)$ where t is replaced by V.

Example:



$$\frac{d}{dV} \underbrace{\begin{pmatrix} F_A \\ F_B \\ F_C \end{pmatrix}}_{\underline{Y}} = \underbrace{\begin{pmatrix} -\frac{kF_A F_B}{v_0^2} + \frac{k_{rev} F_C}{v_0} \\ -\frac{kF_A F_B}{v_0^2} + \frac{k_{rev} F_C}{v_0} \\ +\frac{kF_A F_B}{v_0^2} - \frac{k_{rev} F_C}{v_0} \end{pmatrix}}_{F(t, \underline{Y})}$$

$$dV = area \cdot dz$$

Mass flow rate is constant

$$(v\rho A) = const.$$

$$\rho = \sum C_i W_i$$

For a liquid, $\frac{d\rho}{dz} = 0$

$$\frac{d(v\rho A)}{dz} = \rho A \frac{dv}{dz} + \rho v \frac{dA}{dz} + Av \frac{d\rho}{dz} = 0$$

Rearrange:

$$\frac{dv}{dz} = -v \left(\frac{1}{A} \frac{dA}{dz} + \frac{1}{\rho} \frac{d\rho}{dz} \right)$$

For a normal pipe $\frac{dA}{dz} = 0$ and for a liquid $\frac{d\rho}{dz} = 0$

Therefore: $\frac{dv}{dz} = 0 \Rightarrow v = v_0$

(We can't assume this for gases!)

For a PFR:

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

$$F_A = v[A]$$

$$\frac{d(vC_A)}{dV} = r_A$$

For liquids, v is constant so we can take it out of the differential.

$$r_A = \frac{v}{area} \frac{dC_A}{dz}, \text{ for liquids}$$

$$\frac{dC_A}{dz} = \frac{area}{v_0} r_A$$

Instead of t_{react} we have z_{react} !

$$t_{pipe} = \frac{area \cdot length}{v_0}$$

$$t_{PFR} = \frac{area \cdot z}{v_0} = \frac{X_A}{k[A]_0(1-X_A)}$$

Flow is driven by the pressure drop across the pipe.

$$PV = NRT$$

$$\sum C_i = \frac{P}{RT}$$

$$C_i = \frac{P}{RT} \frac{F_i}{\sum_n F_n} \left. \vphantom{C_i} \right\} \text{ turns F's into concentrations}$$

$$\rho = \sum C_i W_i, W_i \text{ is molecular weight of } i.$$

$$v = \frac{\text{mass flowrate}^{\leftarrow \text{const.}}}{\rho(z)}$$

Lecture 6: Reactor Size Comparisons for PFR and CSTR

This lecture covers reactors in series and in parallel, and how the choice of reactor affects selectivity versus conversion. **PFR vs. CSTR: Size and Selectivity**

Material balance:

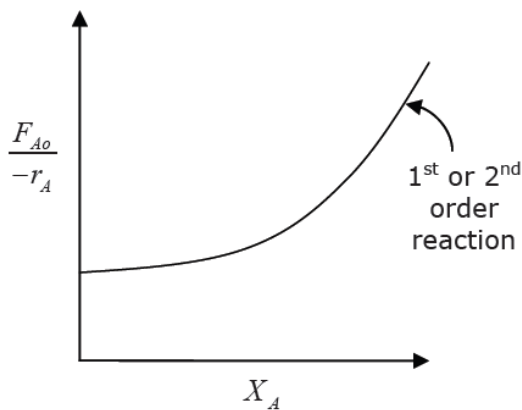
CSTR

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

PFR

$$V = \int_0^{X_A} \frac{F_{A0}}{-r_A} dX_A$$

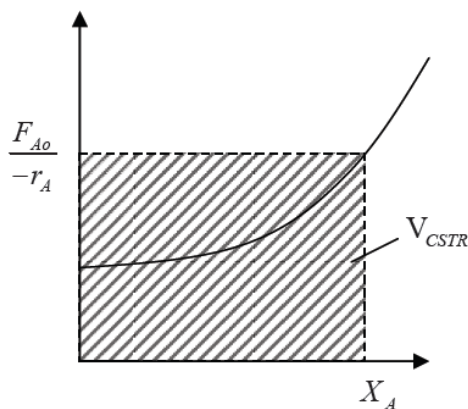
"Levenspiel Plot"



- as X_A increases, C_A decreases
- $-r_A$ decreases, for 1st and 2nd order,
- so $\frac{F_{A0}}{-r_A}$ increases

Figure 1. General Levenspiel Plot.

CSTR Volume



PFR Volume

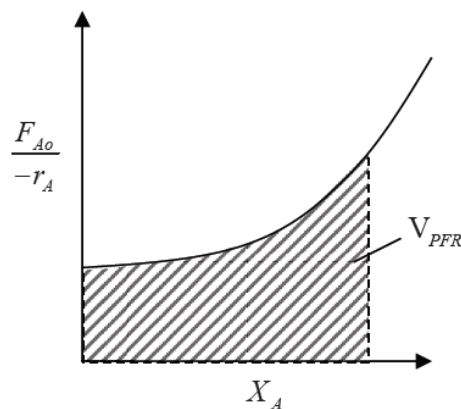


Figure 2. Levenspiel plots for a CSTR and a PFR for positive order reactions.

So PFR is always a smaller reactor for a given conversion when kinetics are positive order.

Non-monotonically positive order kinetics arise:

- Autocatalytic reactions (e.g. cell growth)
- Adiabatic or non-isothermal exothermic reactions
- Product inhibited reactions (some enzymes)

Series of Reactors

Example: 2 CSTRs

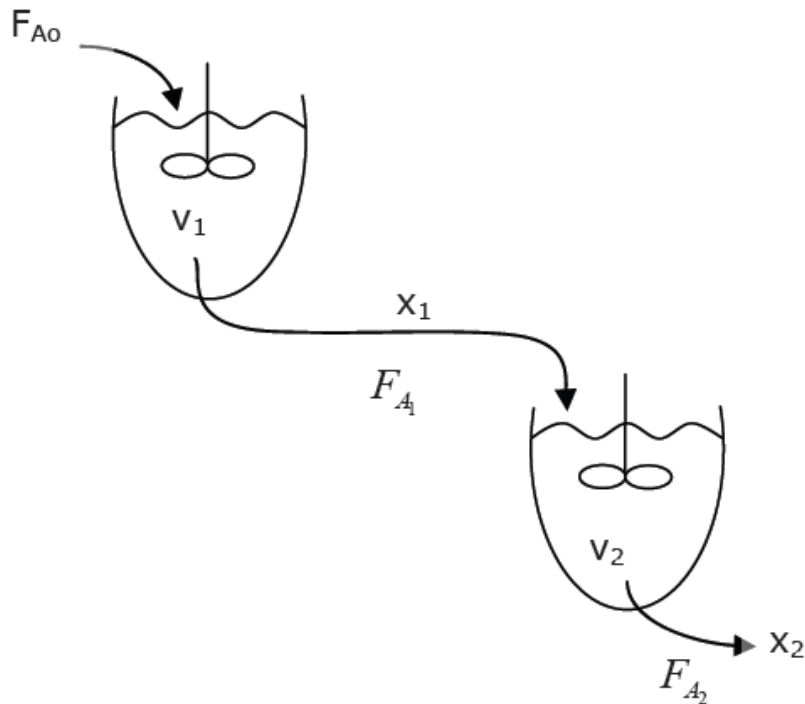


Figure 3. Schematic of two CSTRs in series.

$$V_1 = \frac{F_{A0}}{-r_{A1}} X_1$$

2nd reactor:
 In + Out + Prod = Acc ⁰

$$F_{A1} - F_{A2} + r_{A2} V_2 = \text{Steady state}$$

$$F_{A_2} = F_{A_0} - X_2 F_{A_0} \rightarrow V_2 = \frac{F_{A_0}}{-r_{A_2}} (X_2 - X_1)$$

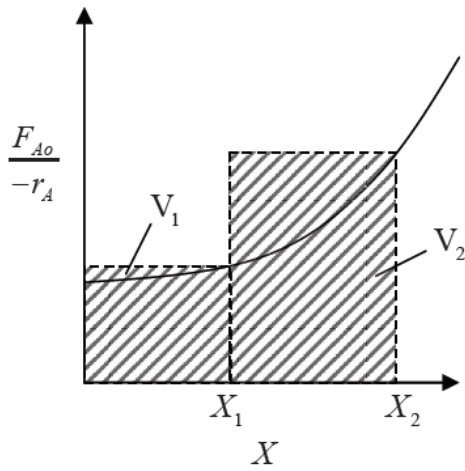
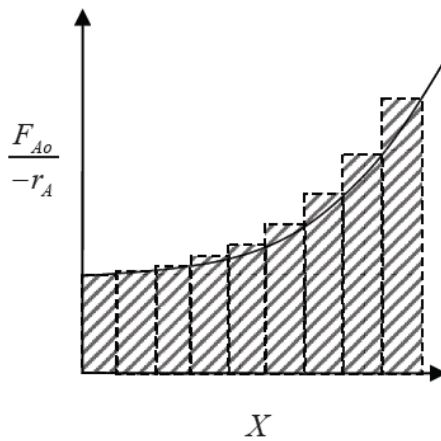


Figure 4. Reactor volumes for 2 CSTRs in series.



Multiple CSTRs begin to approximate a single PFR

Figure 5. Reactor volumes for multiple CSTRs in series.

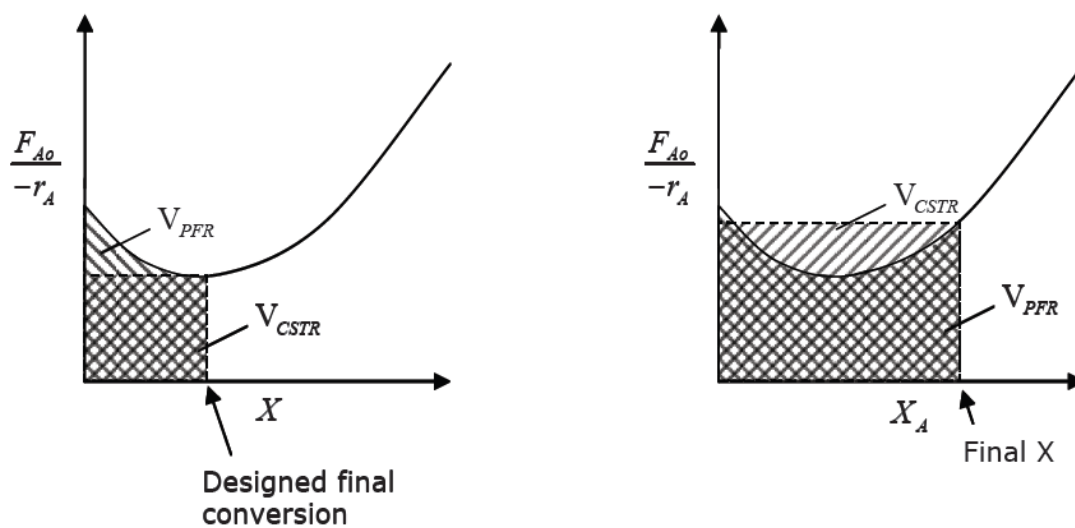


Figure 6. Levenspiel plots comparing CSTR and PFR volumes for changing kinetics. Left: The CSTR has the smaller volume. Right: The PFR eventually has the smaller volume.

Choice of PFR vs CSTR depends on conversion. Choose the reactor that has the smallest volume → reduce cost.

Reactors:

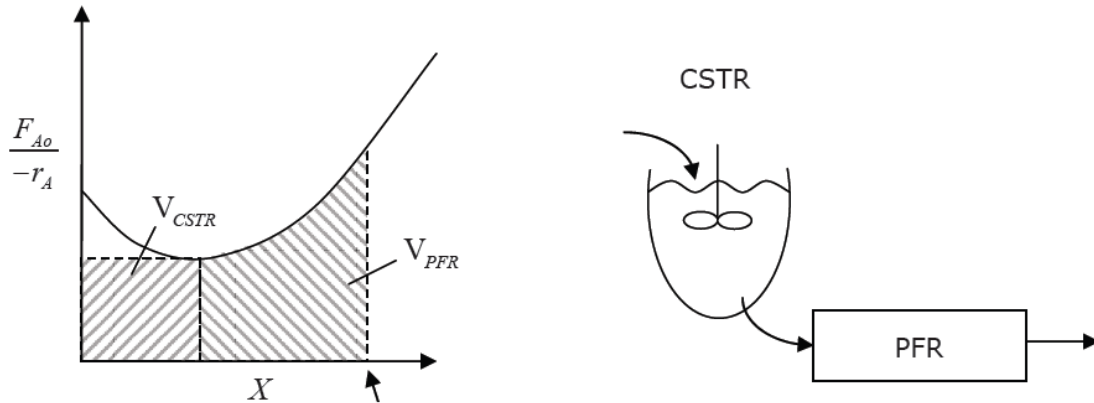
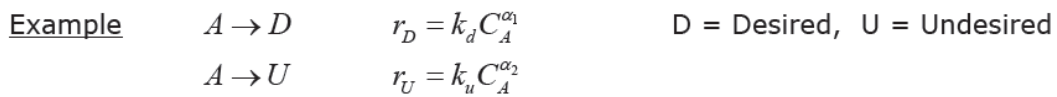


Figure 7. To achieve the desired conversion with smaller reactor volumes, use a combination. In this case, use a CSTR then a PFR. By doing so, the reactor volume is less than the area underneath the curve.

For competing parallel reactions, selectivity for desired product can dominate the choice.



Define "selectivity" $S_{D/U} = \frac{r_D}{r_U} = \frac{k_d}{k_u} C_A^{(\alpha_1 - \alpha_2)}$

If $\alpha_1 > \alpha_2$, as C_A increases, $S_{D/U}$ increases
 -Favors PFR because C_A starts at C_{A0} then drops whereas CSTR concentrations are always at lower C_A .

If $\alpha_1 < \alpha_2$, as C_A increases, $S_{D/U}$ decreases
 -CSTR favored

If $\alpha_1 = \alpha_2$ then $S_{D/U} = \frac{k_d}{k_u}$, no dependence on C_A
 -Therefore no CSTR/PFR preference.

Define a fractional yield

$$\phi = \frac{dC_D}{-dC_A} = \frac{k_d C_A^{\alpha_1}}{k_d C_A^{\alpha_1} + k_u C_A^{\alpha_2}}$$

Overall fractional yield $\Phi = \frac{\text{All } D \text{ produced}}{\text{All } A \text{ consumed}}$

For a CSTR: $\Phi = \phi|_{\text{Exit } C_A}$
 $\Delta C_A = C_{A0} - C_{Af}$

For a PFR: $\Phi = \frac{1}{\Delta C_A} \int_{C_{A0}}^{C_{Af}} \phi dC_A$

If $\alpha_1 = \alpha_2$

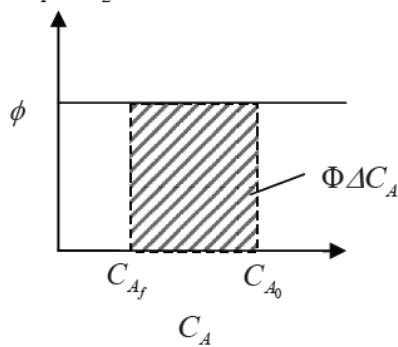


Figure 8. Fractional yield versus concentration. Selectivity does not depend on C_A .

If $\alpha_1 > \alpha_2$

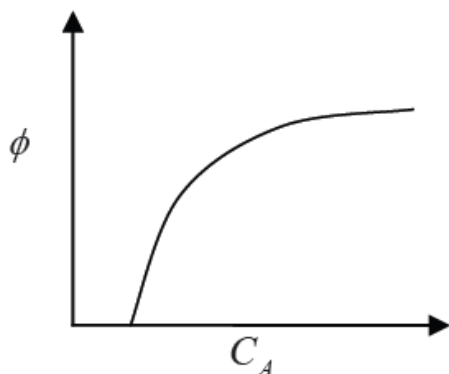


Figure 9. Fractional yield versus concentration when $\alpha_1 > \alpha_2$.

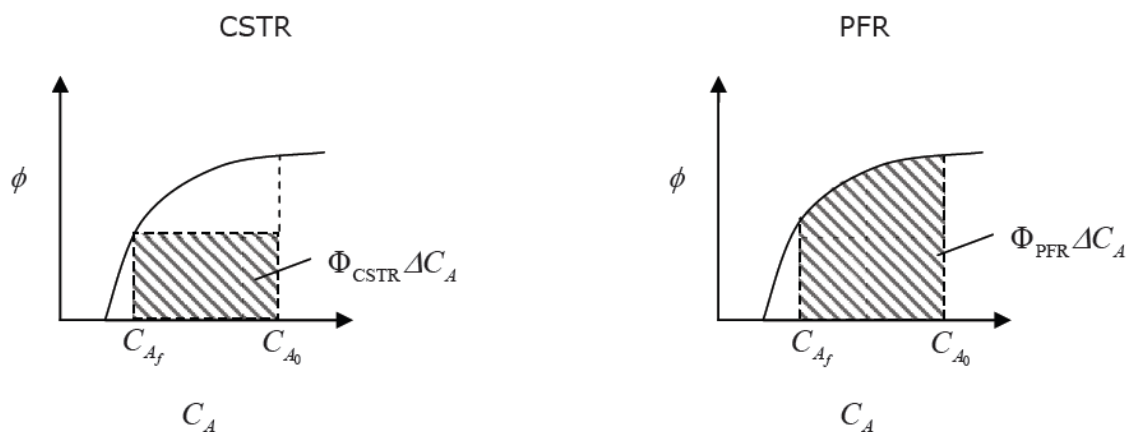


Figure 10. Comparison of overall fractional yield for a CSTR and a PFR when $\alpha_1 > \alpha_2$.

PFR is preferred because $\Phi_{PFR} > \Phi_{CSTR}$, therefore the yield of D per mol A consumed is higher.

If $\alpha_1 < \alpha_2$

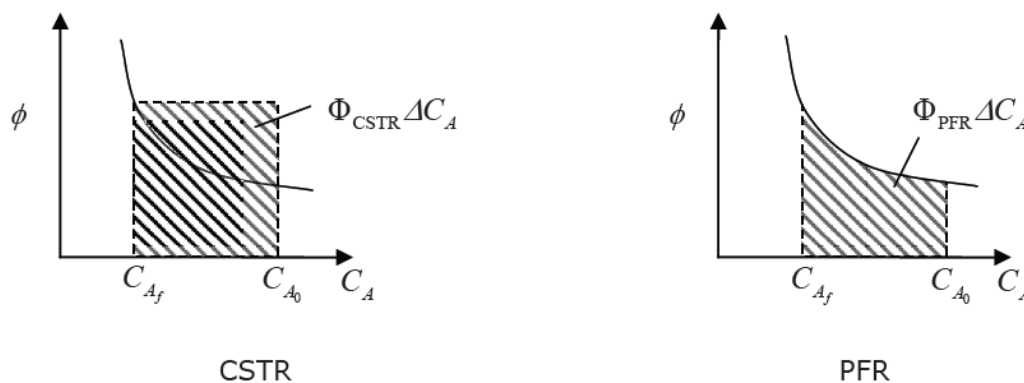


Figure 11. Comparison of overall fractional yield for a CSTR and a PFR when $\alpha_1 < \alpha_2$.

$$\Phi_{PFR} < \Phi_{CSTR}$$

Lecture 7: Nonideal Reactor Mixing Patterns

This lecture covers residence time distribution (RTD), the tanks in series model, and combinations of ideal reactors.

Non Ideal Mixing

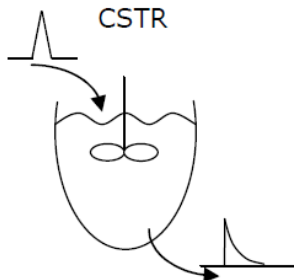


Figure 2. Ideal CSTR with pulse input. A pulse input will yield an output profile that is a sharp peak with a tail.

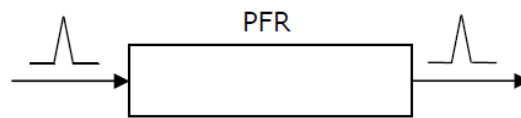


Figure 1. Ideal PFR with pulse input. A pulse input will yield an output profile that is a pulse input.

Real mixed tank

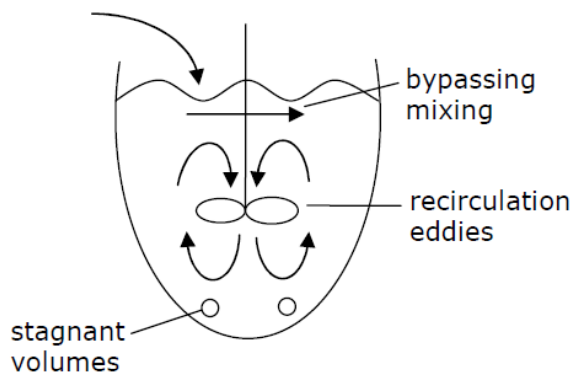


Figure 3. A real mixed tank. In a real mixed tank there are portions that are not well mixed due to stagnant volumes, recirculation eddies, and mixing bypasses.

In a real PFR there is back-mixing and axial dispersion. In a packed bed reactor (PBR) channeling can occur. This is where the fluid channels through the solid medium.

Residence Time Distribution

A useful diagnostic tool is the residence time distribution (RTD). The residence time is how long a particle stays in the reactor once entering.

$E(t)dt \equiv$ Probability that a fluid element entering the vessel at $t=0$ exits between time t and $t+dt$.

$$\int_0^t E(t) dt \text{ Probability that fluid element exits before time } t.$$

$$\int_t^\infty E(t) dt \text{ Probability of exiting at time later than } t.$$

$$\text{mean } t = \int_0^\infty tE(t) dt = \tau$$

$$\text{normalized} = \int_0^\infty E(t) dt = 1$$

$$\text{variance} = \sigma^2 = \int_0^\infty (t - \tau)^2 E(t) dt \text{ (measures the broadness of the distribution)}$$

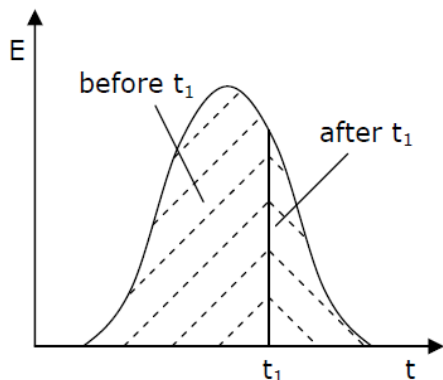


Figure 4. E(t) versus t. At a given time point, some material has exited and some material will still exit at a later time.

Experimental Determination of E(t)

Inflow should be something measurable

- Absorbance
- Fluorescence
- pH
- salt-conductivity
- radioactivity

Use one of two types of input concentration curves:

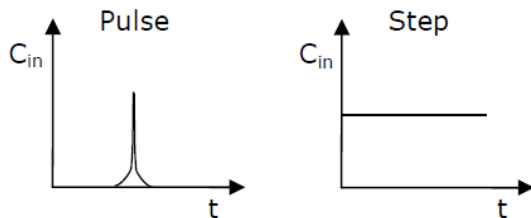


Figure 5. Two types of input. A pulse input is a spike of infinite height but zero width, ideally. A step input is a constant concentration over a period of time.

A pulse input allows for easy interpretation because all materials enter the reactor at once.

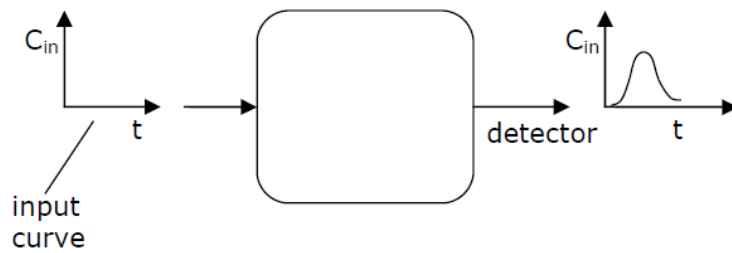


Figure 6. Schematic of a residence-time distribution experiment. The input curve enters the reactor; a detector detects concentration changes in the output stream.

$$E(t) = \frac{C_{out}(t)}{\int_0 C_{out}(t) dt}$$

PFR (Ideal)

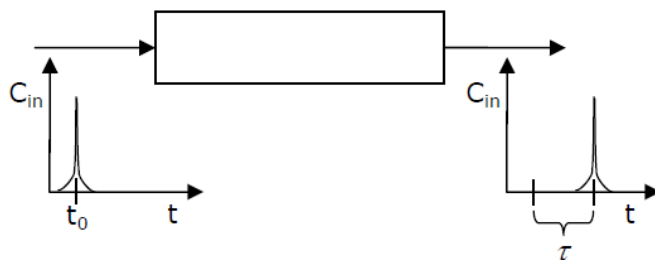


Figure 7. Pulse input in ideal PFR. A pulse input in an ideal PFR becomes a pulse output.

$$E(t) = \delta(t - \tau)$$

$$\delta(x) = \begin{cases} = 0 & x \neq 0 \\ = \infty & x = 0 \end{cases}$$

$$\int_{-\infty}^{\infty} \delta(x) dx = 1$$

$$\int_{-\infty}^{\infty} f(x) \delta(x - a) dx = f(a)$$

CSTR (Ideal)

Transient material balance:
In-Out+Production=Accumulation

Since all the material is added at once, $In=0$. The tracer used is non-reactive. Therefore there is no production. This gives:

$$0 - v_0 C + 0 = V \frac{dC}{dt}$$

$$C(t) = C_0 e^{-t/\tau}, \quad \tau = \frac{V}{v_0}$$

$$E(t) = \frac{C(t)}{\int_0^\infty C(t) dt} = \frac{e^{-t/\tau}}{\tau}$$

CSTR

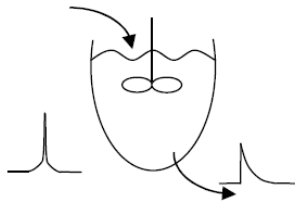


Figure 8. Pulse input in an ideal CSTR. In an ideal CSTR, a pulse input leads to a sharp peak with a tail.

$$\text{mean residence time} = \int_0^\infty \frac{te^{-t/\tau}}{\tau} dt = \tau$$

CSTR (non-ideal mixing)

Bypassing: Divide input into 2 streams

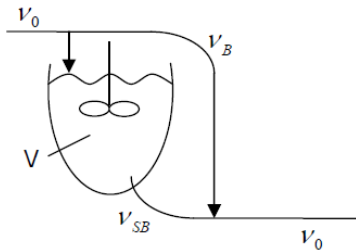


Figure 9. A bypass is modeled by dividing the input stream into two streams, one of which does not enter the reactor.

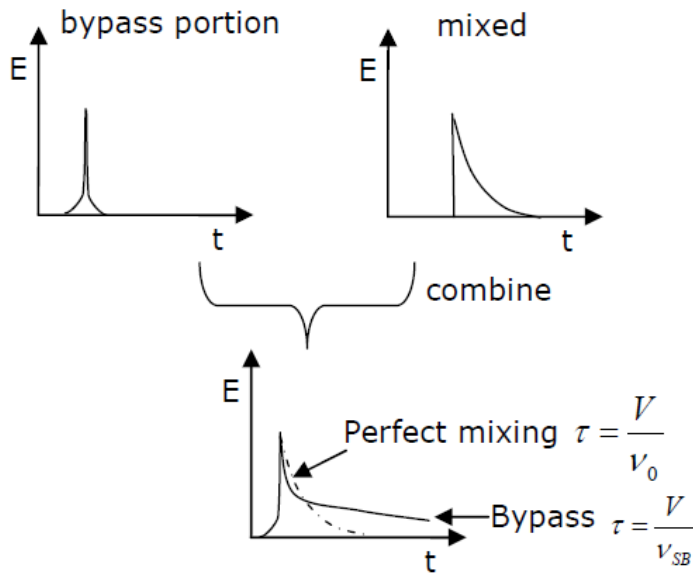


Figure 10. Residence-time distribution determination for a bypass.

Dead volumes: Stagnant regions not getting mixed

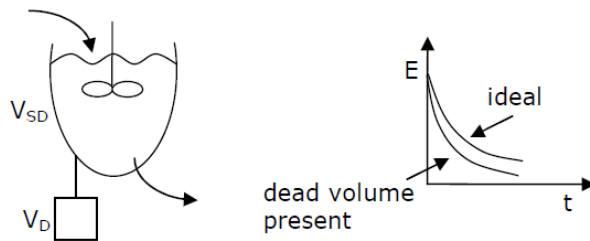


Figure 11. Residence-time distribution for dead volumes. When a dead volume is present, a decreased amount of material is observed in the output stream.

measurable $V = V_{SD} + V_D$

$$\tau_{SD} = \frac{V_{SD}}{v_0} < \tau_{ideal}$$

PFR (Non-ideal)

Channeling

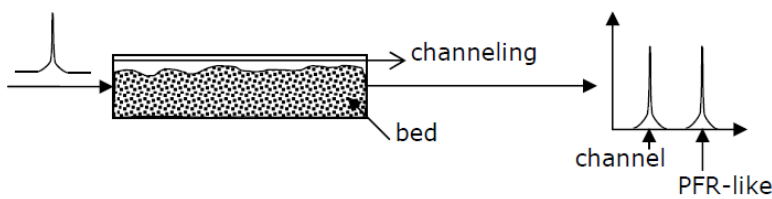


Figure 12. Channeling. In channeling, the residence-time distribution will show peaks for each channel as well as the one for the main portion of the reactor.

Axial Dispersion

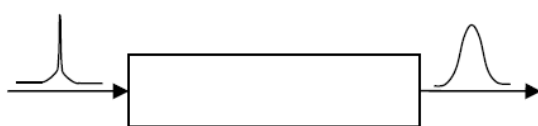


Figure 13. A pulse input can become an axially dispersed pulse output in a non-ideal PFR.

There are two common models for dispersion in a tubular reactor:

- Tanks in a series
- Taylor dispersion model (based on the Peclet number)

To model the PFR as several tanks in a series, break the reactor volume, V , into n CSTRs of volume $\frac{V}{n}$ each.

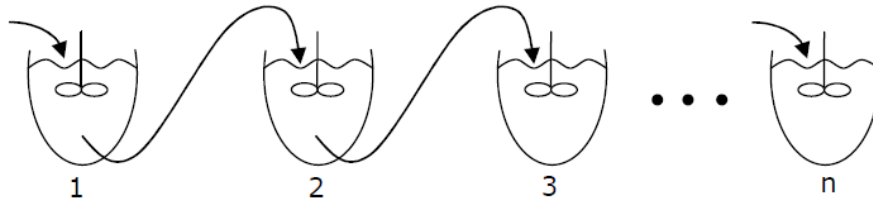


Figure 14. n tanks in series. The output of tank 1 is the input to tank 2. The output is sampled at tank n for dispersion.

$$E(t) = \frac{t^{n-1}}{(n-1)! \tau_i^n} e^{-t/\tau_i}, \quad \tau_i = \frac{\tau}{n}$$

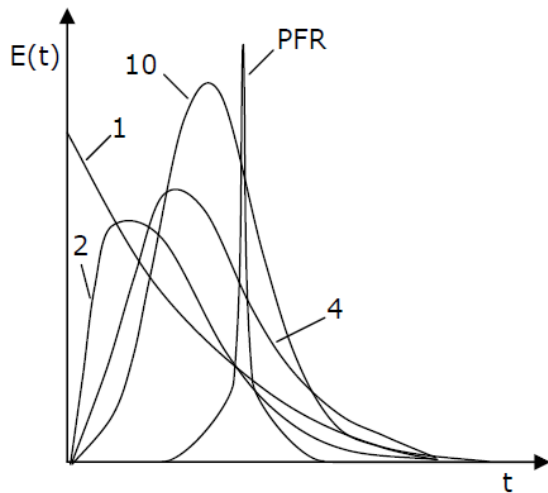


Figure 15. $E(t)$ plots for 1, 2, 4, and 10 tanks and a PFR. Notice how the $E(t)$ curve approaches the PFR pulse as more tanks are used.

The numbers above represent numbers of CSTRs. Without enough CSTRs, the peak is not a good approximation to the narrow peak for a PFR when there is a pulse input.

$$\sigma^2 = \frac{\tau^2}{n}$$

$$n = \frac{\tau^2}{\sigma^2}$$

We can physically measure τ and we can determine σ from experimentally measuring $E(t)$.

RTD (residence time distribution) are useful for diagnosis, but not for reactor design.

To calculate conversion, the most straightforward tactic is to model the non-ideal system as compartmental combinations of ideal reactors.

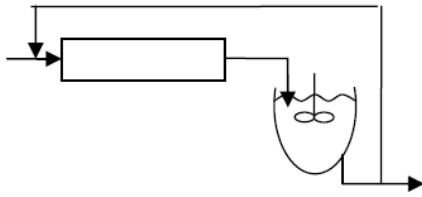


Figure 16. Recirculation. Recirculation can be modeled by a PFR followed by a CSTR with a recycle stream.



Figure 17. Partially dead volumes. Dead volumes can be modeled as separate CSTRs that exchange material with each other.

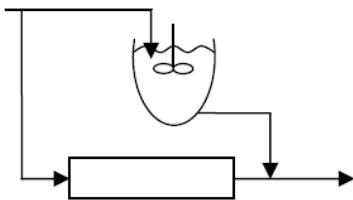


Figure 18. Bypass. A bypass can be modeled as a CSTR along one route with a PFR along the bypass route.

Lecture 8: Non-isothermal Reactors, equilibrium limitations, and stability

This lecture covers: Derivation of energy balances for ideal reactors; equilibrium conversion, adiabatic and non-adiabatic reactor operation.

Non-isothermal Reactors

$$\frac{dN_i}{dt} = \sum_{m=1}^{N \text{ streams}} F_{i,m} + V_{cv} \sum_{l=1}^{N \text{ rxns}} \nu_{i,l} r_l$$

↑
stoichiometric coefficient

- r_i - depends on concentration
 - T
 - catalyst

$$\frac{dU_{cv}^{total}}{dx} + P \frac{dV_{cv}}{dt} = \sum_{m=1}^{N \text{ streams}} H_m^{conc}(T_m) F_m^{total} + \dot{Q} + \dot{W}_s + (\text{other energy terms})$$

↑ extensive work ↑ intensive expansion work ↑ flow work ↑ heat ↑ shaft work

do work → \dot{W}_s negative

If small control volume, pressure constant.

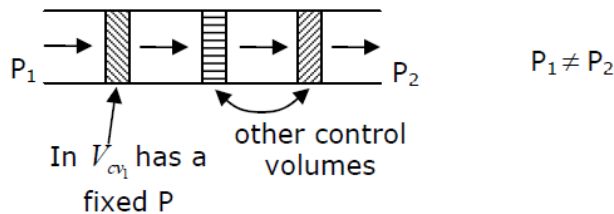


Figure 1. Schematic of a PFR with small control volumes, each with a fixed P.

PFR has many small control volumes, each with its own constant P.

- For isothermal - \dot{Q} adjusted to keep T constant
 - Practical - have big cooling bath
 - or just operate at a particular temperature found after reactor built
 ⇒ not a good strategy, for design we want to know ahead of time
 - before assumed uniform T, actually have hot spots

Where is T? In U_{cv}^{total} and $r_i(T)$.

$$\frac{dU_{cv}^{total}}{dt} = \frac{dU_{cv}^{total}}{dT} \frac{dT}{dt} + \sum_{i=1}^{N \text{ streams}} \left(\frac{dU_{cv}^{total}}{dN_i} \right) \frac{dN_i}{dt}$$

↑
↑
↑

heat capacity of system
intensive contribution of each species
substitute for $\frac{dN_i}{dt}$

Want $\frac{dY}{dt} = F(Y)$

Assume ideal mixtures

$$U_{cv}^{total} \approx \sum N_i U_i(T_{cv})$$

↑
↑

extensive
intensive

$$\frac{dU_{cv}^{total}}{dN_i} = U_i(T_{cv})$$

If P=Constant (Isobaric)

$$\frac{dH^{total}}{dt} = \frac{d(U + PV)}{dt} = \frac{dU}{dt} + \underbrace{\frac{dP}{dt} V}_0 + P \frac{dV}{dt}$$

$$\underbrace{\frac{dU_{cv}^{total}}{dt} + P \frac{dV_{cv}}{dt}}_{\frac{dH^{total}}{dt}}$$

Assume isobaric, all ideal mixtures, neglecting K.E., P.E., other energies

$$\left(\sum_i^{N \text{ species}} N_i C_{p,i} \right) \frac{dT_{cv}}{dt} = \sum_m^{N \text{ streams}} \sum_i^{N \text{ species}} F_{i,m} (H_i(T_m) - H_i(T_{cv})) - \sum_i^{N \text{ streams}} \sum_l^{N \text{ rxns}} H_i(T_{cv}) V_{cv} \nu_{i,l} r_l(T_{cv}) + \dot{Q} + \dot{W}_s$$

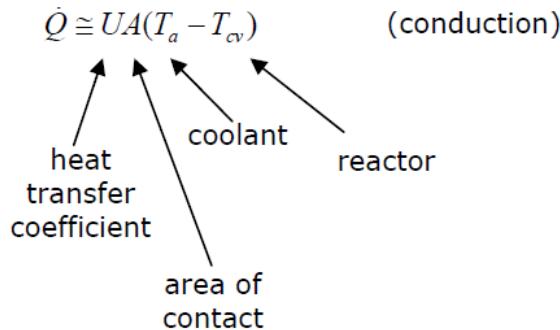
$$\sum_i \nu_{i,l} H_i(T_{cv}) \equiv \Delta H_{rxn,l}(T_{cv})$$

↑

stoichiometric coefficient

$$-\sum_i \sum_l^{N \text{ streams } N \text{ rxns}} H_i(T_{cv}) V_{cv} \nu_{i,l} r_l(T_{cv}) = -\sum_l V_{cv} r_l(T_{cv}) \Delta H_{rxn,l}(T_{cv})$$

Assume



$\dot{W}_s \approx 0$ (As a stirrer, heat negligible)
 If designing engines $\dot{W}_s \neq 0$.

Now just put into MATLAB and solve

Chapter 8 in Fogler – lots of special case equations
 – be careful of assumptions

Special case: Start up CSTR to a steady state
 want to know ultimate T

$$\frac{dT_{cv}}{dt} = 0 \cong \sum_m \sum_i^{N \text{ streams } N \text{ species}} F_{i,m} (H_i(T_m) - H_i(T_{cv})) - \sum_l V_{cv} r_l \Delta H_{rxn,l} + UA(T_a - T_{cv})$$

All depend on T_{cv}

When we reach steady state, no more accumulation

$$F_{A,in} - F_{A,out} + r_A V = 0 \text{ at steady-state}$$

See Fogler: 8.2.3

If just one reaction, one input stream, one output stream, and the system is at steady-state:

$$X_A = \frac{UA(T - T_a) + \sum F_{i,input} C_{p,i} (T - T_{in})}{F_{A0} (-\Delta H_{rxn})}$$

In this special case, conversion and T linear
 1 reaction making heat as product is made.

When $\Delta H_{rxn} = (-)$ Exothermic, reactor is hotter than cooling reactor (heat transfer important)
 (+) Endothermic, reactor must be heated so that reaction will run

$$G(T) \equiv (-\Delta H_{rxn})(-r_A V / F_{Ao}) \quad \text{Generation}$$

$$R(T) = \left(\sum \frac{F_{i,in}}{F_{Ao}} C_{p,i} \right) \left(1 + \frac{UA}{\underbrace{\sum F_{i,in} C_{p,i}}_K} \right) (T - T_c)$$

Heat removal

$K = 0$ Adiabatic
 $K = \text{Big}$ Cooling

$$T_c = \frac{KT_a + T_m}{1 + K}$$

$R(T)$ linear with T

$G(T) \rightarrow$ constant at high T
 - not linear with T

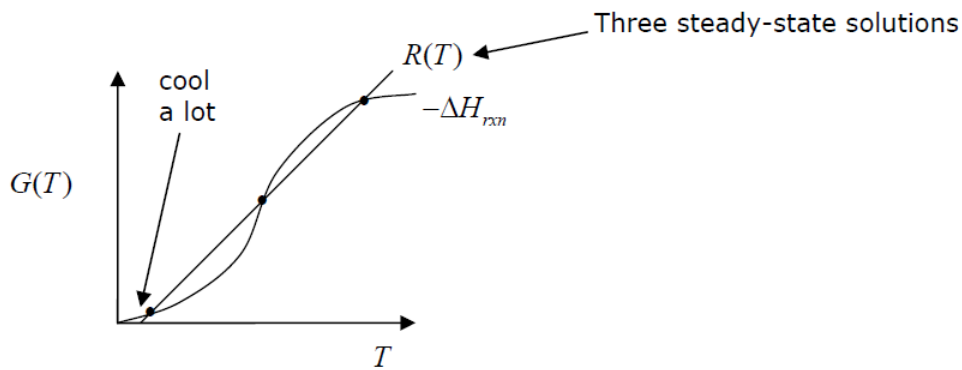


Figure 2. Graph of $G(T)$ versus T . Three steady-state points are shown where $R(T)$ intersects with the heat of reaction.

With multiple steady states must consider stability.

Lecture 9: Catalysis

This lecture covers: Inorganic and enzyme catalysis and their properties; kinetics of heterogeneous catalytic reactions; adsorption isotherms, derivation of rate laws; and Langmuir-Hinshelwood kinetics What initiates the reaction? $AB \rightarrow$ starts upon mixing

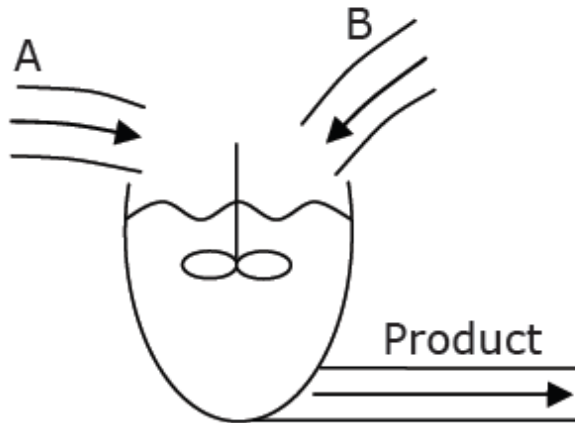


Figure 1. Bi-molecular reaction in a CSTR.

Temperature drastically increases reaction rate.

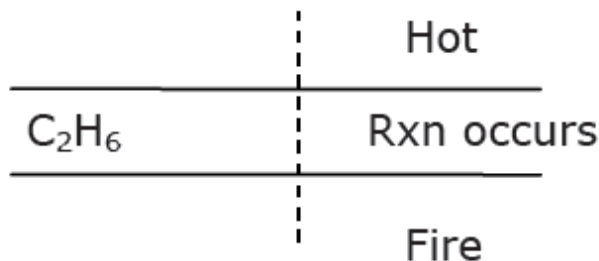


Figure 2. Schematic of tube reactor.

Catalyst dramatically increases reaction rate.

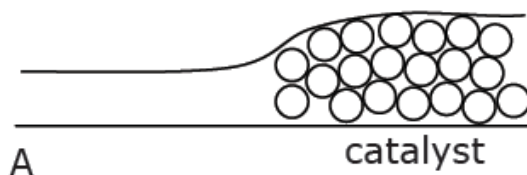


Figure 3. Schematic of packed bed reactor.

Catalyst: Accelerates rate of reaction but is not consumed

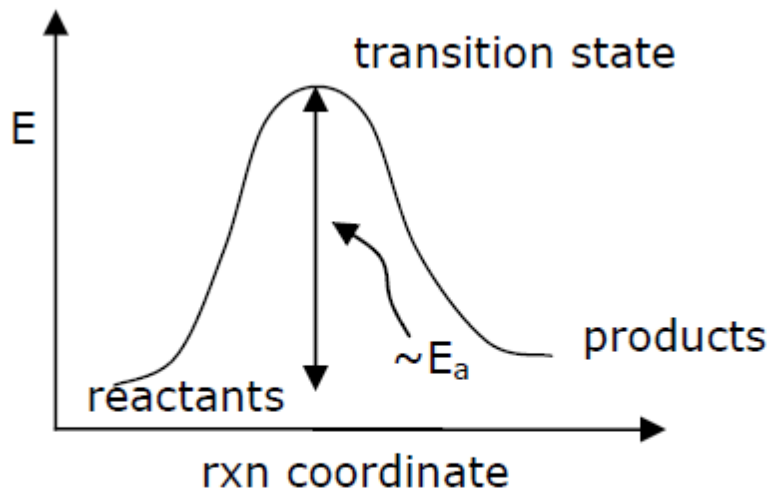


Figure 4. Reaction diagram.

rate constant:

$$k = \frac{k_B T}{h} \exp \left[-\frac{(G_{ts} - G_{\text{reactants}})}{RT} \right]$$

$$G = H - TS$$

$$e^{-G/RT} = e^{-H/RT} e^{S/R}$$

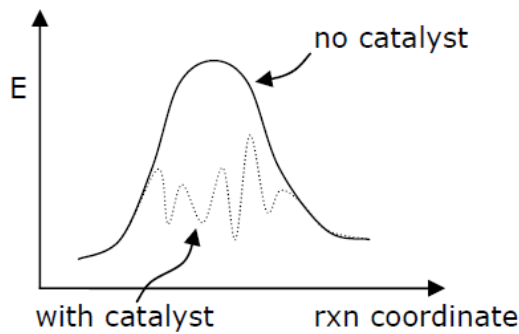
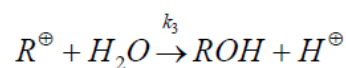
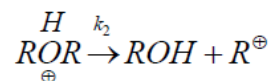
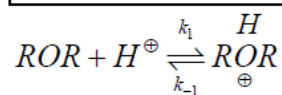
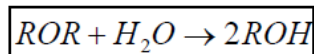


Figure 5. Reaction diagram with and without catalyst.

The reaction forms many intermediates. A catalyst lowers the energy of these intermediates.

Acid/Base catalysis



$$0 \approx \frac{d \left[\overset{H}{ROR}^{\oplus} \right]}{dt} = k_1 [H^+] [ROR] - (k_{-1} + k_2) \left[\overset{H}{ROR}^{\oplus} \right]$$

$$\left[\begin{matrix} H \\ ROR \\ \oplus \end{matrix} \right]_{QSSA} = \frac{k_1}{k_{-1} + k_2} [H^+] [ROR]$$

$$\frac{d[ROH]}{dt} = 2k_2 \left[\begin{matrix} H \\ ROR \\ \oplus \end{matrix} \right]_{QSSA}$$

$$\frac{d[ROH]}{dt} \approx \frac{2k_1k_2}{k_{-1} + k_2} [H^+] [ROR] = r$$

$$r_A \sim [A]$$


$$r_A \sim [\text{catalyst}] \quad (\text{where } \sim \text{ denotes "proportional to"})$$

$$[H^+] + \left[\begin{matrix} H \\ ROR \\ \oplus \end{matrix} \right] + [R^+] = \frac{N_{H^+ \text{ added}}}{V} = [H^+]_{\text{added}}$$

$$[H^+] \left(1 + \frac{k_1 [ROR]}{k_{-1} + k_2} + \frac{k_1 k_2 [ROR]}{k_3 (k_{-1} + k_2) [H_2O]} \right) = [H^+]_{\text{added}}$$

$$r = \frac{k_{\text{eff}} [ROR] [H^+]_{\text{added}}}{1 + k [ROR]}$$

$$r = \frac{k [\text{catalyst}] [A]}{1 + k_A [A] + k_B [B] + \dots}$$



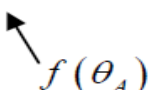
 All the things that the catalyst binds to

Langmuir-Hinshelwood: all reagents bind to catalyst, bound forms react

Eley-Rideal: one reagent binds, 2nd reagent reacts with bound form

$$\frac{dN_A}{dt} = Vr_A \longleftarrow f([A], [H^+])$$

$$\frac{dN_A}{dt} = (\text{area of metal}) r_A'' \longleftarrow \frac{\text{moles}}{\text{area s}}$$



 $f(\theta_A)$

where $\theta_A = \frac{N_{A \text{ bound}}}{N_{\text{total sites on surface}}}$