Competitive Inhibition: I competes with S for E binding site

$(EI <-> I +) E + S <-> ES -> E + P$

$K_m = [E][S] / [ES]$; $K_I = [E][I] / [EI]$

$[E_0] = [E] + [ES] + [EI] = [E] + [ES] + [E][I]/K_I$

$= [E](1 + [I]/K_I) + [ES]$

$[E] = ([E_0]-[ES])/(1+[I]/K_I)$

$K_m = \{([E_0]-[ES])/(1+[I]/K_I)\}[S]/[ES]$

$K_m(1+[I]/K_I) = ([E_0]-[ES])[S]/[ES] = K_m'$

$v = V_m[S]/\{[S] + K_m(1 + [I]/K_I)\}$

$= V_m[S]/([S] + K_m')$ (Note: $K_m' > K_m$)

LB Linearized: $1/v = (K_m'/V_m)(1/[S]) + 1/V_m$

V_m is unchanged, overcome inhibition by increasing $[S]$

K_m' increases as $[I]$ increases

Uncompetitive Inhibition

$E + S {}_2{<->}_1 ES (+ I {}_5{<->}_4 ESI) {->}_3 E + P$

$K_I = K_5/K_4$

Non-Competitive Inhibition
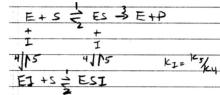
General Model for Inhibition

$v = V_f[S]/(K_f + [S])$; $V_f = f_V V_M$; $K_f = f_k K_M$

if $\alpha = \infty$, $\beta = 0$: competitive inhibition

$f_V = 1$, $f_k = 1 + [I]/K_I$; $v = V_M[S]/\{[S] + K_m(1+[I]/K_I)\}$

if $\alpha = 1$, $\beta = 0$: non-competitive inhibition

$f_V = 1/(1+[I]/K_I)$, $f_k = 1$; $v = V_M\{1/(1+[I]/K_I)\}[S]/\{[S]+K_m\}$

Substrate Inhibition Model

$v = V_M/(1+K_M/[S] + [S]/K_S)$
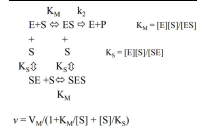
Rate Equation for a Reacting Component

$r_i = (1/V)(dN_i/dt)_{by\ reaction} = f(V)$

Ideal Batch Reactor

Assumptions: composition varies with time, uniform composition, constant volume

Very simple, needs very little supporting equipment, ideal for small-scale experimental studies on rxn kinetics

Flow terms are zero

Performance measure is t (time)

Time to achieve a conversion: $t = N_{A0}\int_0^{X_A} dX_A/(-r_A)V$

For constant density fluid: $t = -\int_{C_{A0}}^{C_A} dC_A/(-r_A)$

Rxn time = area under curve of $1/-rV$ vs X_A

Nth Order ($\epsilon_A = 0$): $(n-1)C^{n-1}_{A0}kt = (C_A/C_{A0})^{1-n}-1 = (1-X_A)^{1-n}-1$

$t = \int dC/r = C_0\int dX/-r$

Mixed Flow Reactor

Assumptions: uniform composition in position, composition does not vary with time, outlet concentration = reactor concentration, constant volume

Accumulation is zero

$C_{A0}v_0 - C_A v_0 + Vr_A = 0$

$-Vr_A = C_{A0}v_0 - C_A v_0$

$V/v_0 = (C_{A0} - C_A)/-r_A = \tau = C_{A0}V/F_{A0} = C_{A0}X_A/-r_A$

$F_{A0} = v_0C_{A0}$

For constant density:

$X_A = 1-C_A/C_{A0}$

$\tau = (C_{A0} -C_A)/-r_A = $ area $X_A * -1/r_A$ or $(C_{A0} - C_A)*-1/r_A$

First order: $k\tau = X_A/(1-X_A) = (C_{A0}-C_A)/C_A$; $C_A = C_{A0}/(1+k\tau)$; $X_A = k\tau/(1+k\tau)$

Second Order: $k\tau = (C_{A0}-C_A)/C_A^2$; $C_A = [-1+(1+4C_{A0}k\tau)^{1/2}]/2k\tau$

Nth Order: $k\tau = (C_{A0}-C_A)/C_A^n = X_A/[C^{n-1}_{A0}(1-X_A)^n]$

$\tau = [C_0-C]/-r = C_0X/-r$

Plug Flow Reactor

Assumptions: Composition varies with axial position, composition does not vary with time, constant volume, no axial mixing, homogeneous radial composition

Accumulation is zero

$\tau = V/v_0 = VC_{A0}/F_{A0} = C_{A0}\int_0^{X_{Af}} -1/r_A\ dX_A = -\int_{C_{A0}}^{C_{Af}} -1/r_A\ dC_A = $ area under curve of X_A vs. $(C_{A0} – C_A)$ vs. $-1/r_A$

Zero order: $k\tau = kC_{A0}V/F_{A0} = C_{A0}X_A$

First order: $k\tau = -\ln(1-X_A) = -\ln(C_A/C_{A0})$

Second Order Irreversible: $C_{A0}k\tau = X_A/(1-X_A)$

Nth Order ($\epsilon_A = 0$): $(n-1)C^{n-1}_{A0}k\tau = (C_A/C_{A0})^{1-n}-1 = (1-X_A)^{1-n}-1$

$t = \int dC/r = C_0\int dX/-r$

Space-Time

Steady flow reactor performance measure

Time required to process one reactor volume of feed measured at specific conditions; units time

$\tau = 1/s = V/v_0 = C_{A0}V/F_{A0}$ (molar flowrate)

PFR has better performance as tau is lower

PFR provides same conversion as MFR for a smaller area

$(\tau C_{A0}^{n-1})_m/(\tau C_{A0}^{n-1})_p = [X_A/(1-X_A)]_m / [\{(1-X_A)^{1-n}-1\}/n-1]_p$ when $n \neq 1$

$(\tau C_{A0}^{n-1})_m/(\tau C_{A0}^{n-1})_p = [X_A/(1-X_A)^n]_m / -\ln(1-X_A)_p$ when $n=1$

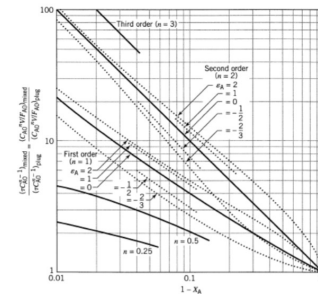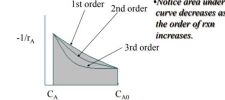**Figure 6.1** Comparison of performance of single mixed flow and plug flow reactors for the nth-order reactions.

Higher Order Reactions

- Reactors containing higher order reactions get a better performance.
- As the order of reaction increases, you want to use a plug flow reactor.
- Notice area under curve decreases as the order of rxn increases.

Space-Velocity

Steady flow reactor performance measure

Number reactor volumes of feed at specified conditions which can be treated in unit time; units 1/time

$s = 1/\tau$

Plug Flow Reactors in Series

$$\tau = \frac{1}{k}\ln\left(\frac{1}{1-x}\right) \qquad \text{1st order}$$
$$e^{\tau k} = \frac{1}{1-x} \Rightarrow x = 1-e^{-\tau k}$$
for series pfr $\tau_{overall} = n\tau_i$
$$X_{overall} = 1-e^{-n\tau_i k}$$

Plug Flow Reactors in Parallel

1) X for each path must be the same (any other system is less efficient)
2) Therefore, issue is how to split flows.

[diagram: reactors V_1, V_2, V_3 in parallel with flows q_1, q_2, q_3, concentrations C_1, C_2, C_3]
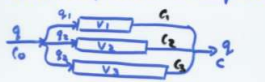
$$\tau_1 = \frac{V_1}{q_1} \quad \tau_2 = \frac{V_2}{q_2} \quad \tau_3 = \frac{V_3}{q_3}$$
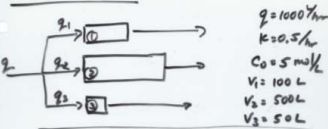for equal conversion, $\tau_1 = \tau_2 = \tau_3$
$$\frac{V_1}{q_1} = \frac{V_2}{q_2} = \frac{V_3}{q_3} \Rightarrow q_2 = \frac{V_2}{V_1}q_1$$
$$q_3 = \frac{V_3}{V_1}q_1$$
$$q = q_1 + \frac{V_2}{V_1}q_1 + \frac{V_3}{V_1}q_1 = \left(1+\frac{V_2}{V_1}+\frac{V_3}{V_1}\right)q_1$$
∴ parallel pfrs must split flowrates in ratio to their volumes
General, n reactors in parallel
$$q = \left(1+\sum \frac{V_i}{V_1}\right)q_1$$

3 reactors in parallel!

[diagram of 3 reactors in parallel]

$q = 1000 /hr$
$k = 0.5/hr$
$C_0 = 5\ mol/L$
$V_1 = 100\ L$
$V_2 = 500\ L$
$V_3 = 50\ L$

Split flow as $q_1 = 300 /hr$
$q_2 = 500 /hr$ } $\Sigma = 1000 /hr$
$q_3 = 200 /hr$

$X = 1-e^{-k\tau}$ $X q C_0 = $ total mols product
$$\tau_1 = \frac{100}{300} = 0.3333 \quad \tau_2 = \frac{500}{500}=1 \quad \tau_3 = \frac{50}{200} = 0.25$$
$X_1 = 0.1535$ $X_2 = 0.3935$ $X_3 = 0.1175$
230.25 983.75 117.5
$$\frac{1331.5}{(5 \times 1000)} = 0.2663 = X_{net}$$

$$q = \left(1+\frac{500}{100}+\frac{50}{100}\right)q_1 = 6.5 q_1$$
$$q_1 = \frac{q}{6.5} = \frac{1000}{6.5} = 153.85 /hr$$
$$q_2 = \frac{500}{100}q_1 = 769.23 /hr$$
$$q_3 = 76.92 /hr$$
$$q_1+q_2+q_3 = 1000 /hr \checkmark$$
$$\tau_1 = \frac{100}{153.85} = \tau_2 = \frac{500}{769.23} = \tau_3 = \frac{50}{76.92}$$
$$= 0.65$$
$$X = 1-e^{-k\tau} = \underline{0.2775} \quad \text{overall conversion}$$
Better conversion by having equal τ

Mixed Flow Reactors in Series

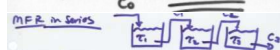[diagram: reactors 1, 2, 3 in series, $C_0 \to C_1 \to C_2 \to C_3$, $q = $ const]
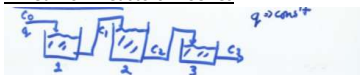
$$\tau_i = \frac{C_{i-1}-C_i}{-r}$$
1st order rxn, $-r = kC$
$$\tau_1 = \frac{C_0-C_1}{kC_1} \Rightarrow \frac{C_0}{C_1} = 1+k\tau_1$$
$$\tau_2 = \frac{C_1-C_2}{kC_2} \Rightarrow \frac{C_1}{C_2} = 1+k\tau_2$$
$$\tau_3 = \frac{C_2-C_3}{kC_3} \Rightarrow \frac{C_2}{C_3} = 1+k\tau_3$$
$$\left(\frac{C_0}{C_1}\right)\left(\frac{C_1}{C_2}\right)\left(\frac{C_2}{C_3}\right) = (1+k\tau_1)(1+k\tau_2)(1+k\tau_3)$$
$$\frac{C_0}{C_3} = \prod_i(1+k\tau_i)$$

For equal volume mfr, $\tau_1 = \tau_2 = \tau_3 = \cdots \tau_n$
$$\frac{C_0}{C_n} = (1+k\tau_i)^n$$
$$\Rightarrow \tau_i = \frac{1}{k}\left[\left(\frac{C_0}{C_n}\right)^{1/n}-1\right]$$
$$\tau_{overall} = n\tau_i = \frac{n}{k}\left[\left(\frac{C_0}{C_n}\right)^{1/n}-1\right]$$
$$= \frac{n}{k}\left[\left(\frac{1}{1-x}\right)^{1/n}-1\right]$$
Note: As $n \to \infty$, $n\left[\left(\frac{C_0}{C_n}\right)^{1/n}-1\right]\to \ln\frac{C_0}{C_n}$
$$\Rightarrow \tau_{overall} \to \frac{1}{k}\ln\left(\frac{C_0}{C_n}\right) \Rightarrow pfr$$

Mixed Flow Reactors in Series

All same volume, $V = 10 L$
$v = 1 L/hr$, $C_0 = 10\ mol/L$, $k = 0.04 \frac{1}{hr}$
What is overall conversion?
What are intermediate concentrations?
1st order rxn
$$C_1 = \frac{C_0}{1+k\tau} \qquad k\tau = \left(.04 \times \frac{10}{1}\right) = 0.4$$
So, $C_1 = \frac{C_0}{1+.4} = \frac{10}{1.4} = 7.1429\ mol/L$
$$C_2 = \frac{C_1}{1+0.4} = \frac{7.1429}{1.4} = 5.102\ mol/L$$
etc.
$$C_8 = \frac{C_0}{(1+k\tau)^n} = \frac{C_0}{(1+0.4)^8} = 0.6776\ mol/L$$
$$X = \frac{C_0-C_8}{C_0} = 0.9322$$

MFR in Series

[diagram of reactors in series]

Zero order rxn
$$\frac{k\tau}{C_0} = \frac{C_0-C}{C_0} = X$$
re-arrange,
$$C = C_0 - k\tau$$
For reactor 1
$$C_1 = C_0 - k\tau_1$$
For reactor 2
$$C_2 = C_1 - k\tau_2 = C_0 - k\tau_1 - k\tau_2$$
For reactor 3
$$C_3 = C_2 - k\tau_3 = C_1 - k\tau_2 - k\tau_3 = C_0 - k\tau_1 - k\tau_2 - k\tau_3$$
In general
$$C_n = C_0 - \sum k\tau_i$$
If τ all the same,
$$C_n = C_0 - nk\tau$$

MFR in Series
1st order rxn
$$k\tau = \frac{C_0-C}{C} \Rightarrow C = \frac{C_0}{1+k\tau}$$
So,
$$C_1 = \frac{C_0}{1+k\tau_1}$$
$$C_2 = \frac{C_1}{1+k\tau_2} = \frac{C_0}{(1+k\tau_1)(1+k\tau_2)}$$
$$C_3 = \frac{C_3}{1+k\tau_3} = \frac{C_0}{(1+k\tau_1)(1+k\tau_2)(1+k\tau_3)}$$
In general,
$$C_n = \frac{C_0}{\prod_i(1+k\tau_i)}$$
If all τ are the same
$$C_n = \frac{C_0}{(1+k\tau)^n}$$

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mfr
2nd order $r = -kC^2$ equal volume ⇒ τ
$$\tau = \frac{C_0-C_1}{kC_1^2} \Rightarrow k\tau C_1^2 + C_1 - C_0 = 0$$
$$C_1 = \frac{-1+\sqrt{1+4\tau k C_0}}{2\tau k}$$
$$= \frac{1}{4\tau k}\left(-2+2\sqrt{1+4\tau k C_0}\right)$$
$$\tau = \frac{C_1-C_2}{kC_2^2} \Rightarrow C_2 = \frac{1}{4\tau k}\left(-2+2\sqrt{1+4\tau k C_1}\right)$$
$$C_2 = \frac{1}{4\tau k}\left(-2+2\sqrt{1+4\tau k\left(\frac{1}{4\tau k}\left(-2+2\sqrt{1+4\tau k C_0}\right)\right)}\right)$$
$$= \frac{1}{4\tau k}\left(-2+2\sqrt{1+2\sqrt{1+4\tau k C_0}}\right)$$
$$C_3 = \frac{1}{4\tau k}\left(-2+2\sqrt{1+4\tau k C_2}\right)$$
$$= \frac{1}{4\tau k}\left(-2+2\sqrt{1+\left(-2+2\sqrt{1+2\sqrt{1+4\tau k C_0}}\right)}\right)$$
$$= \frac{1}{4\tau k}\left(-2+2\sqrt{-1+2\sqrt{-1+2\sqrt{1+4\tau k C_0}}}\right)$$

[diagram: N-stage mixed flow reactor system in series, $C_0, X_0 = 0$, F_0, v; C_1, X_1; C_2, X_2; C_{i-1}, X_{i-1}; C_i, X_i; C_{N-1}, X_{N-1}; C_N, X_N, v]

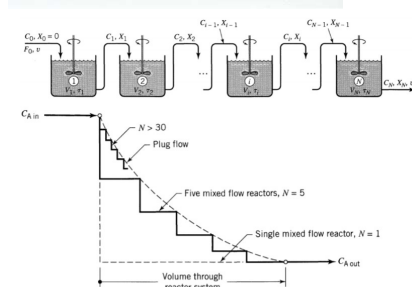[graph: $C_{A\,in}$ vs Volume through reactor system, showing $N > 30$ Plug flow, Five mixed flow reactors $N = 5$, Single mixed flow reactor $N = 1$, $C_{A\,out}$]

Figure 6.3 Concentration profile through an N-stage mixed flow reactor system compared with single flow reactors.

[graph: First-order reaction; curves for $N = 50, N = 20, N = 2, N = 3, N = 4, N = 6, N = 10, N = \infty$; x-axis $1 - X_A = \frac{C_A}{C_{A0}}$]
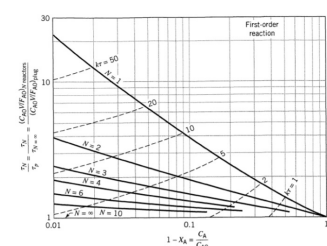
Figure 6.5 Comparison of performance of a series of N equal-size mixed flow reactors with a plug flow reactor for the first-order reaction

$$A \to R, \qquad \varepsilon = 0$$