10.37 Chemical and Biological Reaction Engineering, Spring 2007
Exam 1 Review

In-Out+Production=Accumulation

Accumulation=0 at steady state

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

$$F_{A0} = [A]_0 \nu_0$$

$$F_A = [A]\nu$$

For a liquid phase with constant density: $\nu_0 = \nu$

For $A \rightarrow B$ the reaction moles are the same, so $\nu_0 = \nu$

For $A \rightarrow 2B$, $\nu_0 \neq \nu$

ξ [=] moles (extent of reaction) (-) for a reactant and (+) for a product

$$N_i = N_{i0} + \sum_{n=1}^{N_{rxns}} \upsilon_{i,n}\xi_n$$

Suppose $A \rightarrow B + C$

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

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

Thermodynamics

Suppose $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2C$

$$K_e = e^{-\Delta G/RT}$$

$$\Delta G = \Delta G^{\circ}_{f,products} - \Delta G^{\circ}_{f,reactants}$$

$K_c = \frac{[B][C]}{[A]}$ has units. You need to use standard states, such as 1M, to make it dimensionless.

Enzyme Catalysis

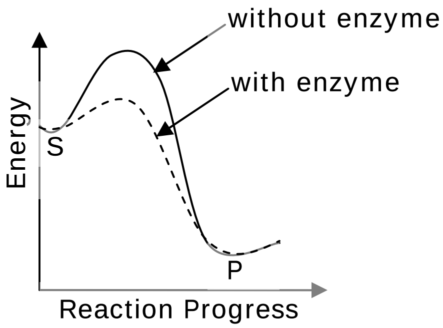

Figure 1. Energy diagram for a reaction with and without enzyme.

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$$E + S \rightleftharpoons ES$$
$$ES \rightarrow E + P$$

Pseudo steady state approximation:

$$\frac{d\left[ES\right]}{dt} = 0$$
$$\left[ES\right] = f(\text{other species})$$

Cell Growth

$$N = \frac{\text{\# cells}}{\text{volume}}$$
$$N = N_0 e^{\mu t}$$

Monod kinetics:

$$\mu = \frac{\mu_{\max}\left[S\right]}{K_S + \left[S\right]}$$
$$Y_{\frac{A}{B}} = \frac{\Delta A}{\Delta B}$$

Rate Constants

$$k(T) = Ae^{-E_a/RT}$$

Given k_1 and k_2, you can calculate k and a different temperature.

CSTRs

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

Incorporates changing volumetric flow rate

If the reaction is 1st order and it consists of liquids with constant density:

$$\tau = \frac{X_A}{k(1 - X_A)}$$
$$\tau = \frac{V}{v_0} = \frac{\text{volume}}{\text{volumetric flow rate}}$$
$$X_A = \frac{\tau k}{1 + \tau k}$$

$Da = \tau k$ = Damköhler number: ratio of kinetic effect to volumetric effect or ratio of reaction rate to dilution rate

2nd order reaction:

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

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

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

For constant density and 1st order reaction:

$$F_{A0} - F_A + r_A V = \frac{dN_A}{dt}$$

$$C_{A0} - C_A + r_A \tau = \tau \frac{dC_A}{dt}$$

Let:

$$\hat{C}_A = \frac{C_A}{C_{A0}} \qquad \hat{t} = \frac{t}{\tau}$$

Nondimesionalize:

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

Solve given $\hat{C}_A = 0$ at $\hat{t} = 0$

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

Tanks in series: 1st order reaction

$$C_{A,n} = \frac{C_{A,0}}{\left(1+Da\right)^n}$$

Reactor Design Equations

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

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

$N_A = V\left[A\right]$ If V changes, then V must remain in the differential

PFR: $\frac{dX_A}{Adz} = \frac{-r_A}{F_{A0}}$

PBR: Pressure drop consideration

If $A_{(g)} \rightarrow 2B_{(g)}$

Use $v_0\rho_0 = v\rho$ (conservation of mass)

Introduce ideal gas law $\rho = \frac{P\dot{m}}{F_T RT}$ $\left(\dot{n}RT = P\nu = P\frac{\dot{m}}{\rho} = F_T RT\right)$

$F_T = F_{T0}\left(1+\varepsilon X\right)$

Reactor volume:

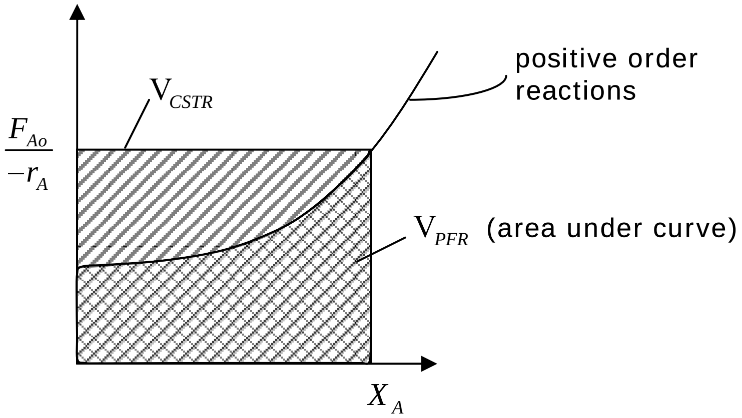

Figure 2. Levenspiel plot for a CSTR and a PFR for positive order reactions.

Selectivity

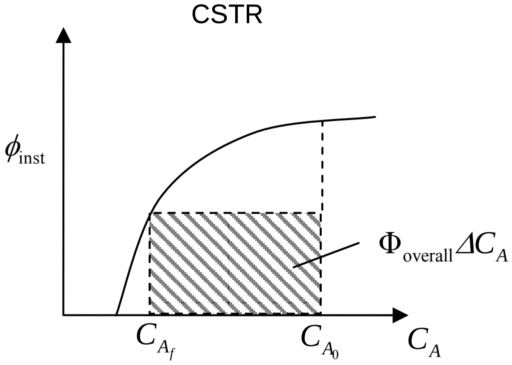

Figure 3. Fractional yield versus concentration. Overall yield times concentration difference shown for a CSTR.

CSTR

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

$$A \xrightarrow{k_3} U$$

$$\left(k_1\left[A\right]+k_3\left[A\right]\right)V = F_{A0} - \left[A\right]\nu$$

Non-ideal reactors

Residence time distribution E(t)

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$$\delta(t)\xrightarrow{reactor}C(t)$$

E(t) must have a pulse trace

$$E(t)=\frac{C(t)}{\int_0^\infty C(t)dt} \qquad \int_0^\infty E(t)=1$$

$$t_m=\int_0^\infty tE(t)dt$$

Mean residence time, t_m, for an:
Ideal CSTR: τ
Ideal PFR: τ

$$\sigma^2=\int_0^\infty \left(t-t_m\right)^2 E(t)dt$$

Variance, σ^2, for an:
Ideal CSTR: τ^2
Ideal PFR: 0 $\left(E(t)=\delta\left(t-\frac{V}{\nu}\right)\right)$

$$\int_0^\infty f(t)\delta(t-t_0)dt=f(t_0)$$ ←property of a dirac delta function

For a CSTR, $E(t)=\frac{e^{-t/\tau}}{\tau}$

Example 1

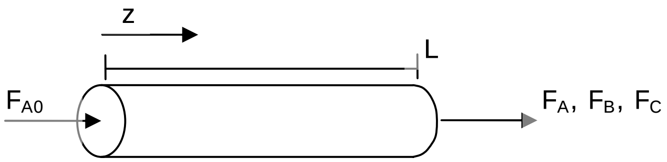

Figure 4. Schematic of a PFR with inflow of A and outflow of A, B, and C.

$$A\xrightarrow{r_1}B\xrightarrow{r_2}C$$
$$r_1=k_1C_A \qquad r_2=k_2C_B$$
$$Y_B=\frac{\text{moles of B produced}}{\text{moles of A in}}=\frac{F_B(L)}{F_{A0}}$$

Mole balance on B

$$\frac{1}{A_{xs}}\frac{dF_B}{dz}=r_B=r_1-r_2=k_1C_A-k_2C_B$$
$$F_B=C_B\nu_0$$
$$F_{A0}=C_{A0}\nu_0$$

$$\frac{\nu_0}{A_{xs}}\frac{dC_B}{dz} = k_1 C_A - k_2 C_B$$

$$\frac{\nu_0}{A_{xs}}\frac{dC_A}{dz} = -k_1 C_A$$

$$\frac{dC_A}{C_A} = \frac{-k_1 A_{xs}}{\nu_0} dz$$

$$\ln C_A = \frac{-k_1 A_{xs}}{\nu_0} z + \phi$$

Initial condition at z=0 gives:

$$\ln C_{A0} = 0 + \phi$$

$$C_A = C_{A0} \exp\left[\frac{-k_1 A_{xs}}{\nu_0} z\right]$$

$$\frac{dC_B}{dz} + \frac{k_2 A_{xs}}{\nu_0} C_B = \frac{k_1 A_{xs}}{\nu_0} C_{A0} \exp\left[\frac{-k_1 A_{xs}}{\nu_0} z\right]$$

$\frac{A_{xs}}{\nu_0} z [=]$ time, call it τ

This is the time it takes for something to flow to the end of the reactor (of length z).

$\frac{\nu_0}{A_{xs}} = \vec{V}$ velocity

$$\frac{dC_B}{d\tau} + k_2 C_B = k_1 C_{A0} e^{-k_1 \tau}$$

Integrating factor: $e^{k_2 \tau}$

$$\frac{d}{d\tau}\left[C_B e^{k_2 \tau}\right] = k_1 C_{A0} e^{(k_2 - k_1)\tau}$$

$$C_B e^{k_1 \tau} = \frac{k_1 C_{A0}}{k_2 - k_1} e^{(k_2 - k_1)\tau} + \phi$$

Initial condition: z=0, C_B=0

$$0 = \frac{k_1 C_{A0}}{k_2 - k_1} + \phi$$

$$C_B(\tau) = \frac{k_1 C_{A0}}{k_2 - k_1}\left[e^{-k_1 \tau} - e^{-k_2 \tau}\right]$$

$$\frac{1}{A_{xs}}\frac{dF_C}{dz} = +r_2$$

$$\frac{1}{A_{xs}}\frac{dF_A}{dz} = -r_1$$

$$\frac{1}{A_{xs}}\frac{dF_B}{dz} = r_1 - r_2$$

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$$\frac{1}{A_{xs}}\left[\frac{dF_A}{dz}+\frac{dF_B}{dz}+\frac{dF_C}{dz}\right]=0$$

$$F_{A0}=F_A+F_B+F_C$$

$$F_C=F_{A0}-F_A+F_B$$

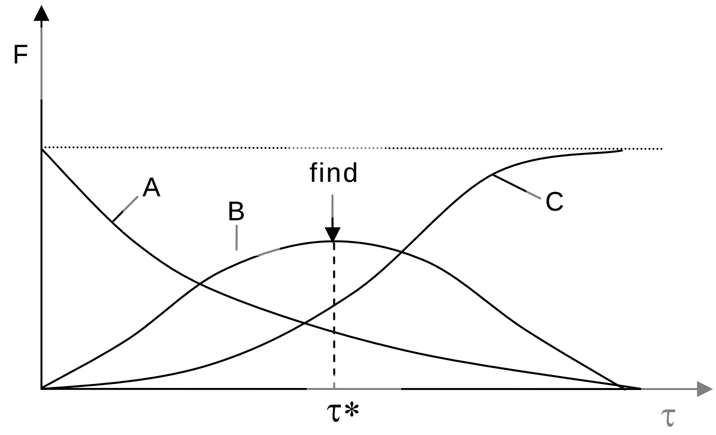

Figure 5. Graphs of flow rates of A, B, and C as a function of residence time.

$$\frac{dC_B}{d\tau}=\frac{k_1C_{A0}}{k_2-k_1}\left(-k_1e^{-k_1\tau^*}+k_2e^{-k_2\tau^*}\right)=0$$

$$k_1e^{-k_1\tau^*}=k_2e^{-k_2\tau^*}$$

$$\ln k_1-k_1\tau^*=\ln k_2-k_2\tau^*$$

$$\ln\frac{k_1}{k_2}=\left(k_1-k_2\right)\tau^*$$

$$\tau^*=\frac{\ln\frac{k_1}{k_2}}{k_1-k_2}$$

L'Hopital's rule: $\lim\limits_{x\to x^*}\frac{A(x)}{B(x)}=\frac{0}{0}\ \ do\ \ \lim\limits_{x\to x^*}\frac{\frac{dA(x)}{dx}}{\frac{dB\frac{dy}{dx}(x)}{dx}}$

Find τ^* for $k_1=k_2$

$$\lim_{k_1\to k_2}\tau^*=\lim_{k_1\to k_2}\frac{{}^{1}\!/_{k_1}}{1}=\frac{1}{k_2}=\frac{1}{k}$$

$$\tau^*=\frac{A_{xs}L}{\nu_0}\qquad\tau=\frac{A_{xs}z}{\nu_0}$$

$$\boxed{L = \frac{\tau * v_0}{A_{xs}} = \text{length of reactor}}$$

Example 2

If $A \rightarrow 2B$ (Assume negligible pressure drop)

$r = kC_A$

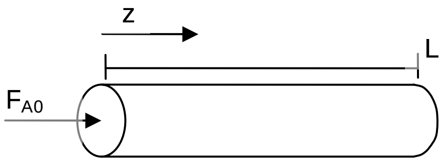

Figure 6. Schematic of a PFR.

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

$$v_0 \leftrightarrow v$$

$$P\dot{V} = \dot{n}RT \quad (F_{total} = \dot{n}\, ,\, v = \dot{V})$$

$$v = F_{total}\frac{RT}{P} = F_{total}C_{total}^{-1}$$

$$F_{total} = F_A + F_B$$

$$F_A = C_A v = y_A F_{total}$$

$$\frac{dF_A}{dV} = -ky_A C_{total} = -k\frac{F_A}{F_A + F_B}\frac{P}{RT}$$

$$\frac{dF_B}{dV} = +2ky_A C_{total} = +2k\frac{F_A}{F_A + F_B}\frac{P}{RT}$$

If P or T changes, you need other equations.

Derivation of E(t) for a CSTR

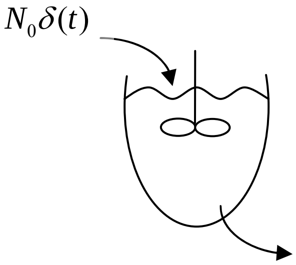

Figure 7. Schematic of a CSTR.

No reaction:

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$$\frac{dN}{dt} = N_0\delta(t) - \nu C$$

$$= N_0\delta(t) - \nu\frac{N}{V}$$

$$\frac{dN}{dt} + \frac{\nu}{V}N = N_0\delta(t)$$

Integrating factor: $\exp\left(\frac{\nu}{V}t\right)$

$$\frac{d}{dt}\left(N\exp\left(\frac{\nu}{V}t\right)\right) = \exp\left(\frac{\nu}{V}t\right)N_0\delta(t)$$

$$N\exp\left(\frac{\nu}{V}t\right) = N_0\cdot\exp\left(\frac{\nu}{V}0\right) = N_0 + \phi$$

Initial condition: $t=0$, $N=N_0$ → $\phi=0$

$$N = N_0\exp\left(-\frac{\nu}{V}t\right)$$

$$\frac{\nu}{V} = \frac{1}{\tau}$$

$$C = C_0\exp\left(\frac{-t}{\tau}\right)$$

$$E(t) = \frac{C}{\int_0^\infty C\,dt}$$

$$\int_0^\infty C\,dt = \int_0^\infty C_0 e^{-t/\tau}dt = C_0\left[-\tau\,\mathrm{e}^{-t/\tau}\right]_0^\infty = C_0\left[-\tau\left(0-1\right)\right] = C_0\tau$$

$$E(t) = \frac{C_0 e^{-t/\tau}}{C_0\tau} = \frac{e^{-t/\tau}}{\tau}$$

Long-chain approximation

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} P + E$$

$$tRNA \xrightarrow{k_3} E$$

$$E \xrightarrow{k_4} \text{Deactivate}$$

Enzyme propagates a long time before it is destroyed.

LCA: $k_3\left[tRNA\right] = k_4\left[E\right]$

(assume 1st order)

If there are other steps, add them into the equation

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$ES \xrightarrow{k_5}$ destruction

$k_3[tRNA] = k_4[E] + k_5[ES]$

Suppose there is a production term

$C \xrightarrow{k_6} E$

Add another term

$k_6[C] + k_3[tRNA] = k_4[E] + k_5[ES]$

$$\frac{dX}{Adz} = \frac{F_{A0}}{-r_A}, \ -r_A = kC_A$$

This is a single differential equation in terms of X. Use for PFR with gas flow.

$\rho_0 \nu_0 = \rho \nu$

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

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