KINETICS

Levenspiel

$aA + bB \rightarrow rR + sS$

$$C_{A0} X_A = \frac{b}{a} C_{B0} X_B$$

$$\frac{-r_A}{a} = -\frac{r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s}$$

elementary rxn : rate eqn corresponds to stoichiometric eqn

$$\text{extent} = X = \frac{N_j - N_{j0}}{\nu_j} = \frac{N_{A0} - N_A}{a} = \frac{N_D - N_{D0}}{d}$$

Pseudo-steady state assumption : $R_X = 0$ for intermediates

Rate-limiting step assumption : other rates in equilibrium

Arrhenius : $k = k_0 e^{-E/RT}$

Constant volume :

$$X_A = \frac{N_{A0} - N_A}{N_{A0}} = 1 - C_A/C_{A0}$$

$$-r_A = -\frac{dC_A}{dt} = kC_A \quad (1^{st} \text{ order})$$

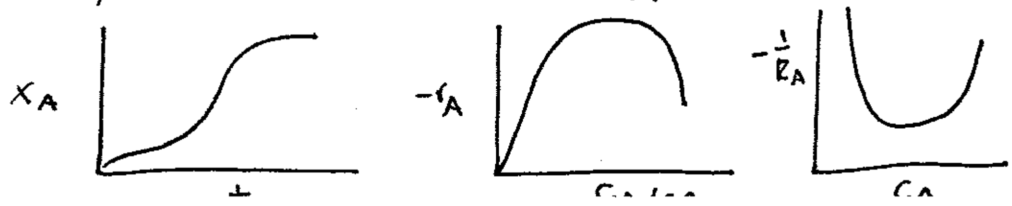
$$-\ln \frac{C_A}{C_{A0}} = kt$$

n^{th} order

$$-r_A = \frac{-dC_A}{dt} = kC_A^n$$

$$C_A^{1-n} - C_{A0}^{1-n} = (1-n)kt$$

Autocatalytic rxns : $A + R \rightarrow R + R$



Varying P: $\frac{C_A}{C_{Ao}} = \frac{(1-X_A)}{(1+\varepsilon_A X_A)} \frac{P}{P_0} \frac{T_o}{T}$

Varying volume

$$V = V_o\,(1+\varepsilon_A X_A)\left(\frac{P_o}{P}\right)\left(\frac{T}{T_o}\right)$$

$A = N_{Ao}(1-X_A)$ always

$$C_A = \frac{N_A}{V} = \frac{N_{Ao}(1-X_A)}{V_o\,(1+\varepsilon_A X_A)} = C_{Ao}\,\frac{1-X_A}{1+\varepsilon_A X_A}$$

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = \frac{N_{Ao}\,dX_A/dt}{V_o\,(1+\varepsilon_A X_A)} = \frac{C_{Ao}}{1+\varepsilon_A X_A}\,\frac{dX_A}{dt}$$

or $$\frac{dX_A}{dt} = \frac{1}{\varepsilon_A}\frac{dV}{dt}$$

$$-r_A = \frac{C_{Ao}}{V\varepsilon_A}\,\frac{dV}{dt}$$

$$\varepsilon_A = \frac{y_{Ao}\sum_{j=1}^{N} \nu_j}{|\nu_A|} = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}}$$

Batch Reactor

in - out + gen = acc

$$0 - 0 + r_A V = \frac{dN_A}{dt} = \frac{d\,[N_{Ao}\,(1-X_A)]}{dt} = -N_{Ao}\,\frac{dX_A}{dt}$$

$$t = N_{Ao}\int_0^{X_A} \frac{dX_A}{(-r_A)\,V}$$

Const V:

$$t = C_{Ao}\int_0^{X_A} \frac{dX_A}{(-r_A)} = -\int_{C_{Ao}}^{C_A} \frac{dC_A}{(-r_A)}$$

Varying V:

$$t = N_{Ao}\int_0^{X_A} \frac{dX_A}{(-r_A)\,V_o\,(1+\varepsilon_A X_A)} = C_{Ao}\int_0^{X_A} \frac{dX_A}{(-r_A)(1+\varepsilon_A X_A)}$$

CSTR

in - out + gen = acc

$$F_{A0} - F_A + (r_A)V = 0 = \frac{dN_A}{dt}$$

$$F_{A0}(1 - (1 - X_A)) = (-r_A)V$$

$$F_{A0}X_A = (-r_A)V$$

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

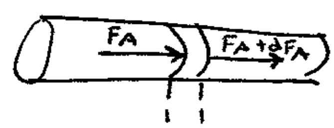
Constant V:

$$\frac{V}{F_{A0}} = \frac{1 - C_A/C_{A0}}{(-r_A)}$$

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

PF

in - out + gen = acc



$dX_A \longrightarrow dV$

$$F_A - (F_A + dF_A) + (r_A)dV = 0$$

$$-dF_A = (-r_A)dV$$

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

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

$$+F_{A0}\,dX_A = (-r_A)\,dV$$

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

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

$$\tau = C_{A0}\int_0^{X_A} \frac{dX_A}{(-r_A)} = \frac{V}{\varphi}$$

space time

Const. V:

$$\tau = -\int_{C_{A0}}^{C_A} \frac{dC_A}{-r_A}$$

τ = space time = $\frac{V}{Q}$ = time to treat 1 reactor volume of feed

$\bar{t}$ = mean residence time

$$= C_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)(1+\varepsilon_A X_A)}$$

Const V: $\bar{t} = \tau$

PFR's in series

$$\frac{V_i}{F_0} = \int_{X_{i-1}}^{X_i} \frac{dX}{-r}$$

$$\frac{V}{F_0} = \int_0^{X_N} \frac{dX}{-r} = \int_{X_0}^{X_1} \frac{dX}{-r} + \int_{X_1}^{X_2} \frac{dX}{-r} + \dots \int_{X_{N-1}}^{X_N} \frac{dX}{-r}$$

CSTR's in series

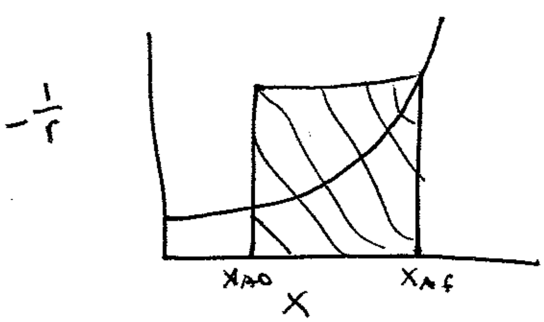
$$\tau_i = \frac{V_i}{Q} = \frac{C_0 (X_i - X_{i-1})}{-r_{Ai}} = \frac{C_{i-1} - C_i}{k C_i}$$

$$\frac{C_{i-1}}{C_i} = 1 + k\tau_i$$

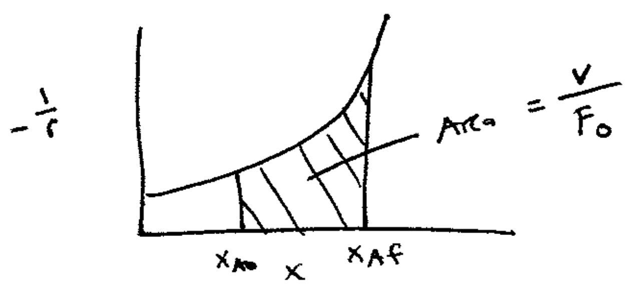
$$\frac{C_0}{C_N} = (1 + k\tau_i)^N = \frac{C_0}{C_1}\frac{C_1}{C_2}\frac{C_2}{C_3}\dots\frac{C_{N-1}}{C_N}$$

$$\tau_{N \text{ reactors}} = N\tau_i = \frac{N}{k}\left[\left(\frac{C_0}{C_N}\right)^{1/N} - 1\right]$$

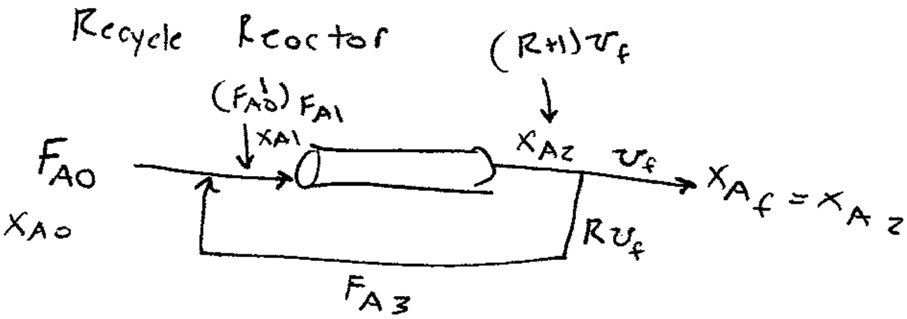
CSTR:



PFR:



Recycle Reactor



$$R = \frac{\text{volume recycled}}{\text{volume leaving}} = \frac{R v_f}{(R+1) v_f}$$

$$\frac{V}{F_{A0}'} = \int_{X_{A1}}^{X_{A2}} \frac{dX_A}{-r_A}$$

$$F_{A0}' = R F_{A0} + F_{A0} = (R+1) F_{A0} = F_{A1} \quad \text{(if no conv of A)}$$

$$C_{A1} = \frac{F_{A1}}{v_1} = \frac{F_{A0} + F_{A3}}{v_0 + R v_f} = \cancel{\frac{F_{A0} + F_{A1}(1-X_{Af})\left(\frac{R}{R+1}\right)}{v_0 + R v_0 (1+\varepsilon_A X_{Af})}}$$

$$\cancel{= F_{A0} +}$$

$$F_{A3} = R F_{A0} (1 - X_{Af}), \quad v_f = v_0 (1 + \varepsilon_A X_A)$$

$$C_{A1} = \frac{F_{A1}}{v_1} = \frac{F_{A0} + R F_{A0}(1 - X_{Af})}{v_0 + R v_0 (1 + \varepsilon_A X_{Af})}$$

$$= \frac{C_{A0}(1 + R - R X_{Af})}{1 + R + R \varepsilon_A X_{Af}}$$

$$\frac{C_{A1}}{C_{A0}} = \frac{1 - X_{A1}}{1 + \varepsilon_A X_{A1}}, \quad \cancel{C_{A1}(1 + \varepsilon_A X_{A1}) = C_{A0}(1 - X_{A1})}$$

$$\cancel{X_{A1}(C_{A1}\varepsilon_A + C_{A0}) = C_{A0} - C_{A1}}$$

$$\cancel{X_{A1}} = \frac{C_{A0} - C_{A1}}{\ldots}$$

$$C_{A1} \quad \cancel{\frac{C_{A0} - C_{AX}}{C_{A0} + \varepsilon_A C_A}} = C_{A0}\left(\frac{1 + R - R X_{Af}}{1 + R + R\varepsilon_A X_{Af}}\right)$$

$$\frac{C_{A0}(1 - X_{A1})}{1 + \varepsilon_A X_{A1}} = C_{A0}\left(\frac{1 + R - R X_{Af}}{1 + R + R\varepsilon_A X_{Af}}\right)$$

$$(1 - X_{A1})(1 + R + R\varepsilon_A X_{Af}) = (1 + R + R X_{Af})(1 + \varepsilon_A X_{A}$$

$$X_{A1}[\varepsilon_A + \varepsilon_A R - \varepsilon_A R X_{Af} + 1 + R + R\varepsilon_A X_{Af}]$$

$$= -(1 + R - R X_{Af}) + 1 + R + R\varepsilon_A X_{Af}$$

$$X_{A1}(\varepsilon_A(1+R) + 1 + R) = (+R X_{Af}(1 + \varepsilon_A))$$

$$X_{A1} = \frac{+R X_{Af}}{1+R}$$

$$\frac{V}{F_{A0}'} = \int_{X_{A1}}^{X_{Af}} \frac{dX_A}{-r_A}$$

$$\frac{V}{(R+1)F_{A0}} = \int_{\left(\frac{R}{R+1}\right)X_{Af}}^{X_{Af}} \frac{dX_A}{-r_A}$$

$R = 0$: plus flow

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

$R \to \infty$: CSTR

Parallel Reactions

$$A \begin{array}{l} \nearrow R \\ \searrow S \end{array}$$

high C_A favors rxn of higher order
low C_A favors rxn of lower order
C_A has no effect when $n = m$

$$r_R = k_1 C_A^n$$

$$r_S = k_2 C_A^m$$

$$\frac{r_R}{r_S} = \frac{k_1}{k_2} C_A^{n-m}$$

want this large (R is desired)
$n > m$, high C_A
$m > n$, low C_A

φ = instantaneous fractional yield

$$= \frac{dC_R}{-dC_A} = \frac{dC_R}{dC_R + dC_S}$$

selectivity = $\dfrac{\text{moles desired prod}}{\text{moles undesired prod}}$

Φ = overall fractional yield

$$= \frac{C_{Rf}}{C_{A0} - C_{Af}} = \bar{\varphi} \text{ in reactor}$$

PFR : $\Phi_p = \dfrac{-1}{C_{A0} - C_{Af}} \displaystyle\int_{C_{A0}}^{C_{Af}} \varphi \, dC_A$

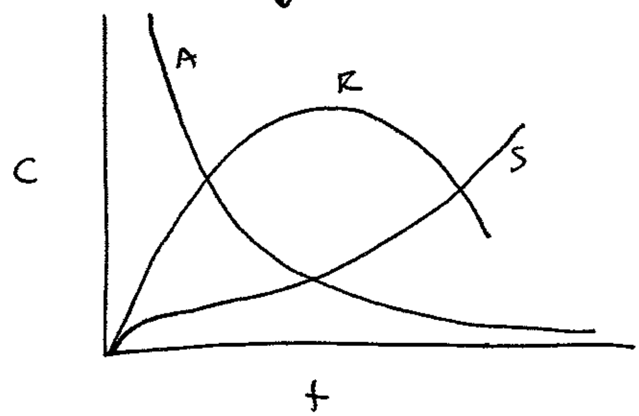
CSTR : $\Phi_m = \varphi$ evaluated at C_{Af}

$$\Phi_m = \left(\frac{d\Phi_p}{dC_A}\right)_{\text{at } C_{Af}} \qquad \Phi_p = \frac{1}{C_{Af} - C_{A0}} \int_{C_{A0}}^{C_{Af}} \Phi_m \, dC_A$$

Series Reactions

$A \xrightarrow{K_1} R \xrightarrow{K_2} S$

PFR or batch

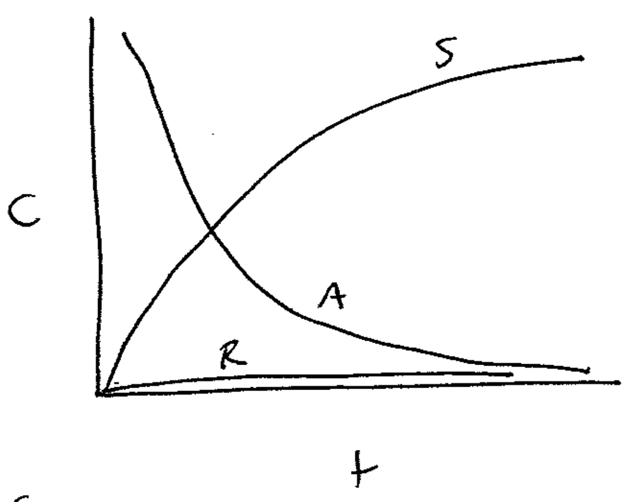


Maximize intermediate if fluids obtained at different compositions do not mix

$\longrightarrow$ batch or PFR

A reacts to form R. A is in excess, so driving force is that A reacts. When there is enough R, then will form S and $C_R \downarrow$.

CSTR



A reacts to completion and is mixed with fresh A

Find $C_{R,max}$

PFR : $\tau_{opt} = \dfrac{1}{K_{lm}} = \dfrac{\ln(K_2/K_1)}{K_2 - K_1}$

plug into rate eqn. Find C_A/C_{A0} and plug into C_R/C_{R0} w/ τ_{opt}

CSTR : Find C_A/C_{A0} , Find C_R/C_{R0}

$F_{A0} = F_A + (-r_A)V$ $\qquad$ $vC_{R0} = vC_R + (-r_R)V$

$C_{R,max}$ at $dC_R/d\tau_m = 0$ $\qquad$ $\tau_m = V/v$

Denbigh Rxns

$$\begin{array}{ccccc} A & \xrightarrow{1} & R & \xrightarrow{3} & S \\ {\scriptstyle 2}\downarrow & & {\scriptstyle 4}\downarrow & & \\ T & & U & & \end{array}$$

$$k_{12} = k_1 + k_2$$
$$k_{34} = k_3 + k_4$$

$$-r_A = k_{12} C_A$$
$$r_R = k_1 C_A - k_{34} C_R$$
$$r_S = k_3 C_R$$
$$r_T = k_2 C_A$$
$$r_U = k_4 C_R$$

Nonisothermal Operation

CSTR:

mass balance: $\varphi C_{A0} X_A = -R_A V$

energy balance: $\varphi \rho C_{pm} (T - T_0) + \varphi C_{A0} X_A \Delta H_{r_A} = \dot{q}$

$$-R_A = k_0 e^{-E/RT} C_{A0}^{\alpha} (1 - X_A)^{\alpha}$$

plug T into $-R_A$

plug $-R_A$ into mass balance

PFR:

mass: $\varphi C_{A0} \frac{dX_A}{dV} = -R_A$

energy: $\varphi \rho C_{pm} \frac{dT}{dV} + \varphi C_{A0} \Delta H_{r_A} \frac{dX_A}{dV} = \dot{q}_V$ per volume

$$\frac{d \ln K}{dT} = \frac{\Delta H_r}{RT^2}$$

(equil. composition from K)

$K = \frac{C_R}{\ } = \frac{X_{Ae}}{\ }$

RTD's

$$\int_0^\infty E \, dt = 1$$

Pulse expt:

$$E = \frac{C_{pulse}}{Area} \qquad Area = M/Q = \int_0^\infty C \, dt$$

$$\bar{t} = \frac{\int_0^\infty t \, C dt}{\int_0^\infty C dt} = \frac{V}{Q}$$

$$E_\theta = \bar{t} E$$

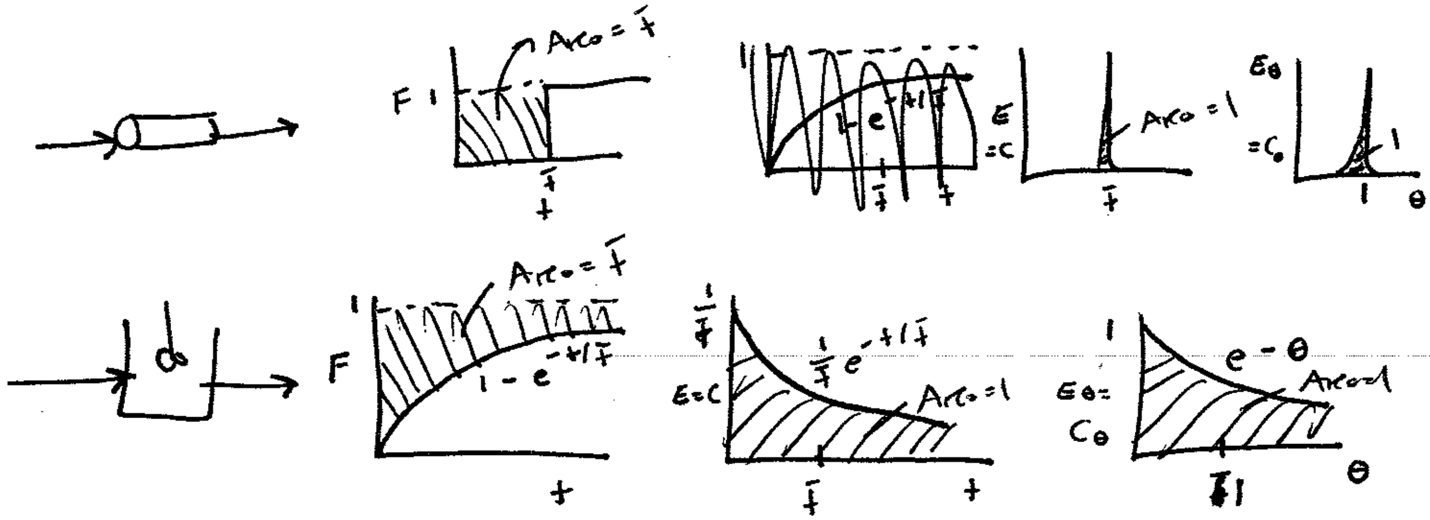
Step expt:

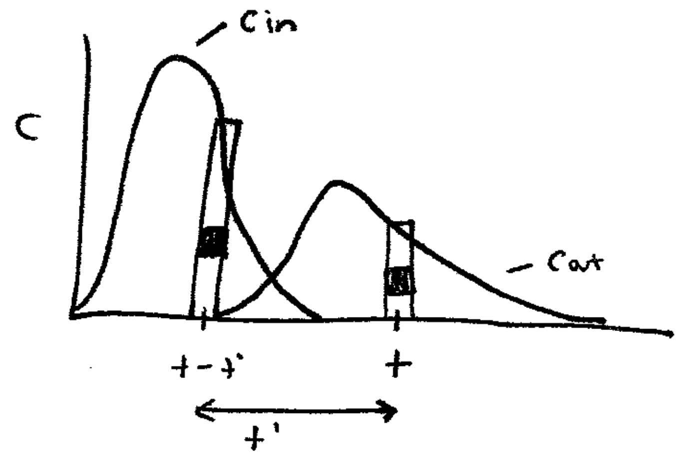
$$C_{max} = \dot{m}/Q$$

$$\bar{t} = \frac{\int_0^{C_{max}} t \, dC_{step}}{\int_0^{C_{max}} dC_{step}} = \frac{1}{C_{max}} \int_0^{C_{max}} t \, dC_{step}$$

$$F = \int_0^t E \, dt$$

$$\frac{dF}{dt} = E$$





$$C_{out} = \int_0^t C_{in}(t-t')\,E(t')\,dt'$$

$$= \int_0^t C_{in}(t')\,E(t-t')\,dt'$$

Macrofluids:

$$\overline{\left(\frac{C_A}{C_{A0}}\right)}_{exit} = \int_0^\infty \left(\frac{C_A}{C_{A0}}\right)_{element} \cdot E\,dt$$

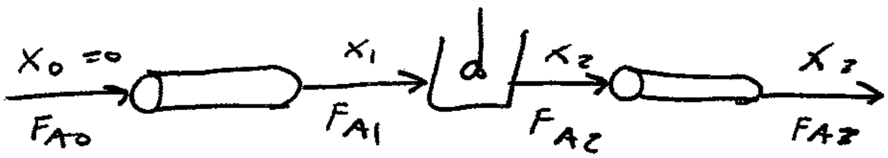
$$\overline{X_A} = \int_0^\infty (X_A)_{element} \cdot E\,dt$$

$$\left(\frac{C_A}{C_{A0}}\right)_{element} = \underbrace{e^{-kt}}_{1^{st}\text{ order}} = \underbrace{\frac{1}{1+kC_{A0}t}}_{2^{nd}\text{ order}}$$

Microfluids: like before

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

Fogler



$$F_{A1} = F_{A0} - X_1 F_{A0}$$

$$F_{A2} = F_{A0} - X_2 F_{A0}$$

$$F_{A3} = F_{A0} - X_3 F_{A0}$$

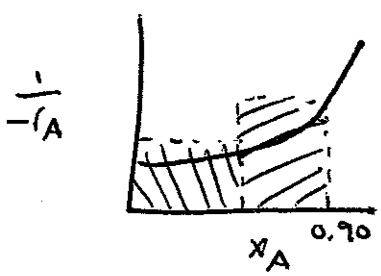
$$X_2 = \frac{\text{total moles of A reacted up to point 2}}{\text{total mol of A fed to 1st reactor}}$$

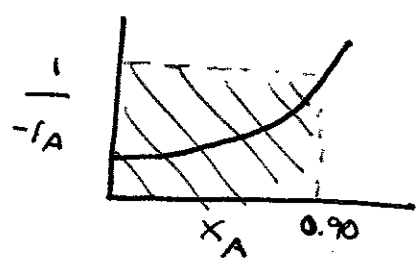
$$V_1 = F_{A0} \int_0^{X_{A1}} \frac{dx}{-r_A}$$

$$V_2 = \frac{F_{A1} - F_{A2}}{-r_{A2}} = \frac{F_{A0}\,(X_2 - X_1)}{-r_{A2}}$$

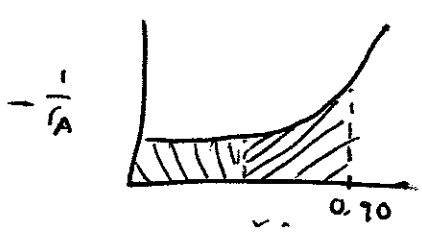
$$V_3 = F_{A0} \int_{X_2}^{X_3} \frac{dx}{-r_A}$$

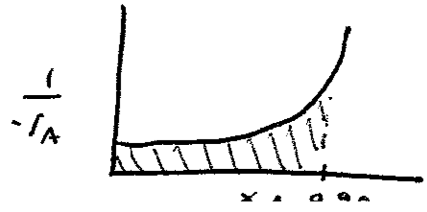
2 CSTR's in series have a smaller volume than 1 CSTR for a given conversion





2 PFR's in series have same volume as 1 PFR for a given conversion





Appendix C:

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

$$K = \frac{a_C^{c/a}\, a_D^{d/a}}{a_A\, a_B^{b/a}} \qquad a_i = \frac{f_i}{f_i^0} = \gamma_i P_i$$

$$= \frac{\gamma_C^{c/a}\,\gamma_D^{d/a}}{\gamma_A\,\gamma_B^{b/a}} \cdot \frac{P_C^{c/a}\, P_D^{d/a}}{P_A\, P_B^{b/a}} = K_\gamma K_p$$

ideal gases: $K_\gamma = 1.0$, $K = K_p$

$$P_i = C_i RT$$

$$K_c = \frac{C_C^{c/a}\, C_D^{d/a}}{C_A\, C_B^{b/a}}$$

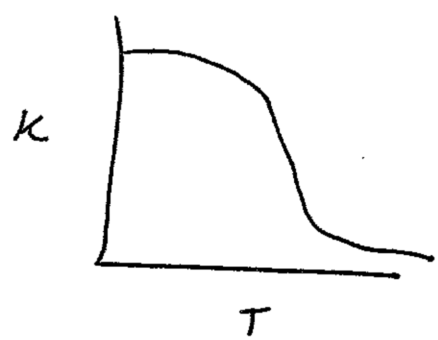
$$K_p = K_c (RT)^\delta \qquad \delta = \frac{\Sigma \nu_i}{|\nu_A|} = \frac{c}{a} + \frac{d}{a} - \frac{b}{a} - 1$$

if $\delta = 0$: $K_p = K_c$

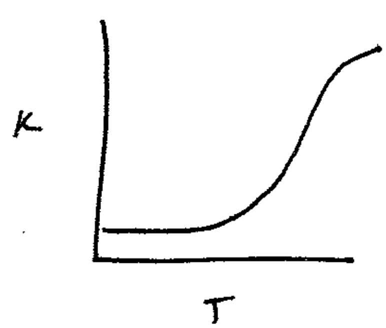
Van't Hoff's Eqn

$$\frac{d \ln K_p}{dT} = \frac{\Delta H_R(T)}{RT^2} = \frac{\Delta H^\circ_R(T_R) + \Delta \hat{C}_p (T - T_R)}{RT^2}$$

exothermic: shift left if $T \uparrow$



exothermic



endothermic

const. V batch

Equilibrium Conversion

For $A \rightleftharpoons 2B$ find X_{Ae}:

$$K_c = \frac{C_{Be}^2}{C_{Ae}}$$

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

$$C_B = \frac{N_B}{V} = \frac{N_B}{V_0} = \frac{N_{B0}(1-X_B)}{V_0} = \frac{2N_{A0}X_A}{V_0} = 2C_{A0}X_A$$

$$K_c = \frac{(2C_{A0}X_{Ae})^2}{C_{A0}(1-X_{Ae})} = \frac{4C_{A0}X_{Ae}^2}{1-X_{Ae}}$$ solve for X_{Ae}

Varying V Flow system

$$C_A = \frac{F_A}{\varphi} = \frac{F_{A0}(1-X_A)}{\varphi_0(1+\varepsilon_A X_A)} = \frac{C_{A0}(1-X_A)}{1+\varepsilon_A X_A}$$

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

$$C_B = \frac{F_B}{\varphi} = \frac{2F_{A0}X_A}{\varphi_0(1+\varepsilon_A X_A)} = \frac{2C_{A0}X_A}{1+\varepsilon_A X_A}$$

Phase Change

$$\varphi = \frac{\varphi_0(1-X_A)}{1-Y_{c,e}} \qquad Y_{c,e} = \frac{P_{vc}}{P_T}$$ after condensation

$Y_{c,e} = \frac{P_{vc}}{P_0}$ = mol fraction at which condensation begins n-CSTR's in series : 1^{st} order, no vol change

$$C_{A1} = \frac{C_{A0}}{1+\tau_1 k_1} \qquad C_{A2} = \frac{C_{A1}}{1+\tau_2 k_2}$$

if $\tau_1 = \tau_2 = \dots \tau_n$, $k_1 = k_2 = \dots k_n$

$$X_A = 1 - \frac{1}{(1+\tau k)^n}$$

n-CSTR's in parallel:

$$V_i = F_{A0}\left(\frac{X_i}{-r_{Ai}}\right)$$

equal size, same feed, same T , same Q : $X_1 = X_2 = \dots X_n$

$$V_i = V/n \qquad F_{A0i} = F_{A0}/n$$

$$\frac{V}{n} = \frac{F_{A0}}{n}\left(\frac{X_i}{-r_{A_i}}\right) = \frac{F_{A0}\ X_i}{-r_{A_i}} = \frac{F_{A0}\, X}{-r_A}$$

Same as 1 large CSTR of where $V = V_i n$

Pressure drop in packed beds

$$-r_A' = F_{A0}\frac{dX_A}{dW} \qquad W = \text{grams catalyst}$$

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

plug into rate law, and then into above equation

solve for $\frac{dX_A}{dW} = F_1(X, P)$

Now use Ergun equation for calculating pressure drop

$$\frac{dP}{dz} = -\frac{G}{\rho g_c D_p}\left(\frac{1-\phi}{\phi^3}\right)\left(\frac{150(1-\phi)\mu}{D_p} + 1.75G\right)$$

ϕ = porosity, G = mass superficial velocity $= \rho u$

ρ = gas density

change to $\frac{dP}{dW} = F_2(X, P)$ Solve equations simultaneously

$$W = (1-\phi)A_c z \cdot \rho_c$$

$$\rho_b = \rho_c(1-\phi)$$

Start-up of a CSTR : how long until reach steady state?

V = const.

$$C_{A0} - C_A + r_A\tau = \tau\frac{dC_A}{dt}$$ 1st order : $-r_A = kC_A$

$$\frac{dC_A}{dt} + \frac{1+\tau k}{\tau}C_A = \frac{C_{A0}}{\tau}$$

$$C_A = \frac{C_{A0}}{1+\tau k}\left[1-\exp\left(-(1+\tau k)\frac{t}{\tau}\right)\right]$$

t_s = time to reach 99% steady state conc C_{AS}

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

$$C_A = C_{AS}(0.99)$$

$$t_s = 4.6\frac{\tau}{1+\tau k}$$

if $\tau k \ll 1$, $t_s = 4.6\,\tau$ 3-4 space times

If $\tau k \gg 1$, $t_s = 4.6/k$

Parallel Rxns

$A \xrightarrow{k_D} D$ (desired) $\qquad -r_A = k_D C_A^{\alpha_1}$

$A \xrightarrow{k_U} U$ (undesired) $\qquad -r_A = k_U C_A^{\alpha_2}$

Selectivity $S = \dfrac{r_D}{r_U} = \dfrac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$

if $\alpha_1 > \alpha_2$, want C_A as high as possible

→ batch or plug flow

if $\alpha_1 < \alpha_2$, want C_A as low as possible

→ dilute the feed

→ CSTR

Also look at temperature

$$\frac{k_D}{k_U} = \frac{A_D}{A_U} e^{-(E_D - E_U)/RT}$$

$E_D > E_U$, run at high T

$E_D < E_U$, run at low T

Series rxns

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

max yield of intermediate

do mole balance on A and solve for C_A

do mole balance on B, plug in C_A, solve for C_B

Enzyme Kinetics

$$E + S \xrightarrow{k_1} E\cdot S$$

$$E\cdot S \xrightarrow{k_2} E + S$$

$$E\cdot S + W \xrightarrow{k_3} P + E$$

$$-r_S = \frac{-dC_S}{dt} = k_1 C_E C_S - k_2 C_{E\cdot S}$$

PSSH:

$$r_{E\cdot S} = \frac{dC_{E\cdot S}}{dt} = k_1 C_E C_S - k_2 C_{E\cdot S} - k_3 C_{E\cdot S} C_W = 0$$

$$E_t = E + E\cdot S$$ (easier to measure)

$$0 = k_1 C_S (C_{E_t} - C_{E\cdot S}) - k_2 C_{E\cdot S} - k_3 C_{E\cdot S} C_W$$

$$-C_{E\cdot S}(k_3 C_W + k_2 + k_1 C_S) = -k_1 C_S C_{E_t}$$

$$C_{E\cdot S} = \frac{k_1 C_{E_t} C_S}{k_3 C_W + k_2 + k_1 C_S}$$

$$-r_S = k_1 C_S (C_{E_t} - C_{E\cdot S}) - k_2 C_{E\cdot S}$$

$$= k_1 C_S C_{E_t} - \frac{(k_1 C_S + k_2)\, k_1 C_{E_t} C_S}{k_3 C_W + k_2 + k_1 C_S}$$

$$-r_S = \frac{k_1 k_3 C_W C_{E_t} C_S}{k_3 C_W + k_2 + k_1 C_S} \cancel{+ k_1 k_2 C_S C_{E_t} + k_1^2 C_S^2 C_{E_t}}$$

For Michaelis-Menten :

Water in excess, $C_W \sim$ constant

let $k_3' = k_3 C_W$

$$-r_S = \frac{k_1 k_3' C_{E_T} C_S}{k_1 C_S + k_2 + k_3'} = \frac{k_3' C_{E_T} C_S}{C_S + \frac{k_2 + k_3'}{k_1}}$$

let $$K_m = \frac{k_2 + k_3'}{k_1}$$

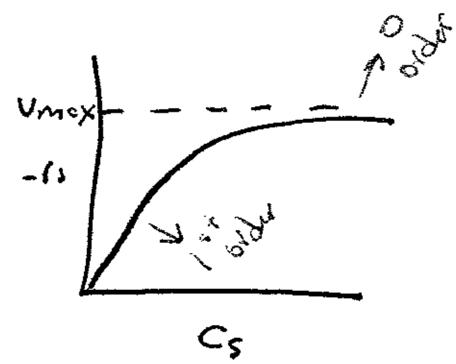
$$-r_S = \frac{k_3' C_{E_T} C_S}{C_S + K_m}$$

V_{max} = max rate of rxn for a given C_{E_T} $= k_3' C_{E_T}$

$$\boxed{-r_S = \frac{V_{max} C_S}{C_S + K_m}}$$

At low C_S, $-r_S = \frac{V_{max}}{K_m} C_S$

At high C_S, $-r_S = V_{max}$



At $-r_S = \frac{V_{max}}{2} = \frac{V_{max} C_S}{C_S + K_m} \longrightarrow K_m = C_{S_{1/2}}$

$K_m = C_S$ when rate $= \frac{1}{2}$ max rate

$\boxed{\text{Reactor Energy Balance}}$

$$d\hat{E} = \delta Q - \delta W$$

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W} + \overbrace{F_{in} E_{in} - F_{out} E_{out}}^{\text{Energy flow in - out}}$$

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W} + \sum_{i=1}^{n} E_i F_i \Big|_{in} + \sum_{i=1}^{n} E_i F_i \Big|_{out}$$

$$\dot{W} = -\sum_{i=1}^{n} F_i P V_i \Big|_{in} + \overbrace{\sum_{i=1}^{n} F_i P V_i \Big|_{out}}^{\text{PV work}} + \dot{W}_s$$

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n} F_i (E_i + P V_i) \Big|_{in} - \sum_{i=1}^{n} F_i (E_i + P V_i) \Big|_{out}$$

$$E_i = U_i + \underbrace{E_{K_i} + E_{P_i} + \text{etc.}}_{\text{negligible}} \qquad = U_i$$

$$\boxed{H_i = U_i + P V_i}$$

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n} F_i H_i \Big|_{in} - \sum_{i=1}^{n} F_i H_i \Big|_{out}$$

subscript "0" for inlet

$$\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n} F_{i0} H_{i0} - \sum_{i=1}^{n} F_i H_i$$

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

Now, steady state $\quad \frac{d\hat{E}_{sys}}{dt} = 0$

$$\sum H_{i0} F_{i0} = H_{A0} F_{A0} + H_{B0} F_{B0} + H_{C0} F_{C0} + H_{D0} F_{D0} + H_{I0} F_{I0}$$

$$\sum H_i F_i = H_A F_A + H_B F_B + H_C F_C + H_D F_D + H_I F_I$$

* get rid of F_i and put in terms of F_{i0}

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

$$F_B = F_{B0} (1 - X_B) = F_{B0} - F_{B0} X_B = F_{B0} - \frac{b}{a} F_{A0} X_A$$

$$= F_{A0} \left(\frac{F_{B0}}{F_{A0}} - \frac{b}{a} X_A \right)$$

$$F_C = F_{C0}(1 - X_C) = F_{C0} - F_{C0} X_C = F_{C0} + \frac{c}{a} F_{A0} X_A$$

$$= F_{A0} \left(\frac{F_{C0}}{F_{A0}} + \frac{c}{a} X_A \right)$$

$$F_D = F_{A0} \left(\frac{F_{D0}}{F_{A0}} + \frac{d}{a} X_A \right)$$

$$F_I = F_{I0}$$

$$\sum_{i=1}^{n} H_{i0} F_{i0} - \sum_{i=1}^{n} H_i F_i = F_{A0} (H_{A0} - H_A) + F_{B0} (H_{B0} - H_B)$$
$$+ F_{C0} (H_{C0} - H_C) + F_{D0} (H_{D0} - H_D)$$
$$+ F_{I0} (H_{I0} - H_I) + F_{A0} X_A H_A + F_{B0} X_A \frac{b}{a} H_B$$
$$- \frac{c}{a} F_{A0} X_A H_C - \frac{d}{a} F_{A0} X_A H_D$$

ΔH_{rx} falls out!

$$\Delta H_{Rx} = \frac{d}{a} H_D + \frac{c}{a} H_C - \frac{b}{a} H_B - H_A$$

let $\Theta_i = \frac{F_{i0}}{F_{A0}}$

$$\sum_{i=1}^{n} H_{i0} F_{i0} - \sum_{i=1}^{n} H_i F_i = F_{A0} \sum_{i=1}^{n} \Theta_i (H_{i0} - H_i) - \Delta H_{rx} X_A F_{A0}$$

$$\boxed{\dot{Q} - \dot{W}_s + F_{A0} \sum_{i=1}^{n} \Theta_i (H_{i0} - H_i) - \Delta H_{Rx} F_{A0} X_A = 0}$$

In the absence of phase change : $\underline{\Delta H = \int C_p \, dT}$

$$H_i = H_i^\circ(T_R) + \Delta H_{Qi} = H_i^\circ(T_R) + \int_{T_R}^{T_i} C_{pi}\, dT$$

$$\dot{Q} - \dot{W}_S - F_{A0} \sum_{i=1}^{n} \int_{T_{i0}}^{T} \Theta_i C_{p_i}\, dT - \Delta H_{Rx}(T)\, F_{A0} X_A = 0$$

~~Constant or mean heat capacity~~:

$$\Delta H_{rx} = \Delta H_{rx}^\circ(T_R) + \int_{T_R}^{T} \Delta C_p \, dT$$

Const or mean C_p :

$$\Delta H_{rx} = \Delta H_{rx}^\circ(T_R) + \Delta \hat{C}_p (T - T_R)$$

$$\dot{Q} - \dot{W}_S - F_{A0} \sum_i \Theta_i C_{p_i} (T - T_{i0}) - F_{A0} X_A [\Delta H_{rx}^\circ(T_R) + \Delta \hat{C}_p (T - T_R)] = 0$$

all reactants enter at same temp

$$T_{i0} = T_0$$

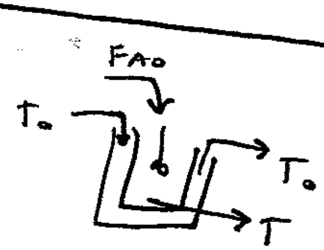
in + in   + in - out C_{i0}/C_{A0} - out

$$\boxed{\dot{Q} - \dot{W}_S - F_{A0} \sum_i \Theta_i C_{p_i} (T - T_0) - F_{A0} X_A [\Delta H_{rx}^\circ(T_R) + \Delta \hat{C}_p (T - T_R)] = 0}$$

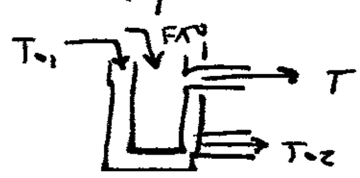
heat added to reactor :

CSTRs :

$$\underline{\dot{Q} = UA\,(T_a - T)}$$



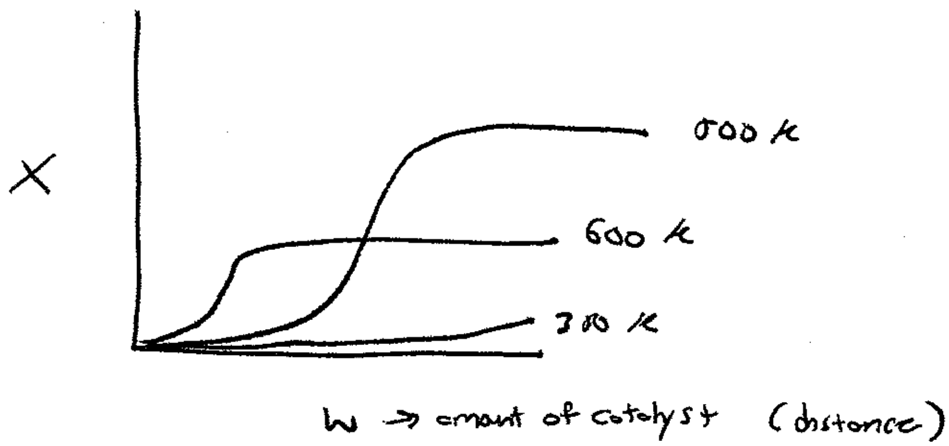
$$\dot{Q} = UA \, \frac{(T_{a1} - T_{a2})}{\ln (T - T_{a1}) / (\ldots)}$$



Tubular :

$$Q = \int^{A} U (T_o - T)\, dA = \int^{V} U_a (T_o - T)\, dV$$

U_a → heat exchange area / unit vol.



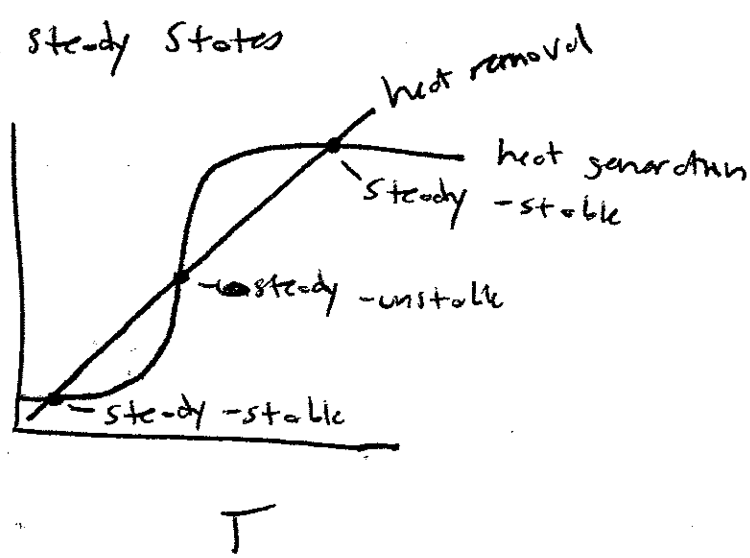
sharp increase - ignition temp

At first, when increase T, rate and X_A ↑.

When equil. conversion is approached, ↑T will ↓ X_A due to decreasing equilibrium conversion.

↑ T, reach equil. conv faster but it is a lower value

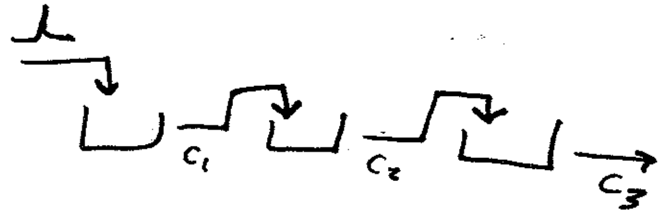
Multiple steady states



Tanks in Series

$V_1 = V_2 = V_i$, $\varphi_1 = \varphi_2 = \varphi_i$, $\tau_1 = \tau_2 = \tau_i$

balance on CSTR



$$V_i \frac{dc_1}{dt} = -\varphi c_1 \longrightarrow c_1 = c_0 e^{-t/\tau_i}$$

$$V_i \frac{dc_2}{dt} = \varphi c_1 - \varphi c_2 \longrightarrow c_2 = \frac{c_0 t}{\tau_i} e^{-t/\tau_i}$$

$$\frac{V_i dc_3}{dt} = \varphi c_2 - \varphi c_3 \longrightarrow c_3 = \frac{c_0 t^2}{2\tau_i^2} e^{-t/\tau_i}$$

$$E(t) = \frac{c_3(t)}{\int_0^\infty c_3(t)\,dt}$$

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

$$\boxed{n = \frac{1}{\sigma_\theta^2} = \frac{\tau^2}{\sigma^2}}$$

$$\sigma_\theta^2 = \int_0^\infty (\theta - 1)^2 E(\theta)\,d\theta$$

Dispersion Model

tracer flow by convection and dispersion

$$F_T = \underbrace{-D_a A_c \frac{\partial C_T}{\partial z}}_{\text{Fick's law}} + U A_c C_T$$

U: Superficial velocity

mol balance on inert tracer T :

$$-\frac{\partial F_T}{\partial z} = A_c \frac{\partial C_T}{\partial t}$$

$$D_a \frac{\partial^2 C_T}{\partial z^2} - \frac{\partial (U C_T)}{\partial z} = \frac{\partial C_T}{\partial t}$$

let $\psi = C_T / C_{T0}$, $\lambda = z/L$, $\theta = tU/L$

$$\frac{D_a}{UL} \frac{\partial^2 \psi}{\partial \lambda^2} - \frac{\partial \psi}{\partial \lambda} = \frac{\partial \psi}{\partial \theta}$$

$$Pe = \frac{UL}{D_a}$$

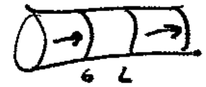
$$\boxed{\frac{1}{Pe} \frac{\partial^2 \psi}{\partial \lambda^2} - \frac{\partial \psi}{\partial \lambda} = \frac{\partial \psi}{\partial \theta}}$$

no rxn

$$\frac{DC_A}{Dt} = D \nabla^2 C_A$$

$$\frac{\partial C_A}{\partial t} + V_z \frac{\partial C_A}{\partial z} = D \frac{\partial^2 C_A}{\partial z^2}$$

nondimensionalize with $Pe = \frac{V_z L}{D}$



At $z=0$:

N_A in $= N_A$ out (1)

$(-D_{AB}\nabla C_A)_{out} + \upsilon C_{out} = \upsilon C_{in}$

closed-closed BC's (Danckwertz)

- dispersion between $z=0^+$ and $z=L^-$
- plug flow at $z=0^-$ and $z=L^+$

At $z=0$, $F_T(0^-, t) = F_T(0^+, t)$

$$\upsilon A_c C_T(0^-, t) = -A_c D_a \left(\frac{\partial C_T}{\partial z}\right)_{z=0^+} + \upsilon A_c C_T(0^+, t)$$

$$C_T(0^-, t) = C_{T0} = -\frac{D_a}{\upsilon}\left(\frac{\partial C_T}{\partial z}\right)_{z=0^+} + C_T(0^+, t)$$

At $z=L$, $C_T(L^-) = C_T(L^+)$

$$\frac{\partial C_T}{\partial z} = 0$$

At $z=L$

N_A in $= N_A$ out

$(-D_{AB}\nabla C_A)_{in} + \upsilon C_{in} = \upsilon C_{out}$

neg. quant. in + $\rightarrow C_{out} > C_{in}$

not physically possible

(1) $\frac{\partial C_A}{\partial z} = 0$

(2) $C_{in} = C_{out}$

At $t=0$, $z>0$, $C_T(0^+, 0) = 0$

$t_m = \tau$

$$\frac{\sigma^2}{t_m^2} = \frac{1}{\tau^2}\int_0^\infty (t-\tau)^2 (E(t))\,dt$$

Open-open BC's

$$F_T(0^-, t) = F_T(0^+, t)$$

$$-D_a\left(\frac{\partial C_T}{\partial z}\right)_{z=0^-} + \upsilon C_T(0^-, t) = -D_a\left(\frac{\partial C_T}{\partial z}\right)_{z=0^+} + \upsilon C_T(0^+, t)$$

$$C_T(0^-, t) = C_T(0^+, t)$$

$$C_T(L^-, t) = C_T(L^+, t)$$

$$t_m = \left(1 + \frac{2}{Pe_r}\right)\tau$$

$$\frac{\sigma^2}{t_m^2} = \frac{2}{Pe_r} + \frac{8}{Pe_r^2}$$

Flow, rxn + dispersion

mol balance : $-\frac{1}{A_c}\frac{dF_A}{dz} + r_A = 0$

$$D_a \frac{d^2 C_A}{dz^2} - \frac{dC_A}{dz} u + r_A = 0$$

Derive RTD for CSTR:

in − out = acc (balance on inert tracer)

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

perfectly mixed : C = within reactor

pulse input, $C_{in} = 0$

$C = C_0$ at $t = 0$

$$\frac{dC}{C} = -\frac{\varphi}{V}dt$$

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

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt} = \frac{C_0 e^{-t/\tau}}{\int_0^\infty C_0 e^{-t/\tau}\,dt}$$

$$= \frac{C_0 e^{-t/\tau}}{C_0(-\tau)(0-1)} = \frac{1}{\tau}e^{-t/\tau}$$

Derive RTD for laminar flow reactor

$$U = U(r)$$

$$t(r) = \frac{L}{U(r)}$$

$$\frac{d\varphi}{\varphi} = \frac{U(r)\,2\pi r\,dr}{\varphi_0}$$ = fraction of fluid passing between r and $(r+dr)$

$$= E(t)\,dt$$

Lindemann Mechanism

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + A^*$$

$$A^* \xrightarrow{k_2} B$$

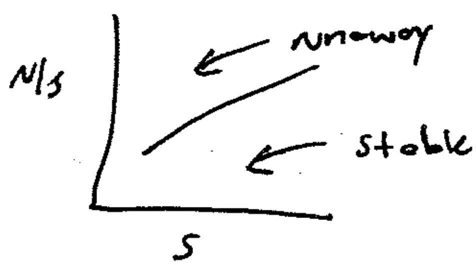
$$\frac{dA^*}{dt} = k_1 A^2 - k_{-1} AA^* - k_2 A^*$$

$$PSSH: A^* \quad \frac{dA^*}{dt} = 0$$

$$\frac{dB}{dt} = k_2 A^*$$

1. Catalytic packed bed reactors

   - write mass + energy balance like a PFR
   - use U_0 - superficial velocity and ρ_B - bed density in the equations (rxn only occurs on catalyst particles)
   - stability: divide energy by mass balance ~~(they should be~~ and non-dimensionalize to get N + S

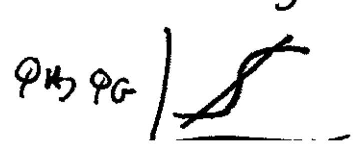


2. - CSTR stability

   - write transient mass and energy balances
   - subtract steady state
   - expand r_A + Q_H in a 1st order Taylor's expansion
   - solve - $e^{mt/\tau}$, m must be negative

     $m^2 + a_1 m + a_0 = 0$, $a_1 > 0$ and $a_0 > 0$

   - another method
     - rearrange energy balance so that $r_A(-\Delta H)$ is on one side $\longrightarrow$ Q_G (heat generation). Plot left and right hand sides, intersection = steady state



Q_H = heat removal - linear

③ TST

$$A + B \rightarrow (AB)^{\ddagger}$$

$$K = \frac{k_B T}{h} \frac{(\varphi_{\ddagger}^{\circ})^{1}}{(\varphi_A^{\circ})(\varphi_B^{\circ})} e^{-E/k_B T}$$

$$\varphi^{\circ} = \varphi_t^{\circ} \, \varphi_r^{\circ} \, \varphi_v^{\circ} \, \varphi_e^{\circ}$$

$$\downarrow \quad \downarrow \quad \downarrow$$

$$f_t^{3} \quad f_r^{3} \quad f_v^{(3N-6)}$$

$$f_r^{2} \quad f_v^{(3N-5)}$$

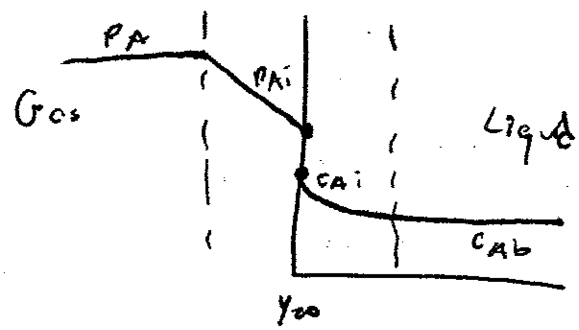
$f_t \propto T^{1/2}$

$f_r \propto T^{1/2}$

$f_v \propto 1$ at low T or high v

$\propto T$ low v

④ Multiphase Reactors



$p_{Ai} = H C_{Ai}$

← slow rxn

Langmuir

adsorption

- all adsorption centers alike
- only monolayer adsorption

$$A + \ell \underset{r_d}{\overset{r_a}{\rightleftharpoons}} A\cdot\ell$$

$$r_a = k_a C_A C_\ell$$

$$r_d = k_d C_{A\cdot\ell}$$

At equilibrium, $r_a = r_d$

$$k_a C_A C_\ell = k_d C_{A\ell}$$

$$C_t = C_{A\ell} + C_\ell$$

$$k_a C_A (C_t - C_{A\ell}) = k_d C_{A\ell}$$

$$C_{A\ell} = \frac{C_t K_a C_A}{1 + K_a C_A}$$

$$\theta_A = \frac{C_{A\ell}}{C_t} = \frac{K_A C_A}{1 + K_A C_A}$$

- assumes all sites have ΔH_{ra}

Freundlich

- continuous distribution of heats of adsorption

$$\varphi_a = -\varphi_{om} \ln \theta$$

$$\theta = a C_A^m$$

$$\Theta = \int_0^1 \frac{(A_o/A_d) \exp\left[\left(\frac{\varphi_a}{\theta_i}\right)/RT\right] C_A}{1 + \left(\frac{A_o}{A_d}\right)\exp\left[\left(\frac{\varphi_a}{\theta_i}\right)/RT\right] C_A}$$

Temkin

$$-\varphi_a = \varphi_{ao}(1 - \alpha\theta)$$

$$\Theta = \left(\frac{RT}{\alpha\varphi_{ao}}\right) \ln\left(\frac{A_o}{A_d} C_A\right)$$

$$= a \ln(m C_A)$$

$$\frac{KC_A}{1 + KC_A}$$

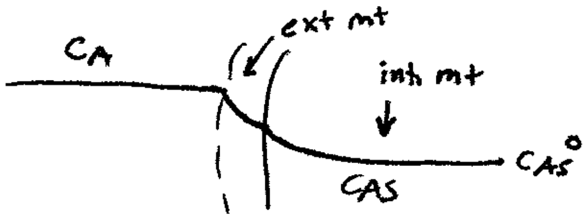
$$E = \frac{-\varphi_a}{\theta_i}$$

$$K = \frac{K_a}{K_d} = \frac{A e^{-E/RT}}{A_d e^{-E/RT}}$$

Longmuir - Hinshelwood - surface rxn controlling

$$r_A = \frac{kKC_A}{1+KC_A} = k\theta_A$$

Porous Catalyst

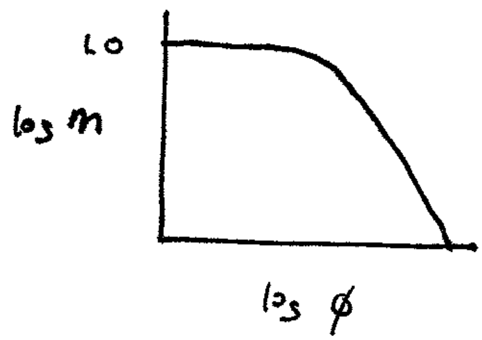


$r_{A,obs} = \eta (r_A)$

$$\eta = \frac{\text{rate with pore diffusion}}{\text{rate w/o pore diffusion}}$$

$$= \frac{D_e \left.\frac{dC_s}{dy}\right|_{y=L} \cdot \frac{1}{L\rho_s}}{r_A}$$

$$= \frac{\tanh\phi}{\phi}$$ 1st order, slab



$\eta \to 0 \quad \phi \to \infty$

$\eta \to 1 \quad \phi \to 0$

large ϕ : $\eta \to 1/\phi$ strong mt limitation

small ϕ : no mt limitations

$$\phi = \frac{V}{S}\sqrt{\frac{k\rho_s}{D_{eA}}} \text{ (1st order)} \qquad \phi = \frac{V}{S}\sqrt{\frac{(n+1)}{2}\frac{k\rho_s (C_s^s)^{n-1}}{D_{eA}}}$$

nth order

$\frac{V}{S} = L$ slab

$= R/2$ cylinder

$= R/3$ sphere

Derive ϕ, the shape factor

no conc inside catalyst

$$D_{eA} \frac{d^2 C_s}{dy^2} - k_{es} C_s = 0$$

diffusion + rxn

$$C_s(L) = C_s^s \quad \text{surface}$$

$$\frac{dC_s(0)}{dy} = 0 \quad \text{center}$$

soln: $$\frac{C_s(y)}{C_s^s} = \frac{\cosh \sqrt{\frac{k_{es}}{D_{eA}}}\, y}{\cosh \sqrt{\frac{k_{es}}{D_{eA}}}\, L}$$

$$(r_A)_{obs} = \eta\, r_A(C_s^s)$$

$$r_A = k_{es} C_s$$

$$\eta = \frac{\frac{1}{W_c} \int r_A(C_s)\, dW_c}{r_A(C_s^s)}$$

integrate over catalyst wt.

1st order rxn in a slab:

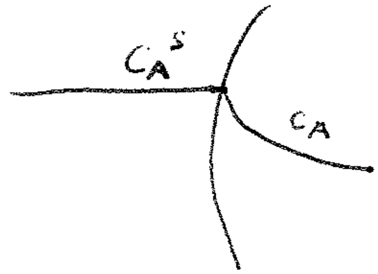
$$\eta = \frac{\tanh \phi}{\phi}$$

$\phi \to 0,\ \eta \to 1$ no res.

$\phi \to \infty,\ \eta \to 1/\phi$

Effectiveness Factors

$$\eta = \frac{(r_A)_{obs}}{(r_A)_{C_A^s}}$$



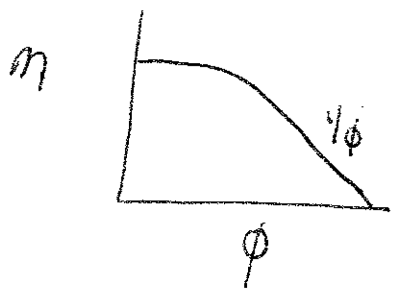
For 1st order rxn in a spherical pellet

$$\eta = \frac{(r_A)_{obs}}{K C_A^s}$$

$$\phi = \frac{R}{3}\sqrt{\frac{K}{D_{eA}}}$$

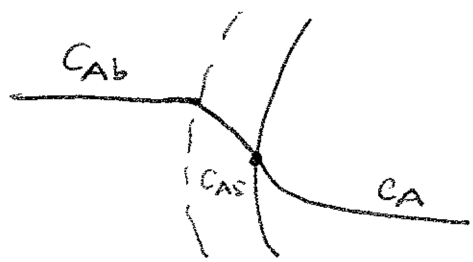
$$\eta = \frac{\tanh \phi}{\phi} \quad \text{for slab}$$

$$\phi = L\sqrt{K/D_{eA}}$$



$$D_{eA} = \frac{\varepsilon_s}{\tau} D_A$$

$$\eta_G = \frac{(r_A)_{obs}}{(r_A)_{C_{Ab}}}$$



At surface of pellet:

$$(4\pi R^2) N_A\big|_{r=R} = \eta K C_A^s \left(\tfrac{4}{3}\pi R^3\right)$$

$$\eta_G = \frac{\eta K C_A^s}{(r_A)_{C_{Ab}}} = \frac{\eta K C_A^s}{K C_{Ab}} = \eta \frac{C_A^s}{C_{Ab}}$$

$$N_A\big|_{r=R} = K_G (C_{Ab} - C_{As})$$

$$K_G (C_{Ab} - C_{As}) = \eta K C_A^s \tfrac{1}{3} R$$

$$C_{Ab} = \frac{C_{As}}{K_G}\left(\eta K \frac{R}{3} + K_G\right)$$

$$\eta_G = \eta \frac{C_A^s \; k_G}{C_A^s\left(\eta k \frac{R}{3} + k_G\right)} = \frac{\eta \, k_G}{\eta k \frac{R}{3} + k_G}$$

$$\eta_G = \frac{k_G}{k \frac{R}{3} + \frac{k_G}{\eta}}$$

$$\frac{1}{\eta_G} = \frac{\eta k \frac{R}{3} + k_G}{\eta \, k_G} = \frac{k R}{k_G 3} + \frac{k_G}{\eta k_G}$$

$$\phi = \frac{R}{3}\sqrt{\frac{k}{D_{eA}}}$$

$$k = D_{eA} \frac{\phi^2 9}{R^2}$$

$$\frac{1}{\eta_G} = \frac{D_{eA}\,\phi^2\, 3}{R\, k_G} + \frac{k_G}{\eta k_G}$$

$$\boxed{\frac{1}{\eta_G} = \frac{1}{\eta} + \frac{\phi^2}{Sh}}$$

$$Sh = \frac{R k_G}{3 D_{eA}}$$ for a sphere