CBE 40455

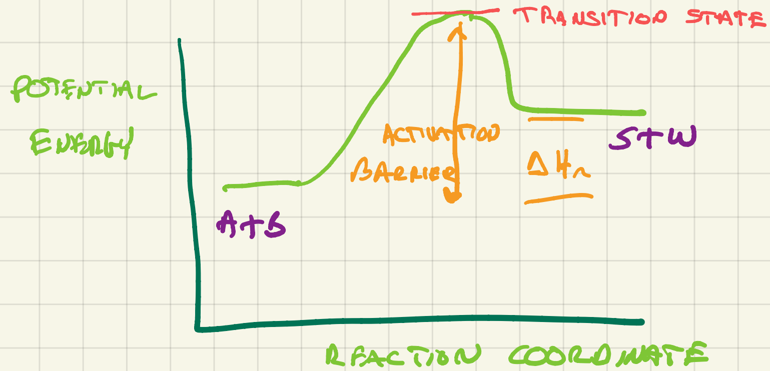
8/24/20

REVIEW

$$k = A \exp\left(\frac{E}{RT}\right)$$

"TRANSITION STATE THEORY"

$A + B \rightleftharpoons S + W$



GENERAL RELATION!

$$r = \left(\frac{k_B T}{h}\right) \exp\left[\frac{\Delta S_0^{\ddagger}}{R}\right] \exp\left[\frac{-\Delta H_0^{\ddagger}}{RT}\right] C_A C_B$$

$$\bar{A} \doteq \frac{\bar{k} T}{h} \cong 10^{13}/s$$

COLLISION FREQUENCY FOR NORMALIZED BOLTZMAN DISTRIBUTION OF MOLECULES

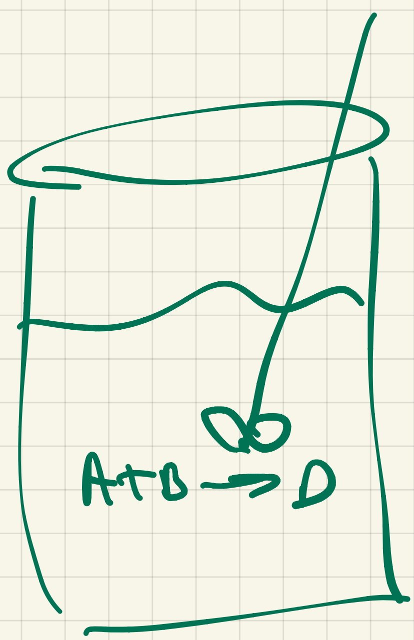
TODAY

ANALYSIS OF DIFFERENT REACTOR CONFIGURATIONS...

CHAPTER 3

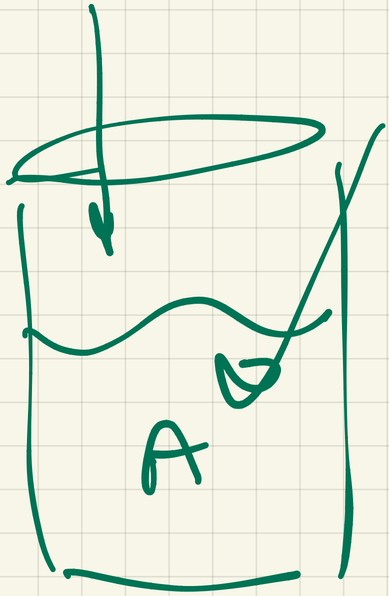
HOW DO WE GET KINETIC DATA?

IN A LAB, YOU USUALLY USE A BATCH OR SEMIBATCH REACTOR



BATCH

FEED IN
B



SEMI BATCH

USED TO CAREFULLY CONTROL CONCENTRATION OF 2ND REACTANT, (PERHAPS BECAUSE OF SELECTIVITY ISSUES)

ANALYSIS OF A BATCH REACTOR

(MOLES)

MASS BALANCE

SPECIES i

RATE OF CHANGE OF MOLES OF i IN REACTOR = FLOW RATE OF i INTO REACTOR − FLOW RATE OF i OUT OF REACTOR

+ RATE AT WHICH i IS PRODUCED/CONSUMED BY REACTION

FIRST CONSIDER A BATCH REACTOR

THUS IN TERMS OF MOLES...

REACTION RATE / VOLUME

$$\frac{dm_i}{dt} = 0 - 0 + \nu_i r V$$

STOICHIOMETRIC COEFFICIENT

VOLUME

GENERALLY AN INITIAL VALUE PROBLEM

COULD ALSO WRITE

$$\frac{d VC_i}{dt} = \nu_i r V$$

IF $r = k C_A$ $\quad A \rightarrow S$

$$\frac{d V C_A}{dt} = -k C_A V$$

IF V = CONST

$$\cancel{V} \frac{dC_A}{dt} = -k C_A \cancel{V}$$

COULD ALSO WRITE:

$$m_i^o \frac{df_i}{dt} = -\nu_i r V \qquad f_i(t=0) = 0$$

SUPPOSE $A + B \longrightarrow S$

$$r = k C_A C_B$$

$$C_{A0} \neq C_{B0}$$

$$dC_A = dC_B$$

$$C_{A0} - C_A = C_{B0} - C_B$$

$V = \text{CONST}$

$C_B = (C_{B0} - C_{A0}) + C_A$

$$\frac{dC_A}{dt} = -k C_A C_B$$

$$\frac{dC_A}{dt} = -k C_A (C_{B0} - C_{A0} + C_A)$$

$$\frac{dC_A}{C_A(C_A - (C_{A0} - C_{B0}))} = -k\,dt$$

CORRECTIONS

$$\frac{dC_A}{C_A\left(C_A-\left(C_{A0}-C_{B0}\right)\right)}=-k\,dt$$

$$\cancel{\ln\left(\frac{C_{A0}\left(C_A(t)-\left(C_{A0}-C_{B0}\right)\right)}{C_{A0}-C_{B0}}\right)=kt}$$

$$\frac{\ln\left(\frac{C_A-C_{A0}+C_{B0}}{C_A}\right)}{\left(C_{A0}-C_{B0}\right)}=-kt$$

$$\frac{C_A}{C_{A0}}=\frac{\left(C_{A0}-C_{B0}\right)}{C_{A0}-\exp\left(\left(C_{B0}-C_{A0}\right)kt\right)}$$

WE WOULD USE THIS

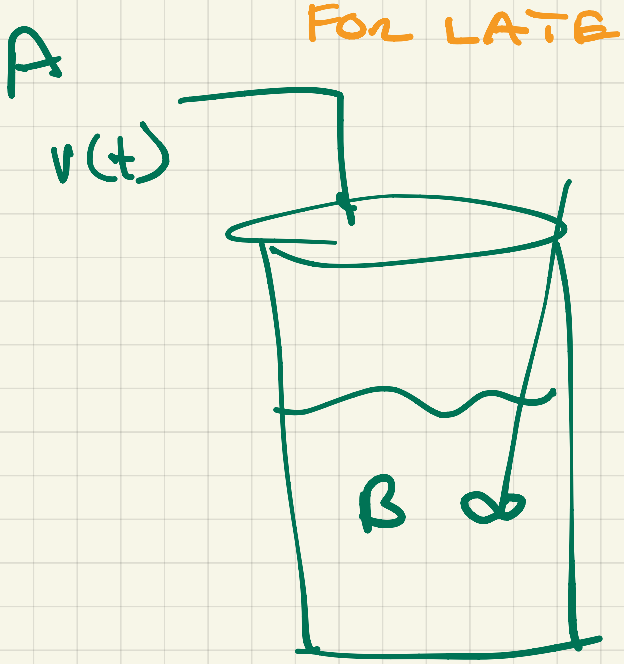
AS EXPECTED!

$c(t)$ DATA $\longrightarrow k$

NOW CONSIDER A "SEMI-BATCH" REACTOR

$$A + B \longrightarrow M$$

SAVE OTHER REACTIONS FOR LATER . . .



WOULD ADJUST IF NECESSARY

FOR COMPONENT i

$$\frac{dm_i}{dt} = f(t)\,C_i^{0}(t) - 0 + (\nu_i r)\,V$$

MIGHT CHANGE

IF RECIPE IS COMPLEX

FOR $A + B \longrightarrow M$

$$r = k C_A C_B \qquad C_B^{\circ} \rightarrow \text{INITIAL IN REACTOR}$$

$$\frac{dm_A}{dt} = q\, C_A^{\circ} - k C_A C_B V$$

$$\frac{dm_B}{dt} = 0 - k C_A C_B V$$

$$V = V_0 + q * t$$

$$k C_A C_B V = k \frac{m_A}{V} \frac{m_B}{V} V$$

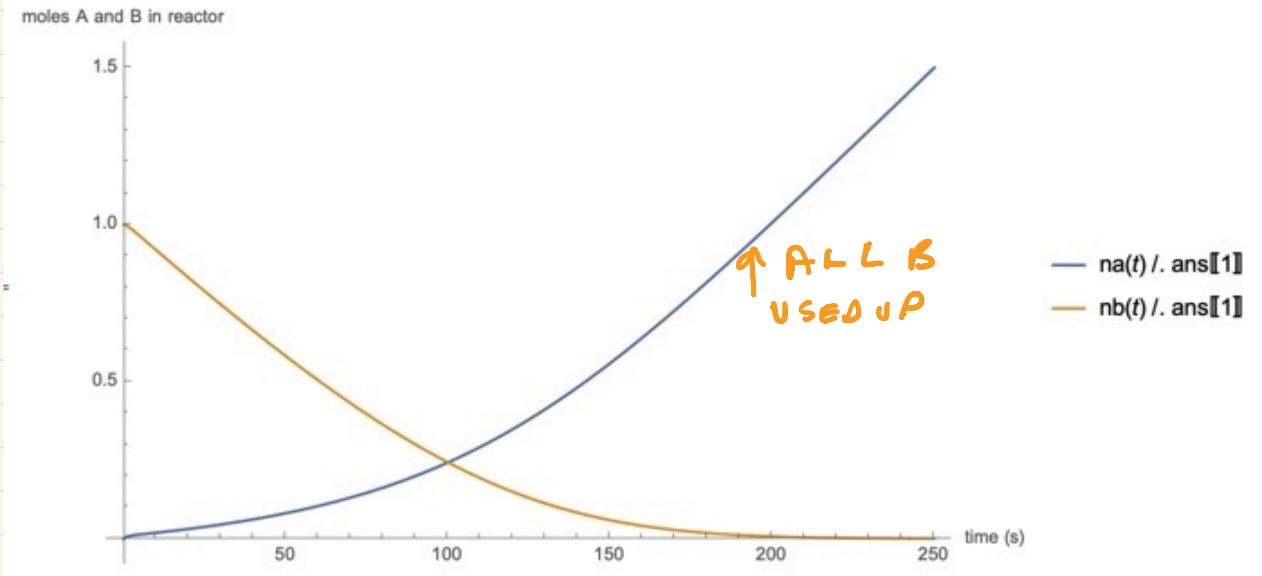
$$= \frac{k\, m_A m_B}{(V_0 + q * t)}$$

$$\frac{dm_A}{dt} = v^{\circ} C_A^{\circ} - \frac{k\, m_A m_B}{(V_0 + q * t)}$$

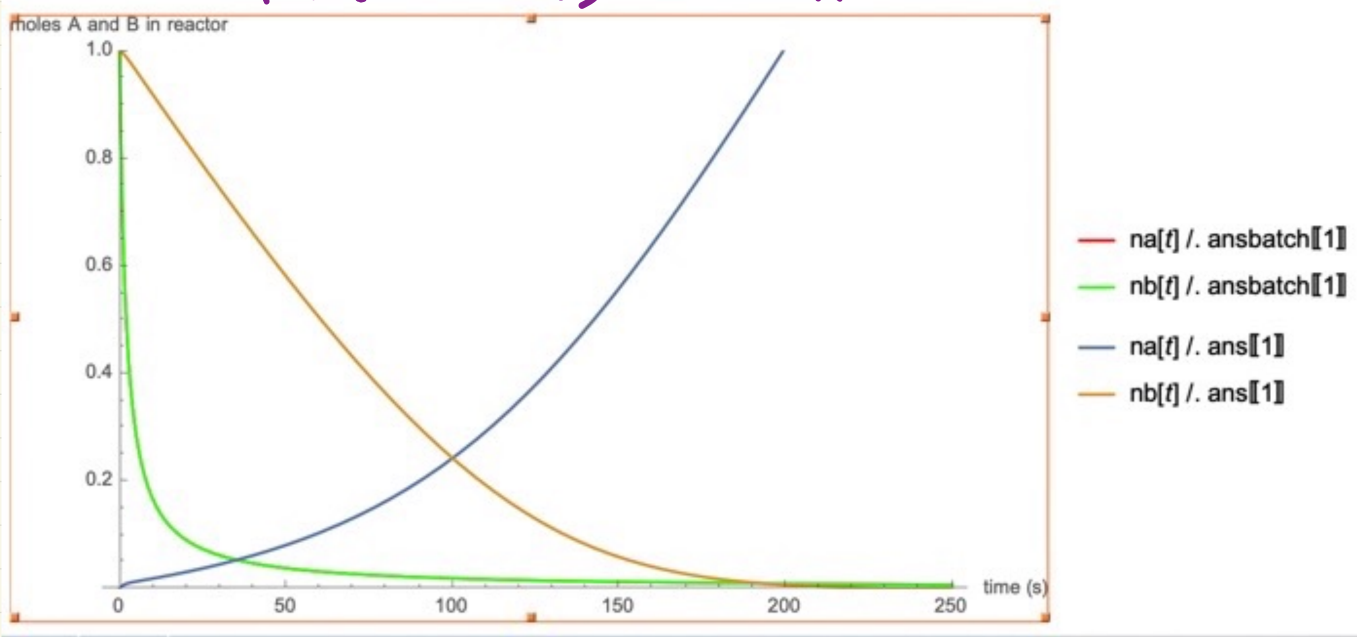
$$\frac{dm_B}{dt} = - \frac{k\, m_A m_B}{(V_0 + q * t)}$$

SOLVE NUMERICALLY

```
Plot[{na[t] /. ans[[1]], nb[t] /. ans[[1]]}, {t, 0, 250},
 AxesLabel → {"time (s)", "moles A and B in reactor"}, PlotLegends → "Expressions"]
```



IF ALL A IS ADDED AT BEGINNING, REACTION IS MUCH FASTER



IF YOU REALLY WANT TO, AN ANALYTICAL SOLUTION IS POSSIBLE . . .

```
analyticalans =
 FullSimplify[DSolve[{eq1 == 0, eq2 == 0, na[0] == na0, nb[0] == nb0}, {na[t], nb[t]}, t,
   Assumptions → {V0 > 0, v0 > 0, ca0 > 0, k > 0, na0 ≥ 0, nb0 > 0, t > 0}]]
```

$$
\Bigg\{\Bigg\{\mathrm{na}[t] \to \Bigg(e^{-\frac{\mathrm{ca0}\,k\,(t\,\mathrm{v0}+\mathrm{V0})}{\mathrm{v0}}}
\Bigg(e^{\frac{\mathrm{ca0}\,k\,\mathrm{V0}}{\mathrm{v0}}}\,\mathrm{nb0}\,\mathrm{v0}\,(t\,\mathrm{v0}+\mathrm{V0})^{\frac{k\,(-\mathrm{na0}+\mathrm{nb0}+\mathrm{ca0}\,\mathrm{V0})}{\mathrm{v0}}} + (\mathrm{na0}-\mathrm{nb0}+\mathrm{ca0}\,t\,\mathrm{v0})\Bigg(e^{\frac{\mathrm{ca0}\,k\,(t\,\mathrm{v0}+\mathrm{V0})}{\mathrm{v0}}}\,\mathrm{v0}\,\mathrm{V0}^{\frac{k\,(-\mathrm{na0}+\mathrm{nb0}+\mathrm{ca0}\,\mathrm{V0})}{\mathrm{v0}}} +
e^{\mathrm{ca0}\,k\left(t+\frac{2\,\mathrm{V0}}{\mathrm{v0}}\right)}\,k\,\mathrm{nb0}\left(\frac{\mathrm{v0}}{\mathrm{ca0}\,k}\right)^{\frac{k\,(-\mathrm{na0}+\mathrm{nb0}+\mathrm{ca0}\,\mathrm{V0})}{\mathrm{v0}}}\Bigg(\mathrm{Gamma}\Big[\frac{k\,(-\mathrm{na0}+\mathrm{nb0}+\mathrm{ca0}\,\mathrm{V0})}{\mathrm{v0}},\frac{\mathrm{ca0}\,k\,\mathrm{V0}}{\mathrm{v0}}\Big] -
\mathrm{Gamma}\Big[\frac{k\,(-\mathrm{na0}+\mathrm{nb0}+\mathrm{ca0}\,\mathrm{V0})}{\mathrm{v0}},\frac{\mathrm{ca0}\,k\,(t\,\mathrm{v0}+\mathrm{V0})}{\mathrm{v0}}\Big]\Bigg)\Bigg)\Bigg)\Bigg)\Bigg/
\Bigg(\mathrm{v0}\,\mathrm{V0}^{\frac{k\,(-\mathrm{na0}+\mathrm{nb0}+\mathrm{ca0}\,\mathrm{V0})}{\mathrm{v0}}} + e^{\frac{\mathrm{ca0}\,k\,\mathrm{V0}}{\mathrm{v0}}}\,k\,\mathrm{nb0}\left(\frac{\mathrm{v0}}{\mathrm{ca0}\,k}\right)^{\frac{k\,(-\mathrm{na0}+\mathrm{nb0}+\mathrm{ca0}\,\mathrm{V0})}{\mathrm{v0}}}\Bigg(\mathrm{Gamma}\Big[\frac{k\,(-\mathrm{na0}+\mathrm{nb0}+\mathrm{ca0}\,\mathrm{V0})}{\mathrm{v0}},\frac{\mathrm{ca0}\,k\,\mathrm{V0}}{\mathrm{v0}}\Big] -
\mathrm{Gamma}\Big[\frac{k\,(-\mathrm{na0}+\mathrm{nb0}+\mathrm{ca0}\,\mathrm{V0})}{\mathrm{v0}},\frac{\mathrm{ca0}\,k\,(t\,\mathrm{v0}+\mathrm{V0})}{\mathrm{v0}}\Big]\Bigg)\Bigg),
$$

$$
\mathrm{nb}[t] \to \Bigg(e^{-\mathrm{ca0}\,k\,t}\,\mathrm{nb0}\,\mathrm{v0}\,(t\,\mathrm{v0}+\mathrm{V0})^{\frac{k\,(-\mathrm{na0}+\mathrm{nb0}+\mathrm{ca0}\,\mathrm{V0})}{\mathrm{v0}}}\Bigg)\Bigg/\Bigg(\mathrm{v0}\,\mathrm{V0}^{\frac{k\,(-\mathrm{na0}+\mathrm{nb0}+\mathrm{ca0}\,\mathrm{V0})}{\mathrm{v0}}} + e^{\frac{\mathrm{ca0}\,k\,\mathrm{V0}}{\mathrm{v0}}}\,k\,\mathrm{nb0}\left(\frac{\mathrm{v0}}{\mathrm{ca0}\,k}\right)^{\frac{k\,(-\mathrm{na0}+\mathrm{nb0}+\mathrm{ca0}\,\mathrm{V0})}{\mathrm{v0}}}
\Bigg(\mathrm{Gamma}\Big[\frac{k\,(-\mathrm{na0}+\mathrm{nb0}+\mathrm{ca0}\,\mathrm{V0})}{\mathrm{v0}},\frac{\mathrm{ca0}\,k\,\mathrm{V0}}{\mathrm{v0}}\Big] - \mathrm{Gamma}\Big[\frac{k\,(-\mathrm{na0}+\mathrm{nb0}+\mathrm{ca0}\,\mathrm{V0})}{\mathrm{v0}},\frac{\mathrm{ca0}\,k\,(t\,\mathrm{v0}+\mathrm{V0})}{\mathrm{v0}}\Big]\Bigg)\Bigg)\Bigg\}\Bigg\}
$$

$$\frac{d\,n_B}{dt} = -k\,C_A C_B V$$

$$\frac{d\,V C_B}{dt} = -k\,C_A C_B\,V$$

$$C_B \frac{dV}{dt} + V\frac{dC_B}{dt} = -k\,C_A C_B\,V$$

$$V = V_0 + q\,t$$

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

$$V\frac{dC_B}{dt} = -k\,C_A C_B V - C_B\,q$$

$$\frac{dC_B}{dt} = -C_B\frac{q}{V} - k\,C_A C_B$$

$$\frac{dC_B}{dt} = -C_B\frac{q}{V} - kC_AC_B$$

$$\frac{dVC_A}{dt} = qC_A^\circ - kC_AC_BV$$

$$V\frac{dC_A}{dt} + C_A q = qC_A^\circ - kC_AC_BV$$

$$\frac{dC_A}{dt} = \frac{q(C_A^\circ - C_A)}{V} - kC_AC_B$$

SUBTRACT EQ'S

$$\frac{dC_B}{dt} - \frac{dC_A}{dt} = -C_B\frac{q}{V} - C_A^\circ\frac{q}{V} + C_A\frac{q}{V}$$

$$\frac{dC_A}{dt} - \frac{dC_B}{dt} = (-C_B + C_A - C_A^\circ)\frac{q}{V}$$

BUT WE CAN NONDIMENSIONALIZE

$$x_B = \frac{C_B}{C_{A0}} \qquad \xi = \frac{V}{q}$$

$$x_A = \frac{C_A}{C_{A0}} \qquad \tau = \frac{t}{\xi}$$

$$\frac{dC_B}{dt} = -C_B \frac{q}{V} - k C_A C_B$$

$$C_{A0} \frac{dx_B}{dt} = \frac{C_{A0} x_B}{\xi} - k C_{A0}^2 x_A x_B$$

$$\frac{dx_B}{d\tau} = x_B - \left(k C_{A0} \xi\right) x_A x_B$$

$$\frac{dx_B}{d\tau} = x_B - D_a x_A x_B$$

$$\frac{dC_A}{dt} = \frac{q\left(C_A^{\circ} - C_A\right)}{V} - k C_A C_B$$

$$C_{A0} \frac{dX_A}{dt} = \frac{(1 - X_A) C_{A0}}{\xi} - k C_{A0}^2 X_A X_B$$

$$\begin{cases} \dfrac{dX_A}{d\tau} = (1 - X_A) - Da\, X_A X_B \\[2ex] \dfrac{dX_B}{d\tau} = - X_B - Da\, X_A X_B \end{cases}$$

WE CAN MAKE ~~THESE~~ THESE

SIMPLER TO LOOK AT !!

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Show[%, %225, %223]
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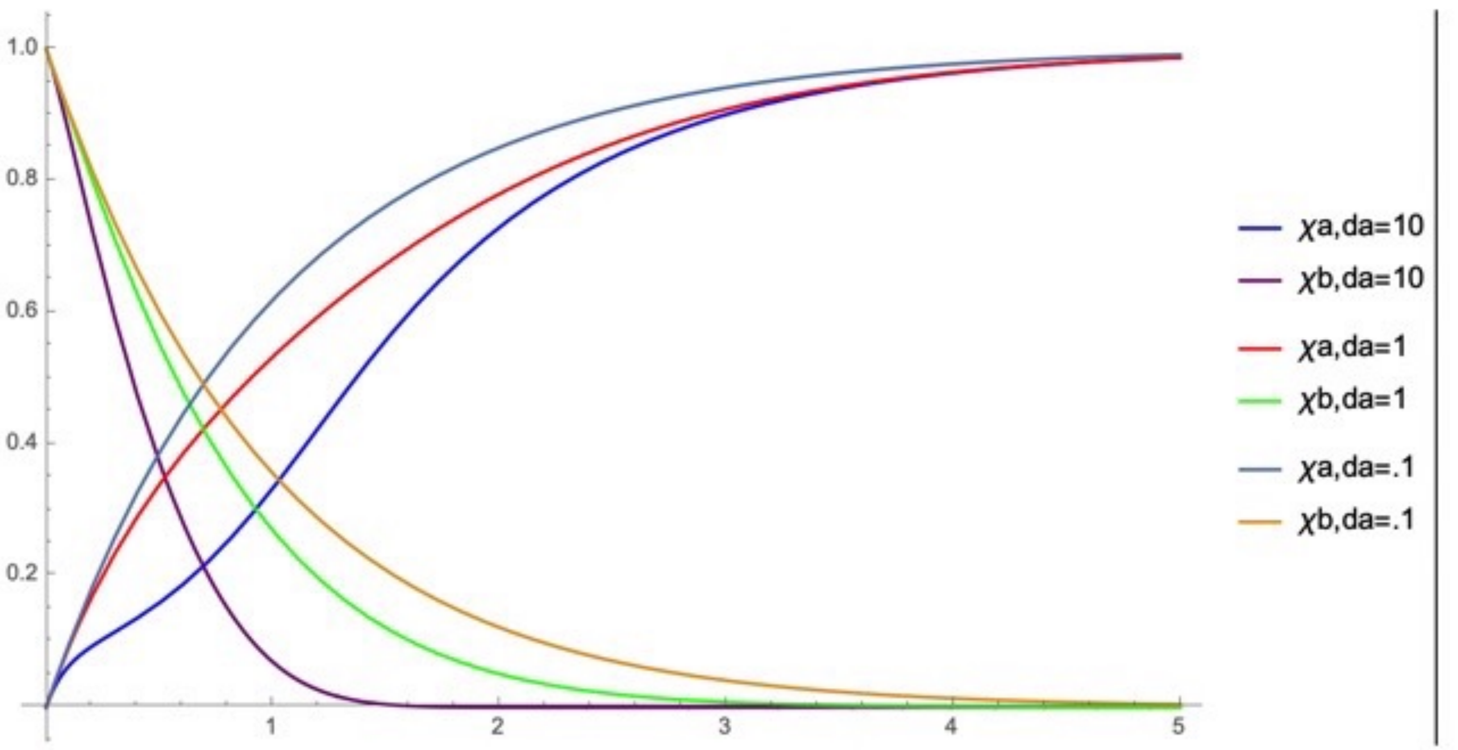
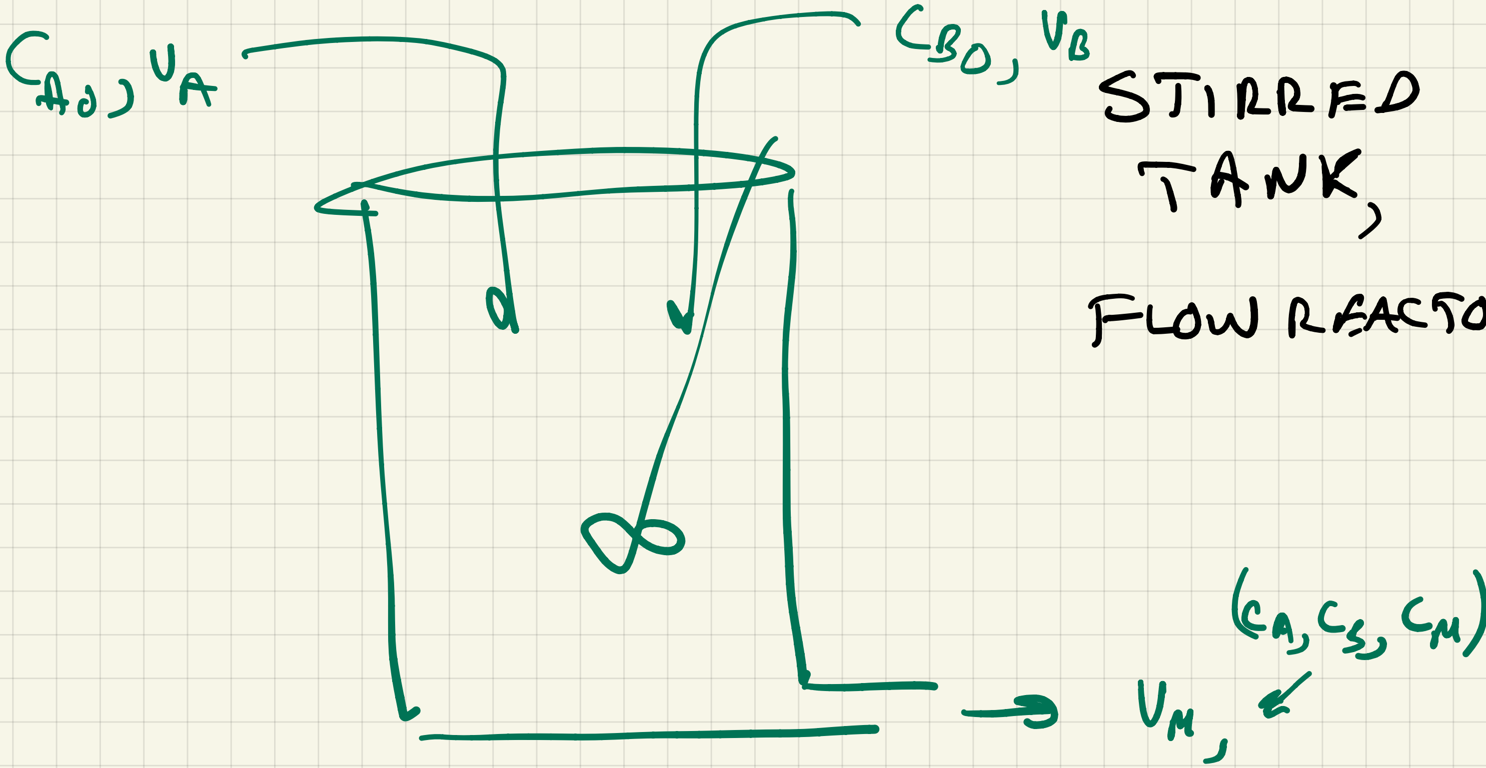


AS Da ↑ FASTER REACTION

BUT THIS IS MITIGATED SOME WHAT BY "A" GETTING USED UP

STIRRED TANK, FLOW REACTOR



$$A + B \rightarrow 2M$$

GENERAL EQUATIONS!

OVERALL MASS BALANCE

$$\frac{d\rho V}{dt} = \rho_A q_A + \rho_B q_B - \rho q$$

$$q = q_A + q_B$$

CHANGE IN DENSITY IS NOT AN ISSUE FOR LIQUIDS IF NO ΔV_{mix}

$$\frac{dV}{dt} = q_A + q_B - q$$

COULD BE FILLING UP.

COMPONENT A $\quad \frac{d}{dt} V C_A = q_A C_{A0} - q C_A + r_A V$

COMPONENT B $\quad \frac{d}{dt} V C_B = q_B C_{B0} - q C_B + r_B V$

COMPONENT M $\quad \frac{d}{dt} V C_M = 0 - q C_M + r_M V$

STANDARD ASSUMPTIONS FOR STEADY-STATE OPERATION.

$$\frac{d}{dt}(\ ) = 0$$

JUST LOOK AT COMPONENT A. $\rightarrow$ $A + B \rightarrow 2M$

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

$$C_A = \frac{q_A}{q} C_{A0} + r_A \frac{V}{q}$$

OR

$$-\nu_A r = \frac{q_A C_{A0} - q C_A}{V}$$

WE CAN WRITE:

$$\frac{\text{MOLES}}{\text{TIME}}$$

$$-\nu_A r = \frac{F_{A0} - F_A}{V}$$

WE COULD ALSO WRITE!

$$f = \frac{F_{A0} - F_A}{F_{A0}}$$

WHICH GIVES:

$$-\nu_A r = \frac{F_{A0}}{V} f_A$$

MOST USEFUL FOR LIMITING REACTANT.