ChE 344
Reaction Engineering and Design

Lecture 9: Thurs, Feb 3, 2022

Pressure drop + semi-batch reactors

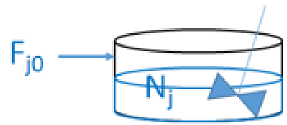
Reading for today's Lecture: Chapter 6.5-6.6

Homework 3 due Friday by 11:59pm

Reading for Lecture 10: Chapter 6.4

Lecture 9: Semi-batch reactors
Related Text: Chapter 6.6

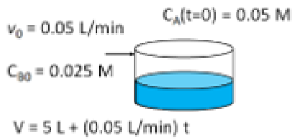
Semi-batch reactors: Liquid phase, feed into the reactor with pre-loaded amount of liquid volume.



Assumptions:

- Not at steady state
- Feed in
- Well-mixed in reactor itself
- Not constant volume with time (for a different reason than expansion from gases!)

For a feed of reactant species B into a reactor with reactant species A, different ways of writing the mole balances for semi-batch reactors:



Mole basis	Concentration basis	Conversion basis
$\frac{dN_A}{dt} = r_A V$	$\frac{dC_A}{dt} = r_A - C_A \frac{v_0}{V}$	$\frac{dX}{dt} = \frac{-r_A V}{N_{Ai}(t=0)}$
$\frac{dN_B}{dt} = F_{B0} + r_B V$	$\frac{dC_B}{dt} = r_B + (C_{A0} - C_B)\frac{v_0}{V}$	

Definition of conversion of limiting reactant (A) here:

$$X = \frac{C_A(t=0)V_0 - C_A(t)V}{C_A(t=0)V_0} = \frac{N_A(t=0) - N_A}{N_A(t=0)}$$

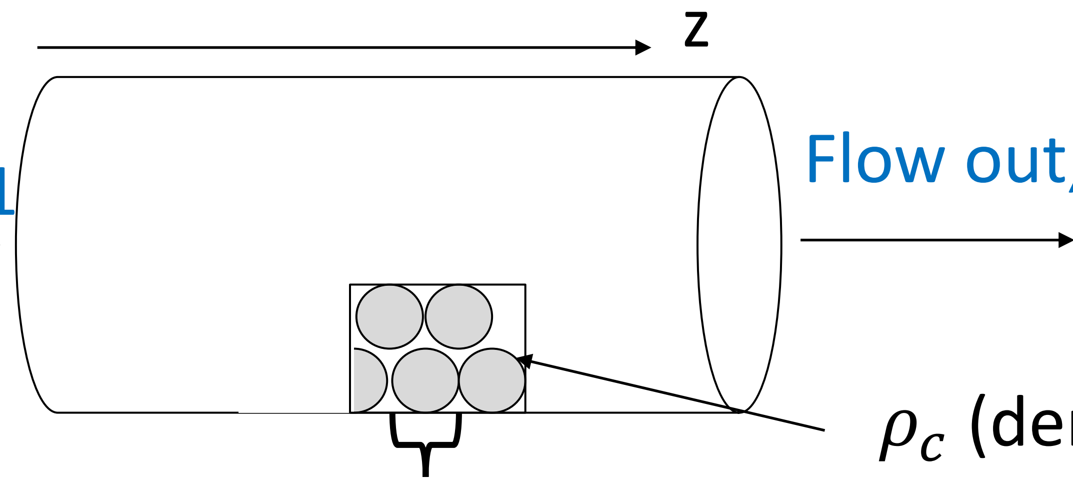
To solve problems: Example for elementary as written liquid phase reaction: $2A + B \rightarrow C$, B being fed in:

Mole balance	$\frac{dN_A}{dt} = r_A V;\ \frac{dN_B}{dt} = F_{B0} + r_B V;\ \frac{dN_C}{dt} = r_C V$
Rate law	$r = -\frac{r_A}{2} = -r_B = r_C = kC_A^2 C_B$
Stoichiometry	$C_j = \frac{N_j}{V}$
Additional equation for semi-batch!	$V = V_0 + v_0 t$
Evaluate	Solve system of equations (usually numerically)

Reminder of terms for pressure drop in gas phase packed bed reactors

Flow in,

$P = P_0$, $p=1$



Flow out, $P < P_0$, $p < 1$

$$p \equiv \frac{P}{P_0}$$

ρ_c (density of catalyst)

Diameter particle=D_P

$$\rho_{bed} = \rho_c(1-\phi_b)$$

Cons. of mass/IG law/define β_0

$$\beta_0 \equiv \frac{G}{\rho_0 g_c D_P}\left(\frac{1-\phi_b}{\phi_b{}^3}\right)\left[\underbrace{\frac{150(1-\phi_b)\mu}{D_P}}_{Laminar} + \underbrace{1.75G}_{Turbulent}\right]$$

$$\alpha \equiv \frac{2\beta_0}{\rho_c(1-\phi_b)A_{CS}P_0}$$

Gas-phase PBRs:

Our simple analytical soln only for $\varepsilon = 0$

$$F_{A0}\frac{dX}{dW} = -r_A' \qquad \frac{dp}{dW} = -\frac{\alpha}{2p}\frac{T}{T_0}(1+\varepsilon X)$$

Rate often depends on concentrations/partial pressures. Therefore, incorrectly ignoring pressure drop can cause you to overestimate r_A' (if positive order in concentrations). This will lead to lower than predicted conversions!

For the gas reaction A → bB with r_A' = - kC_A

No longer 1!!!

$$F_{A0}\frac{dX}{dW} = -r_A' = kC_A = k\frac{C_{A0}(1-X)}{1+\varepsilon X}\frac{P}{P_0}\frac{T_0}{T}$$

$$F_{A0}\frac{dX}{dW} = k\frac{C_{A0}(1-X)}{1+\varepsilon X}p\frac{T_0}{T}$$

Gas only!

X (dep), p (dep), W (ind), two coupled diff equations

With neighbors: $$C_A = \frac{C_{A0}(1-X)}{1+\varepsilon X} p \frac{T_0}{T}$$

For an isothermal gas-phase PBR, which of the following are always true?

i) $C_A(X) < C_{A0}$ for X > 0

ii) $C_A(X = 0.3, pressure\ drop) < C_A(X = 0.3, p = 1)$

iii) Reaction rate with pressure drop will be lower for a reaction that is positive order in A

A) i and ii

B) ii and iii

C) i, ii, and iii

D) i and iii

Recall epsilon min > -1

Example problem:

Make ethylene oxide from ethylene and air in a PBR:

$$C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O; A + \frac{1}{2}B \rightarrow C$$

Conditions: $ $$$

Stoichiometric feed, F_{A0} = 0.3 lbmol/second @ 10 atm

Isothermal PBR @ 260 °C

10 banks of 1 ½" tube x 100 tubes/batch, 1,000 tubes

Assume reaction gas properties are the same as air

ρ_c = 120 lbm/ft^3, ¼" catalyst pellets and void fraction = 0.45

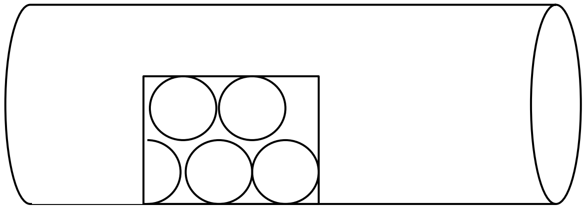
$$r'_A = -kP_A^{1/3}P_B^{2/3}$$

Rate law given for pressures not C_j

k = 0.0141 lbmol/(lbm$_{cat}$ * atm * hr)

- Plot X and concentration profile vs. W
- Calculate X at W = 50 lb_{cat} (single tube)
- Calculate W where X = 0.6
- Calculate the pressure drop at that weight of catalyst

F_{A0} = 0.0003 lbmol/s
(1,000 tubes total)



Consider single tube

F_{B0} = 0.00015 lbmol/s

F_{C0} = 0 lbmol/s

$F_{N2,0}$ = 0.00015 lbmol/s *0.79 mol N_2/ 0.21 mol O_2 = 0.0005643 lbmol/s of inert nitrogen

Design Equation
+ Rate Law

$$F_{A0}\frac{dX}{dW} = -r_A' = kP_A^{1/3}P_B^{2/3}$$

$$= k(C_ART)^{1/3}(C_BRT)^{2/3}$$

$$F_{A0}\frac{dX}{dW} = kRTC_A^{1/3}C_B^{2/3}$$

Stoichiometry:

Reactant A (ethylene)

Isothermal

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

Reactant B (oxygen)

$$C_B = \frac{C_{A0}(\theta_B - \frac{b}{a}X)}{(1+\varepsilon X)}p$$

$$C_B = \frac{C_{A0}(0.5-0.5X)}{(1+\varepsilon X)}p$$

Combine (Design Eqn, Rate Law, Stoichiometry (for gases), and now also have Ergun Eqn):

$$C_A = \frac{C_{A0}(1-X)}{(1+\varepsilon X)}p \quad C_B = \frac{C_{A0}(0.5-0.5X)}{(1+\varepsilon X)}p$$

Not pseudo

$$k' \equiv \frac{kRTC_{A0}}{2^{2/3}}$$

$$\frac{dX}{dW} = \frac{-r_A'}{F_{A0}} = \frac{k}{F_{A0}}RTC_A^{1/3}C_B^{2/3} = \frac{k'}{F_{A0}}\frac{(1-X)}{(1+\varepsilon X)}p$$

Ergun Equation:

Isothermal

$$\frac{dp}{dW} = -\frac{\alpha}{2p}\frac{T}{T_0}(1+\varepsilon X) \qquad \alpha \equiv \frac{2\beta_0}{\rho_c(1-\phi_b)A_{CS}P_0}$$

$$\beta_0 \equiv \frac{G}{\rho_0 g_c D_P}\left(\frac{1-\phi_b}{{\phi_b}^3}\right)\left[\frac{150(1-\phi_b)\mu}{D_P} + 1.75G\right]$$

Solve using Polymath, Mathematica, Matlab, etc.

$$\frac{dX}{dW} = \frac{k'}{F_{A0}} \frac{(1-X)}{(1+\varepsilon X)} p \qquad \frac{dp}{dW} = -\frac{\alpha}{2p}(1+\varepsilon X)$$

ICs: p(W = 0) = 1, X(W=0) = 0

Per (identical) tube:

$$A + \frac{1}{2}B \rightarrow C$$

F_{A0} = 0.0003 lbmol/s

F_{B0} = 0.00015 lbmol/s

$$\varepsilon = y_{A0}\delta = \frac{F_{A0}}{F_{T0}}(-1/2) = -0.15$$

$F_{N2,0}$ = 0.0005643 lbmol/s

$$P_{A0} = y_{A0}P_0 = 0.3(10atm)$$

F_{A0} = 1.08 lbmol/**hr** from 0.0003 *3600

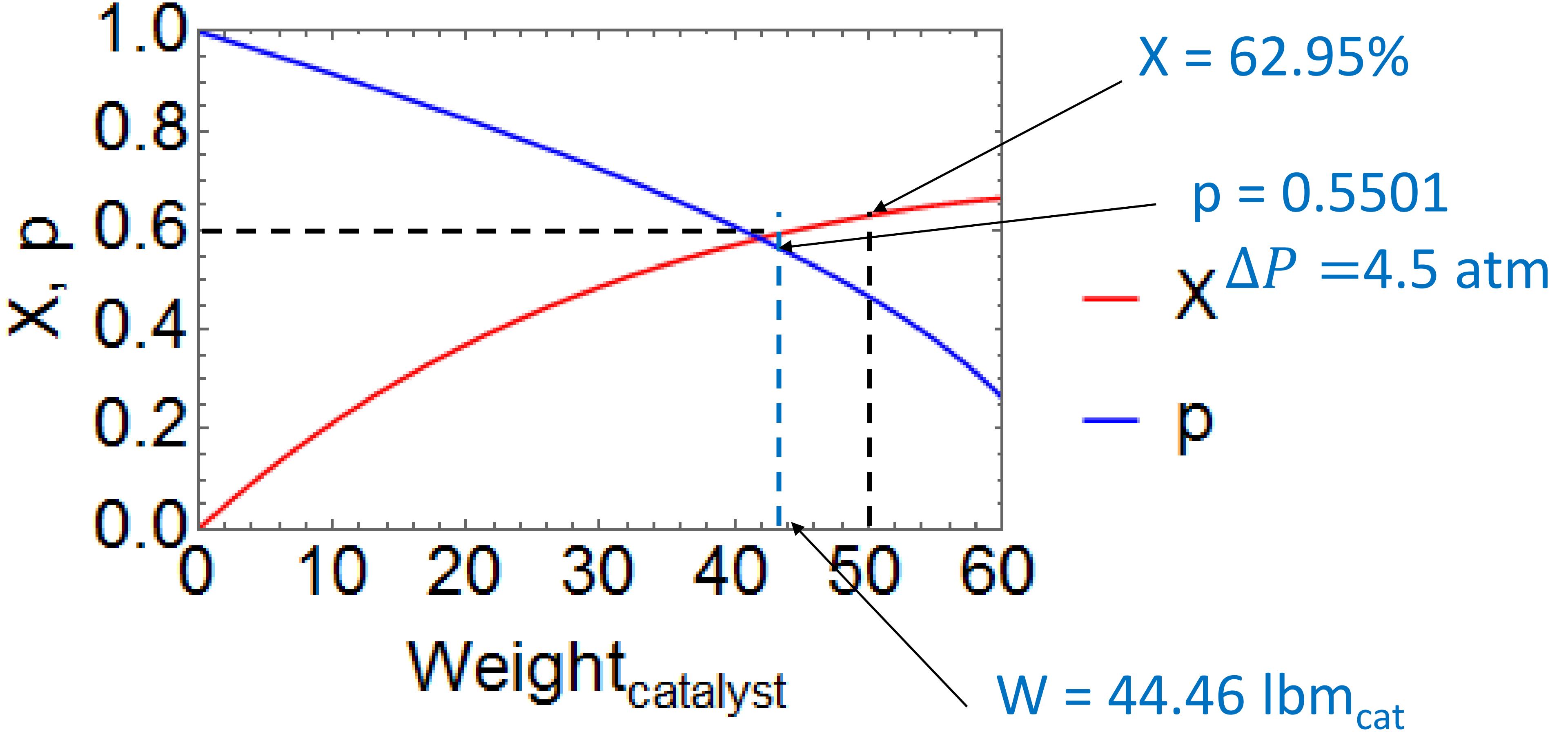
k = 0.0141 lbmol/(lbm$_{cat}$ * atm * hr)

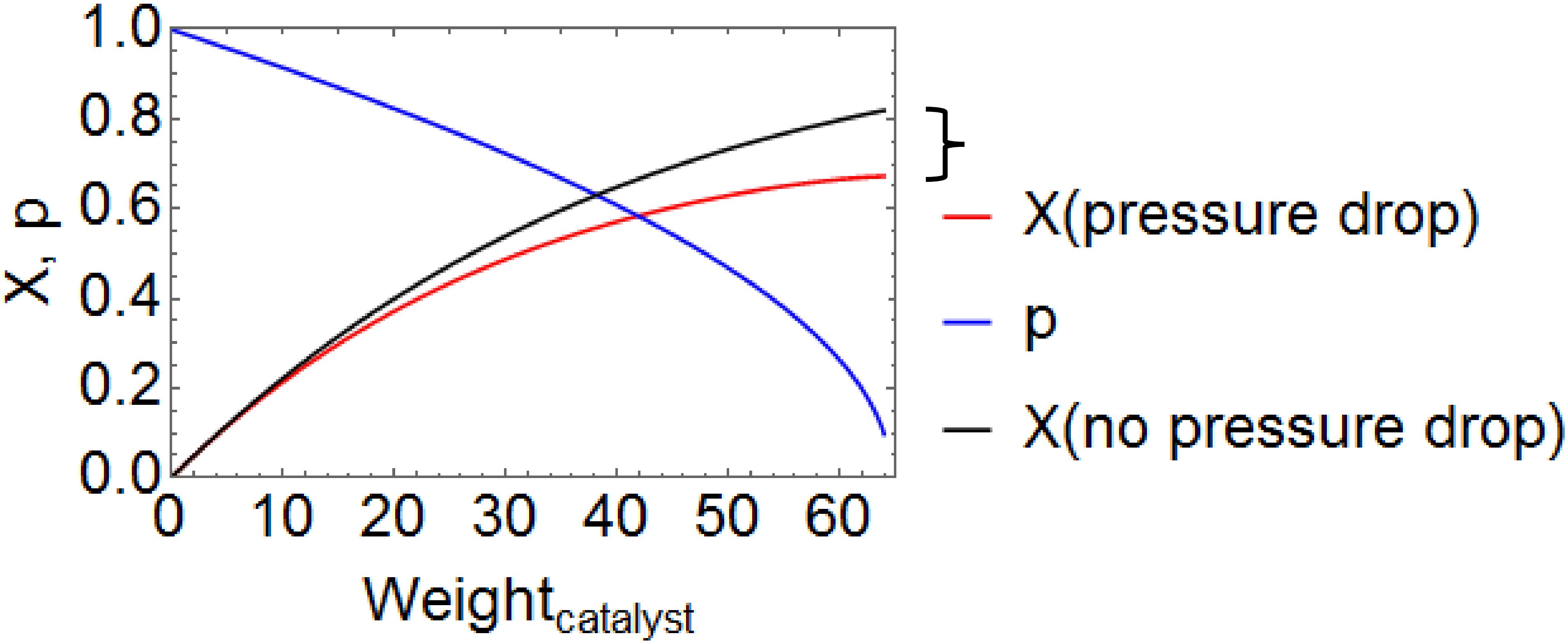
$$k' = \frac{kRTC_{A0}}{2^{2/3}} = \frac{k}{2^{2/3}}RT\frac{P_{A0}}{RT} = 0.0266 \text{ lbmol/(lbmcat*hr)}$$

g_c= 32.174 lb_m*ft/(s^2*lb_f) (convert from mass to force)

$\alpha = 0.0166$ $(lbm_{cat})^{-1}$

$$\frac{dX}{dW} = \frac{k'}{F_{A0}} \frac{(1-X)}{(1+\varepsilon X)} p \qquad \frac{dp}{dW} = -\frac{\alpha}{2p}(1+\varepsilon X)$$





About 15% drop in conversion indicated. Could be millions of dollars in unpredicted losses (less ethylene oxide made) if pressure drop is not accounted for.

Example PBR pressure drop

$$\frac{dX}{dW} = \frac{k'}{F_{A0}} \frac{(1-X)}{(1+\varepsilon X)} p$$

$$\frac{dp}{dW} = -\frac{\alpha}{2p}(1+\varepsilon X)$$

```
(* Define terms for Ergun equation, rate *)

α = 0.0166; ϵ = -0.15; F = 1.08; k1 = 0.0266;

sol1 = NDSolve[{y'[w] == -α / (2 * y[w]) * (1 + ϵ * X[w]),
    X'[w] == k1 / F * (1 - X[w]) / (1 + ϵ * X[w]) * y[w], X[0] == 0, y[0] == 1},
   {y[w], X[w]}, {w, 64.6}];

(* Plot X as a function of catalyst weight,
pressure ratio as a function of weight *)

Show[Plot[X[w] /. sol1, {w, 0, 64}, Frame → True, PlotRange → {{0, 60}, {0, 1}},
  FrameLabel → {"Weight_catalyst", "X, y"}, PlotStyle → Red, PlotLegends → {"X"},
  LabelStyle → {Large, Black}],
 Plot[y[w] /. sol1, {w, 0, 64}, PlotRange → {{0, 60}, {0, 1}}, PlotStyle → Blue,
  PlotLegends → {"y"}, LabelStyle → {Large, Black}]]
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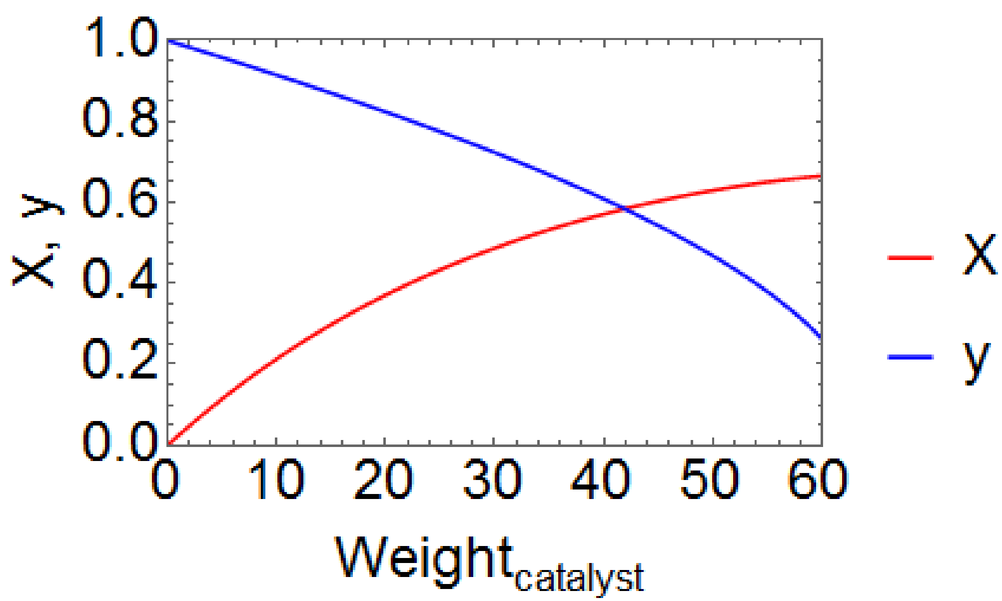

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(* Function applying interpolating function for conversion solved above *)

In[4]:= ex[w_] = X[w] /. sol1[[1]];

ex[50]

0.629527

(* Solve for value of w when X = 0.6 *)

In[5]:= NSolve[ex[w] == 0.6, w]

Out[5]= {{w → 44.4604}}

(* Find the pressure drop for this weight of catayst *)

(* Another way to do it with mma using FindRoot *)

In[54]:= FindRoot[(X[w] /. sol1) == 0.6, {w, 50}]

Out[54]= {w → 44.4604}

In[48]:= why[w_] = y[w] /. sol1[[1]];

In[55]:= why[44.4604]

Out[55]= 0.550114

In[56]:= %*10 (* y = P/P0 and P0 = 10 atm *)

Out[56]= 5.50114

(* ΔP = 10 atmospheres - 5.5 atmosphere = 4.5 atm drop through the PBR *)
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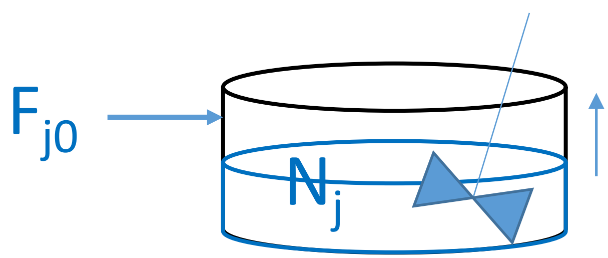
Calculate X at W = 50 lbm

Calculate W where X = 0.6

Calculate the pressure drop at that weight of catalyst

New reactor type! Semi-batch reactors



Liquid level and reactor volume increases

V not just vol. container

Back to our **general** mole balance equation

$$F_{j0} - F_j + G_j = \frac{dN_j}{dt}$$

Well-mixed (like batch reactor), but NOT steady state!

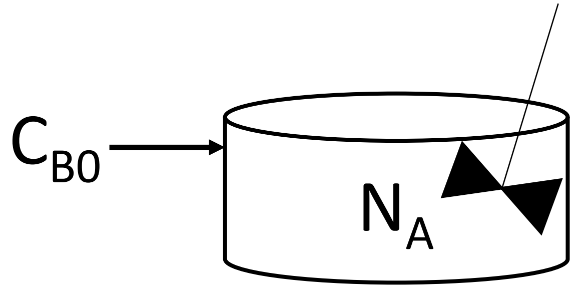
$$F_{j0} - F_j + r_j V(t) = \frac{dN_j}{dt}$$

$$C_{j0} v_0 + r_j V = \frac{dC_j V}{dt} = V\frac{dC_j}{dt} + C_j \boxed{\frac{dV}{dt}}$$

v_0 for const dens.

$$\frac{dC_j}{dt} = r_j + \frac{v_0 [C_{j0} - C_j]}{V}$$

Usually, feed one species (B) into a limiting reactant (A)



Caution: C_{B0} is the concentration of B entering the reactor, NOT the initial concentration of B.

Reminder: V here is not constant!

If constant density, $V = V_0 + v_0 t$. V_0 is initial volume (V(t=0)).

For species B being fed into a semi-batch reactor:

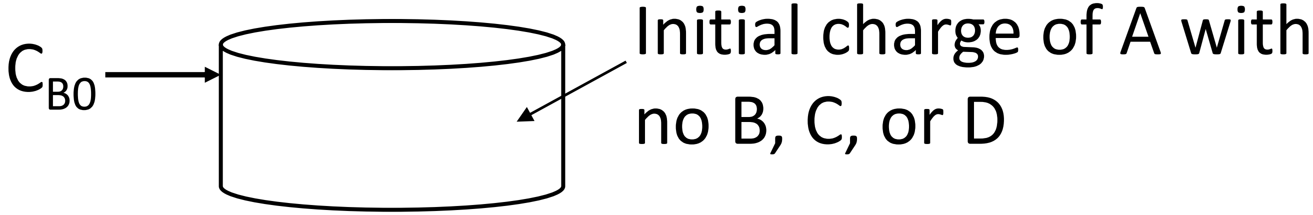
$$\frac{dC_A}{dt} = r_A - \frac{v_0[C_A]}{V} \qquad \frac{dC_B}{dt} = r_B + \frac{v_0[C_{B0} - C_B]}{V}$$

$$C_A(t=0) = \frac{N_A(t=0)}{V_0} \qquad C_B(t=0) = \frac{N_B(t=0)}{V_0}$$

Sample elementary liquid phase reaction

$$CNBr + CH_3NH_2 \rightarrow CH_3Br + NCNH_2$$

$$A + B \rightarrow C + D$$



$$\frac{dC_A}{dt} = r_A + \frac{v_0[0 - C_A]}{V}$$

$$\frac{dC_C}{dt} = r_C + \frac{v_0[0 - C_C]}{V}$$

$$\frac{dC_B}{dt} = r_B + \frac{v_0[C_{B0} - C_B]}{V}$$

$$\frac{dC_D}{dt} = r_D + \frac{v_0[0 - C_D]}{V}$$

$$V = V_0 + v_0 t$$

Rate law

$$r = -r_A = -r_B = r_C = r_D$$

A + B → C + D

$$r = kC_AC_B = -r_A$$

Define conversion of A (limiting reactant because B is continuously being fed).

$$X = \frac{C_A(t=0)V_0 - C_A(t)V}{C_A(t=0)V_0}$$

I'm using $C_A(t=0)$ because that is the concentration of A in the batch reactor to begin, not the inlet concentration of A of the incoming stream (which for this particular problem is 0). Also (in book) $C_A(t=0)$ is called C_{Ai}

Solving semi-batch problem in Polymath

$$A + B \rightarrow C + D$$

Differential equations

1 d(Cd)/d(t) = -ra-v0*Cd/V

Mole balance on D

2 d(Cc)/d(t) = -ra-v0*Cc/V

Mole balance on C

3 d(Cb)/d(t) = ra+(Cb0-Cb)*v0/V

Mole balance on B

4 d(Ca)/d(t) = ra-v0*Ca/V

Mole balance on A

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	Ca	0.05	7.731E-06	0.05	7.731E-06
2	Cb	0	0	0.0125077	0.0125077
3	Cb0	0.025	0.025	0.025	0.025
4	Cc	0	0	0.0121468	0.0083256
5	Cd	0	0	0.0121468	0.0083256
6	k	2.2	2.2	2.2	2.2
7	ra	0	-0.0001644	0	-2.127E-07
8	t	0	0	500.	500.
9	V	5.	5.	30.	30.
10	V0	5.	5.	5.	5.
11	v0	0.05	0.05	0.05	0.05

Explicit equations

1 V0 = 5

Initial reactor volume

2 v0 = 0.05

Inlet volumetric flow rate

3 k = 2.2

Rate constant

4 Cb0 = 0.025

Inlet concentration of B, NOT initial concentration of B!

5 ra = -k*Ca*Cb

Rate law for irreversible elementary reaction

6 V = V0+v0*t

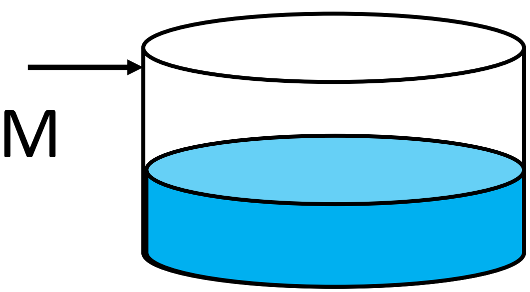
Reactor volume as a function of time

$2.2\ \mathrm{L\ mol^{-1}\ min^{-1}}$

$C_A(t=0) = 0.05\ \mathrm{M}$

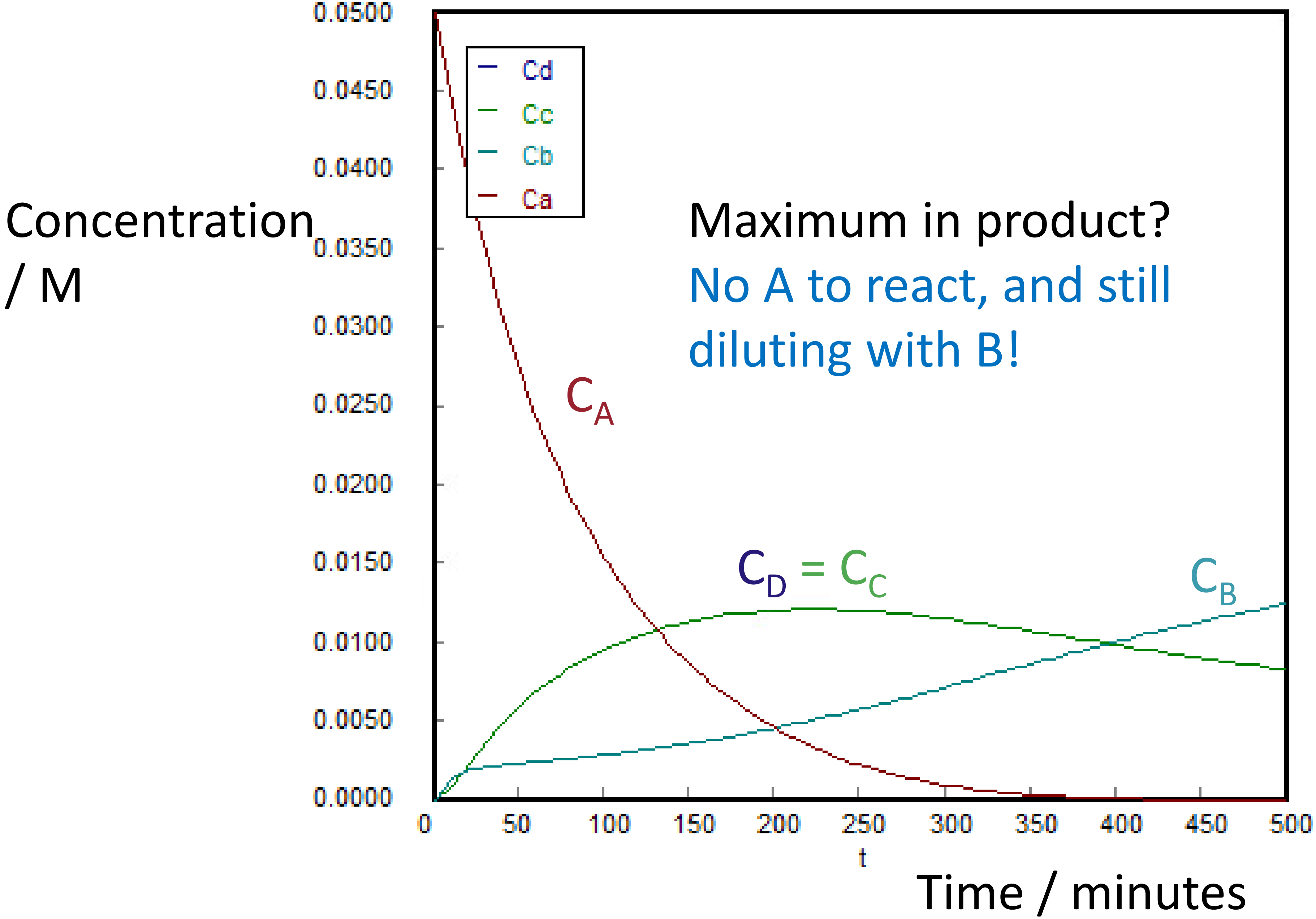
$v_0 = 0.05\ \mathrm{L/min}$

$C_{B0} = 0.025\ \mathrm{M}$



$V = 5\ \mathrm{L} + (0.05\ \mathrm{L/min})\ t$

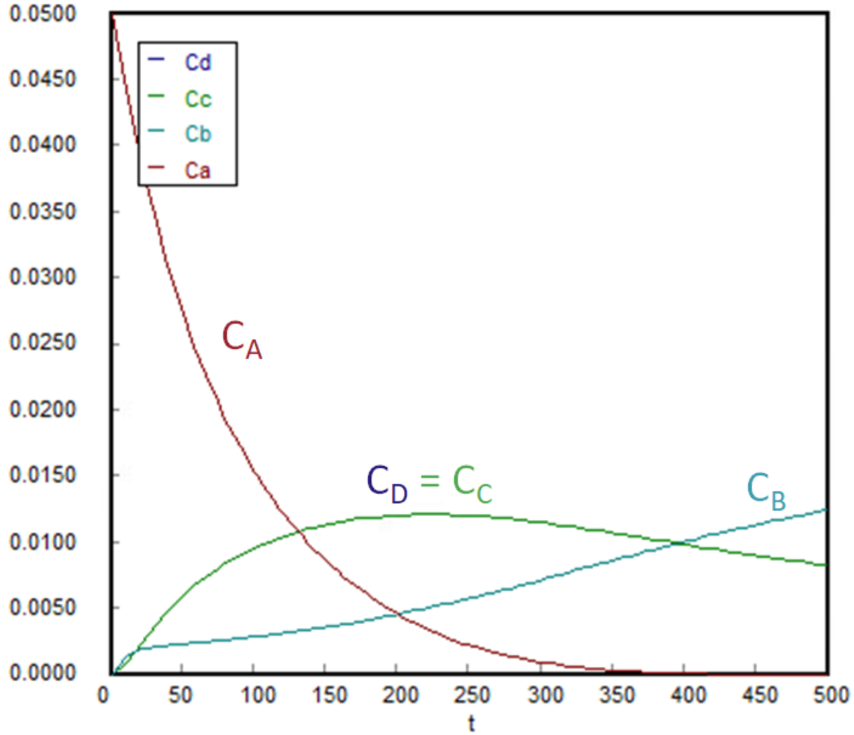
Plotting semi-batch solution in Polymath (see video)



Maximum in product?

No A to react, and still diluting with B!

Why semi batch?



Control the concentrations rather than loading all in at once

Temperature (lower rate if necessary)

Selectivity (more when we discuss multiple reactions)

Next Thursday: Membrane reactors