ChE 344
Reaction Engineering and Design

Lecture 10: Thursday, Feb 10, 2022

Selectivity, membrane reactors

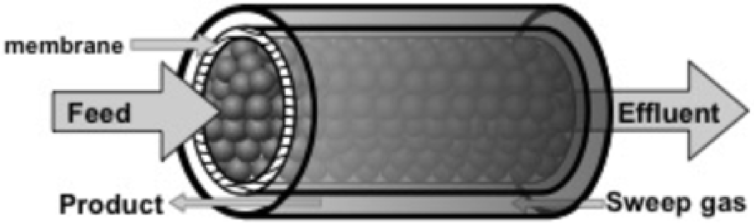
Reading for today’s Lecture: Chapter 6.4 (also 6.1-6.3)

Reading for Lecture 11: Chapter 7

Lecture 10: Selectivity, Membrane Reactors

Related Text: Chapter 6.4

Membrane reactors allow us to control the addition or removal of a specific species, which is sometimes useful to try and get out of limitations from equilibrium:



We model the flow of a species *j* through the side walls of the membrane reactor:

$$R_j = k_C\left(C_j - C_{j,sweep}\right)$$

- R_j is the molar rate of flux of species j per unit volume reactor [=] mol volume^{-1} time^{-1}
- k_C is the mass transfer coefficient [=] time^{-1}
- $C_{j,sweep}$ is the concentration of *j* in the sweep gas (outside the reactor). Often assume as 0.

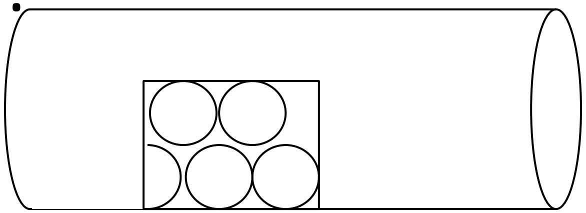
R_j is the term for flux through the membrane per volume reactor, but we can convert it to flux per weight of catalyst by using the catalyst bed density (**$R_j' = R_j\rho_{bed}^{-1}$**). This is similar to the difference between r_j and r_j' for PFRs/PBRs. You can tell which it is by the units given.

Because membrane reactors involve this additional removal term that PFRs or PBRs do not have, we cannot solve them in terms of conversion, and will instead need to use our molar flow balance equations.

So for a reaction $A \rightarrow B + C$ that is gas-phase, isothermal, and elementary as written in a PBR, but the membrane is permeable only to B, with extremely high volumetric flow rate sweep gas:

Mole Balance	$r_A' = \frac{dF_A}{dW};\ r_B' - R_B\rho_{bed}^{-1} = \frac{dF_B}{dW};\ r_C' = \frac{dF_C}{dW}$
Rate Law/Membrane Flux	$r = -r_A = r_B = r_C = kC_A;\ R_B = k_C(C_B - 0)$
Stoichiometry	$C_j = \frac{F_j}{v}$ $F_T = F_A + F_B + F_C$
Match/combine	$v = v_0\left(\frac{F_T}{F_{T0}}\right)\left(\frac{T}{T_0}\right)\left(\frac{1}{p}\right)$ $\frac{dp}{dW} = -\frac{\alpha}{2p}\left(\frac{F_T}{F_{T0}}\right)\frac{T}{T_0}$
Evaluate	Solve system of equations (usually numerically).

What do we have control over for controlling pressure drop in a packed bed reactor?



Catalyst pellet/particle size can be varied to modify Ergun equation constants. A_{CS} as well, but usually practical reasons not to (channeling and heat exchange)

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

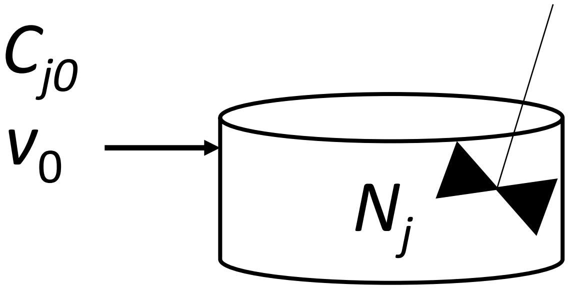
Laminar Turbulent

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

Smaller α, less pressure drop

$$\frac{dp}{dW} = -\frac{\alpha}{2p}\frac{T}{T_0}(1+\varepsilon X)$$

Last time, **semi-batch** reactors (liquid phase)



Initial conditions (t=0)

$$V = V_0$$

$$N_j = N_j(t = 0)$$

At some time t

$$V = V_0 + v_0 t$$

$$C_j = \frac{N_j}{V}$$

Definitions:

V_0 is **initial** 'reactor' volume (t = 0)

C_{ji} or $C_j(t = 0)$ is initial concentration

C_j is concentration in reactor at time t

V is volume of reactor at time t

v_0 is **inlet** vol. flow rate

C_{j0} is inlet conc.

F_{j0} is inlet molar flow rate

Conversion of limiting reactant A

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

Discuss with your neighbors:

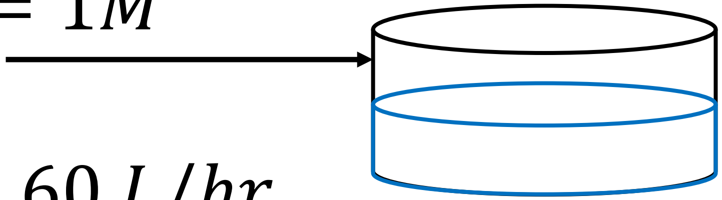
For a constant density liquid phase semi-batch reactor:

What is the conversion after ten minutes?

$C_{B0} = 1M$

No A

$v_0 = 60\ L/hr$



$C_A(t = 0) = 1M$

$C_A(t = 10\ min) = 0.5M$

$V_0 = 10\ L$

[✓ A) X = 0]

B) X = 0.5

C) X = 1

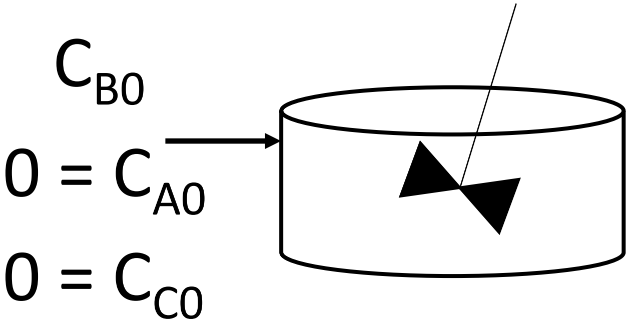
D) X = 0.75

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

From mole balance we'd know C_B(t=10 min) also 0.5 M.

Different forms of semi-batch design equation for example reaction:

$$2A + B \rightarrow C$$



C_{B0}

$0 = C_{A0}$

$0 = C_{C0}$

Mole

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

$$\frac{dN_B}{dt} = F_{B0} + r_B V$$

$$\frac{dN_C}{dt} = r_C V$$

Concentration

$$\frac{dC_A}{dt} = r_A - C_A \frac{v_0}{V}$$

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

$$\frac{dC_C}{dt} = r_C - C_C \frac{v_0}{V}$$

Conversion*

$$\frac{dX}{dt} = \frac{-r_A V}{N_A(t=0)}$$

Use rate law, stoichiometry, and combine/evaluate to solve

Discuss with your neighbors:

The elementary liquid reaction A + B $\rightarrow$ C + D is to be carried out with equimolar amounts of A and B.

Process 1: A and B loaded into a batch reactor.

Process 2: A is loaded into the reactor and B is fed in a semi-batch mode.

In both processes, the same amount of A and B are reacted, 90% conversion is reached, and the final volume of fluid in the reactor is the same. Which process takes less time?

[✓ A) Batch]

B) Semi-batch

C) Time will be the same

D) None of the above

Initial (t=0) rate in semi-batch is zero!

No B present to react until it is fed in

$$-r_A = kC_AC_B$$

Why use semi batch?

If using semi-batch means a lower concentration of B to begin, why would we run a reaction in semi-batch mode?

- Control the concentrations rather than loading all at once
- Control the temperature (lower rate if necessary)
- Control the selectivity of the reactions

Multiple reactions are possible (in almost all real cases)

Desired product

$$A + B \xrightarrow{k_1} D$$

$$$

Undesired product

$$A + 2B \xrightarrow{k_2} U$$

☠

Could also be

$$A + B \xrightarrow{k_1} D$$

$$D + B \xrightarrow{k_2} U$$

$$Selectivity \equiv S_{D/U} = \frac{r_D}{r_U} \ or \ \tilde{S}_{\frac{D}{U}} = \frac{F_D}{F_U} \ or \ \frac{N_D}{N_U}$$

Instant (rates) or overall (flow rates/moles) selectivity

$$Yield \equiv Y_{\frac{D}{A}} = -\frac{r_D}{r_A} \ or \ \tilde{Y}_{D/A} = \frac{F_D}{F_{A0} - F_A} \ or \ \frac{N_D}{N_{A0} - N_A}$$

Selectivity and yield can affect the choice of reactor:

We know that usually rate ∝ C_j^{α}

So for instantaneous selectivity (relative rates) for the following two elementary reactions:

$$A + B \overset{k_1}{\rightarrow} D \qquad A + 2B \overset{k_2}{\rightarrow} U$$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2}\frac{C_A {C_B}^1}{C_A {C_B}^2} = \frac{k_1}{k_2}{C_B}^{-1}$$

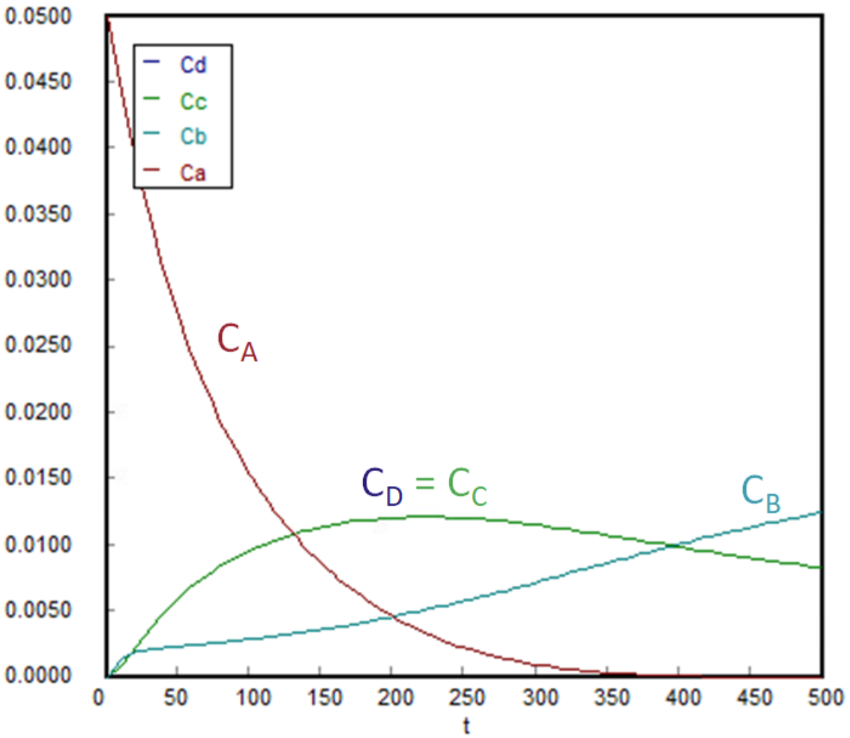
To get higher rates for desired product: Maximize C_A, C_B

1. Use a PFR for flow (higher C_A, C_B on average than CSTR)
2. $C_j = P_j/RT$, so operate at high pressure
3. Batch reactor
4. Do not use diluents

To get higher selectivity for D over U want to:

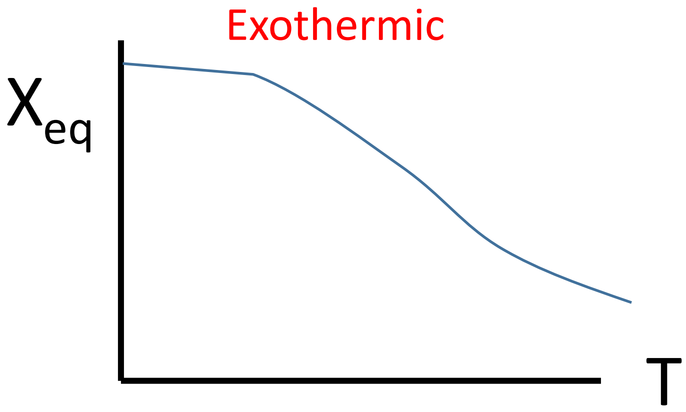
Minimize C_B

1. Use a CSTR (all is at the outlet concentration)
2. Maintain low pressure
3. Use diluents
4. Semi-batch reactor with B fed in



Membrane reactors for thermodynamically limited reactions

If our goal is to increase our reactor yield…



↑ T, ↑ k, but ↓ X_{eq}

↓ T, ↓ k, but ↑ X_{eq}

$$C_6H_{12} \rightleftarrows C_6H_6 + 3H_2$$

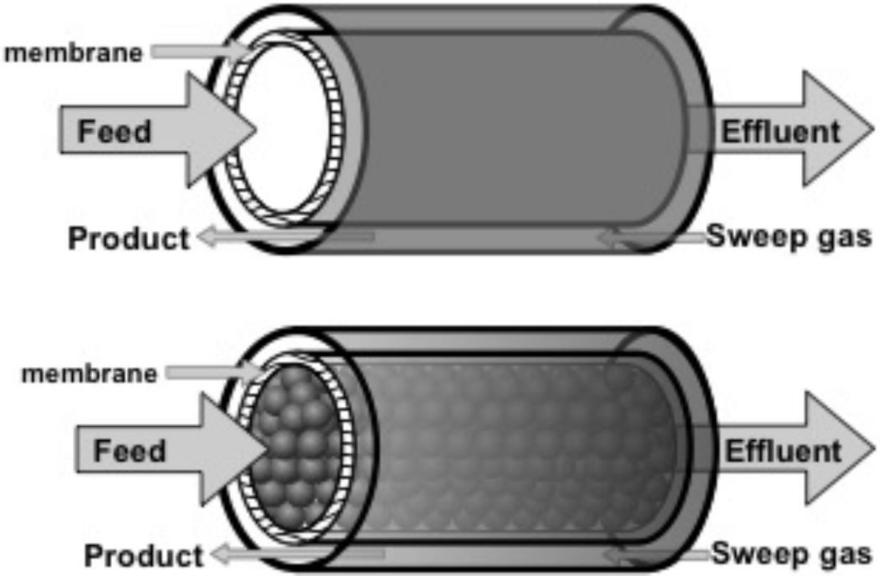
$$A \overset{\longrightarrow}{\cancel{\longleftarrow}} B + 3C$$

Remove C

How can we do this? If we have a membrane that can transport C, but not A or B

PFR

PBR



Membrane reactor

Sweep products away to go ‘beyond’ equilibrium.

How can we model this reactor?

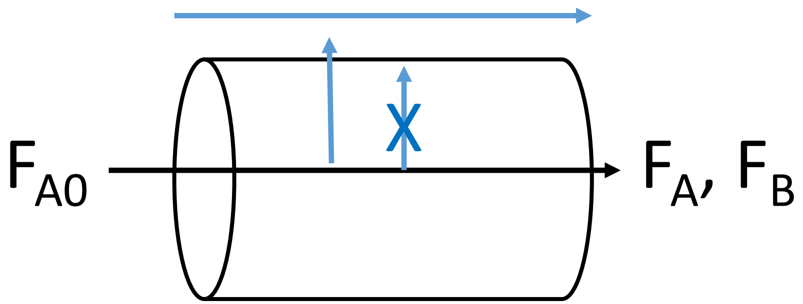
Start with general mole balance:

$$\text{In} - \text{Out} + \text{Gen} = \cancelto{0}{\text{Accumulation}}$$

Steady state operation

$$\text{In} - \text{Out} - \text{Out}_{\text{membrane}} + \text{Gen} = 0$$

Let's consider a reaction $A \rightarrow B$ and reactor with a membrane where B can pass through, but A cannot.



Mole balance on A will be the same as we have been using for a PFR/PBR:

$$F_{A0} - F_A + \int r_A dV = 0 \qquad F_{A0} - F_A + \int r_A' dW = 0$$

PFR/PBR design equations in terms of molar flow for A:

$$\frac{dF_A}{dV} = r_A \qquad \frac{dF_A}{dW} = r_A'$$

Mole balance on B will have the additional 'out' term for molar flow through the membrane

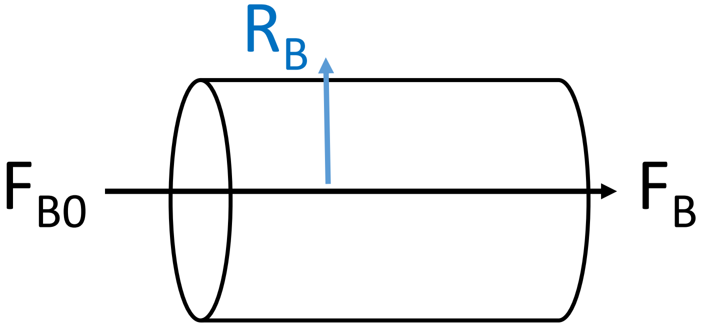
$$F_{B0} - F_B - F_{B,membrane} + \int r_B \, dV = 0$$

$$R_B \equiv \frac{F_{B,membrane}}{\Delta V} = \frac{\text{moles of B through sides/time}}{\text{volume of reactor}}$$

$$\frac{dF_B}{dV} = r_B - R_B$$

New term from B leaving through membrane

Note: R_B is written so that a positive value means exiting reactor, but R_B could also be negative (feeding in through side)



The molar flow out of the membrane will be related to the surface area of the membrane (surface area of cylinder):

$$W_B = k'_C\left(C_B - C_{B,sweep}\right) = \frac{\text{molar flow rate through membrane}}{\text{surface area of membrane}}\left[\frac{mol}{m^2 s}\right]$$

$$F_{B,membrane} = W_B \pi D \Delta L = k'_C\left(C_B - C_{B,sweep}\right)\pi D \Delta L$$

$$R_B \equiv \frac{F_{B,membrane}}{\Delta V}$$

$$a = \frac{\pi D L}{\frac{\pi D^2}{4} L} = \frac{4}{D} = \frac{\text{membrane surface area}}{\text{reactor volume}}\left[\frac{m^2}{m^3}\right]$$

$$k_C \equiv k'_C a$$

$$R_B = W_B a = k'_C a\left(C_B - C_{B,sweep}\right)$$

$$R_B = k_C\left(C_B - C_{B,sweep}\right)$$

If flow rate of inert sweep gas is sufficiently high,

$C_{B,sweep} \approx 0$

$$R_B = k_C C_B$$

k_C mass transfer coefficient wrt $V_{reactor}$, here units 1/time

A note on conversions for semi-batch and membrane reactors where species are being removed or added:
Although you can define conversions for these systems, often it is simpler just to solve the problems in terms of molar flow rates/concentrations (like we did for semi-batch).

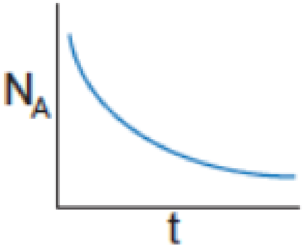
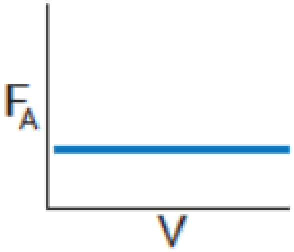
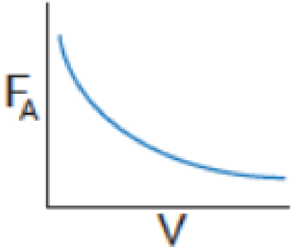
This is even more true for multiple reactions, which we will be treating in greater detail next Thursday (Lecture 12).

$$A + B \overset{k_1}{\rightarrow} D$$

$$A + 2B \overset{k_2}{\rightarrow} U$$

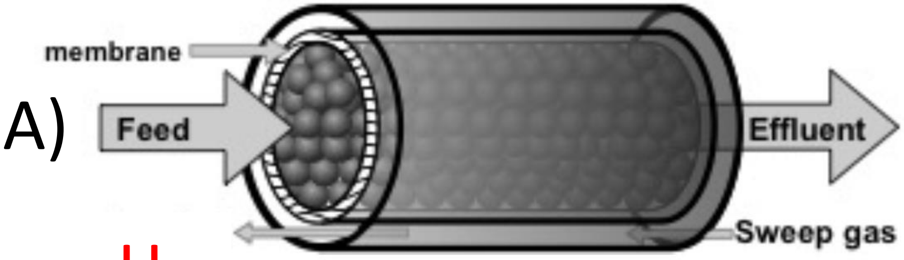
Just thinking of conversion of A, does it go D? Or U?

Chapter 1 Reminder: Reactor Mole Balances/Design Eqs

Reactor	Assumptions	Mole Balance	Reactant Profile
Batch	Spatially uniform, no inlet/outlet streams	$r_j V = \frac{dN_j}{dt}$	
CSTR	Spatially uniform, steady state	$V = \frac{F_j - F_{j0}}{r_j}$	
PFR	No radial variation, steady state	$r_j = \frac{dF_j}{dV}$	
PBR	W is catalyst weight $W = V\rho_{bed} = V\rho_c(1-\phi_b)$	$r_j' = \frac{dF_j}{dW}$	

Example problem: Membrane reactor, isothermal, gas-phase but no pressure drop. Membrane is permeable to H_2 only. Elementary as written, and only A is fed into the reactor.

C_6H_{12} (A)



C_6H_6 (B) + H_2 (C)

H_2


Never ever forget pressure drop in a gas phase reaction.

$$C_6H_{12} \rightleftarrows C_6H_6 + 3H_2$$

$$A \rightleftarrows B + 3C$$

Remove C

Need to work out with our molar flow rates F_A, F_B, F_C:

$$r_A' = \frac{dF_A}{dW};\ r_B' = \frac{dF_B}{dW};\ \frac{dF_C}{dW} = r_C' - R_C \boldsymbol{\rho}_{\boldsymbol{bed}}^{-1} = r_C' - (k_C C_C)\boldsymbol{\rho}_{\boldsymbol{b}}^{-1}$$

$$r_A = \rho_b r_A'$$

Derivation for PBR membrane design equation

PFR + Membrane Design equation: $$\frac{dF_C}{dV} = r_C - R_C$$

Definitions:

$$W = V\rho_{bed} = V\rho_c(1-\phi_b) \qquad r_C = \rho_b r_C'$$

$$\frac{dW}{dV} = \rho_{bed} \equiv \rho_b$$

Rearranging:

$$\frac{dF_C}{dV} = \frac{dF_C}{dW}\frac{dW}{dV} = \frac{dF_C}{dW}\rho_b \qquad r_C - R_C = \rho_b r_C' - \frac{\rho_b}{\rho_b}R_C$$

$$\frac{dF_C}{dW}\rho_b = \rho_b r_C' - \frac{\rho_b}{\rho_b}R_C$$

$$\frac{dF_C}{dW} = r_C' - \frac{1}{\rho_b}R_C$$

Rate law (for elementary, reversible reaction): $A \rightleftarrows B + 3C$

$$\boldsymbol{r} = -r_A' = k\left[C_A - \frac{C_B C_C^3}{K_C}\right]$$

$$\frac{r_A'}{-1} = \frac{r_B'}{+1} = \frac{r_C'}{+3}$$

Stoichiometry: Recall definitions (here not using conversion, but same concept). Here we have isothermal, no pressure drop reactor.

$$C_A = \frac{P_0}{RT_0}\frac{F_A}{F_T} \qquad C_B = \frac{P_0}{RT_0}\frac{F_{\boldsymbol{B}}}{F_T} \qquad C_C = \frac{P_0}{RT_0}\frac{F_{\boldsymbol{C}}}{F_T}$$

$$F_T = F_A + F_B + F_C$$

Can solve using Polymath if we have some parameters

$C_{total,0} = P_0/(RT_0) = 0.2\ \text{M}$

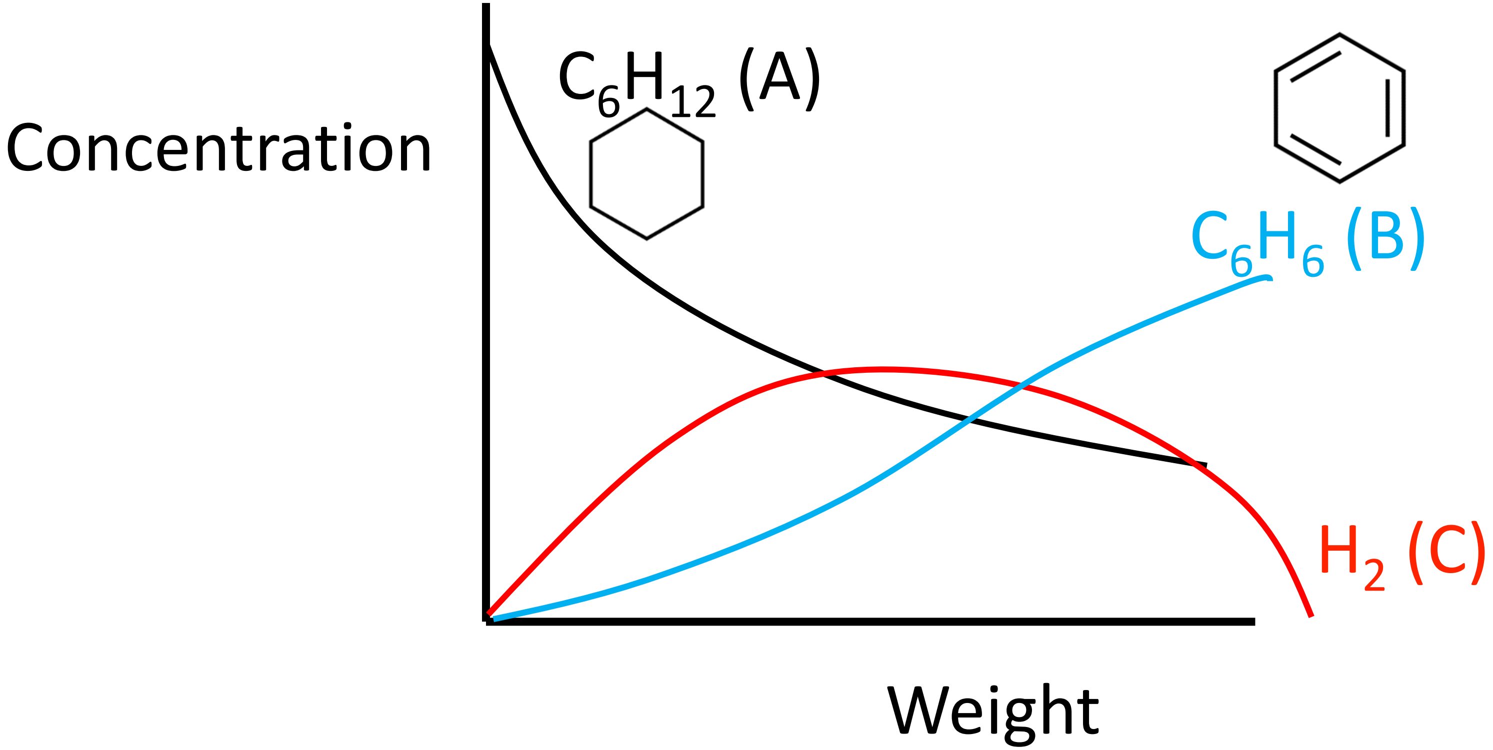
$k = 10\ \text{L kg}_{cat}^{-1}\ \text{s}^{-1}$

$F_{A0} = 10\ \text{mol/s}$

$K_C = 200\ \text{M}^2$ Equilibrium constant!

k_C Mass transfer constant

$k_C \boldsymbol{\rho_b^{-1}} = 0.5\ \text{L kg}_{cat}^{-1}\ \text{s}^{-1}$



Polymath code tip if you need to change a variable between two different values

```
v0 = if(t<1) then (1) else (0)
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