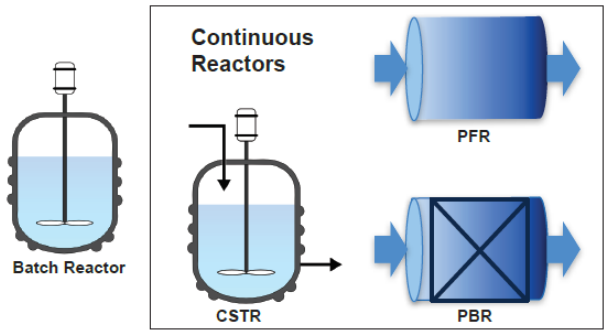
Lecture 1: Introduction and Moles Balances
Related Text: Syllabus, Chapter 1

Main Reactor Types

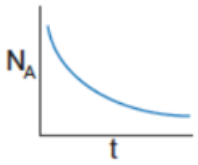
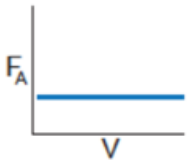
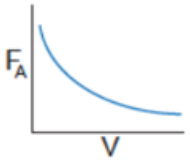


$$F_j = C_j v$$

General mole balance

$$F_{j0} - F_j + \int_0^V r_j dV = \frac{dN_j}{dt}$$

Mole balances (aka Design Equations) for reactor types (actually covered in Lecture 2, here for space purposes)

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	$r_j = \frac{dF_j}{dV}$	
Modifications for solid catalyst loading*			
PBR	Same as PFR, plus uniform catalyst	$r_j' = \frac{dF_j}{dW}$	
Fluidized CSTR**	Same as CSTR, plus uniform catalyst	$W = \frac{F_j - F_{j0}}{r_j'}$	

*$W = \rho_b V$. $r_j' \rho_b = r_j$.

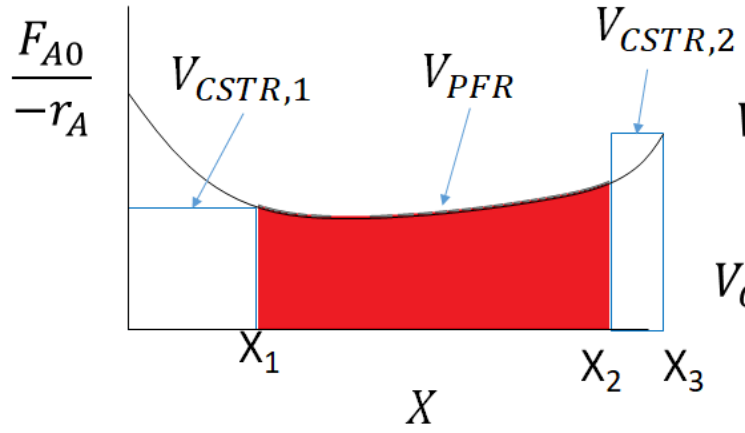
**Not covered specifically in class, but same concept as PFR/PBR relationship.

Lecture 2: Reactor Sizing Using Conversion
Related Text: Chapter 2

If there is only one significant reaction, and A is the limiting reactant we can use conversion.

Reactor	Conversion Definition	Mole balance	Mole Balance (aka Design Equation)
Batch	$X = \frac{N_{A0} - N_A}{N_{A0}}$	$N_A = N_{A0}(1 - X)$	$\frac{dX}{dt} = -\frac{r_A V}{N_{A0}}$
CSTR	$X = \frac{F_{A0} - F_A}{F_{A0}}$	$F_A = F_{A0}(1 - X)$	$V_{CSTR} = \frac{F_{A0}(X_{out} - X_{in})}{-r_A}$
PFR	$X = \frac{F_{A0} - F_A}{F_{A0}}$	$F_A = F_{A0}(1 - X)$	$V_{PFR} = \int_{X_{in}}^{X_{out}} \frac{-F_{A0}}{r_A} dX$
PBR	Same as PFR, plus uniform catalyst	$r_j' = \frac{dF_j}{dW}$	$W_{PBR} = \int_{X_{in}}^{X_{out}} \frac{-F_{A0}}{r_A'} dX$

Levenspiel Plots:



$$V_{PFR} = \int_{X_{in}}^{X_{out}} \frac{-F_{A0}}{r_A} dX$$

$$V_{CSTR} = \frac{F_{A0}(X_{out} - X_{in})}{-r_A}$$

Lecture 3: Introduction to Rate Laws
Related Text: Chapter 3

Space time: $\frac{V}{v_0} = \tau$; Space velocity = $\frac{1}{\tau}$

Reaction orders (overall reaction order determines units of rate constant)

$$-r_A = kC_A^{\alpha}C_B^{\beta}; n = \alpha + \beta$$

Elementary Rate Laws

Powers in the rate law agree with magnitude of stoichiometric coefficient of the reaction as written.

$$aA + bB \rightarrow C; \frac{-r_A}{a} = kC_A^a C_B^b$$

Relative rates (true even if the reaction is not elementary)

$$aA + bB \rightarrow cC + dD$$

$$\frac{r_j}{v_j} = r; r = \frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}$$

v_j is the stoichiometric coefficient of species j. It is positive if j is a product, and negative if j is a reactant. For example, if the reaction is elementary 'as written' above:

$$r = \frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d} = kC_A^a C_B^b$$

Temperature dependence of rate constant (Arrhenius equation)

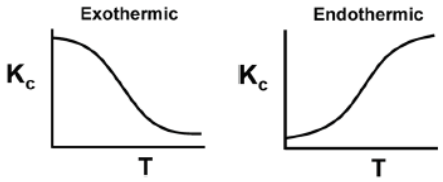
$$k(T) = A\exp\left(-\frac{E_a}{RT}\right) \qquad \text{or} \qquad k(T) = k(T_1)\exp\left(\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right)$$

Arrhenius plot: $\ln(k) = \ln(A) - \frac{E_a}{R}\frac{1}{T}$

Temperature dependence of concentration equilibrium constant

$$K_C(T) = K_C(T_1)\exp\left[-\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)\right]$$

Equilibrium constant can tell you whether a reaction is irreversible (→) or reversible (⇄).



Where do rate laws come from? (not covered in Lecture 3)

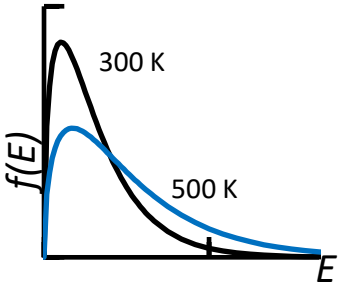
Collision theory: Frequency of collisions qualitatively gives you the frequency factor/pre-exponential factor for Arrhenius equation, and the concentration dependence (reaction orders).

Maxwell-Boltzmann distribution gives you the probability of a collision having a certain energy.

$$f(E,T)dE = \frac{2\pi}{(\pi RT)^{3/2}}\exp\left[\frac{-E}{RT}\right]E^{1/2}dE$$

The integral of the probability gives you the fraction of collisions with energy above some threshold energy (E_a).

$$F(E > E_a, T) = \int_{E_a}^{\infty} f(E,T)dE = \frac{2}{\sqrt{\pi}}2\left(\frac{E_a}{RT}\right)^{1/2}\exp\left[\frac{-E_a}{RT}\right]$$



The exp $\left[\frac{-E_a}{RT}\right]$ is where the exponential portion in the Arrhenius equation comes from! At higher temperatures, a higher fraction of molecular collisions have higher kinetic energies.

Lecture 4: Stoichiometry and relation of concentration to conversion
Related Text: Chapter 4.1-4.2

Variables

For a reaction with A as the limiting reactant:

$$aA + bB \longrightarrow cC + dD$$

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

$$\delta = \frac{\text{change in number of moles with reaction}}{\text{moles A reacted}} = \frac{c + d - b - a}{a}$$

$$y_{A0} \equiv \frac{P_{A0}}{P_0} = \frac{N_{A0}}{N_{T0}} = \frac{F_{A0}}{F_{T0}}$$

$$\varepsilon = y_{A0}\delta$$

$$\theta_j = \frac{\text{initial/inlet number of moles "j"}}{\text{initial/inlet number of moles "A"}} = \frac{N_{j0}}{N_{A0}} = \frac{F_{j0}}{F_{A0}} = \frac{C_{j0}}{C_{A0}} = \frac{y_{j0}}{y_{A0}}$$

Stoichiometry Tables (for A as limiting reactant)

Batch

Species	Symbol	Initial	Change	Remaining
Reactant A	A	N_{A0}	$-N_{A0}X$	$N_A = N_{A0}(1-X)$
Reactant B	B	$N_{A0}\Theta_B$	$-b/a\ N_{A0}X$	$N_B = N_{A0}(\Theta_B - b/a\ X)$
Product C	C	$N_{A0}\Theta_C$	$+c/a\ N_{A0}X$	$N_C = N_{A0}(\Theta_C + c/a\ X)$
Product D	D	$N_{A0}\Theta_D$	$+d/a\ N_{A0}X$	$N_D = N_{A0}(\Theta_D + d/a\ X)$
Inert	I	$N_{A0}\Theta_I$		$N_{A0}\Theta_I$
Total		N_{T0}		$N_T = N_{T0}(1+\varepsilon X)$

Flow

Species	Symbol	Inlet	Change	Outlet
Reactant A	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
Reactant B	B	$F_{A0}\Theta_B$	$-b/a\ F_{A0}X$	$F_B = F_{A0}(\Theta_B - b/a\ X)$
Product C	C	$F_{A0}\Theta_C$	$+c/a\ F_{A0}X$	$F_C = F_{A0}(\Theta_C + c/a\ X)$
Product D	D	$F_{A0}\Theta_D$	$+d/a\ F_{A0}X$	$F_D = F_{A0}(\Theta_D + d/a\ X)$
Inert	I	$F_{A0}\Theta_I$		$F_{A0}\Theta_I$
Total		F_{T0}		$F_T = F_{T0}(1+\varepsilon X)$

For gas-phase, volume can change. No change in volume for liquid!

$$V = V_0 \frac{N_T}{N_{T0}} \frac{T}{T_0} \frac{P_0}{P};\ v = v_0 \frac{F_T}{F_{T0}} \frac{T}{T_0} \frac{P_0}{P};\ C_A = C_{A0} \frac{(1-X)}{1+\varepsilon X} \frac{T_0}{T} \frac{P}{P_0};\ C_j = C_{A0} \frac{(\theta_j - \frac{\nu_j}{\nu_A}X)}{1+\varepsilon X} \frac{T_0}{T} \frac{P}{P_0}$$

In the final equation, for C_j, remember if we write the reaction in terms of limiting reactant A, $\nu_A = -1$.

Lecture 5: Stoichiometry and equilibrium conversion for reversible reactions
Related Text: Chapter 4.3

Reminder: Reversible reactions

$$2A + B \rightleftarrows 3C$$

Two rate constants, k_f (forward rate constant) and k_r (reverse rate constant). For elementary reaction:

$$-\frac{r_A}{2} = -r_B = \frac{r_C}{3} = k_f C_A^2 C_B - k_r C_C^3 = k_f \left[C_A^2 C_B - \frac{C_C^3}{K_C} \right]$$

Please note that when we say it is elementary, that is referring to how the reaction is originally written ($2A + B \rightleftarrows 3C$), including the stoichiometric coefficients as written. If you rewrite the reaction to be in terms of a limiting reactant, that would not change the rate law. For example, if we were to take the elementary reaction above and rewrite it as ($A + \frac{1}{2}B \rightleftarrows \frac{3}{2}C$), the rate law is **still**:

$$-\frac{r_A}{2} = -r_B = \frac{r_C}{3} = k_f C_A^2 C_B - k_r C_C^3$$

because it was elementary for the originally written reaction.

Concentration equilibrium constant:

$$K_C = \frac{k_f}{k_r} = \frac{C_{C,eq}^3}{C_{A,eq}^2 C_{B,eq}}$$

Equilibrium conversion

For irreversible reactions, conversion will go to 1, but for reversible reactions it goes to X_{eq}. We can determine this conversion if we know the concentration equilibrium constant. From last lecture for a gas-phase reaction where volume changes:

$$C_j(X) = C_{A0} \frac{(\theta_j - \frac{\nu_j}{\nu_A} X)}{1 + \varepsilon X} \frac{T_0}{T} \frac{P}{P_0}$$

This is a more general form of what we wrote in class, when we used terms like (-b/a) in the numerator instead of $-\frac{\nu_j}{\nu_A}$. Remember ν_j is the stoichiometric coefficient of species *j*. The symbol here is a "nu". I don't use it in class unless necessary because it looks very similar in writing to a *v* (which we use for volumetric flow rate). They are two different things! An example of the concentration of B for $A \rightleftarrows B$:

$$C_B(X) = C_{A0} \frac{\left(\theta_B - \frac{\nu_B}{\nu_A} X\right)}{1 + \varepsilon X} \frac{T_0}{T} \frac{P}{P_0} = C_{A0} \frac{\left(\theta_B - \frac{+1}{-1} X\right)}{1 + \varepsilon X} \frac{T_0}{T} \frac{P}{P_0} = C_{A0} \frac{(\theta_B + X)}{1 + \varepsilon X} \frac{T_0}{T} \frac{P}{P_0}$$

Equilibrium is where the net rate of reaction is zero. We can use that along with the concentrations as a function of conversion to solve for X_{eq}. For instance:

$$K_C = \frac{\left(C_C(X_{eq})\right)^3}{\left(C_A(X_{eq})\right)^2 C_B(X_{eq})}$$

Equilibrium conversion (for the same K_C) can change if volume varies (gas-phase), so long as there is a change in stoichiometry of the reaction (i.e., $\delta \neq 0$).

Lecture 6: Isothermal reactor design
Related Text: Chapter 5.1-5.4

The order we will solve problems:

0. Assumptions
1. Mole Balance: Reactor design equation for the selected reactors
2. Rate Law: To get reaction rate as a function of rate constant and concentrations
3. Stoichiometry: To get concentration as a function of conversion
4. Combine: Parts 1-3
5. Evaluate: Use values to get numerical answer

Concept of pseudo-orders:

If a concentration does not change significantly with conversion then we can in some cases approximate it as constant. For example if B is in large excess compared to A such that C_B remains constant with conversion (here for liquid reaction).

$$-r_A = kC_BC_A \approx kC_{B0}C_A = kC_{B0}C_{A0}(1-X) = k'C_{A0}(1-X)$$

where $k' \equiv kC_{B0}$. k' is a pseudo-first order rate constant here.

Recall space time:

$$\frac{V}{v_0} = \tau$$

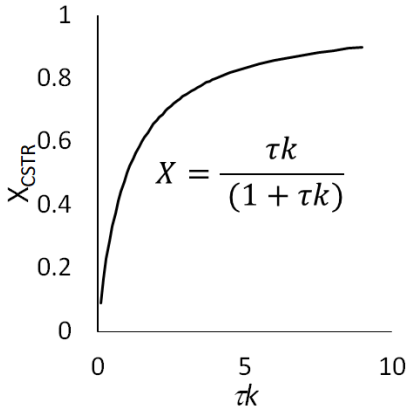
For first order (or pseudo first-order) reactions we get out a term that is called the Damköhler number, or Da_1, which is the ratio of the reaction rate to convection rate).

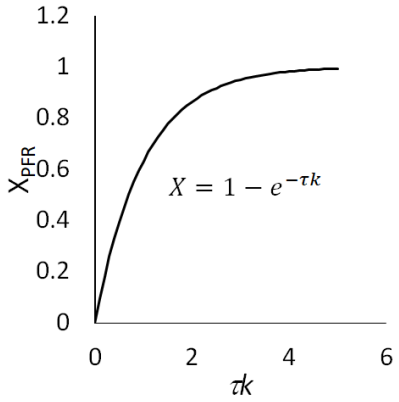
$$Da_1 = k\tau$$

This shows up in the solution for the first order PFR and CSTR:

$$X_{CSTR} = \frac{\tau k}{(1+\tau k)}$$

$$X_{PFR} = 1 - e^{-\tau k}$$





Lecture 7: Isothermal reactor design – Reactors in series
Related Text: Chapter 5.1-5.4

For reactors in series with only one reaction we will use the same design equations we were introduced to when we discussed Levenspiel plots (see Lecture 2). However, now we will need to solve the equations rather than having a generated Levenspiel plot already.

We will define the conversion based on the feed to the first reactor (this is the way we were defining it for Levenspiel plots).

$$X = \frac{moles\ A\ reacted\ at\ a\ point\ along\ the\ reactor\ series}{moles\ A\ fed\ to\ the\ initial\ reactor}$$

For a CSTR when we can solve with X (single reaction, etc.):

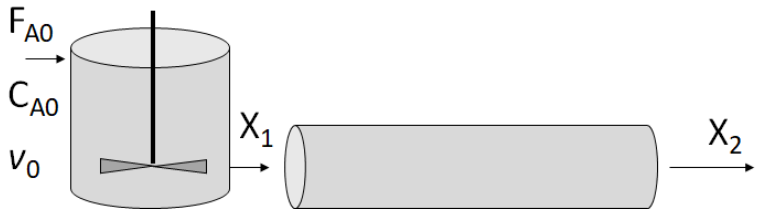
$$V = \frac{F_{A0}(X_{out} - X_{in})}{(-r_A)_{out}}$$

For a PFR when we can solve with X:

$$V = \int_{X_{in}}^{X_{out}} \frac{F_{A0}dX}{-r_A}$$

You could also redefine the conversion for each reactor, then at the end determine the overall conversion (not recommended, but technically can also be correct).

Example: CSTR first, followed by a PFR.



Solving for X_1 for the CSTR. Here $X_{in,CSTR} = 0$ and $X_{out,CSTR} = X_1$.

$$V_{CSTR} = \frac{F_{A0}(X_{out} - X_{in})}{(-r_A)_{out}} = \frac{F_{A0}(X_1)}{(-r_A)_{at\ X_1}}$$

Use this mole balance, rate law, and stoichiometry to solve for X_1. Recall for CSTR that $-r_A$ is evaluated at the conversion at the outlet (X_1) since the reactor is well-mixed.

Next, solving for the PFR. Here $X_{in,PFR} = X_1$ and $X_{out,PFR} = X_2$.

$$V = \int_{X_{in}}^{X_{out}} \frac{F_{A0}dX}{-r_A} = \int_{X_1}^{X_2} \frac{F_{A0}dX}{-r_A}$$

For the PFR r_A is a function of the conversion, which is changing through the reactor, but we are looking for X_2.

Lecture 8: Isothermal reactor design – Pressure drop
Related Text: Chapter 5.5-5.6

Pressure drop definition:

$$\Delta P = P_0 - P$$

Pressure drop is how much the total pressure decreases from one point in flowing fluid to another. We will only (in this class) model using pressure drop through PBRs (packed bed reactors). We will assume pressure drop (to drive flow) is negligible in pipes, CSTRs, and PFRs.

The **Ergun equation** for gas-phase pressure drop through a packed bed:

$$\frac{dP}{dz} = \frac{-G}{\rho g_c D_P}\left(\frac{1-\phi_b}{{\phi_b}^3}\right)\left[\underbrace{\frac{150(1-\phi_b)\mu}{D_P}}_{Laminar} + \underbrace{1.75G}_{Turbulent}\right]$$

New variables/parameters related to catalyst:

$$\phi_b = \text{porosity of bed} = \frac{\text{volume of void}}{\text{total bed volume}} = \text{void fraction} = \text{vol. for flow[=]unitless}$$

$$\rho_c(1-\phi_b) = \rho_b = (\text{catalyst density})\left(\frac{\text{volume of solid}}{\text{total volume}}\right) = \text{density of bed[=]}\frac{\text{mass}}{\text{volume}}$$

$$D_P = \text{diameter of the catalyst pellet/particle[=]length}$$

New variables/parameters related to fluid:

$$\rho = \text{gas density[=]}\frac{\text{mass}}{\text{volume}}$$

$$G = \rho u = \rho\left(\frac{v}{A_{CS}}\right)[=]\frac{\text{mass}}{\text{area}\cdot\text{time}}$$

$$\mu = \text{fluid viscosity[=]}\frac{\text{mass}}{\text{length}\cdot\text{time}}$$

G is the superficial mass velocity, *u* is the superficial velocity. A_{CS} is the cross sectional area (of the reactor bed).

150 and 1.75 are from empirically fitting.

g_c is a conversion factor (sometimes called gravitational conversion constant) used to convert between mass and force. For example 32.174 lb_m ft s^{-2} lb_f^{-1}.

Often we will rearrange the Ergun equation:

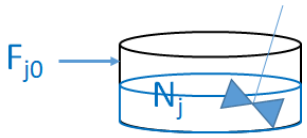
$$\frac{dp}{dW} = -\frac{\alpha}{2p}\frac{T}{T_0}(1+\varepsilon X) = -\frac{\alpha}{2p}\frac{T}{T_0}\frac{F_T}{F_{T0}}$$

$$p \equiv \frac{P}{P_0}[=]\text{unitless};\ \alpha \equiv \frac{2\beta_0}{\rho_c(1-\phi_b)A_{CS}P_0}[=](\text{catalyst mass})^{-1}$$

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

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

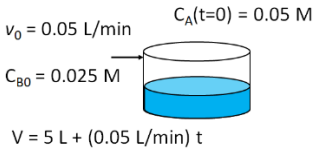
Semi-batch reactors: Liquid phase, feed into the reactor with pre-loaded amount of liquid volume.



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:

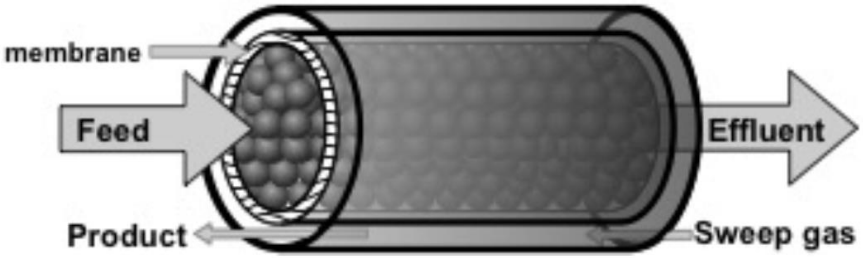
$$X = \frac{C_A(t=0)V_0 - C_A(t)V}{C_A(t=0)V_0} = \frac{N_A(t=0) - N_A}{N_A(t=0)}$$

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)

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 ($R_j' = R_j\boldsymbol{\rho_{bed}^{-1}}$**)**. 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	$\boldsymbol{r} = -r_A = r_B = r_C = kC_A;\ R_B = k_C(C_B - 0)$
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).

Lecture 11: Collecting and Analyzing Rate Data
Related Text: Chapter 7

Thus far we have always assumed we already know the rate law, but sometimes to design a reactor you must first determine the rate law from doing experiments yourself, or interpreting experiments that someone else did.

Steps to deriving kinetic parameters from experimental data.

0. **Gather data**, noting given or assumed knowledge about its collection

1. **Postulate a form of the rate law**. A common form will be a power law expression:

$$r = kC_A^{\alpha} C_B^{\beta}$$

2. **Mole balance on the type of reactor used** (usually either constant volume batch, or differential PFR or PBR).

3. **Process data** in terms of measured variables

4. **Simplify equations** as appropriate for the problem (for example, using method of excess where you assume pseudo-orders).

5. **Calculate rate law** using appropriate methods for your data

i. Integral method, assume a reaction order, solve the design equation and plot your data to see if it matches the expression (useful if you expect whole/integer order dependence on concentration).

ii. Differential method (differentiate the experimental data to allow comparison with a differential rate law). For batch reactors this requires determining $\frac{dC_A}{dt}$ through graphical, numerical, or fitting to a polynomial and taking its derivative wrt time. For example:

$$\ln\left[-\frac{dC_A}{dt}\right] = \ln[-r_A] = \ln[k] + \alpha \ln[C_A]$$

The slope of $\ln\left[-\frac{dC_A}{dt}\right]$ vs. $\ln[C_A]$ will be α **<u>iff</u>** the intercept is constant for all the data. Here that would mean the rate constant *k* would need to be constant, usually by operating at the same temperature.

iii. Non-linear regression. Minimize the difference between your calculated values and the measured values for your proposed rate law and parameters. Use an Excel Solver or regression tool to determine the parameters that give the best fit.

$$s^2 = \sum_{i=1}^{N} \left(t_{i,measured} - t_{i,calculated}\right)^2$$

6. **Check** "goodness of fit", for example through a correlation coefficient. If your rate law cannot fit the data, you may need to propose another rate law, for example in heterogeneous catalysis we often see rate laws of the form:

$$r = \frac{kP_A}{1 + K_A P_A}$$

Lecture 12: Multiple Reactions
Related Text: Chapter 8

Updating the chemical reaction engineering algorithm/menu.

0. Assumptions
- Isothermal?
- Isobaric?
- Rate law elementary as written?

1. Mole balance (for multiple reactions in terms of number of moles or molar flow rates)
Example for packed bed flow reactors with A, B, and C:

$$\frac{dF_A}{dW} = r'_A$$

$$\frac{dF_B}{dW} = r'_B$$

$$\frac{dF_C}{dW} = r'_C$$

2. Rate law(s), for example elementary reactions

$$A \rightarrow B$$
$$A \rightarrow C$$
$$r'_1 = k_1 C_A;\ r'_2 = k_2 C_A$$
$$r'_{1A} = -r'_1;\ r'_{2A} = -r'_2$$
$$r'_{1B} = +r'_1;\ r'_{2B} = 0$$
$$r'_{1C} = 0;\ r'_{2C} = r'_2$$

$$\boxed{r'_A = -k_1 C_A - k_2 C_A}$$
$$\boxed{r'_B = k_1 C_A}$$
$$\boxed{r'_C = k_2 C_A}$$

3. Stoichiometry on molar flow rate or number of moles:

$$C_j = N_j / V$$
$$C_j = F_j / v$$

4. Any remaining required equations? For example, Ergun equation for pressure drop, etc.

5. Combine equations

6. Evaluate

Note: To optimize selectivity, can look at the effect of different parameters on selectivity, for example does increasing the concentration of species *j* increase or decrease selectivity:

$$\left(\frac{dS_{D/U}}{dC_j}\right)_{C_{i\neq j}, T}$$

Lecture 13: Non-isothermal Reactor Design
Related Text: Chapter 11.1-11.4

Due to the strong dependence of the reaction rate on temperature, we need to know how to properly account for temperature change in non-isothermal reactors.

Some key definitions from **thermodynamics**:

$C_{P,i}$ is heat capacity of species *i* (in this class we assume to be constant, and assume no phase changes)

H_i is molar enthalpy of species *i*, in units of J/mol

$$H_i(T) = H_i(T_1) + (T - T_1)C_{P,i}$$

$$\Delta C_P \equiv \sum \nu_i C_{P,i}$$

$$\Delta H_{rxn} = \sum \nu_i H_i$$

For example reaction $aA + bB \rightarrow cC + dD$:

$$\Delta H_{rxn} = -aH_A - bH_B + cH_C + dH_D$$

$$\Delta C_P = -aC_{P,A} - bC_{P,B} + cC_{P,C} + dC_{P,D}$$

The Energy Balance

Open system, sums refer to all species *i* in the reactor.

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

For most chemical reactors (kinetic and potential energy are small, no shear stress):

$$\sum F_{i0} H_{i0} - \sum F_i H_i + \dot{Q} - \dot{W}_s = \frac{d\hat{E}_{sys}}{dt}$$

For systems that can be solved in terms of conversion, X, assuming X = 0 at inlet, and no phase change:

$$F_{A0}\left[\left(\sum -\theta_i C_{P,i}[T - T_0]\right) - \left[\Delta H_{rxn}(T_{ref}) + \Delta C_P(T - T_{ref})\right]X\right] + \dot{Q} - \dot{W}_s = \frac{d\hat{E}_{sys}}{dt}$$

For adiabatic reactors in this class:

- No heat added/removed from reactor
- No shaft work
- Steady state

$$\frac{\left(\sum -\theta_i C_{P,i}[T - T_0]\right)}{\left[\Delta H_{rxn}(T_{ref}) + \Delta C_P(T - T_{ref})\right]} = X$$

Lecture 14: Non-isothermal Reactor Design
Related Text: Chapter 11.1-11.4

Non-isothermal Algorithm:

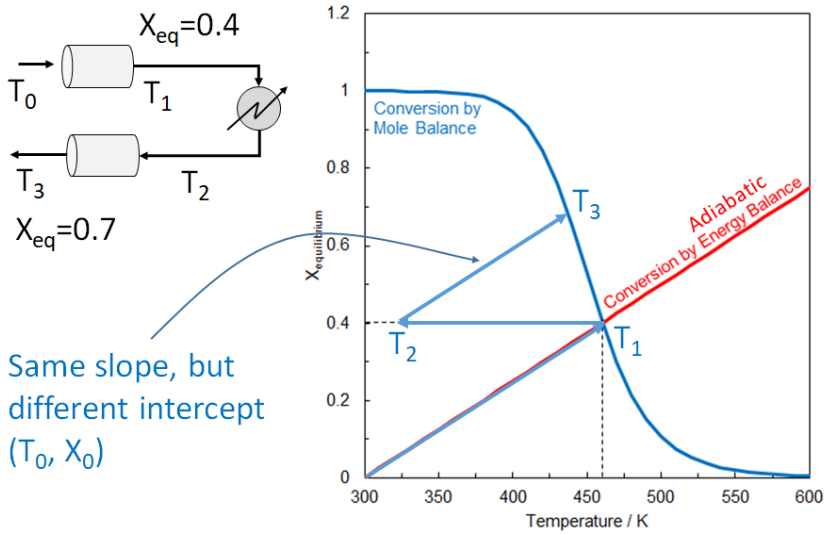
Start with normal algorithm used for isothermal reactors:

0. Assumptions
1. Mole Balance: Reactor design equation for the selected reactors
2. Rate Law: To get reaction rate as a function of rate constant, equilibrium constant (for reversible reactions), and concentrations or pressures
    - K_C(T), k(T)
3. Stoichiometry: Consider gas or liquid phase species.
4. Combine: Parts 1-3
    - If needed, may have to include Ergun equation
5. **Solve with energy balance to relate T and X**
6. Evaluate: Use values to get numerical answer

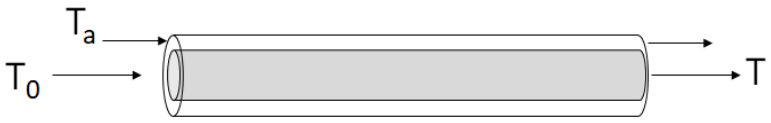
Lecture 15: Non-isothermal Reactor Design
Related Text: Chapter 11.6, 12.1

Interstage heat exchangers

For an exothermic reaction, $A \rightleftarrows B$ we can view the equilibrium conversion vs. the conversion from the adiabatic energy balance. The intercept (T1) is the maximum conversion you can achieve in a single adiabatic reactor. However, by cooling the reactants/products, you can get a higher conversion in a second reactor.



For a heat exchanger coupled with a reactor (PFR)



From PFR energy balance

$$\frac{dT}{dV} = \frac{r_A \Delta H_{rxn} - Ua(T - T_a)}{\sum F_i C_{P,i}} = \frac{r_A \Delta H_{rxn} - Ua(T - T_a)}{F_{A0}\left[\sum \theta_i C_{P,i} + \Delta C_P X\right]} = \frac{Q_g - Q_r}{\sum F_i C_{P,i}}$$

T_a is the temperature of the heat exchanger fluid at volume V.

Q_g is the heat 'generated' by the reaction, and Q_r is the heat 'removed' by the heat exchanger (positive if $T > T_a$, negative if $T < T_a$).

U is the heat transfer coefficient with units of $J/m^2 \cdot s \cdot K$

a is the shape factor, or heat transfer area divided by unit reactor volume.

From PFR mole balance

$$F_{A0}\frac{dX}{dV} = -r_A$$

Can solve this coupled set of equations for PFR design.

Lecture 16: Non-isothermal Reactor Design-PFR with heat exchangers
Related Text: Chapter 12.1-12.2

PFR heat exchanger energy balance on **reactor**

$$\frac{dT}{dV} = \frac{r_A \Delta H_{rxn} - Ua(T - T_a)}{\sum F_i C_{P,i}}$$

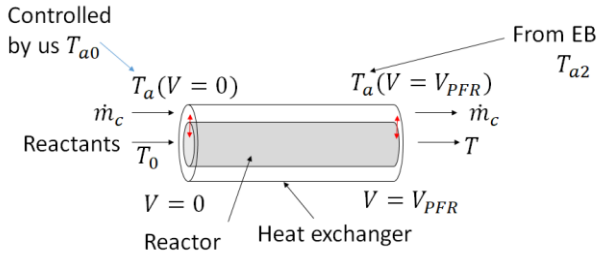
T_a is the temperature of the heat exchanger fluid at volume V.
Q_g is the heat 'generated' by the reaction, and Q_r is the heat 'removed' by the heat exchanger (positive if $T > T_a$, negative if $T < T_a$).
U is the heat transfer coefficient with units of $J/m^2 \cdot s \cdot K$
a is the shape factor, or heat transfer area divided by unit reactor volume.

PBR heat exchanger energy balance

$$\frac{dT}{dW} = \frac{\frac{Ua}{\rho_b}(T_a - T) + r'_A \Delta H_{rxn}}{\sum F_i C_{P,i}}$$

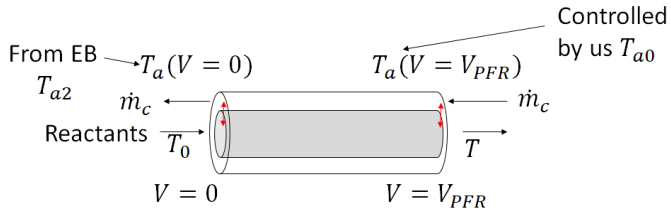
Co-current heat exchanger balance on **heat exchanger fluid**

$$\frac{-Ua(T_a - T)}{\dot{m}_c C_{P,c}} = \frac{dT_a}{dV}$$



Counter-current heat exchanger balance on **heat exchanger fluid**

$$\frac{Ua(T_a - T)}{\dot{m}_c C_{P,c}} = \frac{dT_a}{dV}$$



For counter-current we need to **iteratively solve** by guessing a T_{a2}, then solving for T_{a0} and comparing to our actual T_{a0}, then modifying our T_{a2} guess.

To solve, need to simultaneously solve the coupled i) mole balance equation ii) heat exchanger energy balance on the reactor, iii) energy balance on the heat exchanger fluid.

"Lecture 16-Heat exchanger T profiles.nb" goes through the setup for a zero-order, irreversible reaction.

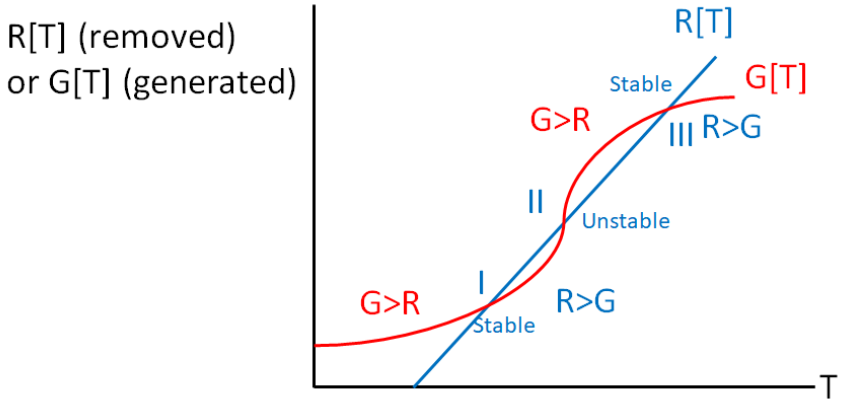
Lecture 17: Non-isothermal Reactor Design-CSTR with heat exchangers + multiple reactions
Related Text: Chapter 12.4-12.6

CSTR with high coolant flow rates:

$$\underbrace{-\left[\Delta H_{rxn}(T_{ref})\right]X}_{Reaction\ heat\ generated=G[T]} = \underbrace{C_{P0}(1+\kappa)(T-T_c)}_{\substack{Heat\ removed\ by:\\ coolant\ and\ reactor\ effluent=R[T]}}$$

$$C_{P0} \equiv \sum \theta_i C_{P,i}\ ;\ \kappa \equiv \frac{UA}{F_{A0}C_{P0}};\ T_c \equiv \frac{\kappa T_a + T_0}{1+\kappa}$$

Steady states are determined when G[T] = R[T].
A steady state is stable if a perturbation from the steady state temperature would force the reactor temperature to go back to the original steady state temperature.



Multiple reactions:
Reaction 1: $A \rightarrow B;\ \Delta H_{rxn,1A} = -10\ kJ/mol\ A$
Reaction 2: $A \rightarrow 2C;\ \Delta H_{rxn,2A} = -15\ kJ/mol\ A$

For PFR: *n* number of reactions, involving some species *j*.

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + \sum_{i=1}^{n} r_{ij}\Delta H_{rxn,ij}}{\sum F_j C_{P,j}}$$

CSTR negligible shaft work, single reaction:

$$\sum -\theta_i C_{P,i}[T - T_0] - \left[\Delta H_{rxn}(T_{ref}) + \Delta C_P(T - T_{ref})\right]X + \frac{UA(T_a - T)}{F_{A0}} = 0$$

If ΔC_P=0 and re-writing without using conversion:

$$\left(\sum -\theta_i C_{P,i}[T - T_0]\right) + \left[\Delta H_{rxn}(T_{ref})\right]\frac{r_A V}{F_{A0}} + \frac{UA(T_a - T)}{F_{A0}} = 0$$

For *n* multiple reactions:

$$\left(\sum -\theta_j C_{P,j}[T - T_0]\right) + \frac{V}{F_{A0}}\sum_{i=1}^{n} r_{ij}\Delta H_{rxn,ij} + \frac{UA(T_a - T)}{F_{A0}} = 0$$

Lecture 18: Non-isothermal Reactor Design-CSTR with heat exchangers + multiple reactions
Related Text: Chapter 12.3, 12.6

Algorithm for solving CSTRs with heat effects with conversion.

If temperature is specified in the problem (recall assumptions necessary):

$$X = \frac{C_{P0}(1+\kappa)(T-T_c)}{-\left[\Delta H_{rxn}(T_{ref})\right]}$$

If conversion is specified in the problem:

$$T = \frac{-\left[\Delta H_{rxn}(T_{ref})\right]X}{C_{P0}(1+\kappa)} + T_c$$

Once you have both T and X, you can solve for the reactor volume using the mole balance equation for a CSTR:

$$V = \frac{F_{A0}X}{-r_A(X, k(T))}$$

If reactor volume is specified in the problem you will need to plot R(T) and G(T) and find intersections, as there may be multiple steady states.

For CSTR with multiple reactions:

Cannot solve with conversion so need mole balance for each individual species. For the energy balance below:

$$\sum -\theta_i C_{P,i}[T-T_0] + \frac{V}{F_{A0}}\sum_{i=1}^{n} r_{ij}\Delta H_{rxn,ij} + \frac{UA(T_a-T)}{F_{A0}} = 0$$

The first term is positive if $T_0 > T$ (feed in is heating up the reactor contents), the third term is positive if $T_a > T$ (heat exchanger fluid is heating the reactor contents). The middle term is positive if the reaction rate of species j is negative and the heat of reaction is negative (exothermic). The middle term is our generation of heat, and the first and last terms are our removal of heat (combined into one for CSTR, as heat can be changed without reaction either by a heat exchanger or by the feed in being different temperature than the reactor/outlet temperature). For large coolant flow rate you may use (see Lecture 17 summary for definitions):

$$R(T) = C_{P0}(1+\kappa)(T-T_c)$$

$$G(T) = \frac{V}{F_{A0}}\sum_{i=1}^{n} r_{ij}\Delta H_{rxn,ij}$$

Example for two reactions:

$$G(T) = \frac{\tau}{C_{A0}}\left(-k_1 C_A \Delta H_{rxn,1A} - k_2 C_B \Delta H_{rxn,\,2B}\right)$$

Lecture 19: Unsteady state reactor energy balance and Safety
Related Text: Chapter 13

Unsteady state operation is a particularly risky portion of operating chemical reactors. It is important to understand the risks involved with loss of temperature control for exothermic reactions which can cause fatal accidents.

As a note, we won't cover unsteady state PFRs/PBRs as they require more complex solvers since the dependent variables depend both on volume (location in reactor) and time.

For a semi-batch or CSTR with no shaft work and a large coolant flow rate such that the heat exchange fluid temperature is constant

$$\frac{dT}{dt} = \frac{\overbrace{(\Delta H_{rxn})(r_A V)}^{\dot{Q}_{gs}} - \left[\overbrace{F_{A0}\sum \theta_i C_{P,i}\,(T - T_0) + \big(UA(T - T_a)\big)}^{\dot{Q}_{rs}}\right]}{\sum N_i C_{P,i}}$$

For a batch reactor with no flows in/out and no shaft work, and large coolant flow rate:

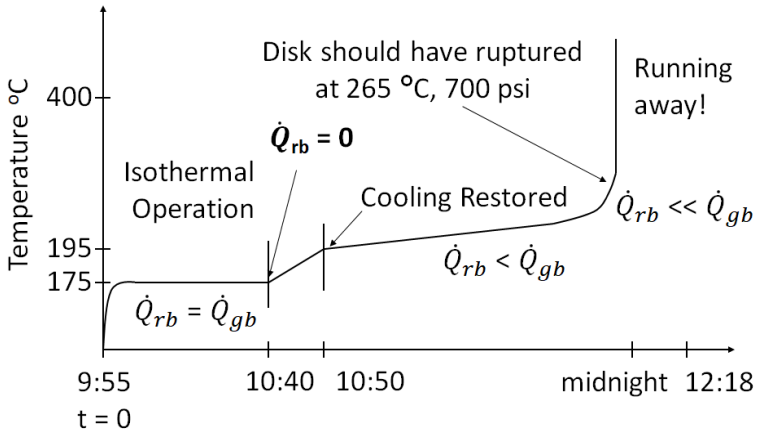
$$\frac{dT}{dt} = \frac{\overbrace{(\Delta H_{rxn})(r_A V)}^{\dot{Q}_{gb}} - \left[\overbrace{\big(UA(T - T_a)\big)}^{\dot{Q}_{rb}}\right]}{\sum N_i C_{P,i}}$$

A change in temperature with time will occur if the generation and removal terms are not equal. For a first order reaction in a batch reactor:

$$\dot{Q}_{gb} = (\Delta H_{rxn})(r_A V) = -kC_A(\Delta H_{rxn} V) = -Ae^{-E_a/RT} C_A(\Delta H_{rxn} V)$$

$$\dot{Q}_{rb} = UA(T - T_a)$$

While both terms will increase with temperature, the generation term will increase exponentially, while the removal term will only increase linearly. This increase with temperature will lead to a larger difference between generation and removal, and will cause the temperature to 'runaway'. Safety Module 1 discusses this, and here is the reactor temperature profile with time.



Lecture 20: Unsteady state reactor energy balance with CSTR startup example
Related Text: Chapter 13

From the energy balance we have used before we can get equations to describe the change in temperature with respect to time, which will need to be coupled to the mole balance equations, as a change in temperature will affect the reaction rates.
One example for adiabatic batch reactor with no shaft work, constant heat capacity with T and no phase change:

$$T = T_0 + \frac{[-\Delta H_{rxn}(T_0)]X}{C_{P0} + \Delta C_P X}$$

For <u>multiple reactions</u>:

$$\frac{dT}{dt} = \frac{\overbrace{\sum_{i=1}^{n} r_{ij} V \Delta H_{rxn,ij}}^{\dot{Q}_{gs}} - \left[\overbrace{F_{A0}\sum_{j=1}^{m}\theta_j C_{P,j}(T - T_0) + \left(UA(T - T_a)\right)}^{\dot{Q}_{rs}}\right]}{\sum_{j=1}^{m} N_j C_{P,j}}$$

Here n is the number of reactions, and m is the number of species in the reactor.

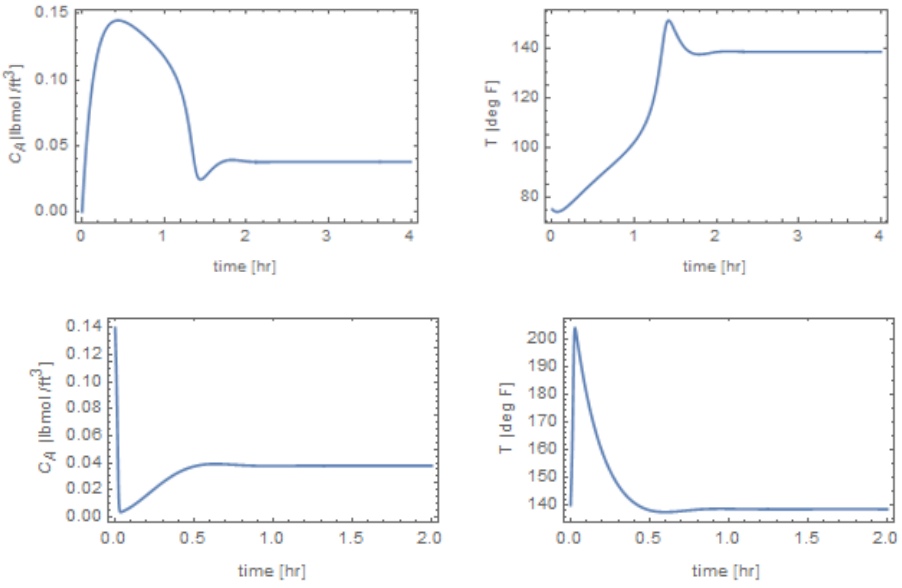
<u>Unsteady state CSTR (CSTR during startup):</u>
Mole balance and rate law can give us expressions for the change in concentrations with time for constant volumetric flow rate in and out of reactor (V is constant):

$$C_{i0}v_0 - C_i v_0 - \nu_i r_A V = \frac{dC_i V}{dt}$$

Using energy balance (here coolant flow rate is not necessarily large):

$$\frac{\sum F_{i0}\left[C_{P,i}(T_0 - T)\right] + \Delta H_{rxn} r_A V + \dot{m}_c C_{P,c}(T_{a1} - T)\left(1 - \exp\left[\frac{-UA}{\dot{m}_c C_{P,c}}\right]\right)}{\sum N_i C_{P,i}} = \frac{dT}{dt}$$

Depending on <u>initial</u> (t=0) conditions, steady state is reached but in different pathways (time profiles):



Lecture 21: Reaction mechanisms and pseudo steady-state hypothesis
Related Text: Chapter 9

Clarifying some definitions:

- **Reaction mechanism**: sequence of events (elementary reactions) that converts reactant molecules into product molecules
- **Elementary step/reaction**: reaction that occurs in one step with one transition state, follows elementary rate law
    - Reactions that follow an elementary rate law are not necessarily elementary steps/reactions, but all elementary reactions will follow elementary rate law
- **Active intermediate**: chemical species that reacts as fast as it is formed, generally not observed or measured. As a result its concentration is typically very low.
- **PSSH**: pseudo-steady-state hypothesis, which assumes that the net rate for an active intermediate is zero

Postulating rate law:

1. Start with the overall balanced reaction based on experiment
2. Postulate elementary steps to form your reaction mechanism, trying to minimize the number of simultaneous collisions
    a. Avoid elementary steps where more than 2 molecules react together
    b. Make use of experimental clues
    c. Ensure that the elementary steps lead to the overall reaction from Step 1
3. Postulate whether any species are active intermediates
4. Use the PSSH hypothesis to simplify/remove variables
5. Check whether the resulting rate law from your reaction mechanism is consistent with experiment, if not, use the experimental data to postulate a different set of elementary steps (back to Step 2)

Example reaction and reaction mechanism:

Overall reaction:

$$2NO + O_2 \rightarrow 2NO_2$$

Three step reaction mechanism (each step is an elementary reaction, step 2 is just the reverse of step 1):

$$NO + O_2 \rightarrow NO_3$$

$$NO_3 \rightarrow NO + O_2$$

$$NO_3 + NO \rightarrow 2NO_2$$

Summing up reaction 1 and 3 (don't include reaction 2 b/c it is the reverse of reaction 2) will give overall reaction.

Notes on safety (ICP 19):

Chain reactions consist of initiation, where radicals form from a molecule, propagation, and termination steps. Generally they are exothermic so can be very dangerous as we have noted before.

A branching step is a step where more reactive intermediates are formed than consumed.

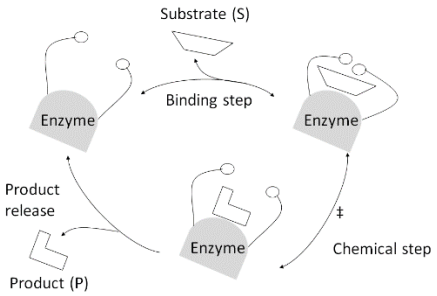
Lecture 22: Enzyme kinetics
Related Text: Chapter 9

Catalyst: A species which itself is not consumed or produced in a reaction, but which affects the rate of reaction. Typically, this comes in the form of interacting with the reactants in a specific way such that the energy associated with a given reaction mechanism is changed. Often catalysts lower activation barriers.

Homogeneous catalysts: Catalysts that are in the same phase (of matter) as the reactants/products*

Heterogeneous catalysts: Catalysts that are in a different phase than the reactants and products

Enzymes are an example of a homogeneous catalyst, specifically biocatalysts. They are usually proteins that fold to create an active center that interacts with the reactants.



The reaction mechanism can be written as:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} EP \overset{k_3}{\longrightarrow} E + P$$

where E is the enzyme, ES is the substrate bound to the enzyme, and EP is the product bound to the enzyme. Importantly, because enzymes are not consumed we can do a balance on the enzyme, where the total enzyme concentration ($C_{E,total}$) is controlled by how much we put into the reactor. In general, we add much less of the enzyme than the substrate, such that $C_{E,total}$ is low, and we can apply PSSH to E, ES, EP.

Solving for the rate of reaction in the absence of diffusion limitations:

$$v = \frac{r_P}{C_{E,total}} = \frac{v_M C_S}{C_S + K_M}$$

$$v_M = k_2 k_3 (k_3 + k_{-2} + k_2)^{-1}$$

$$K_M = \frac{k_{-1}k_{-2} + k_{-1}k_3 + k_3 k_2}{k_1(k_3 + k_{-2} + k_2)}$$

A simplified case is the Briggs-Haldane mechanism:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \overset{k_2}{\longrightarrow} E + B$$

$$v_{M,BH} \approx k_2$$

$$K_{M,BH} \approx \frac{k_{-1} + k_2}{k_1}$$

Lecture 23: Enzyme review; quasi-equilibrium and rate-determining step + heterogeneous catalysis
Related Text: Chapter 10

Quasi-equilibrium: A given step can rapidly equilibrate with respect to other steps in the same mechanism. Result is that you can say the net rate of that step is approximately zero. Can be applied to reversible or irreversible step.

$$A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$$

Here we can apply QE to the second step, essentially saying C_B must be zero.

$$r_2 = k_2 C_B \approx 0$$

Then the other concentrations can be solved for a batch reactor:

$$C_A = C_{A0} e^{-k_1 t}$$

$$C_C = C_{A0}\left(1 - e^{-k_1 t}\right)$$

Rate-determining step: The "slowest" step such that other steps are assumed to be at quasi-equilibrium. We could possibly apply it to a heterogeneous catalyst reaction mechanism:

$$A + * \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A* \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} B* \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} B + *$$

where * is an active catalyst site, A* is A bound to the catalyst site, and B* is bound to the catalyst site. If step 2 is the rate-determining step, and we assume once B is formed it cannot go back to A:

$$A + * \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A* \overset{k_2}{\rightarrow} B + *$$

Assuming QE on the first adsorption:

$$K_{A,ads} = \frac{k_1}{k_{-1}} = \frac{[A*]}{C_A[*]}$$

And the rate of the second step is:

$$r_B = k_2[A*]$$

Catalyst site balance:

$$[*]_0 = [*] + [A*]$$

Define coverage:

$$\theta_A \equiv \frac{[A*]}{[*]_0};\ \theta_* \equiv \frac{[*]}{[*]_0}$$

$$\theta_A = \frac{K_{A,ads} C_A[*]}{[*]_0} = \frac{K_{A,ads} C_A[*]}{[*] + [A*]} = \frac{K_{A,ads} C_A[*]}{[*] + K_{A,ads} C_A[*]} = \frac{K_{A,ads} C_A}{1 + K_{A,ads} C_A}$$

We can write the rate as:

$$\frac{r}{[*]_0} = k_2 \frac{K_{A,ads} C_A}{1 + K_{A,ads} C_A}$$

This is the rate law with an irreversible unimolecular surface reaction as the rate-determining step.

Lecture 24: Heterogeneous catalysis continued
Related Text: Chapter 10

Langmuir-Hinshelwood mechanism example:

$$A + * \rightleftarrows A*$$
$$B + * \rightleftarrows B*$$
$$A* + B* \rightleftarrows Product + 2*$$

Catalyst site balance on all catalyst species:

$$[*]_0 = [*] + [A*] + [B*]$$
$$1 = \theta_A + \theta_B + \theta_*$$

If the surface reaction is the rate-determining step, and if we can consider it to be irreversible:

$$A* + B* \rightarrow Product + 2*$$

The rate law for that step is:

$$r_3 = k_3[A*][B*]$$

We are going to write this in terms of coverages:

$$r_{LH,c} = k_{LH,c}\theta_A\theta_B$$

We can get the coverages of A and B from the quasi-equilibrium approximation on reaction steps 1 and 2:

$$A + * \rightleftharpoons A*$$
$$B + * \rightleftharpoons B*$$

By approximating both of those net reaction rates as zero, and using the site balance, we can get:

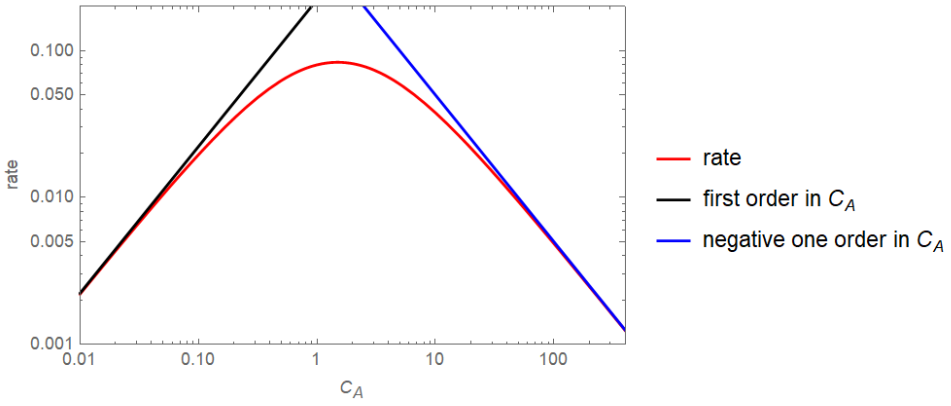
$$\theta_B = \frac{K_B C_B}{(1 + K_A C_A + K_B C_B)}$$
$$\theta_A = \frac{K_A C_A}{1 + K_A C_A + K_B C_B}$$

Thus, the overall rate (forming the product) is:

$$r_{LH,c} = k_{LH,c}\frac{K_A C_A K_B C_B}{(1 + K_A C_A + K_B C_B)^2}$$

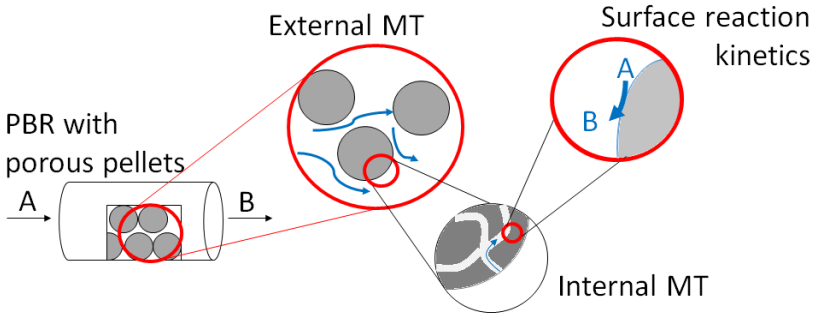
Note that our approximation of the net rate of reaction of A and B is just an approximation to solve more easily, in reality we are converting A and B to product. But if we just use those steps to estimate the rate, we have assumed that they are zero, so we have to estimate the rate law from the rate-determining step.

Langmuir-Hinshelwood will have limiting behavior for very large and small values of $K_A C_A$ (likewise for $K_B C_B$):



Lecture 25: Catalysis-External and internal mass transport
Related Text: Chapter 14/15

In a catalytic gas-phase packed bed reactor, the observed reaction rate (what you would see using the reactor design equations to extract the reaction rate) can be controlled by different reaction regimes, including mass transport (MT). In order for the reaction A → B to occur, the A molecules must flow through the reactor, diffuse through the boundary layer around the catalyst pellet (external diffusion), diffuse through the pores of the porous pellet (internal diffusion), and then react on the surface (through a reaction mechanism, for example, the Langmuir-Hinshelwood mechanism).



By modeling the transport we can get the dependence of the reaction rate (r_A') on different parameters. How the reaction rate changes with these parameters depends on what limits the rate (i.e., which of these three steps is the slowest/limiting). When we say a certain step is limiting, we essentially mean the other steps are at quasi-equilibrium.

*One note, I called the pellet diameter D_p when we discussed the Ergun equation. This is the same as what I call d_p here, the capital vs. lower case is not meant to signify any physical difference.

Limitation	Fluid velocity	Pellet size	Temperature
External	$(\text{Velocity})^{1/2}$	$(d_p)^{-3/2}$	~Linear
Internal	Independent	d_p^{-1}	Exponential(-1/T)
Surface reaction	Independent	Independent	Exponential(-1/T)

There are some useful chemical engineering parameters that are typically used for understanding regimes. One very common one is the Thiele modulus. Here it is for a spherical porous pellet, with a first order reaction:

$$\phi_1 = \sqrt{\frac{k}{\mathfrak{D}_{Eff}}}R$$

It is used to evaluate whether there are internal diffusion limitations. We also define an internal effectiveness factor:

$$\eta \equiv \frac{r_{A,observed}}{r_A(C_{A,s})}$$

$$\eta = \frac{3}{{\phi_1}^2}(\phi_1 \coth \phi_1 - 1)$$

At very large values of the Thiele modulus (where internal diffusion is very slow, and so limits the rate):

$$\eta = \frac{3}{\phi_1}$$

There is also a total effectiveness factor term that incorporates both external and internal mass transport, but we did not cover it yet.