Reactor Design

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Contents

1 Mole Balances

1.1 The Mole Balance

- The variable r_j shall represent the rate of formation of species j per unit volume

  - Alternatively phrased, r_j has units of moles per unit volume per unit time (i.e. concentration per time)

- The rate of reaction is defined as $-r_j$ such that it is a positive number for a reactant being consumed

- The rate equation is a function of the properties of the reacting materials and reaction conditions (not the type of reactor)

- The general mole balance is given as the following for species A:

$$\boxed{F_{A0} - F_A + G_A = \frac{dN_A}{dt}}$$

where F_{A0} is the input molar flow rate, F_A is the output molar flow rate, G_A is the generation, and the differential term is the accumulation (all units are moles/time)

- If the system variables are uniform throughout the system volume, then

$$G_A = r_A V$$

where V is the system volume

- More generally, if r_A changes with position in the system volume,

$$F_{A0} - F_A + \int r_A \, dV = \frac{dN_A}{dt}$$

1.2 Batch Reactor

- A batch reactor has no input or output when the reaction is occurring ($F_{A0} = F_A = 0$), so

$$\frac{dN_A}{dt} = \int r_A \, dV$$

and if the reaction mixture is perfectly mixed so that r_A is independent of position,

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

- The time, t, needed to reduce the number of moles from N_{A0} to N_{A1} is given as

$$t = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{-r_A V}$$

- Since

$$\boxed{N_A = C_A V}$$

it can also be stated that (for a constant-volume batch reactor)

$$\boxed{\frac{dC_A}{dt} = r_A}$$

1.3 Continuous-Flow Reactors

1.3.1 Continuous-Stirred Tank Reactor (CSTR)

- CSTRs are operated at steady state (accumulation $= 0$) and are assumed to be perfectly mixed. This makes the temperature, concentration, and reaction rate independent of position in the reactor

- Since CSTRs are operated at steady state, there is no accumulation, and since r_A is independent of position,

$$\boxed{V = \frac{F_{A0} - F_A}{-r_A}}$$

- If v is the volumetric flow rate (volume/time) and C_A is the concentration (moles/volume) of species A, then[1]

$$\boxed{F_A = C_A v}$$

such that

$$V = \frac{v_0 C_{A0} - v C_A}{-r_A}$$

1.3.2 Packed-Flow Reactor (Tubular)

- The tubular reactor is operated at steady state. The concentration varies continuously down the tube, and, therefore, so does the reaction rate (except for zero order reactions)

- The phrase "plug flow profile" indicates that there is uniform velocity with no radial variation (but there is axial variation) in reaction rate. A reactor of this type is called a plug-flow reactor (PFR) and is homogeneous as well as in steady-state

- For a PFR,

$$\boxed{\frac{dF_A}{dV} = r_A}$$

and is not dependent on the shape of the reactor (only on its total volume)

- The necessary volume, V, needed to reduce the entering molar flow rate, F_{A0}, to some specific value of F_{A1} is given as

$$V = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A}$$

1.3.3 Packed-Bed Reactor (Tubular)

- For a heterogeneous reaction (e.g. fluid-solid interactions), the mass of solid catalyst, W, is what matters instead of the system volume

  - Therefore, the reaction rate has units of moles of A per unit mass of catalyst per unit time

- For a heterogeneous reactor,

$$G_A = r_A W$$

- The packed-bed reactor (PBR), a type of catalytic reactor operated at steady state, can have a reaction rate described by

$$\boxed{\frac{dF_A}{dW} = r_A}$$

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[1]This is a general statement true for all reactors

- If the pressure drop and catalyst decay are neglected,

$$W = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A}$$

where W is the catalyst weight needed to reduce the entering molar flow rate of A, F_{A0}, to some F_{A1}

2 Conversion and Reactor Sizing

2.1 Batch Reactor Design Equations

- Conversion (of substance A) is defined as

$$\boxed{X = \frac{\text{moles of A reacted}}{\text{moles of A fed}}}$$

  - This can be rephrased mathematically as

$$X_i = \frac{N_{i0} - N_i}{N_{i0}} = 1 - \frac{C_i V}{C_{A0} V_0}$$

- The number of moles of A in the reactor after a conversion X has been achieved is

$$\boxed{N_A = N_{A0}\left(1 - X\right)}$$

- By differentiating the above expression with respect to t and plugging it into the expression for the batch reactor, $\dfrac{dN_A}{dt} = r_A V$, we get

$$\boxed{N_{A0}\frac{dX}{dt} = -r_A V}$$

and

$$t = N_{A0} \int_0^X \frac{dX}{-r_A V}$$

2.2 Design Equations for Flow Reactors

2.2.1 The Molar Flow Rate

- The molar flow rate of substance A, F_A, is given as the following for a flow reactor

$$\boxed{F_A = F_{A0}\left(1 - X\right)}$$

  - Note that this is **not** multiplying flow rate by concentration, but, rather, by conversion
  - For a gas, the concentration can be calculated using the ideal gas law (or other gas law if required)

- It can also be stated that

$$\boxed{C_A = C_{A0}\left(1 - X\right)}$$

- For batch reactors, conversion is a function of time whereas for flow reactors at steady state it is a function of volume

2.2.2 CSTR Design Equation

- Using the expression for the volume of a given CSTR derived earlier, we can eliminate F_A by using the conversion of F_{A0} such that the design equation is

$$\boxed{V = \frac{F_{A0} X}{-r_A}}$$

2.2.3 PFR Design Equation

- Similarly, the design equation for a PFR is

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

- Therefore,

$$V = F_{A0}\int_0^X \frac{dX}{-r_A}$$

  - For PBRs, simply swap V for W

2.3 Sizing CSTRs and PFRs

- For an isothermal reactor, the rate is typically greatest at the start of the reaction when the concentration is greatest

  - Recall that the reactor volume for CSTRs and PFRs are functions of the inverse of the reaction rate
  - For all irreversible reactions of greater than zero order, the volume of the reactor approaches infinity for a conversion of 1 (since the reaction rate approaches zero and the slope of the Levenspiel plot approaches infinity)

- For reversible reactions, the maximum conversion is the equilibrium conversion where the reaction rate is zero (and thus the volume of the reactor approaches infinity for a system in equilibrium as well)

- For an isothermal case, the CSTR volume will typically be greater than the PFR volume for the same conditions (except when zero order)

  - This is because the CSTR operates at the lowest reaction rate while the PFR starts at a high rate and decreases to the exit rate (which requires less volume since it is inversely proportional to the rate)

- From a $\dfrac{F_{A0}}{-r_A}$ vs. X plot, the reactor volumes can be found from areas as shown in the sample Levenspiel plot below

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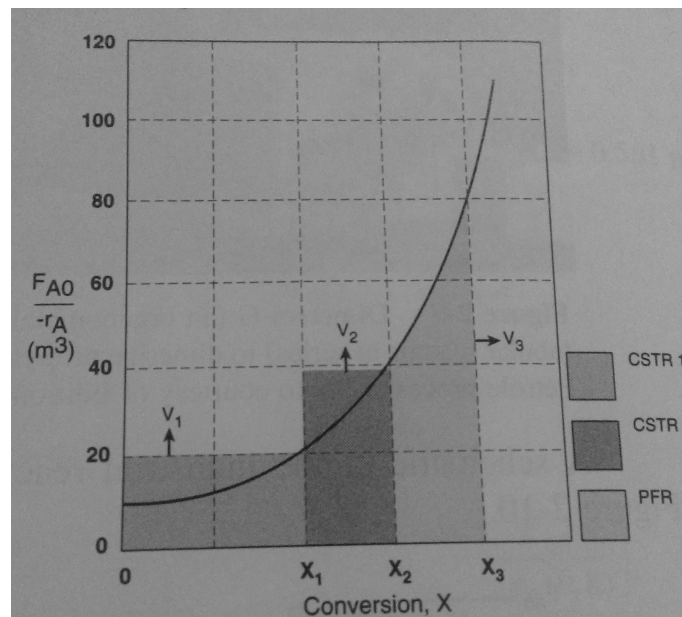
2.4 Reactors in Series

- If we consider two CSTRs in series, we can state the following for the volume of one of the CSTRs (where the f subscript stands for final and the i subscript stands for initial)

$$V = F_{A0} \left(\frac{1}{-r_A} \right) (X_f - X_i)$$

  - If it is the first reactor in the series, then $X_i = 0$

- To achieve the same overall conversion, the total volume for two CSTRs in series is less than that requires for one CSTR (this is not true for PFRs)

- The volume for a PFR where PFRs are in series

$$V = \int_{X_i}^{X_f} F_{A0} \frac{dX}{-r_A}$$

  - PFRs in series have the same total volume for the same conversion as one PFR, as shown below:

$$V_{\text{total}} = \int_0^{X_2} F_{A0} \frac{dX}{-r_A} = \int_0^{X_1} F_{A0} \frac{dX}{-r_A} + \int_{X_1}^{X_2} F_{A0} \frac{dX}{-r_A}$$

  - A PFR can be modeled as infinitely many CSTRs in series

2.5 Space Time and Space Velocity

- Space time is defined as

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

  - The velocity is measured at the entrance condition
  - For a PBR,

$$\tau' = \frac{W}{v_0} = \rho_b \tau$$

- Space velocity is defined as

$$\text{SV} \equiv \frac{v_0}{V}$$

  - For a liquid-hourly space velocity (LHSV), the velocity is the liquid feed rate at 60 F or 75 F
  - For a gas-hourly space velocity (GHSV), the velocity is measured at STP

3 Rate Laws and Stoichiometry

3.1 Rate Laws

- The molecularity is the number of atoms, ions, or molecules colliding in a reaction step

- For a reaction aA+bB→cC+dD,

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

3.2 The Reaction Order and the Rate Law

- A reaction rate is described as (using the reaction defined earlier),

$$-r_A = k_A C_A^\alpha C_B^\beta$$

  where the order with respect to A is α, the order with respect to B is β, and the total order is $\alpha + \beta$

- For a zero-order reaction, the units of k are mol/L·s

- For a first-order reaction, the units of k are 1/s

- For a second-order reaction, the units of k are L/mol·s

- For an elementary reaction, the rate law order is identical to the stoichiometric coefficients

- For heterogeneous reactions, partial pressures are used instead of concentrations

    – To convert between partial pressure and concentration, one can use the ideal gas law

    – The reaction rate per unit volume is related to the rate of reaction per unit weight of catalyst via

$$-r_A = \rho\left(-r_A'\right)$$

- The equilibrium constant is defined (for the general reaction) as

$$K_C = \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{C_{C,eq}^c C_{D,eq}^d}{C_{A,eq}^a C_{B,eq}^b}$$

    – The units of K_C are $(\text{mol/L})^{d+c-b-a}$

- The net rate of formation of substance A is the sum of the rates of formation from the forward reaction and reverse reaction for a system at equilibrium

    – For instance, if we have the elementary, reversible reaction of $2\,\text{A} \rightleftharpoons \text{B} + \text{C}$, we can state that $-r_{A,forward} = k_A C_A^2$ and $r_{A,reverse} = k_{-A} C_B C_C$. Therefore, $-r_A = -\left(r_{A,forward} + r_{A,reverse}\right) = k_A C_A^2 - k_{-A} C_B C_C = k_A\left(C_A^2 - \frac{k_{-A}}{k_A} C_B C_C\right)$. Using $K_C = \frac{C_B C_C}{C_A^2}$, the previous expression can be redefined as $-r_A = k_A\left(C_A^2 - \frac{C_B C_C}{K_C}\right)$

- The temperature dependence of the concentration equilibrium constant is the following when there is no change in the total number of moles and the heat capacity does not change

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

3.3 The Reaction Rate Constant

- The Arrhenius equation states that

$$k_A(T) = A\exp\left(-\frac{E}{RT}\right)$$

- Plotting $\ln k_A$ vs. $\frac{1}{T}$ yields a line with slope $-\frac{E}{R}$ and y-intercept is $\ln A$

- Equivalently,

$$k(T) = k(T_0)\exp\left[\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

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3.4 Batch Systems

- Let us define the following variables:

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

$$\Theta_B = \frac{N_{B0}}{N_{A0}} = \frac{C_{B0}}{C_{A0}} = \frac{y_{B0}}{y_{A0}}$$

- With these definitions, we can state that the total moles is described by

$$N_T = N_{T0} + \delta N_{A0} X$$

- A table like the one below can be used to compute changes and remaining quantities of substances in a constant volume batch reactor

Symbol	Initial	Change	End (Moles)	End (Concentration)
A	N_{A0}	$-N_{A0}X$	$N_{A0}(1-X)$	$C_{A0}(1-X)$
B	$N_{B0} = \Theta_B N_{A0}$	$-\dfrac{b}{a}N_{A0}X$	$N_{A0}\left(\Theta_B - \dfrac{b}{a}X\right)$	$C_{A0}\left(\Theta_B - \dfrac{b}{a}X\right)$
C	$N_{C0} = \Theta_C N_{A0}$	$\dfrac{c}{a}N_{A0}X$	$N_{A0}\left(\Theta_C + \dfrac{c}{a}X\right)$	$C_{A0}\left(\Theta_C + \dfrac{c}{a}X\right)$
D	$N_{D0} = \Theta_D N_{A0}$	$\dfrac{d}{a}N_{A0}X$	$N_{A0}\left(\Theta_D + \dfrac{d}{a}X\right)$	$C_{A0}\left(\Theta_D + \dfrac{d}{a}X\right)$
Total	N_{T0}		$N_T = N_{T0} - N_{A0}X$	

- It is important to make the basis of the reaction (i.e. substance A) the limiting reagent

- Using the mole-fraction definition of Θ, for a constant-volume batch reactor,

$$C_i = C_{A0}(1-X) = \frac{N_{A0}\left[\Theta_i \pm (i/a)X\right]}{V} = C_{A0}(\Theta_i + \nu_i X)$$

  - Note that this is for an arbitrary species $i \neq A$, species A is the limiting reagent, and the variable i in the numerator represents the stoichiometric number of species i. Also, the $\pm$ is addition for generation (i.e. product) and subtraction for consumption (i.e. reactant)

  - Here, we define the stoichiometric coefficient as

$$\nu_I = \pm \frac{i}{a}$$

  for a substance I with stoichiometric number i. It is positive for products and negative for reactants

  - For a gas-phase reaction, constant-volume conditions tend to exist when n moles of reactant form n moles of product and when there is no change in temperature or pressure (i.e. ideal gas law states that volume is unchanged)

  - For a liquid-phase reaction, the solvent dominates the solution, so the density of the solute negligibly impacts the system thus making most liquid-phase reactions essentially constant-volume

3.5 Flow Systems

- For ICE tables with flow systems, we use molar flow rates instead of moles (as shown below)

TABLE 3-4. STOICHIOMETRIC TABLE FOR A FLOW SYSTEM

Species	Feed Rate to Reactor (mol/time)	Change within Reactor (mol/time)	Effluent Rate from Reactor (mol/time)
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	$F_{B0} = \Theta_B F_{A0}$	$-\dfrac{b}{a}F_{A0}X$	$F_B = F_{A0}\left(\Theta_B - \dfrac{b}{a}X\right)$
C	$F_{C0} = \Theta_C F_{A0}$	$\dfrac{c}{a}F_{A0}X$	$F_C = F_{A0}\left(\Theta_C + \dfrac{c}{a}X\right)$
D	$F_{D0} = \Theta_D F_{A0}$	$\dfrac{d}{a}F_{A0}X$	$F_D = F_{A0}\left(\Theta_D + \dfrac{d}{a}X\right)$
I	$F_{I0} = \Theta_I F_{A0}$	—	$F_I = F_{A0}\Theta_I$
	F_{T0}		$F_T = F_{T0} + \left(\dfrac{d}{a} + \dfrac{c}{a} - \dfrac{b}{a} - 1\right)F_{A0}X$
			$F_T = F_{T0} + \delta F_{A0}X$

- To express rate constants as a function of conversion, we can utilize the flowing for gas-phase reactions
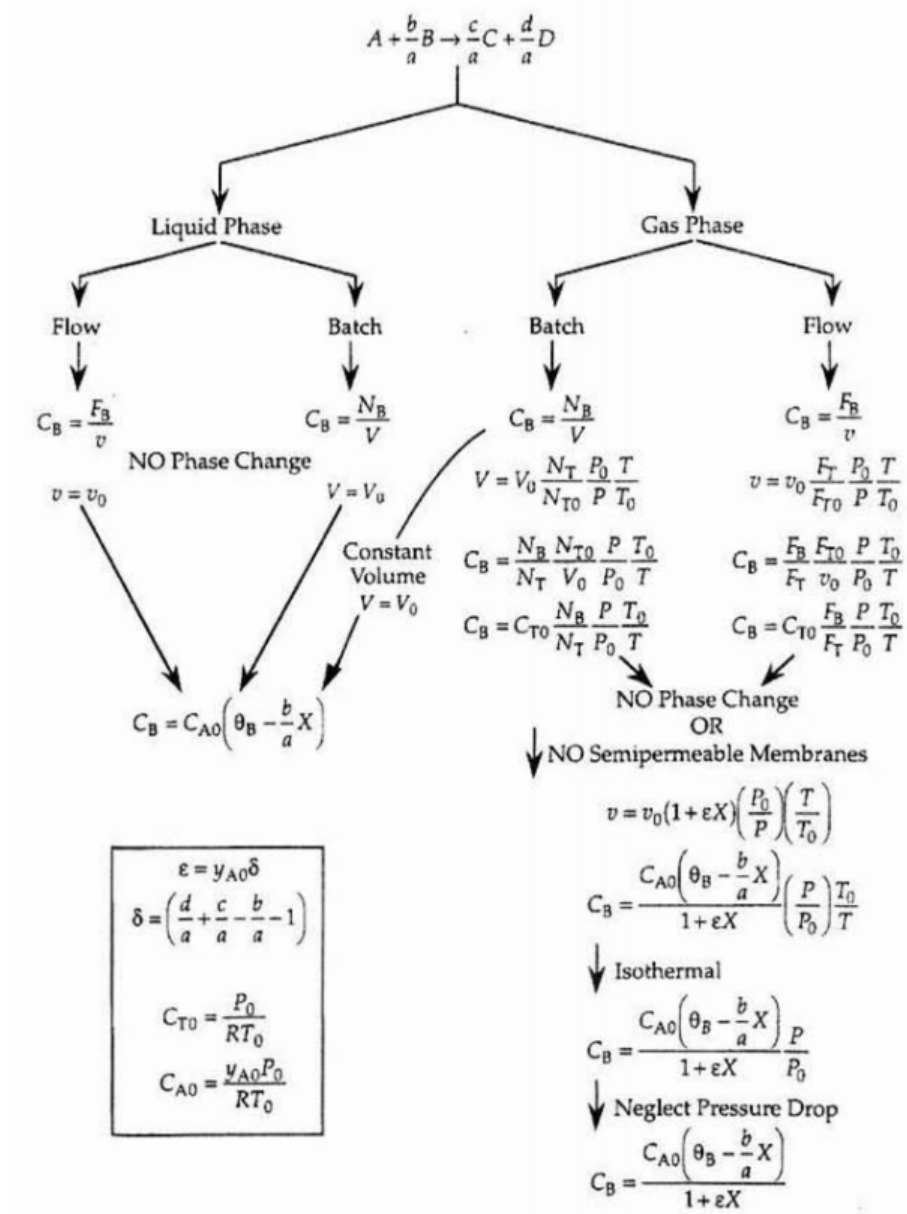
$$PV = ZnRT$$

where Z is the compressibility factor that accounts for unidealities

- Also, we shall define

$$\boxed{\varepsilon = \frac{\Delta N_T}{N_{T_0}}\ (\text{at } X = 1) = y_{A0}\delta}$$

- With this, the following graphic summarizes our possible options for flow systems as well as batch systems

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

Liquid Phase

- Flow
  $$C_B = \frac{F_B}{v}$$
  $$v = v_0$$

- Batch
  $$C_B = \frac{N_B}{V}$$
  NO Phase Change
  $$V = V_0$$
  Constant Volume $V = V_0$

$$C_B = C_{A0}\left(\theta_B - \frac{b}{a}X\right)$$

Gas Phase

- Batch
  $$C_B = \frac{N_B}{V}$$
  $$V = V_0 \frac{N_T}{N_{T0}} \frac{P_0}{P} \frac{T}{T_0}$$
  $$C_B = \frac{N_B}{N_T} \frac{N_{T0}}{V_0} \frac{P}{P_0} \frac{T_0}{T}$$
  $$C_B = C_{T0} \frac{N_B}{N_T} \frac{P}{P_0} \frac{T_0}{T}$$

- Flow
  $$C_B = \frac{F_B}{v}$$
  $$v = v_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0}$$
  $$C_B = \frac{F_B}{F_T} \frac{F_{T0}}{v_0} \frac{P}{P_0} \frac{T_0}{T}$$
  $$C_B = C_{T0} \frac{F_B}{F_T} \frac{P}{P_0} \frac{T_0}{T}$$

NO Phase Change
OR
NO Semipermeable Membranes

$$v = v_0(1+\varepsilon X)\left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)$$

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

Isothermal

$$C_B = \frac{C_{A0}\left(\theta_B - \frac{b}{a}X\right)}{1+\varepsilon X}\frac{P}{P_0}$$

Neglect Pressure Drop

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

$$\varepsilon = y_{A0}\delta$$
$$\delta = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)$$
$$C_{T0} = \frac{P_0}{RT_0}$$
$$C_{A0} = \frac{y_{A0}P_0}{RT_0}$$

- It is important to remember that one can get C_{A0} in the gaseous state from an equation of state such as

$$\boxed{C_{A0} = \frac{Py_{A0}}{RT}}$$

  - The factor of y_{A0} comes in due to the necessity of the partial pressure

- Recall that X is the conversion of substance A

- We can state the following for gases

$$\boxed{C_i = \frac{C_{A0}\left(\Theta_i + \nu_i X\right)}{\left[(1 + \varepsilon X)\frac{P_0 T}{P T_0}\right]}}$$

4 Isothermal Reactor Design

4.1 Design Structure for Isothermal Reactors

The following algorithm can be used to solve problems for isothermal reactors. Note that everything is done with respect to A. If you want to find, let's say, the concentration of substance B in a batch reactor with constant volume, consult the schematic at the end of **Section 3.5**

1. **Mole Balance**

   (a) PFR

      i. $\dfrac{dX}{dV} = \dfrac{-r_A}{F_{A0}}$

   (b) CSTR

      i. $V = \dfrac{F_{A0}X}{-r_A}$

   (c) Batch

      i. $\dfrac{dX}{dt} = \dfrac{-r_A V}{N_{A0}}$

   (d) PBR

      i. $\dfrac{dX}{dW} = \dfrac{-r_A}{F_{A0}}$

2. **Rate Laws**

   (a) Variable for each reaction (e.g. $-r_A = kC_A^\alpha$)

3. **Stoichiometry**

   (a) Flow

      i. $C_A = \dfrac{F_A}{v}$

      ii. $F_A = F_{A0}\left(1 - X\right)$

         - Liquid (constant flow rate)

         A. $v = v_0$

         B. $C_A = C_{A0}\left(1 - X\right)$

         - Ideal gas (variable flow rate)

         A. $v = v_0\left(1 + \varepsilon x\right)\dfrac{P_0}{P}\dfrac{T}{T_0}$

         B. $C_A = \dfrac{C_{A0}\left(1 - X\right)}{\left(1 + \varepsilon X\right)}\dfrac{P}{P_0}\dfrac{T_0}{T}$

   (b) Batch

      i. $C_A = \dfrac{N_A}{V}$ and $N_A = N_{A0}\left(1 - X\right)$

         - Ideal gas (variable volume)

         A. $V = V_0\left(1 + \varepsilon X\right)\dfrac{P_0}{P}\dfrac{T}{T_0}$

         B. $C_A = \dfrac{C_{A0}\left(1 - X\right)}{\left(1 + \varepsilon X\right)}\dfrac{P}{P_0}\dfrac{T_0}{T}$

         - Liquid or gas (constant volume)

         A. $V = V_0$ and $C_A = C_{A0}\left(1 - X\right)$

4. **Combine**

    (a) Combine the results from the mole balance, rate law, and stoichiometry to yield an expression for the rate of change of conversion

5. **Evaluate**

    (a) Integrate the differential equation (if there is one) obtained in Step 4

        i. Isothermal cases will have k constant

        ii. It is usually true that at $t = 0$, $X = 0$. You can then integrate from 0 to t and from 0 to X

        iii. The final expression will yield the reaction time (i.e. the time needed to achieve a conversion X)

4.2 Scale-Up of Liquid-Phase Batch Reactor Data to the Design of a CSTR

- Using the algorithm described in the previous subsection, the first-order reaction time for a batch reactor is

$$t_R = \frac{1}{k} \ln \left(\frac{1}{1 - X} \right)$$

- For second-order,

$$t_R = \frac{X}{k C_{A0} \left(1 - X \right)}$$

- One can then find k to use in a CSTR equation

4.3 Design of Continuous Stirred Tank Reactors

4.3.1 A Single, First-Order CSTR

- Using the previously described algorithm for a first-order liquid-phase reaction in a CSTR, one yields

$$X = \frac{\tau k}{1 + \tau k}$$

- For a first-order reaction, the Damkohler number is defined as

$$\boxed{\mathrm{Da} = \tau k = \frac{-r_{A0} V}{F_{A0}}}$$

so

$$X = \frac{\mathrm{Da}}{1 + \mathrm{Da}}$$

- Combining the equation for the conversion with $C_i = C_{A0} \left(\Theta_i + \nu_i X \right)$ yields the exit-concentration

$$C_A = \frac{C_{A0}}{1 + \mathrm{Da}}$$

4.3.2 CSTRs in Series (First-Order)

- For two CSTRs in series, the volume of the second reactor can be given by

$$V_2 = \frac{F_{A1} - F_{A2}}{-r_{A2}} = \frac{v_0 \left(C_{A1} - C_{A2} \right)}{-r_{A2}}$$

- For a first-order reaction,

$$C_{A2} = \frac{C_{A1}}{1 + \tau_2 k_2} = \frac{C_{A0}}{\left(1 + \tau_2 k_2 \right) \left(1 + \tau_1 k_1 \right)}$$

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- For a series of n CSTRs in series operating at the same temperature (constant k) and the same size (constant τ), the concentration leaving the final reactor is
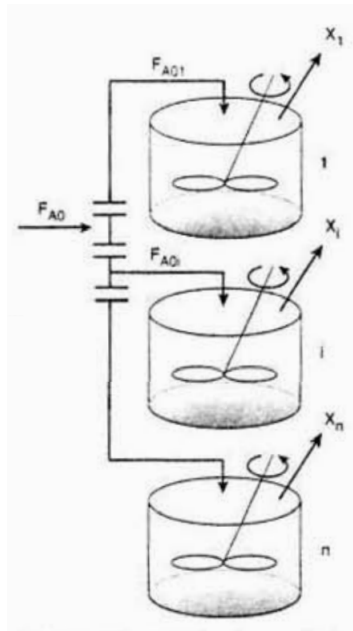
$$C_{An} = \frac{C_{A0}}{(1+\tau k)^n} = \frac{C_{A0}}{(1+\text{Da})^n}$$

- Using $C_{An} = C_{A0}(1-X)$,

$$X = 1 - \frac{1}{(1+\text{Da})^n}$$

- The rate of disappearance of A for n CSTRs with first-order reactions is

$$-r_{An} = kC_{An} = k\frac{C_{A0}}{(1+\tau k)^n}$$

4.3.3 CSTRs in Parallel

- For i reactors in parallel (see diagram),

$$V_i = F_{A0i}\left(\frac{X_i}{-r_{Ai}}\right)$$

- The volume of each individual reactor is related to the total volume of all reactors by

$$V_i = \frac{V}{n}$$

- Similarly,

$$F_{A0i} = \frac{F_{A0}}{n}$$

- Therefore,

$$V = \frac{F_{A0}X}{-r_A}$$

  - The conversion in any one reactor in parallel is identical to what would be achieved if the reactant was fed to one large reactor of volume V

4.3.4 A Second-Order Reaction in a CSTR

- Using the algorithm discussed earlier in this section a second-order liquid-phase reaction in a CSTR has

$$\tau = \frac{C_{A0}X}{kC_{A0}^2\left(1-X\right)^2}$$

- When solved, this yields,

$$X = \frac{\left(1+2\text{Da}\right) - \sqrt{1+4\text{Da}}}{2\text{Da}}$$

4.4 Tubular Reactors

- Using the algorithm discussed earlier in this section, a second-order reaction in a PFR in the liquid-phase yields

$$X = \frac{\tau kC_{A0}}{1+\tau kC_{A0}} = \frac{\text{Da}_2}{1+\text{Da}_2}$$

where

$$\boxed{\text{Da}_2 = \tau kC_{A0}}$$

- For a second-order reaction in a PFR in the gas-phase at constant pressure and temperature[2],

$$V = \frac{v_0}{kC_{A0}}\left[2\varepsilon\left(1+\varepsilon\right)\ln\left(1-X\right) + \varepsilon^2 X + \frac{\left(1+\varepsilon\right)^2 X}{1-X}\right]$$

- This equation states that when $\delta = 0$, $v = v_0$. When $\delta < 0$, the volumetric flow rate decreases as the conversion increases. When $\delta > 0$, the volumetric flow increases as the conversion increases. This comes from the equation $v = v_0\left(1+\varepsilon X\right)$ in this scenario

4.5 Pressure Drop in Reactors

4.5.1 Ergun Equation

- The Ergun equation states that

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

where ϕ is porosity (volume of void divided by total bed volume, or you can say that $1 - \phi$ is the volume of solid divided by total bed volume), g_c is the gravitational constant, D_p is the diameter of the particle in the bed, μ is the viscosity of gas passing through the bed, z is the length down the packed bed of pipe, ρ is the gas density, and $G = \rho u$ where u is the superficial velocity (volumetric flow divided by cross-sectional area of pipe)

4.5.2 PBR

- For a pressure drop through a packed bed,

$$\frac{dP}{dz} = -\beta_0\frac{P_0 T F_T}{PT_0 F_{T0}}$$

where β_0 is a constant composing the right hand side of the Ergun equation (without the negative sign)

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[2]These expressions are quite specific for the reaction conditions but are easily derivable using the algorithm described at the beginning of this section. Although the derivations are not shown in detail (see Fogler), you can check your work with these results. The general procedure does not vary.

- In terms of catalyst weight

$$\frac{dP}{dW} = \frac{-\beta_0}{A_c\left(1-\phi\right)\rho_c}\frac{P_0 T F_T}{P T_0 F_{T0}}$$

- This can be expressed further as

$$\frac{dy}{dW} = -\frac{\alpha}{2y}\frac{T}{T_0}\frac{F_T}{F_{T0}}$$

  where

$$\boxed{\alpha = \frac{2\beta_0}{A_c\rho_c\left(1-\phi\right)P_0}}$$

  and

$$y = \frac{P}{P_0}$$

  - This equation should be used for membrane reactors or multiple reactors

- Some more manipulation yields the important equation,

$$\boxed{\frac{dy}{dW} = -\frac{\alpha}{2y}\left(1+\varepsilon X\right)\frac{T}{T_0}}$$

  - This equation should be coupled with

$$\boxed{\frac{dX}{dW} = -\frac{r_A}{F_{A0}}}$$

  where you plug in the rate law and terms for the concentration

4.5.3   PFR

- For pressure drops in pipes (without packing) can be approximated by

$$\frac{P}{P_0} = \left(1 - \alpha_p V\right)^{1/2}$$

  where

$$\alpha_p = \frac{4fG^2}{A_c\rho_0 P_0 D}$$

  and f is the fanning factor and u is the average velocity of the gas

4.6   Unsteady-State Operation of Stirred Reactors

- The time to reach steady-state for an isothermal CSTR is given by

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

- For a semi-batch reactor, the volume as a function of time is

$$\boxed{V = V_0 + v_0 t}$$

- The mole balance for a batch reactor is

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

- A mole balance on B for a batch reactor (if B is the fed substance) is

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

4.7 Mole Balances on CSTRs, PFRs, PBRs, and Batch Reactors

4.7.1 Liquid Phase

The mole balance for liquid-phase reactions of the type $A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$ is as follows:

1. Batch

   (a) $\dfrac{dC_A}{dt} = r_A$

   (b) $\dfrac{dC_B}{dt} = \dfrac{b}{a}r_A$

2. CSTR

   (a) $V = \dfrac{v_0\left(C_{A0} - C_A\right)}{-r_A}$

   (b) $V = \dfrac{v_0\left(C_{B0} - C_B\right)}{-\left(b/a\right)r_A}$

3. PFR

   (a) $v_0\dfrac{dC_A}{dt} = r_A$

   (b) $v_0\dfrac{dC_B}{dV} = \dfrac{b}{a}r_A$

4. PBR

   (a) $v_0\dfrac{dC_A}{dW} = r_A$

   (b) $v_0\dfrac{dC_B}{dW} = \dfrac{b}{a}r_A$

4.7.2 Gas Phase

The mole balance for a gas-phase reaction is as follows:

$$F_T = \sum_{i=1}^{n} F_i$$

1. Batch

   (a) $\dfrac{dN_i}{dt} = r_i V$

2. CSTR

   (a) $V = \dfrac{F_{i0} - F_i}{-r_i}$

3. PFR

   (a) $\dfrac{dF_i}{dV} = r_i$

The concentrations for a gas-phase reaction is as follows:

$$C_i = C_{T0}\frac{F_i T_0}{F_T T}y$$

5 Collection and Analysis of Rate Data

5.1 Batch Reactor Data

5.1.1 Differential Method

- The following differential applies for constant-volume batch reactors,

$$\ln\left(-\frac{dC_A}{dt}\right) = \alpha \ln\left(C_A\right) + \ln\left(k_A\right)$$

  - Of course, this can be plotted as $y = mx + b$ to find the order, α

5.1.2 Integral Method

- In the integral method, we guess a reaction order and see if a plot gets a straight line

- For a zero-order reaction,

$$C_A = C_{A0} - kt$$

- For a first-order reaction,

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

- For a second-order reaction,

$$\frac{1}{C_A} = kt + \frac{1}{C_{A0}}$$

5.2 CSTR Reaction Data

- Write down the stoichiometry equation relating C_A and X_A and solve for X_A. For a gaseous system,

$$X_A = \frac{1 - C_A/C_{A0}}{1 + \varepsilon_A C_A/2C_{A0}}$$

- Given v_0 and C_A, solve for X_A. Then use the design equation of

$$-r_A = \frac{v_0 C_{A0} X_A}{V}$$

  to find the rate

- From here, plot $\ln\left(-r_A\right)$ vs. $\ln\left(C_A\right)$ to utilize

$$\ln\left(-r_A\right) = \ln\left(k\right) + \alpha \ln\left(C_A\right)$$

- If $\varepsilon = 0$, a plot of C_A vs. τ will be linear for zeroth order with slope k

- If $\varepsilon = 0$, a plot of $\frac{C_{A0}}{C_A}$ vs. τ will be linear for first order with slope k

- If $\varepsilon = 0$, a plot of $\frac{C_{A0}}{C_A}$ vs. τC_A will be linear for second order with slope k

5.3   PFR Reaction Data

- For any ε, a plot of X_A vs. $\dfrac{V}{F_{A0}}$ can be made such that the tangent at any point has the value of $-r_A$

- For zero order, a plot of $\dfrac{C_{A0} - C_A}{C_{A0} + \varepsilon_A C_A}$ vs. $\dfrac{\tau}{C_{A0}}$ will have a slope of k

- For first order, a plot of $(1 + \varepsilon_A) \ln \left(\dfrac{1}{1 - X_A} \right) - \varepsilon_A X_A$ vs. τ will have a slope of k

- For second order, a plot of $2\varepsilon_A (1 + \varepsilon_A) \ln (1 - X_A) + \varepsilon_A^2 X_A + (\varepsilon_A + 1)^2 \dfrac{X_A}{1 - X_A}$ vs. τC_{A0} will have a slope of k

5.4   Method of Initial Rates

- Plot the logarithm of the initial rate (which can be obtained by the derivative at $t = 0$ of a series C_A vs. t plots) as a function of the logarithm of the initial concentration of A. The slope of the line is the reaction order with respect to A since $-r_A = k_A C_A^\alpha$

5.5   Method of Half-Lives

- The equation for the half-life is

$$\ln \left(t_{1/2} \right) = (1 - \alpha) \ln \left(C_{A0} \right) + \ln \left(\dfrac{2^{\alpha - 1} - 1}{(\alpha - 1) k} \right)$$

  - Therefore, by plotting $\ln \left(t_{1/2} \right)$ against $\ln \left(C_{A0} \right)$, the order can be found as $\alpha = 1 - \text{slope}$

5.6   Differential Reactors

- A series of experiments is carried out at different initial concentrations, and initial rate of reaction is determined for each step

  - The value of $-r_{A0}$ can be found by differentiating the data and extrapolating to zero time

- The slope of $\ln \left(-r_{A0} \right)$ vs. $\ln \left(C_{A0} \right)$ will be α for a rate-law that follows a power-law with respect to A

- The design equations for the differential reactor are

$$-r_A' = \dfrac{v_0 C_{A0} - C_{Aexit} v}{\Delta W}$$

and

$$-r_A' = \dfrac{F_{A0} X}{\Delta W} = \dfrac{F_{product}}{\Delta W}$$

6 Multiple Reactions

6.1 Definitions

- The parallel reaction occurs when the reactant is consumed by two different reaction pathways to form different prouncts (e.g. A breaks down to both B and C)

- The series reaction is when the reactant forms an intermediate product, which reacts further to form another product (e.g.. $A \rightarrow B \rightarrow C$)

- Complex reactions are multiple reactions that involve a combination of both series and parallel reactions

- Independent reactions occur are reactions that occur at the same time but neither the products nor reactants react with themselves or one another (e.g. $A \rightarrow B + C$ and $D \rightarrow E + F$)

- The selectivity is defined as

$$S = \frac{\text{rate of formation of desired product}}{\text{rate of formation of undesired product}}$$

- The overall selectivity is defined as

$$\tilde{S} = \frac{\text{exit molar flow rate of desired product}}{\text{exit molar flow rate of undesired product}}$$

  - For a CSTR, the overall selectivity and selectivity are identical

- The reaction yield is defined as the following if we A decomposes to a desired (D) and undesired (U) product

$$Y_D = \frac{r_D}{-r_A}$$

- The overall yield for a batch system is

$$\tilde{Y}_D = \frac{N_D}{N_{A0} - N_A}$$

- The overall yield for a flow system is

$$\tilde{Y}_D = \frac{F_D}{F_{A0} - F_A}$$

  - For a CSTR, the overall yield and instantaneous yield are identical

- For a CSTR, the highest overall yield (i.e. most product formed) occurs when the rectangle under the Y vs. C_A curve has the largest area

- For a PFR, the highest overall yield (i.e. most product formed) occurs when the area under the Y vs, C_A curve is maximized

- If unreacted reagent can be separated from the exit stream and recycled, the highest overall yield (i.e. most product formed) is at the maximu of the Y vs. C_A curve

6.2   Parallel Reactions

6.2.1   Maximizing the Desired Product of One Reactant

Let α_1 be the order of the desired reaction $A + B \rightarrow D$ and α_2 be the order of the undesired reaction $A + B \rightarrow U$. Let E_D be the activation energy of the desired reaction and E_U be the activation of the undesired reaction. We want to maximize selectivity.

- If $\alpha_1 > \alpha_2$:

    - We want the concentration of the reactant to be as high as possible since $C_A^{\alpha_1 - \alpha_2}$ has a positive exponent
    - If in the gas phase, the reaction should be run without inerts and at high pressure
    - If in the liquid phase, the reaction should be run without dilutents
    - A batch or PFR should be used since C_A starts at a high value and drops over the course of the reaction whereas it is always at the lowest concentration in a CSTR (i.e. the outlet concentration)

- If $\alpha_2 > \alpha_1$:

    - We want the concentration of the reactant to be as low as possible since $C_A^{\alpha_1 - \alpha_2}$ has a negative exponent
    - If in the gas phase, the reaction should be run with inerts and at low pressure
    - If in the liquid phase, the reaction should be run without dilutents
    - A CSTR or recycle reactor should be used

- If $E_D > E_U$:

    - High temperature should

- If $E_U > E_D$

    - Low temperature should be used (but not so low that the desired reaction never proceeds)

- For analyzing the effect of activatoin energies on selectivity, one can state the following if the reaction is $A \rightarrow D$ and $A \rightarrow U$

$$S_{D/U} \sim \frac{k_D}{k_U} = \frac{A_D}{A_U} e^{-[(E_D - E_U)/(RT)]}$$

    - For a system of 3 reactions with a total of 2 undesired products, see Example 6-2 in Fogler for how to analyze the temperature

6.2.2   Reactor Selection and Operating Conditions

Let α_1 and β_1 be the order of the desired reaction $A + B \rightarrow D$ and α_2 and β_2 be the order of the desired reaction $A + B \rightarrow D$ if the reaction rates can be described by $r = kC_A^\alpha C_B^\beta$. We want to maximize the selectivity of the desired product:

- If $\alpha_1 > \alpha_2$ and $\beta_1 > \beta_2$:

    - Since $C_A^{\alpha_1 - \alpha_2}$ and $C_B^{\beta_1 - \beta_2}$ both have poisitve exponents, the concentration of both A and B should be maximized. Therefore, a tubular reactor or batch reactor should be used
    - High pressure for a gas phase reaction and a minimization of inerts should be considered

- If $\alpha_1 > \alpha_2$ but $\beta_2 > \beta_1$:

- Since $C_A^{\alpha_1-\alpha_2}$ has a positive exponent but $C_B^{\beta_1-\beta_2}$ has a negative exponent, the concentration of A should be maximized, but the concentration of B should be minimized. Therfore, a semibatch reactor in which B is fed slowly into a large amount of A should be used.
    - A membrane reactor or a tubular reactor with a side stream of B continuously fed into the reactor would also work
    - Another option is a series of small CSTRs with A fed only to the first reactor and small amounts of B fed to each reactor so that B is mostly consumed before the CSTR exit stream flows into the next reactor

- If $\alpha_2 > \alpha_1$ and $\beta_2 > \beta_1$:

    - The concentration of both A and B should be minimized. Therefore, a CSTR should be used. A tubular reactor with a large recycle ratio can also be used
    - The feed can be diluted with inerts and should be at low pressure if in the gas phase

- If $\alpha_1 < \alpha_2$ but $\beta_2 > \beta_1$:

    - The concentration of A should be small but B should maximized. Therefore, a semibatch reactor with A slowly fed to a large amount of B can be used
    - A membrane reactor or a tubular reactor with side streams of A would also work
    - A series of small CSTRs with fres A fed to the reactor would be suitable as well

6.3 Maximizing the Desired Product in Series Reactions

- For a series reaction, such as $A \to B \to C$, the most important variable is the space-time for a flow reactor and real-time for a batch reactor

    - For instance, if the first reaction is slow and the second reaction is fast, there will be very little B present at a given time. Timing is key!

To best illustrate the issue, it is best to analyze an example. Consider a reaction $A \to B \to C$ with rate constant k_1 and k_2, respectively. It is occurring in a PBR. Here is how to analyze the scenario:

1. Break the reaction into a series of steps. In essence, $A \to B$ is reaction 1, and $B \to C$ is reaction 2

2. A mole balance on A yields $\dfrac{dF_A}{dW} = r'_A$ with a rate law of $-r'_A = k_1 C_A$ and stoichiometry of $F_A = C_A v_0$

    (a) Therefore, $v_0 \dfrac{dC_A}{dW} = -k_1 C_A$, which can be rewritten as $\dfrac{dC_A}{d\tau'} = -k_1 C_A$ (where $\tau' \equiv W/v_0$)

    (b) This can be integrated to yield $C_A = C_{A0} e^{-k_1 \tau'}$ for the initial conditions $C_A = C_{A0}$ at $W = 0$

3. A mole balance on yields $\dfrac{dF_B}{dW} = r'_{B,net}$ with a net rate law of $r'_{B,net} = k_1 C_A - k_2 C_B$ and stoichiometry of $F_B = C_B v_0$

    (a) Therefore, $v_0 \dfrac{dC_B}{dW} = k_1 C_A - k_2 C_B$

    (b) Substituting for C_A from 2(b) and introducing τ' yields $\dfrac{dC_B}{d\tau'} + k_2 C_B = k_1 C_{A0} e^{-k_1 \tau'}$

    (c) This can be integrated to yield $C_B = k_1 C_{A0} \left(\dfrac{e^{-k_1 \tau'} - e^{-k_2 \tau'}}{k_2 - k_1} \right)$

4. To find the optimum reactor length to maximize B, one can differentiate C_B with respect to τ' and set it equal to zero. This will yield the optimal τ', which subsequently yields the optimal W. From here, one could find the optimal conversion if desired

5. A mole balance on C yields $v_0 \dfrac{dC_C}{dW} = k_2 C_B$, which can be rewritten as $\dfrac{dC_C}{d\tau'} = k_2 C_B$

6. Plugging in the result of 3(c) and integrating (applying the initial condition of $C_C = 0$ at $\tau' = 0$) will yield an expression for C_C

   (a) Similarly, one could state that $C_C = C_{A0} - C_A - C_B$

6.4 Algorithm for Solution of Complex Reactions

1. Write out the reactions

   (a) Number each reaction. Split up a series reaction into multiple steps

2. Write the mole balance of each mole balance

   (a) Batch

      i. $\dfrac{dN_i}{dt} = r_i V$ or $\dfrac{dC_i}{dt} = r_i$ (for liquids only)

   (b) PFR

      i. $\dfrac{dF_i}{dV} = r_i$ or $\dfrac{dC_i}{dV} = \dfrac{r_i}{v_0}$ (for liquids only)

   (c) PBR

      i. $\dfrac{dF_i}{dW} = r_i$ or $\dfrac{dC_i}{dW} = \dfrac{r_i}{v_0}$ (for liquids only)

   (d) CSTR

      i. $V = \dfrac{F_{i0} - F_i}{-r_i}$ or $V = \dfrac{v_0 \left[C_{i0} - C_i \right]}{-r_i}$ (for liquids only)

   (e) Semibatch B added to A

      i. $\dfrac{dN_A}{dt} = r_A V$, $\dfrac{dN_B}{dt} = F_{B0} + r_B V$ or $\dfrac{dC_A}{dt} = r_A - \dfrac{v_0 C_A}{V}$, $\dfrac{dC_B}{dt} = r_B + \dfrac{v_0 \left[C_{B0} - C_B \right]}{V}$ (for liquids only)

3. Net Rate

   (a) Write the net rate of reaction for each species

      i. Example: $r_A = r_{1A} + r_{2A}$

   (b) Write the rate law for one species in every reaction

      i. Example: $r_{1A} = -k_{1A} C_A C_B$

   (c) In each reaction, relate the rates of reaction of each species to the same basis

      i. If the reaction is $aA + bB \rightarrow cC + dD$, then the relation you would use $\dfrac{r_{iA}}{-a_i} = \dfrac{r_{iB}}{-b_i} = \dfrac{r_{iC}}{c_i} + \dfrac{r_{iD}}{d_i}$

   (d) Combine the net rates, rate laws, and relative rates to write the net rates in terms of the concentration

4. Stoichiometry

   (a) For gas-phase reactions, write the concentrations in terms of the molar flow rates

      i. $C_i = C_{T0} \dfrac{F_i P T_0}{F_T P_0 T}$ with $F_T = \sum F_i$ and $C_{T0} = \dfrac{F_{T0}}{v_0}$

   (b) For liquid-phase reactions, v is constant so $C_i = \dfrac{F_i}{v_0}$

5. Pressure Drop

   (a) Write the gas-phase pressure drop term in terms of molar flow rates

      i. $\dfrac{dy}{dW} = -\dfrac{\alpha}{2y} \dfrac{F_T}{F_{T0}} \dfrac{T}{T_0}$ where $y = \dfrac{P}{P_0}$

6. Solve the system of ODEs

7 Reaction Mechanisms, Pathways, Bioreactions, and Bioreactors

7.1 Active Intermediates and Nonelementary Rate Laws

- The pseudo-steady-state hypothesis states that

$$r_A^* = \sum_{i=1}^{n} r_{iA^*} = 0$$

where A^* is the active intermediate

- Species having the concentration(s) appearing in the denominator of the rate law probably collide with the active intermediate: $A + A^* \rightarrow$ Collision products

- If a constant appears in the denominator, one of the reaction steps is probably the spontaneous deocmposition of the active intermediate: $A^* \rightarrow$ Decomposition products

- Species having the concentration(s) appearing in the numerator of the rate law probably produce the active intermediate in one of the reaction steps: reactant $\rightarrow A^* +$ other products

7.2 Enzymatic Reaction Fundamentals

- One cannot measure the concentration of an enzyme-substrate complex or the unbound enzyme concentration

  - To resolve this, introduce the total enzyme concentration, which is simply the sum of the bound and unbound enzyme concentration

- The Michaelis-Menten equation states that

$$\boxed{-r_S = \frac{V_{max} [S]}{K_M + [S]}}$$

where S is the substrate and $V_{max} = k_{cat} [E_t]$

- K_M is equal to the substrate concentration at which the rate of reaction is equal to one-half the maximum rate

- To linearize the Michaelis-Menten equation (called the Lineweaver-Burk plot),

$$\boxed{-\frac{1}{r_S} = \frac{K_M}{V_{max}} \left(\frac{1}{[S]}\right) + \frac{1}{V_{max}}}$$

- Other linearized forms exist. For instance, the Eadie-Hofstee form states that

$$-r_S = V_{max} - K_M \left(\frac{-r_S}{[S]}\right)$$

and the Hanes-Woolf form states that

$$\frac{[S]}{-r_S} = \frac{K_M}{V_{max}} + \frac{1}{V_{max}} [S]$$

- For a batch enzymatic reaction,

$$t = \frac{K_M}{V_{max}} \ln\left(\frac{1}{1-X}\right) + \frac{[S_0]\,X}{V_{max}}$$

which is equivalent to

$$\frac{1}{t} \ln\left(\frac{[S_0]}{[S]}\right) = \frac{V_{max}}{K_M} - \frac{[S_0] - [S]}{K_M t}$$

7.3 Inhibition of Enzyme Reactions

7.3.1 Competitive Inhibition

- The rate equation for competitive inhibition, where I is the inhibitor, is

$$\boxed{-r_S = \frac{V_{max}\,[S]}{[S] + K_M\left(1 + \dfrac{[I]}{K_I}\right)}}$$

which can be rearranged to

$$-\frac{1}{r_S} = \frac{1}{V_{max}} + \frac{1}{[S]}\frac{K_M}{V_{max}}\left(1 + \frac{[I]}{K_I}\right)$$

  - As the concentration of the inhibitor increases, the slope of the Lineweaver-Burke plot increases while the y-intercept stays the same

- The "apparent" Michaelis constant is $K_{M,app} = K_M\left(1 + \dfrac{[I]}{K_I}\right)$, so competitive inhibition increases the apparent Michaelis constant

7.3.2 Uncompetitive Inhibition

- The rate equation is

$$\boxed{-r_S = \frac{V_{max}\,[S]}{K_M + [S]\left(1 + \dfrac{[I]}{K_I}\right)}}$$

which can be rearranged to

$$-\frac{1}{r_S} = \frac{1}{[S]}\frac{K_M}{V_{max}} + \frac{1}{V_{max}}\left(1 + \frac{[I]}{K_I}\right)$$

  - As the concentration of the inhibitor increases, the slope remains the same but the y-intercept increases

7.3.3 Noncompetitive Inhibition

- The rate equation is

$$\boxed{-r_S = \frac{V_{max}\,[S]}{([S] + K_M)\left(1 + \dfrac{[I]}{K_I}\right)}}$$

which can be rearranged to

$$-\frac{1}{r_S} = \frac{1}{V_{max}}\left(1 + \frac{[I]}{K_I}\right) + \frac{1}{[S]}\frac{K_M}{V_{max}}\left(1 + \frac{[I]}{K_I}\right)$$

  - As the concentration of the inhibitor increases, the slope and y-intercept will increase

8 Appendix

8.1 Integral Table

$$\int_0^X \frac{dX}{1-X} = \ln\left(\frac{1}{1-X}\right)$$

$$\int_{X_1}^{X_2} \frac{dX}{(1-X)^2} = \frac{1}{1-X_2} - \frac{1}{1-X_1}$$

$$\int_0^X \frac{dX}{(1-X)^2} = \frac{X}{1-X}$$

$$\int_0^X \frac{dX}{1+\varepsilon X} = \frac{1}{\varepsilon}\ln\left(1+\varepsilon X\right)$$

$$\int_0^X \frac{(1+\varepsilon X)\,dX}{1-X} = (1+\varepsilon)\ln\left(\frac{1}{1-X}\right) - \varepsilon X$$

$$\int_0^X \frac{(1+\varepsilon X)\,dX}{(1-X)^2} = \frac{(1+\varepsilon)\,X}{1-X} - \varepsilon\ln\left(\frac{1}{1-X}\right)$$

$$\int_0^X \frac{(1+\varepsilon X)^2\,dX}{(1-X)^2} = 2\varepsilon\left(1+\varepsilon\right)\ln\left(1-X\right) + \varepsilon^2 X + \frac{(1+\varepsilon)^2\,X}{1-X}$$

$$\int_0^X \frac{dX}{(1-X)\left(\Theta_i - X\right)} = \frac{1}{\Theta_i - 1}\ln\left(\frac{\Theta_i - X}{\Theta_i\left(1-X\right)}\right) \quad \Theta \neq 1$$

$$\int_0^W (1-\alpha W)^{1/2}\,dW = \frac{2}{3\alpha}\left(1 - (1-\alpha W)^{3/2}\right)$$

$$\int_0^X \frac{dX}{aX^2 + bX + c} = \frac{-2}{2aX + b} + \frac{2}{b} \quad \text{for } b^2 = 4ac$$

$$\int_0^X \frac{dX}{aX^2 + bX + c} = \frac{1}{a\left(p-q\right)}\ln\left(\frac{q}{p}\frac{X-p}{X-q}\right) \quad \text{for } b^2 > 4ac$$

It should be noted that p and q are the roots of the equation.

$$\int_0^X \frac{a+bX}{c+gX}\,dX = \frac{bX}{g} + \frac{ag-bc}{g^2}\ln\left(\frac{c+gX}{c}\right)$$

8.2 Rate Equations

Table 5.1 Performance Equations for nth-order Kinetics and $\varepsilon_A = 0$

	Plug Flow or Batch		Mixed Flow	
$n = 0$ $-r_A = k$	$\dfrac{k\tau}{C_{A0}} = \dfrac{C_{A0} - C_A}{C_{A0}} = X_A$	**(20)**	$\dfrac{k\tau}{C_{A0}} = \dfrac{C_{A0} - C_A}{C_{A0}} = X_A$	
$n = 1$ $-r_A = kC_A$	$k\tau = \ln \dfrac{C_{A0}}{C_A} = \ln \dfrac{1}{1 - X_A}$	**(3.12)**	$k\tau = \dfrac{C_{A0} - C_A}{C_A} = \dfrac{X_A}{1 - X_A}$	**(14a)**
$n = 2$ $-r_A = kC_A^2$	$k\tau C_{A0} = \dfrac{C_{A0} - C_A}{C_A} = \dfrac{X_A}{1 - X_A}$	**(3.16)**	$k\tau = \dfrac{(C_{A0} - C_A)}{C_A^2} = \dfrac{X_A}{C_{A0}(1 - X_A)^2}$	**(15)**
any n $-r_A = kC_A^n$	$(n - 1)C_{A0}^{n-1} k\tau = \left(\dfrac{C_A}{C_{A0}}\right)^{1-n} - 1 = (1 - X_A)^{1-n} - 1$ **(3.29)**		$k\tau = \dfrac{C_{A0} - C_A}{C_A^n} = \dfrac{X_A}{C_{A0}^{n-1}(1 - X_A)^n}$	
$n = 1$ $A \overset{1}{\underset{2}{\rightleftharpoons}} R$ $C_{R0} = 0$	$k_1\tau = \left(1 - \dfrac{C_{Ae}}{C_{A0}}\right) \ln\left(\dfrac{C_{A0} - C_{Ae}}{C_A - C_{Ae}}\right) = X_{Ae} \ln\left(\dfrac{X_{Ae}}{X_{Ae} - X_A}\right)$		$k_1\tau = \dfrac{(C_{A0} - C_A)(C_{A0} - C_{Ae})}{C_{A0}(C_A - C_{Ae})} = \dfrac{X_A X_{Ae}}{X_{Ae} - X_A}$	
General rate	$\tau = \displaystyle\int_{C_A}^{C_{A0}} \dfrac{dC_A}{-r_A} = C_{A0} \int_0^{X_{Ae}} \dfrac{dX_A}{-r_A}$	**(19)**	$\tau = \dfrac{C_{A0} - C_A}{-r_{Af}} = \dfrac{C_{A0} X_A}{-r_{Af}}$	**(13)**

Table 5.2 Performance Equations for nth-order Kinetics and $\varepsilon_A \neq 0$

	Plug Flow		Mixed Flow	
$n = 0$ $-r_A = k$	$\dfrac{k\tau}{C_{A0}} = X_A$	**(20)**	$\dfrac{k\tau}{C_{A0}} = X_A$	
$n = 1$ $-r_A = kC_A$	$k\tau = (1 + \varepsilon_A)\ln \dfrac{1}{1 - X_A} - \varepsilon_A X_A$	**(21)**	$k\tau = \dfrac{X_A(1 + \varepsilon_A X_A)}{1 - X_A}$	**(14b)**
$n = 2$ $-r_A = kC_A^2$	$k\tau C_{A0} = 2\varepsilon_A(1 + \varepsilon_A)\ln(1 - X_A) + \varepsilon_A^2 X_A + (\varepsilon_A + 1)^2 \cdot \dfrac{X_A}{1 - X_A}$	**(23)**	$k\tau C_{A0} = \dfrac{X_A(1 + \varepsilon_A X_A)^2}{(1 - X_A)^2}$	**(15)**
any n $-r_A = kC_A^n$			$k\tau C_{A0}^{n-1} = \dfrac{X_A(1 + \varepsilon_A X_A)^n}{(1 - X_A)^n}$	
$n = 1$ $A \overset{1}{\underset{2}{\rightleftharpoons}} rR$ $C_{R0} = 0$	$\dfrac{k\tau}{X_{Ae}} = (1 + \varepsilon_A X_{Ae})\ln \dfrac{X_{Ae}}{X_{Ae} - X_A} - \varepsilon_A X_A$	**(22)**	$\dfrac{k\tau}{X_{Ae}} = \dfrac{X_A(1 + \varepsilon_A X_A)}{X_{Ae} - X_A}$	
General expression	$\tau = C_{A0} \displaystyle\int_0^{X_A} \dfrac{dX_A}{-r_A}$	**(17)**	$\tau = \dfrac{C_{A0} X_A}{-r_A}$	**(11)**