Chapter 5

Ideal Reactors for a Single Reaction

Single Ideal reactor
Homogeneous reactions

- **Batch reactor** : Unsteady state operation

- **Plug flow reactor** : Slug flow, Piston flow,
  Ideal tubular unmixed flow reactor

- No element of fluid overtaking or mixing

  with any other element ahead or behind

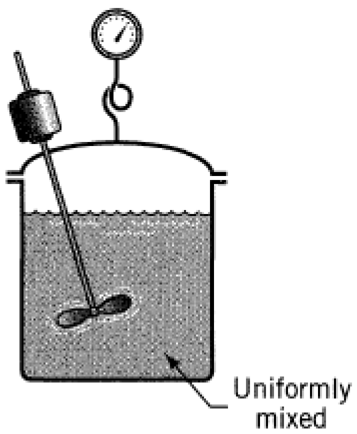
- There may be lateral mixing, no mixing along the flow path
  - **Constant flow stirred tank reactor (CFSTR):**
    Mixed reactor

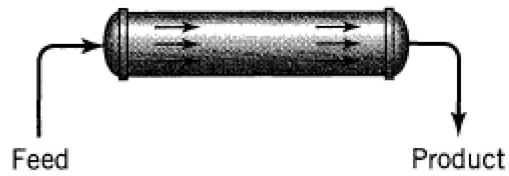
Single Ideal reactor

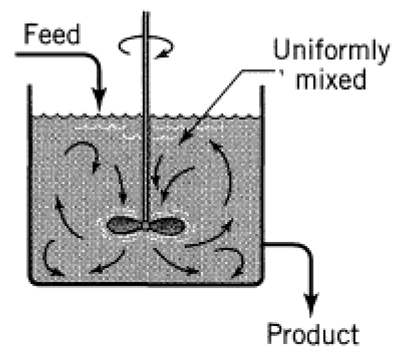
- Internal volume of reactor, V_r
- While V the volume of reacting fluid

voidage ε

$$V = \varepsilon V_r$$







Plug flow reactor, PFR

Batch reactor

Mixed flow reactor, MFR

IDEAL BATCH REACTOR

- Composition is uniform throughout at any instant of time,
- No fluid enters or leaves the reaction mixture during reaction

$$\overbrace{\cancel{\text{input}}}^{=0} = \overbrace{\cancel{\text{output}}}^{=0} + \text{disappearance} + \text{accumulation}$$

$$+\begin{pmatrix}\text{rate of loss of reactant A}\\ \text{within reactor due to}\\ \text{chemical reaction}\end{pmatrix} = -\begin{pmatrix}\text{rate of accumulation}\\ \text{of reactant A}\\ \text{within the reactor}\end{pmatrix}$$

unit

$$\begin{matrix}\text{disappearance of A}\\ \text{by reaction,}\\ \text{moles/time}\end{matrix} = (-r_A)V = \left(\frac{\text{moles A reacting}}{\text{(time)(volume of fluid)}}\right)\text{(volume of fluid)}$$

$$\begin{matrix}\text{accumulation of A,}\\ \text{moles/time}\end{matrix} = \frac{dN_A}{dt} = \frac{d[N_{A0}(1-X_A)]}{dt} = -N_{A0}\frac{dX_A}{dt}$$

IDEAL BATCH REACTOR

$$(-r_A)V = N_{A0}\frac{dX_A}{dt}$$

$$t = N_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)V}$$

If the density of the fluid remains constant

$$t = C_{A0}\int_0^{X_A}\frac{dX_A}{-r_A} = -\int_{C_{A0}}^{C_A}\frac{dC_A}{-r_A} \qquad \text{for } \varepsilon_A = 0$$

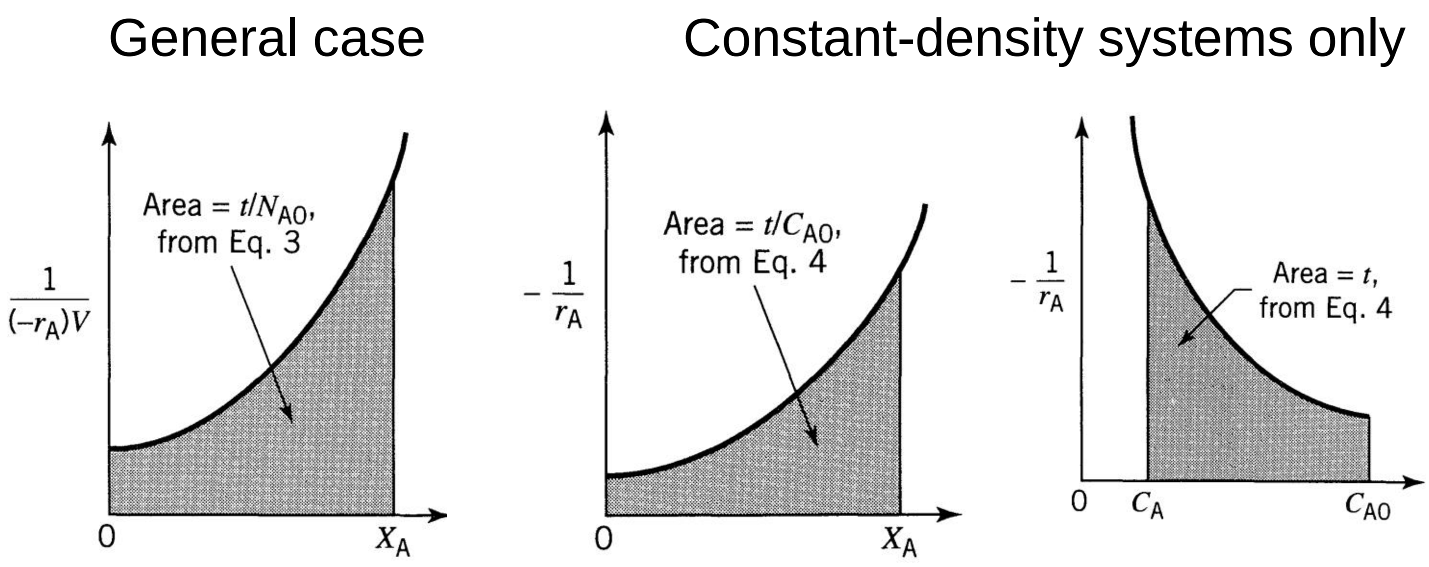
Volume of reacting mixture changes proportionally with conversion

$$t = N_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)V_0(1+\varepsilon_A X_A)}$$

$$= C_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)(1+\varepsilon_A X_A)}$$

IDEAL BATCH REACTOR

Graphical representation of the performance equations for isothermal



Space-Time and Space-Velocity

Proper performance measures of flow reactors

IDEAL BATCH REACTOR

Space-time:

$$\tau = \frac{1}{s} = \left(\begin{array}{c} \text{time required to process one} \\ \text{reactor volume of feed measured} \\ \text{at specified conditions} \end{array} \right) = [\text{time}]$$

Space -velocity

$$s = \frac{1}{\tau} = \left(\begin{array}{c} \text{number of reactor volumes of} \\ \text{feed at specified conditions which} \\ \text{can be treated in unit time} \end{array} \right) = [\text{time}^{-1}]$$

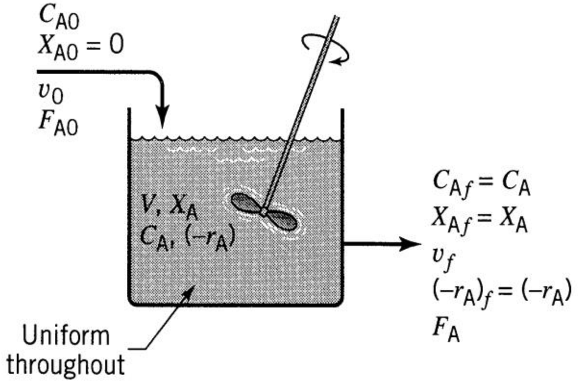
$$\tau = \frac{1}{s} = \frac{C_{A0}V}{F_{A0}} = \frac{\left(\dfrac{\text{moles A entering}}{\text{volume of feed}}\right)(\text{volume of reactor})}{\left(\dfrac{\text{moles A entering}}{\text{time}}\right)}$$

$$= \frac{V}{v_0} = \frac{(\text{reactor volume})}{(\text{volumetric feed rate})}$$

The space-velocity and space-time based on feed at actual entering conditions

STEADY-STATE MIXED FLOW REACTOR

- Composition is uniform throughout reactor
- By selecting reactant A for consideration



$$\text{input} = \text{output} + \text{disappearance by reaction} + \underbrace{\cancel{\text{accumulation}}}_{=0}$$

if $F_{A0} = v_0 C_{A0}$ is the molar feed rate of component A

$$\boxed{\begin{aligned} \text{input of A, moles/time} &= F_{A0}(1 - X_{A0}) = F_{A0} \\ \text{output of A, moles/time} &= F_A = F_{A0}(1 - X_A) \end{aligned}}$$

$$\begin{matrix}\text{disappearance of A}\\ \text{by reaction,}\\ \text{moles/time}\end{matrix} = (-r_A)V = \left(\frac{\text{moles A reacting}}{(\text{time})(\text{volume of fluid})}\right)\left(\begin{matrix}\text{volume of}\\ \text{reactor}\end{matrix}\right)$$

$$F_{A0} X_A = (-r_A)V$$

On rearrangement:

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{\Delta X_A}{-r_A} = \frac{X_A}{-r_A}$$

$$\tau = \frac{1}{s} = \frac{V}{v_0} = \frac{V C_{A0}}{F_{A0}} = \frac{C_{A0} X_A}{-r_A}$$

Steady-State Mixed Flow Reactor

- Where X_A and r_A are measured at exit stream conditions,
- Which are the same as the conditions within the reactor

If the feed enters the reactor, subscript 0

Partially converted, subscript i,

leaves at conditions given by subscript *f*

$$\frac{V}{F_{A0}} = \frac{\Delta X_A}{(-r_A)_f} = \frac{X_{Af} - X_{Ai}}{(-r_A)_f} \qquad \tau = \frac{VC_{A0}}{F_{A0}} = \frac{C_{A0}(X_{Af} - X_{Ai})}{(-r_A)_f}$$

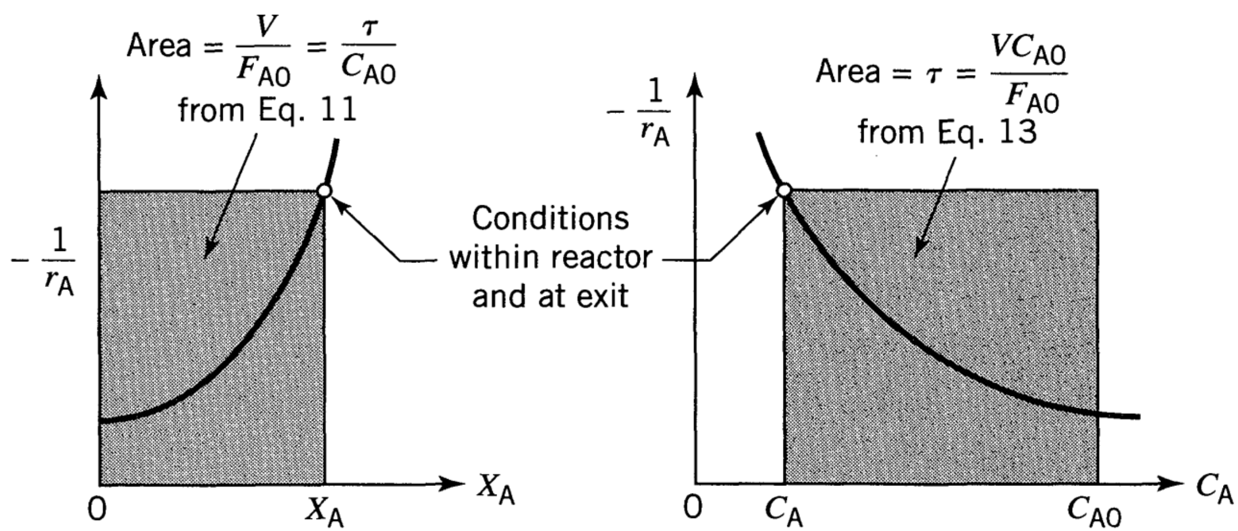
Constant-density systems $X_A = 1 - C_A/C_{Ao}$

$$\frac{V}{F_{A0}} = \frac{X_A}{-r_A} = \frac{C_{A0} - C_A}{C_{A0}(-r_A)}$$

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

Mixed flow reactor

General case | Constant-density systems only



First-order Reaction:

$$k\tau = \frac{X_A}{1 - X_A} = \frac{C_{A0} - C_A}{C_A} \qquad \text{for } \varepsilon_A = 0$$

For linear expansion

$$V = V_0(1 + \varepsilon_A X_A) \qquad \frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A}$$

Mixed flow reactor

- First-order reaction the performance expression

$$k\tau = \frac{X_A(1+\varepsilon_A X_A)}{1-X_A} \qquad \text{for any } \varepsilon_A$$

- Second-order reaction, A -> products,

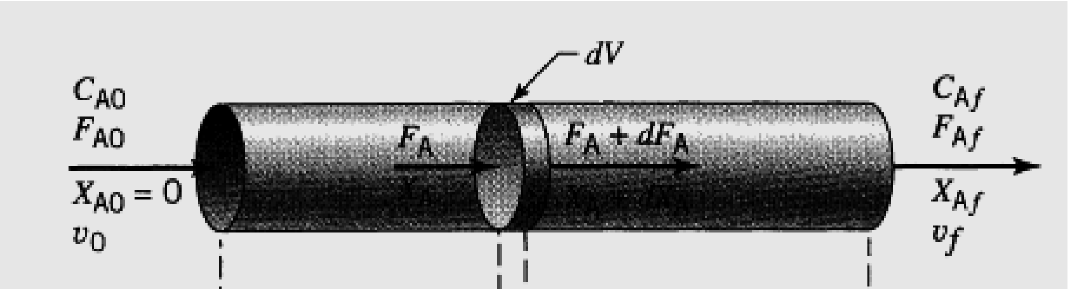
$$-r_A = kC_A^2,\ \varepsilon_A = 0,$$

The performance equation

$$k\tau = \frac{C_{A0}-C_A}{C_A^2} \quad \text{or} \quad C_A = \frac{-1+\sqrt{1+4k\tau C_{A0}}}{2k\tau}$$

STEADY-STATE PLUG FLOW REACTOR

- Composition of the fluid varies from point to point along a flow path



- Material balance for a reaction component made for a differential element of volume dV

$$\text{input} = \text{output} + \text{disappearance by reaction} + \underbrace{\cancel{\text{accumulation}}}_{=0}$$

Input of **A,** moles/time = $\boldsymbol{F_A}$
Output of **A,** moles/time = $\boldsymbol{F_A + dF_A}$
Disappearance of **A** by reaction, moles/time = $(-r_A)dV$

PLUG FLOW REACTOR

- Disappearance of **A** by reaction, moles/time = $(-r_A)dV$

$$= \left(\frac{\text{moles A reacting)}}{\text{(time)(volume of fluid)}}\right)\left(\begin{matrix}\text{volume of}\\ \text{element}\end{matrix}\right)$$

$$F_A = (F_A + dF_A) + (-r_A)dV$$

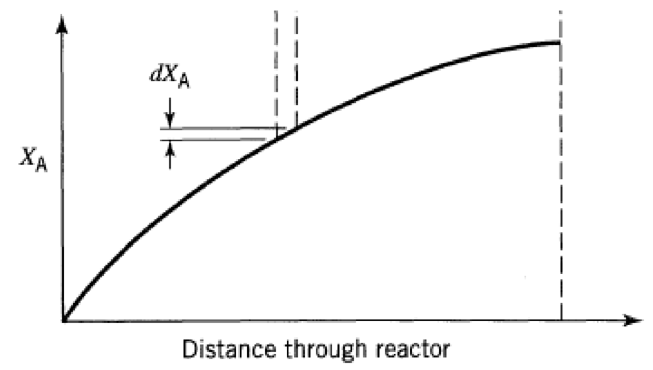
$$dF_A = d[F_{A0}(1 - X_A)] = -F_{A0}dX_A$$

$$F_{A0}dX_A = (-r_A)dV$$

$$\int_0^V \frac{dV}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

$$\tau = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = C_{A0}\int_0^{X_{Af}} \frac{dX_A}{-r_A}$$



PLUG FLOW REACTOR

- Difference in plug flow r_A varies, whereas in mixed flow r_A is constant

$$\frac{V}{F_{A0}} = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}$$

- Case of constant-density systems

$$\tau = C_{A0} \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}$$

$$\varepsilon_A = 0$$

$$X_A = 1 - \frac{C_A}{C_{A0}} \quad \text{and} \quad dX_A = -\frac{dC_A}{C_{A0}}$$

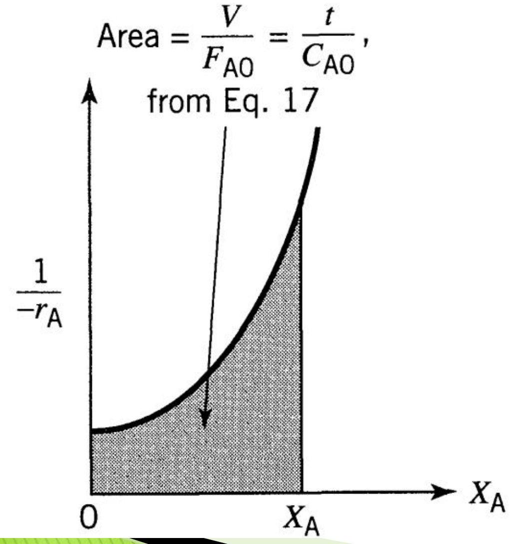
Performance equations for plug flow reactors

$\varepsilon_A = 0$

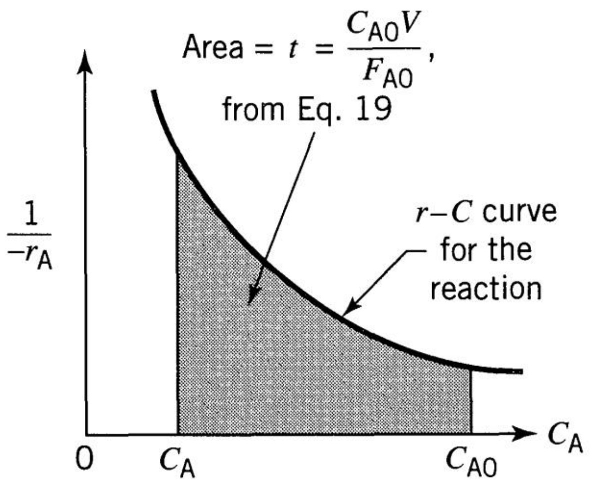
$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A} = -\frac{1}{C_{A0}} \int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A}$$

$$\tau = \frac{V}{v_0} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{-r_A} = -\int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A}$$

General case



Constant-density systems only



Simpler integrated forms for plug flow

Zero-order homogeneous reaction:

$$k\tau = \frac{kC_{A0}V}{F_{A0}} = C_{A0}X_A$$

First-order irreversible reaction:

$$k\tau = -(1+\varepsilon_A)\ln(1-X_A) - \varepsilon_A X_A$$

First-order reversible reaction

$$A \rightleftarrows rR,\ C_{R0}/C_{A0} = M$$

$$-r_A = k_1 C_A - k_2 C_R$$

Equilibrium conversion $\boldsymbol{X_{Ae}}$

$$k_1\tau = \frac{M + rX_{Ae}}{M + r}\left[-(1+\varepsilon_A X_{Ae})\ln\left(1 - \frac{X_A}{X_{Ae}}\right) - \varepsilon_A X_A\right]$$

Second-order irreversible reaction

- Second-order irreversible reaction

  A + B -> Products with equimolar feed or

  2A -> Products

constant ε_A

$$C_{A0}k\tau = 2\varepsilon_A(1+\varepsilon_A)\ln(1-X_A) + \varepsilon_A^2 X_A + (\varepsilon_A+1)^2 \frac{X_A}{1-X_A}$$

Holding Time and Space Time

$$\tau = \begin{pmatrix} \text{time needed to} \\ \text{treat one reactor} \\ \text{volume of feed} \end{pmatrix} = \frac{V}{v_0} = \frac{C_{A0}V}{F_{A0}},$$

$$\bar{t} = \begin{pmatrix} \text{mean residence time} \\ \text{of flowing material} \\ \text{in the reactor} \end{pmatrix}$$

$$= C_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)(1 + \varepsilon_A X_A)}$$

constant density systems

(all liquids and constant density gases)

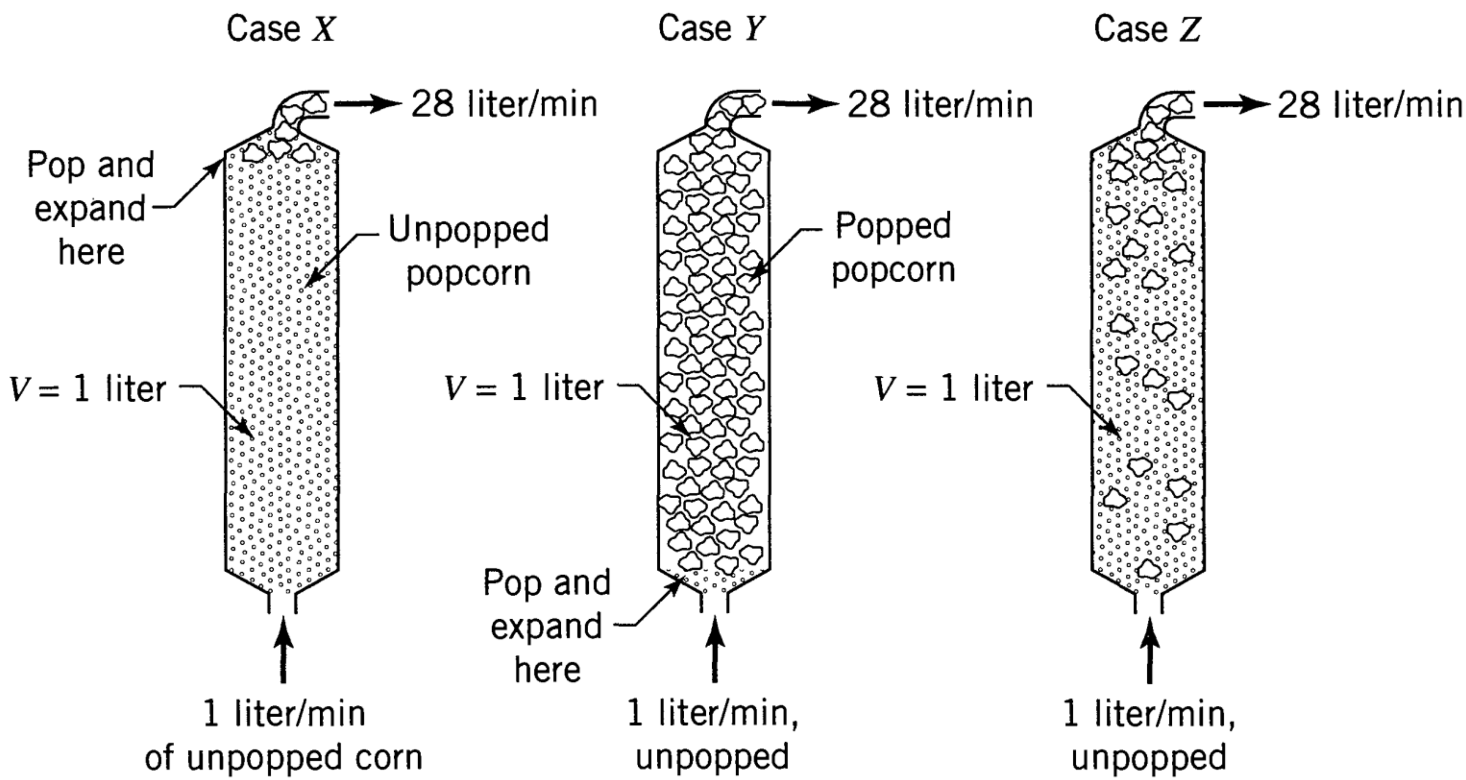
$$\tau = \bar{t} = \frac{V}{v}$$

For changing density systems $\bar{t} \neq \tau$ and $\bar{t} \neq V/v_0$

Holding Time and Space Time

- Consider three cases of the steady-flow popcorn
- Takes in 1 liter/min of raw corn and produces 28 liters/min

Consider three cases, called **X, Y, and Z**,



Holding Time and Space Time

- Case X : All the popping occurs at the back end of the reactor
- Case Y : All the popping occurs at the front end of the reactor
- Case Z : The popping occurs somewhere between entrance and exit

$$\tau_X = \tau_Y = \tau_Z = \frac{V}{v_0} = \frac{1 \text{ liter}}{1 \text{ liter/min}} = 1 \text{ min}$$

Irrespective of where the popping occurs

Residence time in the three cases is very different

$$\bar{t}_X = \frac{1 \text{ liter}}{1 \text{ liter/min}} = 1 \text{ min}$$

$$\bar{t}_Y = \frac{1 \text{ liter}}{28 \text{ liter/min}} \cong 2 \text{ sec}$$

$\bar{t}_Z$ is somewhere between 2 and 60 s

Value of $\bar{t}$ depends on what happens in the reactor, while τ is independent of what happens in the reactor

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

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

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

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

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, $-r_A = kC_A^n$			$k\tau C_{A0}^{n-1} = \dfrac{X_A(1 + \varepsilon_A X_A)^n}{(1 - X_A)^n}$	
$n = 1$, $A \underset{2}{\overset{1}{\rightleftharpoons}} rR$, $C_{R0} = 0$	$\dfrac{k\tau}{X_{Ae}} = (1 + \varepsilon_A X_{Ae})\ln\dfrac{X_{Ae}}{X_{Ae} - X_A} - \varepsilon_A X_A$	**(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)**

Thankyou