## ISOTHERMAL REACTOR DESIGN

In Chapter 1 \& 2, we discussed balances on batch \& flow reactors. In Chapter 3, we discussed rxns. Here, we will combine rxns and reactors.

## Topics

Part 1: Mole Balances in Terms of Conversion

1. Algorithm for Isothermal Reactor Design
2. Applications/Examples of CRE Algorithm
3. Reversible Reactions
4. ODE Solutions to CRE Problems
5. General Guidelines for California Problems
6. PBR with Pressure Drop
7. Engineering Analysis

Part 2: Measures Other Than Conversion

1. Measures Other Than Conversion
2. Membrane Reactors
3. Semibatch Reactors

## Part 1: Mole Balances in Terms of Conversion

1. Algorithm for Isothermal Reactor Design

The algorithm for the pathway of interest can be summarized as:

1. Mole Balance and Design Equation
(choose reactor type)
2. Rate Law
(choose rxn type; gas or liq. phase)
3. Stoichiometry
4. Combine
5. Evaluate

The Evaluate Step can be carried out
A. Graphically (Plots)
B. Numerically (Quadrature Formulas)
C. Analytically (Integral tables)
D. Using Software Packages


## Elementary gas phase reaction in different reactor types

## CSTR

The elementary gas phase reaction $2 \mathrm{~A}+\mathrm{B} \rightarrow \mathrm{C}$
takes place in a CSTR at constant temperature ( 500 K ) and constant pressure (16.4 atm). The feed is equal molar in A and B. $x=0.9, k=10 \mathrm{dm}^{6} / \mathrm{mol}^{2} \mathrm{~s}$
$\mathrm{V}_{\text {CSTR }}=$ ?

Mole balance

$$
V=\frac{F_{A, 0} X}{-r_{A}}
$$

Rate Law

$$
-r_{A}=k C_{A}^{2} C_{B}
$$

Stoichiometry gas phase, isothermal $\left(T=T_{0}\right)$, no pressure drop $\left(P=P_{0}\right)$

$$
\begin{aligned}
& \mathrm{O}_{\mathrm{A}}=\mathrm{C}_{\mathrm{A} 0} \frac{(1-\mathrm{X})}{(1-0.5 \mathrm{X})} \quad \text { Derivation } \\
& \mathrm{O}_{\mathrm{E}}=\mathrm{O}_{\mathrm{A} 0}
\end{aligned}
$$

$$
C_{A, 0}=\frac{Y_{A 0} P_{0}}{R T_{0}}=\frac{(0.5)(16.4 \mathrm{~atm})}{\left(\frac{0.082 \mathrm{~atm} \cdot \mathrm{~m}^{3}}{\mathrm{kmol} \cdot \mathrm{~K}}\right)(500 \mathrm{~K})}=0.2 \frac{\mathrm{kmol}}{\mathrm{~m}^{3}}=0.2 \frac{\mathrm{~mol}}{\mathrm{dm}^{3}}
$$

Combine

$$
\begin{aligned}
& -r_{A}=k C_{A}^{2} C_{B}=k C_{A 0}^{3} \frac{(1-X)^{2}}{(1-0.5 X)^{2}} \\
& -r_{A}=\left(10 \frac{\mathrm{dm}^{6}}{\mathrm{~mol}^{2} \cdot \mathrm{~s}}\right)\left(0.2 \frac{\mathrm{~mol}}{\mathrm{dm}^{3}}\right)^{3} \frac{(1-\mathrm{X})^{2}}{(1-0.5 \mathrm{X})^{2}} \\
& -r_{\mathrm{A}}=\left(0.08 \frac{\mathrm{~mol}}{\mathrm{dm}^{3} \cdot \mathrm{~s}}\right) \frac{(1-\mathrm{X})^{2}}{(1-0.5 x)^{2}}
\end{aligned}
$$

## Evaluate

$$
V=\frac{F_{\mathrm{A}_{0}} \times}{-r_{\mathrm{A}}}=\frac{(5 \mathrm{~mol} / \mathrm{s})(0.9)\left[1-0.5(0.9]^{2}\right.}{\left(0.8 \frac{\mathrm{~mol}}{\mathrm{dm}^{3} \cdot \mathrm{~s}}\right)(1-0.9)^{2}}
$$

```
V = 1701 dm}\mp@subsup{}{}{3
```


## PFR and Batch Reactors

Elementary Gas Phase Reaction: $2 \mathrm{~A}+\mathrm{B} \rightarrow \mathrm{C}$

## PFR

Mole Balance $\quad V=F_{A 0} \int_{0}^{X} \frac{d X}{-r_{A}}$

## Rate Law

$$
-r_{A}=k C_{A}^{2} C_{B}
$$

Stoichiometry

$$
\text { gas phase, isothermal }\left(T=T_{0}\right) \text {, no pressure }
$$

$$
\operatorname{drop}\left(P=P_{0}\right), C_{A 0}=C_{B o}(\Theta=1), v=v_{0}(1+\varepsilon X)
$$

$$
\begin{gathered}
A+\frac{B}{2} \longrightarrow \frac{C}{2} \\
C_{A}=C_{A 0} \frac{(1-x)}{(1+\varepsilon x)} \\
\varepsilon=y_{A 0} \delta=\frac{1}{2}\left(\frac{1}{2}-\frac{1}{2}-1\right)=-\frac{1}{2} \\
v=v_{0}\left(1-\frac{1}{2} x\right) \\
C_{B}=\frac{F_{A 0}}{v}=\frac{F_{A 0}\left(1-\frac{X}{2}\right)}{v_{0}\left(1-\frac{1}{2} x\right)}=C_{A O} \\
C_{B}=C_{A O}
\end{gathered}
$$

Combine

$$
\begin{gathered}
-\mathrm{r}_{\mathrm{A}}=\mathrm{k} C_{\mathrm{A} 0}^{3} \frac{(1-X)^{2}}{(1+\varepsilon X)^{2}} \\
\mathrm{~V}=\frac{\mathrm{F}_{\mathrm{A} 0}}{\mathrm{kC} C_{\mathrm{A} 0}^{3}} \int \frac{(1+\varepsilon X)^{2}}{(1-X)^{2}} \mathrm{dX} \\
\mathrm{~V}=\frac{\mathrm{F}_{\mathrm{A} 0}}{\mathrm{kC}_{A 0}^{3}}\left[2 \varepsilon(1+\varepsilon) \ln (1-X)+\varepsilon^{2} \mathrm{X}+(\varepsilon+1)^{2} \frac{\mathrm{X}}{1-\mathrm{X}}\right\rfloor
\end{gathered}
$$

Parameter Evaluation $\begin{aligned} & \mathrm{C}_{\mathrm{Ao}}=0.2, \mathrm{v}=\mathrm{v}_{\mathrm{o}}=25 \mathrm{dm}^{3} / \mathrm{s}, \mathrm{k}=10 \mathrm{dm}^{6} / \mathrm{mol}^{2} \mathrm{~s}, \varepsilon=-0.5 \text {, } \\ & X=0.9\end{aligned}$ $X=0.9$

$$
\begin{gathered}
\mathrm{V}=\frac{\left(5 \frac{\mathrm{~mol}}{\mathrm{~s}}\right)}{\left(10 \frac{\mathrm{dm}^{6}}{\mathrm{~mol}^{2} \cdot \mathrm{~s}}\right)\left(0.2 \frac{\mathrm{~mol}}{\mathrm{dm}^{3}}\right)^{3}}=\left[2\left(-\frac{1}{2}\right)\left(1-\frac{1}{2}\right) \ln (1-0.9)+\left(-\frac{1}{2}\right)^{2}(0.9)+\left(-\frac{1}{2}+1\right)^{2} \frac{0.9}{1-0.9}\right] \\
\mathrm{V}=6.25 \mathrm{dm}^{3}[1.15+0.23+2.25]=226.9 \mathrm{dm}^{3}
\end{gathered}
$$

$$
V=227 \mathrm{dm}^{3}
$$

## Deriving $C_{A}$ and $C_{B}$

Remember that the reaction is: $\quad 2 A+B \rightarrow C$
For a gas phase system:

$$
\mathrm{C}_{\mathrm{A}}=\frac{F_{A}}{v}=\frac{F_{A_{0}}(1-X)}{v_{0}\left(1+e X^{\prime} P_{0} / P Y^{\prime} T / T_{0}\right)}
$$

If the conditions are isothermal $\left(T=T_{0}\right)$ and isobaric $\left(P=P_{0}\right)$ :

$$
\mathrm{C}_{\mathrm{A}}=\mathrm{C}_{\mathrm{AO}} \frac{(1-X)}{(1+\varepsilon)} \frac{T_{0}}{T} \frac{P}{P_{0}}=C_{A 0} \frac{(1-X)}{(1+\varepsilon)}
$$

We must divide by the stoichiometric coefficient of our basis of calculation yielding:

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

And if the feed is equal molar, then:

$$
\varepsilon=y_{40} \delta=0.5\left(\frac{1}{2}-\frac{1}{2}-1\right)=-0.5
$$

This leaves us with $C_{A}$ as a function of conversion alone:

$$
\mathrm{C}_{\mathrm{A}}=\mathrm{C}_{\mathrm{A} 0} \frac{(1-\mathrm{X})}{(1-0.5 \mathrm{X})}
$$

Similarly for $\mathrm{C}_{\mathrm{B}}$ :

$$
C_{\mathrm{B}}=\mathrm{C}_{\mathrm{A} 0} \frac{\left(\Theta_{\mathrm{B}}-\frac{1}{2} X\right)}{(1+\varepsilon X)}=C_{40} \frac{(1-0.5 X)}{(1-0.5 X)}=C_{A 0}
$$

Batch Reactor Constant Volume, $\mathrm{V}=\mathrm{Vo}$ and the pressure changes.
Mole Balance $\quad \mathrm{t}=\mathrm{N}_{\mathrm{A} 0} \int_{0}^{X} \frac{\mathrm{dX}}{-\mathrm{r}_{\mathrm{A}} V}=\mathrm{C}_{\mathrm{A} 0} \int_{0}^{X} \frac{\mathrm{dX}}{-\mathrm{r}_{\mathrm{A}}}$
$\underline{\text { Rate Law }} \quad-r_{A}=k_{A}^{2} C_{B}$

Stoichiometry $\quad C_{A}=\frac{\mathrm{N}_{\mathrm{A}}}{\mathrm{V}_{0}}=\frac{\mathrm{N}_{\text {AOO }}}{\mathrm{V}_{0}}(1-\mathrm{x})$

$$
C_{B}=\frac{N_{A O}}{V_{0}}\left(\Theta_{B}-\frac{1}{2} x\right)=C_{A O}\left(1-\frac{x}{2}\right)
$$

$\mathrm{P}=\frac{\mathrm{N}_{\mathrm{T}}}{\mathrm{N}_{\mathrm{To}}} \mathrm{P}_{o}=\frac{\mathrm{C}_{\mathrm{T}}}{\mathrm{C}_{\mathrm{To}}} \mathrm{P}_{o}$

Combine

$$
\begin{aligned}
& -r_{A}=k C_{A 0}^{3}(1-X)^{2}\left(1-\frac{X}{2}\right) \\
& t=\frac{1}{{k C_{A 0}^{2}}_{2} \int_{0}^{X} \frac{d X}{(1-X)^{2}\left(1-\frac{X}{2}\right)}}
\end{aligned}
$$

$$
\text { Parameter Evaluation } \quad \mathrm{C}_{\mathrm{A}_{0}}=0.2, \mathrm{k}=10 \mathrm{dm}^{6} / \mathrm{mol}^{2} \mathrm{~s} \text {, }
$$



$$
\mathrm{t}=\frac{1}{\mathrm{kC}_{\mathrm{A} 0}^{2}} \int_{0}^{0.9} \frac{\mathrm{dX}}{(1-\mathrm{X})^{2}\left(1-\frac{X}{2}\right)}
$$

$$
\begin{aligned}
& \left.\mathrm{t}=\frac{1}{\left(10 \frac{\mathrm{dm}^{6}}{\mathrm{~mol}^{2} \bullet \mathrm{~s}}\right)\left(0.2 \frac{\mathrm{~mol}}{\mathrm{dm}^{3}}\right)^{2}} \int_{0}^{0.9} \frac{\mathrm{dX}}{(1-\mathrm{X})^{2}\left(1-\frac{\mathrm{X}}{2}\right)} \right\rvert\, \\
& \mathrm{t}=2.5 \mathrm{~s} \int_{0}^{0.9} \frac{\mathrm{dX}}{(1-\mathrm{X})^{2}\left(1-\frac{\mathrm{X}}{2}\right)} \\
& \mathrm{t}=2.5 \mathrm{~s}\left\{\int_{0}^{1.6} \frac{\mathrm{dX}}{(1-\mathrm{X})^{2}\left(1-\frac{\mathrm{X}}{2}\right)}+\int_{0.6}^{0.9} \frac{\mathrm{dX}}{(1-\mathrm{X})^{2}\left(1-\frac{\mathrm{X}}{2}\right)}\right\}
\end{aligned}
$$

$$
\begin{aligned}
& \mathrm{t}=\frac{1}{\mathrm{kC}_{A 0}^{2}}\left\lceil\frac{\Delta \mathrm{X}_{1}}{3}(\mathrm{f}(\mathrm{X}=0)+4 \mathrm{f}(\mathrm{X}=0.3)+\mathrm{f}(\mathrm{X}=0.6))\right. \\
& \left.+\frac{\Delta \mathrm{X}_{2}}{3}(\mathrm{f}(\mathrm{X}=0.6)+4 \mathrm{f}(\mathrm{X}=0.75)+\mathrm{f}(\mathrm{X}=0.9))\right\rfloor \\
& \mathrm{t}=2.5 \mathrm{~s}\left[\frac{(0.3)}{3}[1+4(2.4)+7.81]\right]+\frac{(0.15)}{3}[7.81+4(25.6)+181] \\
& \mathrm{t}=2.5 \mathrm{~s}\left[\frac{0.3}{3}(18.4)+\frac{0.15}{3}[291]\right]=2.5 \mathrm{~s}[1.84+14.55] \\
& \mathrm{t}=41 \mathrm{~s} \\
& P=\frac{N_{T}}{N_{T 0}} P_{0}=\frac{\left(N_{t 0}+N_{z 0}+\delta N_{A 0} X\right) P_{0}}{N_{T 0}} \\
& =\left(1+y_{A 0} \delta X\right) P_{0} \\
& =\left(1+\left(\frac{1}{2}\right)\left(\frac{-1}{2}\right)(0.9)\right) 164 \\
& =12.7 \mathrm{~atm}
\end{aligned}
$$

## Scale - Up of Liquid - Phase Batch Reactor Data to Design of a CSTR:

Scale - Up a lab experiment to pilot - plant operation of full - scale
production. Find $k$ from experimental data and use it to design a full - scale flow reactor.

Batch Operation:
Liquid phase: (density change is small $\rightarrow \mathrm{V}=\mathrm{V}_{0}$ )
Gas phase with constant volume $\mathrm{V}=\mathrm{V}_{0}$.

$$
\begin{aligned}
& \frac{1}{V} \cdot\left(\frac{d N_{A}}{d t}\right)=r_{A} \\
& \frac{1}{V} \cdot\left(\frac{d N_{A}}{d t}\right)=\frac{1}{V_{0}} \cdot \frac{d N_{A}}{d t}=\frac{d N_{A} / V_{0}}{d t}=\frac{d C_{A}}{d t}=r_{A}
\end{aligned}
$$

Since conc'n is a measured quantity in liquid - phase rxns:

$$
-\frac{d C_{A}}{d t}=-r_{A}
$$

Let's calculate the time necessary to achieve a given conversion X for the irreversible second order rxn:

$$
\begin{align*}
N_{A 0} \cdot \frac{d X}{d t} & =-r_{A} \cdot V_{0} \\
-r_{A} & =k \cdot C_{A}^{2}  \tag{1}\\
C_{A} & =C_{A 0} \cdot(1-X) \tag{2}
\end{align*}
$$

Combine [1], [2] and [3];

$$
\frac{d X}{d t}=k \cdot C_{A 0} \cdot(1-X)^{2}
$$

Rearrange:

$$
\frac{d X}{(1-X)^{2}}=k \cdot C_{A 0} \cdot d t
$$

@ $\mathrm{t}=0 ; \mathrm{X}=0 ; \mathrm{T}=\mathrm{T}_{0}$ (isothermal) $\rightarrow \mathrm{k} \rightarrow$ constant

$$
\int_{0}^{t} t=\frac{1}{k \cdot C_{A 0}} \int_{0}^{X} \frac{d X}{(1-X)^{2}} \Rightarrow t=\frac{1}{k \cdot C_{A 0}} \cdot\left(\frac{X}{1-X}\right)
$$

It is important to know the reaction time, $\mathrm{t}_{\mathrm{R}}$, to achieve a certain conversion.

Flow reactors use characteristic rxn times, $t_{R}$.
The time for a total cycle is much longer than $t_{R}$, as one must account for the time to fill $\left(\mathrm{t}_{\mathrm{F}}\right)$, heat $\left(\mathrm{t}_{\mathrm{h}}\right)$ and clean $\left(\mathrm{t}_{\mathrm{C}}\right)$.

$$
\mathrm{t}=\mathrm{t}_{\mathrm{f}}+\mathrm{t}_{\mathrm{h}}+\mathrm{t}_{\mathrm{C}}+\mathrm{t}_{\mathrm{R}}
$$

## Design of Continuous Stirred Tank Reactors

CSTRs are usually used for liquid phase rxns:
$V=\frac{\overline{F_{A 0}} \cdot X}{\left(-r_{A}\right)_{\text {exit }}}=\frac{\overline{v_{0} \cdot C_{A 0}} \cdot X}{-r_{A}}$
[1] (Design Eq'n for CSTR)

Divide by $\mathrm{v}_{0}: \quad \tau=\frac{V}{v_{0}}=\frac{C_{A 0} \cdot X}{-r_{A}} \quad$ [2]

## A single CSTR:

First order irreversible rxn:

$$
\begin{array}{ll}
-r_{A}=k \cdot C_{A} & {[3]} \\
C_{A}=C_{A 0} \cdot(1-X) & {[4]} \\
\tau=\frac{1}{k} \cdot\left(\frac{X}{1-X}\right) & {[5]} \\
X=\frac{\tau \cdot k}{1+\tau \cdot k} & {[6]}
\end{array}
$$

Combine [4] and [6] $\quad C_{A}=\frac{C_{A 0}}{1+\frac{\tau \cdot k}{}}$
rxn Damköhler \#,
Da: a dimensionless \# that for a first order rxn
says the degree of conversion that can be achieved in cont. flow reactor.

$$
D a=\frac{-r_{A 0} \cdot V}{F_{A 0}}: \frac{\text { rate of rxn of } A}{\text { rate of convective transport of }\left.A\right|_{t=0}}
$$

For a second order rxn:

$$
D a=\frac{-r_{A 0} \cdot V}{F_{A 0}}=\frac{k \cdot C_{A 0}^{2} \cdot V}{v_{0} \cdot C_{A 0}}=\tau \cdot k \cdot C_{A 0}
$$

$D a \leq 0.1 \quad X<0.10$
$D a \geq 10 \quad X>0.90$

$$
\left.X=\frac{D a}{1+D a} \quad \text { First order liq-phase rxn (Eq'n }[6]\right)
$$

## CSTRs in Series



From the mole balance on reactor 2 :

$$
V_{2}=\frac{F_{A 1}-F_{A 2}}{-r_{A 2}}=\frac{v_{0}\left(C_{A 1}-C_{A 2}\right)}{k_{2} \cdot C_{A 2}}
$$

Solving for $\mathrm{C}_{\mathrm{A} 2}$ :

$$
C_{A 2}=\frac{C_{A 1}}{1+\tau_{2} \cdot k_{2}}=\frac{C_{A 0}}{\left(1+\tau_{2} \cdot k_{2}\right)\left(1+\tau_{1} \cdot k_{1}\right)}
$$

If both reactors are of equal size, $\quad\left(\tau_{1}=\tau_{2}=\tau\right)$
and operate at the same $T\left(k_{1}=k_{2}=k\right)$

$$
C_{A 2}=\frac{C_{A 0}}{(1+\tau \cdot k)^{2}}
$$

for $n$ equal sized CSTR system

$$
C_{A n}=\frac{C_{A 0}}{(1+\tau \cdot k)^{n}}=\frac{C_{A 0}}{(1+D a)^{n}}
$$

Substituting for $\mathrm{C}_{\mathrm{An}}$ in terms of conversion

$$
\begin{aligned}
& C_{A 0} \cdot(1-X)=\frac{C_{A 0}}{(1+D a)^{n}} \Rightarrow \\
& X=1-\frac{1}{(1+D a)^{n}}=1-\frac{1}{(1+\tau \cdot k)^{n}}
\end{aligned}
$$

## CSTRs in Parallel:

Equal sized reactors are placed in parallel rather than in series:


Individual volume is given by

$$
\begin{equation*}
V=F_{A 0 i} \cdot\left(\frac{X_{i}}{-r_{A i}}\right) \tag{1}
\end{equation*}
$$

Since $V_{i}=V_{j}$, then $X_{i}=X ; \rightarrow \quad-r_{A 1}=-r_{A 2}=\ldots . .=-r_{A}$

$$
\begin{equation*}
V_{i}=\frac{V}{n} \tag{2}
\end{equation*}
$$

$$
\begin{equation*}
F_{A 0 i}=\frac{F_{A 0}}{n} \tag{3}
\end{equation*}
$$

Substitute [2] \& [3] into [1]

$$
\begin{equation*}
\frac{V}{n}=\frac{F_{A 0}}{n} \cdot\left(\frac{X_{i}}{-r_{A i}}\right)=F_{A 0} \cdot \frac{X}{-r_{A}} \tag{4}
\end{equation*}
$$

Example: 2 ${ }^{\text {nd }}$ order rxn, $v=v_{0}, C_{A}=C_{A 0}(1-X) ; F_{A 0} X=v_{0} C_{A 0} X$
Combine $-\mathrm{r}_{\mathrm{A}}=\mathrm{k} \mathrm{C}_{\mathrm{A} 2}$ and $\mathrm{V}=\mathrm{F}_{\mathrm{A} 0} \mathrm{X} /-\mathrm{r}_{\mathrm{A}}$

$$
V=\frac{F_{A 0} \cdot X}{k \cdot C_{A}^{2}}=\frac{v_{0} \cdot C_{A 0} \cdot X}{k \cdot C_{A 0}^{2} \cdot(1-X)^{2}}
$$

Divide by $\mathrm{v}_{0}$ :

$$
\begin{aligned}
& \tau=\frac{V}{v_{0}}=\frac{X}{k \cdot C_{A 0} \cdot(1-X)^{2}} \\
& X=\frac{\left(1+2 \cdot \tau \cdot k \cdot C_{A 0}\right)-\sqrt{\left(1+2 \cdot \tau \cdot k \cdot C_{A 0}\right)^{2}-\left(2 \cdot \tau \cdot k \cdot C_{A 0}\right)^{2}}}{2 \cdot \tau \cdot k \cdot C_{A 0}} \\
& X=\frac{(1+2 \cdot D a)-\sqrt{1+4 D a} \quad}{2 \cdot D a} \quad \begin{array}{l}
\text { Since } \tau \cdot k \cdot C_{A 0}=D a \\
\text { for a second order rxn. }
\end{array}
\end{aligned}
$$

Since $X$ can not be greater than $1.0,(-)$ sign is chosen.

## Example: The elementary liquid phase reaction

$$
2 A \rightarrow B
$$

is carried out isothermally in a CSTR. Pure A enters at a volumetric flow rate of $25 \mathrm{dm}^{3} / \mathrm{s}$ and at a concentration of $0.2 \mathrm{~mol} / \mathrm{dm}^{3}$.
What CSTR volume is necessary to achieve a $90 \%$ conversion when $k=10$ $\mathrm{dm}^{3} /\left(\mathrm{mol}^{*} \mathrm{~s}\right)$ ?

Mole Balance $\quad V=\frac{F_{A o} X}{-r_{a}}$
Rate Law $\quad-r_{A}=k C_{A}{ }^{2}$
Stoichiometry liquid phase $\left(\mathrm{v}=\mathrm{v}_{\mathrm{o}}\right)$

$$
\begin{aligned}
& F_{A o}=v_{o} C_{A o} \quad F_{A}=v C_{A}=v_{o} C_{A} \\
& C_{A}=\frac{F_{A}}{v}=\frac{F_{A}}{v_{o}}=\frac{F_{A o}(1-X)}{v_{o}} \\
& C_{A}=C_{A o}(1-X)
\end{aligned}
$$

## Combine

$$
V=\frac{v_{o} C_{A 0} X}{k C_{A 0}{ }^{2}(1-X)^{2}}=\frac{v_{o} X}{k C_{A 0}(1-X)^{2}}
$$

Evaluate at $X=0.9$,

$$
V=\frac{25 \frac{\mathrm{dm}^{3}}{\mathrm{~s}}(0.90)}{\left(10 \frac{\mathrm{~mm}^{3} \mathrm{l}}{\mathrm{~mol} .5}\left(0.2 \frac{\mathrm{~mol}}{\mathrm{dol}}{ }^{3}\right)(1-0.9)^{2}\right.}
$$

$V=1125 \mathrm{dm}^{3}$
Space Time

$$
\tau=\frac{V}{v_{0}}=\frac{1125 \mathrm{dm}^{3}}{25 \frac{\mathrm{dm}^{3}}{s}}=45 \mathrm{~s}
$$

## 2. Applications/Examples of the CRE Algorithm

| Gas Phase Elementary Reaction | Additional Information |  |
| :---: | :---: | :---: |
| $2 \mathrm{~A} \rightarrow \mathrm{~B}$ | only A fed | $\mathrm{P}_{0}=8.2 \mathrm{~atm}$ |
|  | $\mathrm{T}_{0}=500 \mathrm{~K}$ | $\mathrm{C}_{\text {A0 }}=0.2 \mathrm{~mol} / \mathrm{dm}^{3}$ |
|  | $\mathrm{k}=0.5 \mathrm{dm}^{3}$ | $\mathrm{v}_{0}=2.5 \mathrm{dm}^{3} / \mathrm{s}$ |

Applying the algorithm to the above reaction occuring in Batch, CSTR, PFR

|  | Batch | CSTR | PFR |
| :---: | :---: | :---: | :---: |
| Mole Balance: | $t=N_{A 0} \int_{0}^{x} \frac{d x}{-r_{A} v}$ | $V=\frac{F_{A A} X}{-r_{A}}$ | $V=F_{A O} \int_{0}^{x} \frac{d X}{-r_{A}}$ |
| Rate Law: | $-r_{A}=k C_{A}^{2}$ | $-r_{A}=k C_{A}^{2}$ | $-r_{A}=K C_{A}^{2}$ |
| Stoichiometry: | $\begin{gathered} \text { Gas: } \mathrm{V}=\mathrm{V}_{0} \\ \text { (e.g., constant volume } \\ \text { steel container) } \end{gathered}$ | Gas: $T=T_{0}, P=P_{0}$ | Gas: $T=T_{0}, \mathrm{P}=\mathrm{P}_{0}$ |
|  |  | Per Mole of A: $\begin{gathered} \mathrm{A} \rightarrow \frac{\mathrm{~B}}{2} \\ \varepsilon=1.0\left(\frac{1}{2}-1\right)=-0.5 \end{gathered}$ | Per Mole of A : $\begin{gathered} \mathrm{A} \rightarrow \frac{\mathrm{~B}}{2} \\ \varepsilon=1.0\left(\frac{1}{2}-1\right)=-0.5 \end{gathered}$ |
|  | $C_{A}=\frac{N_{A}}{V}=\frac{N_{A 0}(1-X)}{V_{0}}$ | $C_{A}=\frac{F_{A}}{v}=\frac{F_{A 0}(1-X)}{v_{0}(1+\varepsilon X)}$ | $C_{A}=\frac{F_{A}}{v}=\frac{F_{A A}(1-X)}{v_{0}(1+\varepsilon X)}$ |
|  | $\mathrm{C}_{\mathrm{A}}=\mathrm{C}_{\text {A0 }}(1-\mathrm{X})$ | $C_{A}=C_{A 0} \frac{(1-X)}{(1+\varepsilon X)}$ | $C_{A}=C_{A 0} \frac{(1-X)}{(1+\varepsilon x)}$ |
|  | $C_{B}=\frac{N_{B}}{V}=\frac{N_{A 0}\left(+\frac{1}{2} x\right)}{V_{0}}$ | $C_{s}=\frac{\mathrm{P}_{\mathrm{e}}}{v}=\frac{\mathrm{F}_{\mu v}\left(+\frac{1}{2} x\right)}{v_{i}(1+e X)}$ | $C_{s}=\frac{\mathrm{P}_{\mathrm{e}}}{v}=\frac{\mathrm{P}_{\mu \prime}\left(+\frac{1}{2} x\right)}{v_{y}(1+e X)}$ |
|  | $C_{B}=\frac{C_{A 0} X}{2}$ | $c_{B}=\frac{c_{A 0} X}{2(1+\varepsilon X)}$ | $C_{B}=\frac{C_{A 0} X}{2(1+\varepsilon X)}$ |


| Combine: | $\mathrm{t}=\frac{1}{\mathrm{kC} \mathrm{C}_{A 0}} \int_{0}^{\mathrm{X}}\left[\frac{1}{(1-X)^{2}}\right] d \mathrm{X}$ | $V=\frac{F_{A 0} X(1-0.5 X)^{2}}{k C_{A 0}^{2}(1-X)^{2}}$ | $V=\frac{F_{A 0}}{k C_{A 0}^{2}} \int_{0}^{x}\left[\frac{(1-0.5 X)^{2}}{(1-X)^{2}}\right] d x$ |
| :---: | :---: | :---: | :---: |
| Integrate | $\mathrm{t}=\frac{1}{\mathrm{kC}} \mathrm{A}, 0\left[\frac{\mathrm{X}}{1-\mathrm{X}}\right]$ |  | $V=\frac{F_{A 0}}{k C_{A 0}^{2}}\left[2 \varepsilon(1+\varepsilon) \ln (1-X)+\varepsilon^{2} X+\frac{(1+\varepsilon)^{2} X}{1-X}\right]$ |
| Evaluate | $\begin{aligned} \mathrm{kC}_{\mathrm{A} 0} & =\left(\frac{0.2 \mathrm{dm}^{3}}{\mathrm{~mol} \cdot \mathrm{~s}}\right)\left(\frac{0.5 \mathrm{~mol}}{\mathrm{dm}^{3}}\right) \\ & =0.1 \mathrm{~s}^{-1} \\ & \mathrm{kC}_{\mathrm{so}}=0.1 \mathrm{sec}^{-1} \end{aligned}$ | $\begin{aligned} \mathrm{KC}_{\mathrm{AD}}^{2} & =0.5 \frac{\mathrm{dm}^{3}}{\mathrm{~mol} \cdot \mathrm{~s}}\left(0.2 \frac{\mathrm{~mol}}{\mathrm{dm}}\right)^{2} \\ & =0.02 \frac{\mathrm{~mol}}{\mathrm{dm}^{3} \cdot \mathrm{~s}} \\ \mathrm{~V} & =\frac{0.5 \frac{\mathrm{~mol}}{\mathrm{~s}}(0.9)}{0.02 \frac{\mathrm{~mol}}{\mathrm{~mm}^{3} \cdot \mathrm{~s}}} \frac{(1-0.5(0.9))^{2}}{(1-0.9)^{2}} \end{aligned}$ | $\begin{gathered} \mathrm{F}_{\mathrm{AO}=}=0.5 \frac{\mathrm{~mol}}{\mathrm{~s}} \\ \mathbf{k C}_{\mathrm{A}_{0}}^{2}=0.02 \frac{\mathrm{~mol}}{\mathrm{dm}^{3} \mathrm{~s}} \\ \mathrm{~V}=\frac{5 \frac{\mathrm{~mol}}{\mathrm{~s}}(.9)}{.02 \frac{\mathrm{~mol}}{\mathrm{~mm}^{3} \cdot \mathrm{~s}}}\left(2(-5)(1-5) \ln (1-.9)+(-5)^{2}(9)+\frac{(1-5)^{2}(.9)}{1-9}\right) \end{gathered}$ |
| For $\mathrm{X}=0.9$ : | $\mathrm{t}=\left(\frac{1}{0.1 \mathrm{~s}^{-1}}\right)\left(\frac{0.9}{1-0.9}\right)$ | $\mathrm{V}=680.6 \mathrm{dm}^{3}$ | $\mathrm{V}=90.7 \mathrm{dm}^{3}$ |
|  | $\mathrm{t}=90 \mathrm{sec}$ | $\tau=\frac{V}{v_{0}}=272.3 \mathrm{sec}$ | $\tau=\frac{V}{v_{0}}=36.3 \mathrm{sec}$ |

## 3. Reversible Reaction

To determine the conversion or reactor volume for reversible reactions, one must first calculate the maximum conversion that can be achieved at the isothermal reaction temperature, which is the equilibrium conversion. (See Example 3-8 in the text for additional coverage of equilibrium conversion in isothermal reactor design.)

$$
\begin{aligned}
& \text { Equilibrium Conversion, } X_{e} \\
& \qquad K_{C}=\frac{C_{C}^{c} C_{D}^{d}}{C_{d}^{d} C_{B}^{b}}
\end{aligned}
$$

## Calculate Equilibrium Conversion ( $\mathrm{X}_{\mathrm{e}}$ ) for a Constant Volume System

Example: Determine Xe for a PFR with no pressure drop, $\mathrm{P}=\mathrm{P}_{0}$
Given that the system is gas phase and isothermal, determine the reactor volume when $\mathrm{X}=0.8 \mathrm{X}_{\mathrm{e}}$

| Reaction | Additional Information |  |
| :---: | :--- | :--- |
| $2 A \Leftrightarrow B$ | $C_{A O}=0.2 \mathrm{~mol} / \mathrm{dm}^{3}$ <br> $K_{C}=100 \mathrm{dm}^{3} / \mathrm{mol}$ | $\mathrm{k}=2 \mathrm{dm}^{3} / \mathrm{mol}-\mathrm{min}$ <br> $\mathrm{F}_{\mathrm{A} O}=5 \mathrm{~mol} / \mathrm{min}$ |

First calculate $X_{e}$ :
$\begin{array}{ll} \\ \text { Equilibrium constant } \mathrm{K}_{\mathrm{c}} \text { is; } \quad K_{C} & =\frac{C_{B e}}{C_{A e}{ }^{2}} \\ C_{A e}=C_{A 0}\left(1-X_{e}\right)\end{array} \quad K_{\mathrm{c}}=\frac{\chi_{e}\left(1+e \mathrm{X}_{e}\right)}{2 C_{A 0}\left(1-\mathrm{X}_{e}\right)^{2}}$

$$
C_{B e}=C_{A 0}\left(\frac{1}{2} X_{e}\right)
$$

$$
\begin{aligned}
& X_{e}=0.89 \\
& X=0.8 X_{e}=0.711
\end{aligned}
$$

## Deriving The Equilibrium Constant ( $\mathrm{K}_{\mathrm{C}}$ ) and Equilibrium Conversion ( $\mathrm{X}_{\mathrm{e}}$ ) for a Non-Constant Volume System:

The reversible reaction:

$$
2 A \Leftrightarrow B
$$

which takes place in gas phase PFR. Since gas phase reactions almost always involve volume changes, we will have to account for volume changes in our calculations. The equilibrium constant, $\mathrm{K}_{\mathrm{C}}$, for this reaction is:

$$
K_{\mathrm{c}}=\frac{\mathrm{C}_{\mathrm{Be}}}{\mathrm{C}_{\mathrm{Ae}}^{2}}
$$

$A$ is the limiting reactant $A \Leftrightarrow B / 2$ where $C_{A e}$ and $C_{B e}$ are:

$$
\begin{aligned}
& \mathrm{C}_{\mathrm{Ae}}=\frac{F_{\mu_{\mathrm{e}}}}{v_{\mathrm{e}}}=\frac{F_{\mu \mathrm{A},}\left(1-\mathrm{X}_{\mathrm{e}}\right)}{v_{0}\left(1+\varepsilon \chi_{\mathrm{e}}\right)}=\frac{\mathrm{C}_{\mathrm{A}, 0}\left(1-\chi_{\mathrm{e}}\right)}{\left(1+\varepsilon \mathrm{X}_{\mathrm{e}}\right)} \\
& C_{B e}=\frac{F_{B e}}{v_{e}}=\frac{F_{A 0}\left(X_{e} / 2\right)}{v_{0}\left(1+\varepsilon X_{e}\right)}=\frac{C_{\mathrm{AO}}\left(X_{\mathrm{e}} / 2\right)}{\left(1+\varepsilon X_{e}\right)}
\end{aligned}
$$

Substituting for $\mathrm{C}_{\mathrm{Ae}}$ and $\mathrm{C}_{\mathrm{Be}}$ gives us:

$$
\begin{aligned}
& K_{C}=\frac{\left[\frac{C_{A 0}\left(0.5 X_{e}\right)}{\left(1+\varepsilon X_{e}\right)}\right]}{\left[\frac{C_{A 0}^{2}\left(1-X_{e}\right)^{2}}{\left(1+\varepsilon X_{e}\right)^{2}}\right]} \\
& K_{\mathrm{C}}=\frac{X_{e}\left(1+\varepsilon X_{e}\right)}{2 C_{\mathrm{AO}}\left(1-\mathrm{X}_{\mathrm{e}}\right)^{2}}
\end{aligned}
$$

Substituting known values ( $\mathrm{C}_{\mathrm{A} 0}=0.2 \mathrm{~mol} / \mathrm{dm}^{3}$ and $\left.\mathrm{K}_{\mathrm{C}}=100 \mathrm{dm}^{3} / \mathrm{mol}\right)$, and realizing that:

$$
\begin{gathered}
\varepsilon=y_{A 0} \delta=(1.0)\left(\frac{1}{2}-\frac{2}{2}\right)=-0.5 \\
100=\frac{X_{e}\left(1-0.5 X_{\mathrm{e}}\right)}{2(0.2)\left(1-X_{\mathrm{e}}\right)^{2}}
\end{gathered}
$$

Solving for the equilibrium conversion, $\mathrm{X}_{\mathrm{e}}$, yields:

$$
X_{e}=0.89
$$

## Batch Reactor With a Reversible Reaction

The following reaction follows an elementary rate law


Initially $77 \% \mathrm{~N}_{2}, 15 \% \mathrm{O}_{2}, 8 \%$ inerts are fed to a batch reactor where $80 \%$ of the equilibrium conversion $\left(X_{e}=0.02\right)$ is reached in $151 \mu \mathrm{~s}$. What is the specific reaction rate constant $\mathrm{k}_{1}$ ?

Additional Information

$$
\mathrm{X}_{\mathrm{e}}=0.02, \mathrm{~V}=0.4 \mathrm{dm}^{3}, \mathrm{~K}_{\mathrm{C}}=0.01, \mathrm{P}=20 \mathrm{~atm}, \mathrm{~T}=2700 \mathrm{~K}
$$

## Mole Balance

Design Equation:

$$
\begin{gathered}
\frac{d N_{A}}{d t}=r_{A} V \\
N_{A 0} \frac{d X}{d t}=-r_{A} \cdot V
\end{gathered}
$$

Rate Law

$$
\begin{gathered}
\mathrm{N}_{2}+\mathrm{O}_{2} \longleftrightarrow 2 \mathrm{NO} \\
\mathrm{~A}+\mathrm{B} \longleftrightarrow 2 \mathrm{C} \\
\mathrm{r}_{\mathrm{A}}=\mathrm{k}_{1}\left(\mathrm{C}_{\mathrm{A}} \cdot \mathrm{C}_{\mathrm{B}}-\frac{\mathrm{C}_{\mathrm{C}}^{2}}{\mathrm{~K}_{\mathrm{C}}}\right) \\
\mathrm{V}=\mathrm{V}_{0} \\
\mathrm{C}_{\mathrm{A}}=\mathrm{C}_{\mathrm{A} 0}(1-\mathrm{X}) \\
\mathrm{C}_{\mathrm{B}}=\mathrm{C}_{\mathrm{A} 0}\left(\Theta_{\mathrm{B}}-\mathrm{X}\right) \\
\mathrm{C}_{\mathrm{C}}=2 \mathrm{C}_{\mathrm{A} 0} \cdot \mathrm{X}
\end{gathered}
$$

Stoichiometry: Constant Volume

## Combining

$$
\begin{gathered}
-\mathrm{r}_{\mathrm{A}}=\mathrm{k}_{1} \mathrm{C}_{\mathrm{A}}^{2}\left[(1-\mathrm{X})\left(\omega_{\mathrm{B}}-\mathrm{X}\right)-\frac{4 \mathrm{X}^{2}}{\mathrm{~K}_{\mathrm{C}}}\right] \\
\frac{\mathrm{N}_{\mathrm{A} 0}}{\mathrm{~V}_{0}} \cdot \frac{\mathrm{dX}}{\mathrm{dt}}=-\mathrm{r}_{\mathrm{A}} \\
\mathrm{C}_{\mathrm{A} 0} \frac{\mathrm{dX}}{\mathrm{dt}}=-\mathrm{r}_{\mathrm{A}}
\end{gathered}
$$

Rearranging and integrating

$$
\mathrm{t}=\mathrm{C}_{\mathrm{A} 0} \int_{0}^{\mathrm{x}} \frac{\mathrm{dX}}{-\mathrm{r}_{\mathrm{A}}}=\frac{1}{\mathrm{k}_{1} \mathrm{C}_{\mathrm{A} 0}} \int_{0}^{\mathrm{x}} \frac{\mathrm{dX}}{(1-\mathrm{X})\left(\Theta_{\mathrm{B}}-\mathrm{X}\right)-4 \mathrm{X}^{2} / \mathrm{K}_{\mathrm{C}}}
$$

Evaluate:

$$
\begin{aligned}
& \mathrm{C}_{\mathrm{A} 0}= \frac{\mathrm{Y}_{\mathrm{A} 0} \bullet \mathrm{P}_{0}}{\mathrm{R} \cdot \mathrm{~T}_{0}}=\frac{(0.77) \bullet(20 \mathrm{~atm})}{\left(0.082 \frac{\mathrm{~atm} \cdot \mathrm{dm}^{3}}{\mathrm{~mol} \cdot \mathrm{~K}}\right)(2700 \mathrm{~K})} \\
& \mathrm{C}_{\mathrm{A} 0}=6.96 \times 10^{-2} \mathrm{~mol} / \mathrm{dm}^{3}
\end{aligned}
$$

For $80 \%$ of equilibrium conversion $X=0.8 X_{e}=0.016$

$$
\Theta_{B}=\frac{y_{B, 0}}{y_{A, 0}}=\frac{0.15}{0.77}=0.195
$$

Solving for $k_{1}$ and substituting for $\mathrm{C}_{\mathrm{A} 0},{ }^{\left({ }_{D}\right.} \mathrm{B}, \mathrm{t}$, and $\mathrm{K}_{\mathrm{C}}$ gives

$$
\mathrm{k}_{1}=\frac{1}{\left(151 \times 10^{-6} \mathrm{~s}\right)\left(0.0696 \mathrm{~mol} / \mathrm{dm}^{3}\right)} \times \int_{0}^{0.016} \frac{\mathrm{dX}}{0.195-1.195 \bullet \mathrm{X}-399 \bullet \mathrm{X}^{2}}
$$

Use Simpson's three point formula to integrate

$$
\begin{array}{ll}
\mathrm{k}_{1}=9.51 \times 10^{4} \frac{\mathrm{dm}^{3}}{\mathrm{~mol} \bullet \mathrm{~s}} & \int_{0}^{0.016} \mathrm{f}(\mathrm{X}) \mathrm{dX} \\
\mathrm{X}_{0}=0 & \mathrm{f}\left(\mathrm{X}_{0}\right)=5.128 \\
\mathrm{X}_{1}=0.008 & \mathrm{f}\left(\mathrm{X}_{1}\right)=6.25 \\
\mathrm{X}_{2}=0.016 & \mathrm{f}\left(\mathrm{X}_{2}\right)=13.56
\end{array}
$$

with $\Delta X=0.016 / 2=0.008$

$$
\begin{gathered}
\int_{\mathrm{X}_{0}}^{\mathrm{X}_{2} \mathrm{f}(\mathrm{X}) \mathrm{dX}=\frac{\Delta \mathrm{X}}{3}\left[\mathrm{f}\left(\mathrm{X}_{0}\right)+4 \mathrm{f}\left(\mathrm{X}_{1}\right)+\mathrm{f}\left(\mathrm{X}_{2}\right)\right]} \\
\mathrm{k}_{1}=9.51 \times 10^{4} \times\left(\frac{0.008}{3}\right)(5.128+4 \times 6.25+13.56) \\
\mathrm{k}_{1}=1.11 \times 10^{4} \mathrm{dm}^{3} / \mathrm{mol} \cdot \mathrm{~s}
\end{gathered}
$$

## Tubular Reactors:

Gas-phase rxns are usually carried out in tubular reactors where the gas is generally turbulent.


Design Eq'n: $\quad F_{A 0} \cdot \frac{d X}{d V}=-r_{A}$
In the absence of pressure drop or heat exchange, integral form of the design equation is used:

$$
V=F_{A 0} \cdot \int_{0}^{X} \frac{d X}{-r_{A}}
$$

## Pressure Drop in Reactors

In liquid-phase rxns, the conc'n of reactants is not effected by the changes in pressure.

However, in gas phase rxns, conc'n is propotional to total pressure.

## Pressure Drop \& Rate Law

Example: Analyze the following second order gas phase reaction that occurs isothermally in a PBR:

$$
A \rightarrow B
$$

## Mole Balance

Must use the differential form of the mole balance to separate variables:

$$
F_{A 0} \frac{d X}{d W^{\prime}}=-r_{A}^{\prime}
$$

Rate Law
Second order in A and irreversible: $-r_{A}{ }^{\prime}=k C_{A}^{2}$

Stoichiometry $\quad C_{A}=\frac{F_{A}}{v}=C_{A 0} \frac{(1-X)}{(1+\varepsilon X)} \frac{P}{P_{0}} \frac{T_{0}}{T}$
Isothermal, $\mathrm{T}=\mathrm{T}_{0}$

$$
\mathrm{C}_{\mathrm{A}}=\mathrm{C}_{\mathrm{A}, 0}\left(\frac{(1-x)}{(1+\varepsilon)} \frac{\mathrm{P}}{\mathrm{P}_{0}}\right.
$$

Combine $\quad \frac{d X}{d W}=\frac{\mathrm{KC}^{2}}{\mathrm{~F}_{\mathrm{AO}}^{2}} \frac{(1-X)^{2}}{(1+\varepsilon)^{2}}\left(\frac{\mathrm{P}}{\mathrm{P}_{0}}\right)^{2}$
Need to find $\left(P / P_{0}\right)$ as a function of $W$ (or $V$ if you have a $P F R$ ).

## Pressure Drop in Packed Bed Reactors

Ergun Equation $\frac{d P}{d z}=\frac{-G}{\mathrm{Pg}_{\mathrm{C}} \mathrm{D}_{\mathrm{P}}}\left(\frac{1-\phi}{\phi^{3}}\right)[\underbrace{\left.\frac{150(1-\phi) \mu}{\mathrm{D}_{\mathrm{P}}}+1.75 \mathrm{G}\right]}$
laminar turbulent

```
\(\mathrm{P}=\) pressure (kPa)
Dp = diameter of particle (m)
\(\Phi=\) porosity = volume of void \(/\) total bed volume
\(\dot{m}_{0}=\dot{m}(s t-s t)\)
\(\rho_{0} \cdot v_{0}=\rho \cdot v\)
\(1-\Phi=\) volume of solid / total V
\(\mathrm{g}_{\mathrm{C}}=1\) (metric)
\(\mu=\) viscosity of gas ( \(\mathrm{kg} / \mathrm{m} \mathrm{s}\) )
\(z=\) length down the packed bed \((\mathrm{m})\)
\(\mathrm{u}=\) superficial velocity \(=\mathrm{v}_{0}\) (volumetric flow) \(/ \mathrm{A}^{2}\) (cross-area)
\(\rho=\) gas density ( \(\mathrm{kg} / \mathrm{m} 3\) )
\(\mathrm{G}=\rho \mathrm{u}=\) superficial mass velocity \(\left(\mathrm{kg} / \mathrm{m}^{2} \mathrm{~s}\right)\)
```

Ergun, S., 1952. Fluid flow through packed columns. Chemical Engineering Progress 48, pp. 89-94.

## Variable Density

$$
\begin{aligned}
& \rho=P_{0} \frac{P}{P_{0}} \frac{T_{0}}{T} \frac{F_{T 0}}{F_{T}} \\
& \frac{d P}{d Z}=\frac{-G}{P_{0} g_{\mathrm{C}} \mathrm{D}_{\mathrm{P}}}\left(\frac{1-\phi}{\phi^{3}}\right)\left[\frac{150(1-\phi) \mu}{\mathrm{D}_{\mathrm{F}}}+1.75 \mathrm{G}\right] \frac{\mathrm{P}_{\mathrm{O}}}{\mathrm{P}} \frac{\mathrm{~T}}{\mathrm{~T}_{0}} \frac{\mathrm{~F}_{\mathrm{T}}}{\mathrm{~F}_{\mathrm{TO}}} \\
& \beta_{0}=\frac{\mathrm{G}}{\mathrm{P}_{0} g_{\mathrm{C}} \mathrm{D}_{\mathrm{P}}}\left(\frac{1-\phi}{\phi^{3}}\right)\left[\frac{150(1-\phi) \mu}{\mathrm{D}_{\mathrm{P}}}+1.75 \mathrm{G}\right]
\end{aligned}
$$

Catalyst Weight

$$
\begin{aligned}
& W^{\prime}=z A_{c} P_{b}=z A_{c}(1-\phi) \rho_{c} \\
& \rho_{b}=\text { bulk density } \\
& \rho_{c}=\text { solid catalyst density } \\
& \phi=\text { porosity (a.k.a., void fraction) } \\
& \frac{d P}{d W^{\prime}}=\frac{-\beta_{0}}{A_{c}(1-\phi) \rho_{c}} \frac{P_{0}}{P} \frac{T}{T_{0}} \frac{F_{T}}{F_{T 0}} \\
& \alpha=\frac{2 \beta_{0}}{A_{c}(1-\phi)} \frac{1}{P_{0}}
\end{aligned}
$$

Then

$$
\begin{aligned}
& \frac{d P}{d W}=-\frac{\alpha}{2} \frac{P_{0}}{\left(P / P_{n}\right)} \frac{T}{T_{0}} \frac{F_{T}}{F_{T 0}} \\
& \frac{d\left(\frac{P}{P_{0}}\right)}{d W}=-\frac{\alpha}{2} \frac{T}{\left(\frac{P}{P_{o}}\right)} \frac{T}{T_{0}} \frac{F_{T}}{F_{T o}}
\end{aligned}
$$

We will use this form for multiple reactions:

$$
\begin{gathered}
\frac{\mathrm{dy}}{\mathrm{dW}}=-\frac{\alpha}{2 y} \frac{\mathrm{~T}}{\mathrm{~T}_{0}} \frac{\mathrm{~F}_{\mathrm{T}}}{\mathrm{~F}_{\mathrm{T}}} \\
\frac{\mathrm{~d}\left(\mathrm{PI} \mathrm{P}_{0}\right)}{\mathrm{dW}}=-\frac{1}{2} \frac{1}{\left(\mathrm{P} / \mathrm{P}_{0}\right)} \frac{\mathrm{T}}{\mathrm{~T}_{0}}(1+\varepsilon X) \\
\text { Since } \quad\left(\mathrm{y}=\frac{\mathrm{P}}{\mathrm{P}_{0}}\right) \\
F_{T}=F_{T 0}+F_{A 0} \delta X=F_{T 0}\left(1+\frac{F_{A 0}}{F_{T 0}} \delta X\right) \\
\frac{F_{T}}{F_{T 0}}=1+\varepsilon \cdot X \quad\left(\varepsilon=y_{A 0} \cdot \delta=\frac{F_{A 0}}{F_{T 0}} \cdot \delta\right)
\end{gathered}
$$

$\frac{d y}{d W}=-\frac{a}{2 y} \frac{T}{T_{0}}(1+e x)$
when $\varepsilon<0 ; \quad \Delta \mathrm{P}$ will be less than $\varepsilon=0$.
when $\varepsilon>0 ; \quad \Delta \mathrm{P}$ will be greater than $\varepsilon=0$.

Isothermal Operation

$$
\frac{d y}{d w^{\prime}}=-\frac{\alpha}{2 y}(1+x)
$$

Recall that

$$
\frac{d X}{d W}=\frac{k C_{A_{0}}^{2}(1-X)^{2}}{F_{A_{0}}(1+\varepsilon X)^{2}} y^{2}
$$

Notice that

$$
\frac{d \mathrm{X}}{d W}=f(X, \mathrm{P}) \text { and } \frac{\mathrm{dP}}{d W}=f(X, \mathrm{P}) \text { or } \frac{d y}{d W}=f(\mathrm{y}, \mathrm{X})
$$

The two expressions are coupled ordinary differential equations. We can solve them simultaneously using an ODE solver such as Polymath. For the special case of isothermal operation and epsilon $=0$, we can obtain an analytical solution.

$$
\text { Analytical Solution } \quad \mathbf{A} \rightarrow \mathbf{B} \quad,[\mathrm{e}], \mathrm{PFR} \text { with } \quad-\dot{\mathbf{r}_{\mathbf{A}}^{\prime}}=\mathbf{k} \mathbf{C}_{\mathbf{A}}^{2}
$$

$$
\begin{aligned}
& \frac{d y}{d W^{\prime}}=-\frac{\alpha}{2 y^{\prime}}\left(1+e^{x}\right) \\
& 2 y \cdot \frac{d y}{d W}=-\alpha \\
& y=1 \quad\left(P=P_{0}\right) @ W=0 \\
& y^{2}=1-\alpha \cdot W
\end{aligned}
$$

IF $\mathrm{T}=\mathrm{T}_{0}$ AND $\varepsilon=0 \quad \mathrm{y}=(1-\mathrm{LN})^{1 / 2}$

CAUTION: Never use this form if $\quad \varepsilon \neq 0$
For $\varepsilon=0 \quad \mathrm{C}_{\mathrm{A}}=\mathrm{C}_{\mathrm{A} 0}(1-\mathrm{X}) \mathrm{y}=\mathrm{C}_{\mu 0}(1-\mathrm{X})(1-\alpha W)^{1 / 2}$

## Combine

$$
-r_{\mathcal{A}}^{\prime}=k C_{\dot{A}}^{2}=k C_{\dot{A}, 0}^{2}(1-X)^{2}\left(1-\alpha W^{\prime}\right)
$$

$$
F_{A O} \frac{d \mathrm{X}}{d \mathrm{~W}^{\prime}}=-r_{A}^{\prime}
$$

$$
\frac{d X}{d W}=\frac{k C_{A O}^{2}}{F_{A O}}(1-X)^{2}(1-\alpha W)
$$

Solve

$$
\frac{X}{1-X}=\frac{\mathrm{KC}_{\mathrm{A}, 0}^{2}}{\mathrm{~F}_{\mathrm{A}, 0}}\left[\mathrm{~W}^{\prime}-\frac{\mathrm{wW}^{2}}{2}\right]
$$

Could now solve for X given W , or for W given X .

For gas phase reactions, as the pressure drop increases, the concentration decreases, resulting in a decreased rate of reaction, hence a lower conversion when compared to a reactor without a pressure drop.




4


Effect of presure drop on P, rate, con'n, and $x$.

## Pressure Drop in Pipes:

Pressure drop for gases flowing through pipes without packing can be neglected. For flow in pipes, $\Delta P$ is given by:

$$
\frac{d P}{d L}=-G \cdot \frac{d u}{d L}-\frac{2 \cdot f \cdot G^{2}}{g \cdot D}
$$

Where
$\mathrm{G}=\rho \mathrm{u}\left(\mathrm{g} / \mathrm{cm}^{3} \mathrm{~s}\right)=$ mass velocity is constant along L .
$\mathrm{u}=$ average velocity of gas, $\mathrm{cm} / \mathrm{s}$.
$\mathrm{f}=$ fanning friction factor
$f=$ fnc (Re, pipe roughness

$$
\frac{P}{P_{0}}=\left[1-\frac{4 \cdot f \cdot G^{2} \cdot V}{\rho_{0} \cdot P_{0} \cdot A_{C} \cdot D}\right]=\left(1-\alpha_{p} V\right)^{1 / 2}
$$

## Optimum Particle Diameter

$$
\begin{aligned}
& A \rightarrow B \\
& -r_{A}=k C_{A 0}(1-X) y, y=P / P_{0} \\
& \frac{d y}{d w}=-\frac{\alpha}{2 y}(1+\varepsilon X) \\
& \text { as } \alpha \text { increases the pressure drop increases } \\
& \alpha=\frac{2 G}{A_{c} \rho_{c} P_{0} \rho_{0} D_{P} \phi^{3}}\left[\frac{150(1-\phi) \mu}{D_{P}}+1.75 G\right]
\end{aligned}
$$

Laminar Flow, Fix $\mathrm{P}_{0}, \rho_{0}, \Phi$

$$
\begin{gathered}
\rho_{0}=P_{0}(\mathrm{MW}) / R T_{0} \\
\rho_{0} P_{0} \sim P_{0}^{2}
\end{gathered}
$$

$\alpha \sim \frac{G}{A_{C} D_{P}{ }^{2} P_{0}{ }^{2}}$
$\alpha_{2}=\alpha_{1}\left(\frac{G_{2}}{G_{1}}\right)\left(\frac{D_{P 1}}{D_{P 2}}\right)^{2}\left(\frac{A_{C 1}}{A_{C 2}}\right)\left(\frac{P_{01}}{P_{C 2}}\right)^{2}$
If $\quad D_{P 2}=2 D_{P 1} \quad G_{1}=G_{2}, \quad A_{C 1}=A_{C 2} \longrightarrow$ Cross-sectional area
$\alpha_{2}=\alpha_{1}\left(\frac{1}{2}\right)^{2}=\frac{\alpha_{1}}{4}$
Superficial mass velocity $=\rho u$


Increasing the particle diameter descreases the pressure drop and increases the rate and conversion.


However, there is a competing effect. The specific reaction rate decreases as the particle size increases, therefore so deos the conversion.
k ~ 1/Dp


$$
\begin{aligned}
\mathrm{D}_{\mathrm{P} 1} & >\mathrm{D}_{\mathrm{P} 2} \\
\mathrm{k}_{1} & >\mathrm{k}_{2}
\end{aligned}
$$

Higher k, higher conversion


The larger the particle, the more time it takes the reactant to get in and out of the catalyst particle. For a given catalyst weight, there is a greater external surgace area for smaller particles than larger particles. Therefore, there are more entry ways into the catalyst particle.

## 7. Engineering Analysis - Critical Thinking and Creative Thinking

We want to learn how the various parameters (particle diameter, porosity, etc.) affect the pressure drop and hence conversion. We need to know how to respond to "What if" questions, such as:
"If we double the particle size, decrease the porosity by a factor of 3 , and double the pipe size, what will happen to D P and X?"

To answer these questions we need to see how a varies with these parameters

$$
\alpha=\frac{2 \mathrm{G}}{\mathrm{~A}_{\mathrm{c}} \rho_{o} \rho_{c} g_{c} D_{P} \not \phi_{o} P_{o}}\left[\frac{150, \mu(1-\not \phi)}{\mathrm{D}_{\mathrm{P}}}+1.75 G\right]
$$

Turbulent Flow

$$
\alpha \sim \frac{G^{2}}{A_{c} D_{P} P_{o}^{2}}
$$

## Compare Case 1 and Case 2:

For example, Case 1 might be our current situation and Case 2 might be the parameters we want to change to.

$$
\alpha_{2}=\alpha_{1}\left(\frac{G_{2}}{G_{1}}\right)^{2}\left(\frac{A_{\mathrm{A}}}{A_{\mathrm{c} 2}}\right)\left(\frac{D_{\mathrm{P} 1}}{D_{\mathrm{P} 2}}\right)\left(\frac{\mathrm{F}_{\mathrm{u} 1}}{\mathrm{P}_{02}}\right)^{2}
$$

For constant mass flow through the system $\dot{\mathrm{m}}=$ constant

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

Laminar Flow

$$
\begin{aligned}
& \alpha \sim \frac{G}{A_{\mathrm{c}} D_{\mathrm{F}}^{2}}, G=\frac{\dot{\mathrm{m}}}{A_{\mathrm{c}}} \\
& \alpha_{2}=\alpha_{1}\left(\frac{D_{P 1}}{D_{P 2}}\right)^{2}\left(\frac{A_{c 1}}{A_{c 2}}\right)^{2}
\end{aligned}
$$

## Part 2: Mole Balances in terms of Conc'n \& Molar Flow Rates

In some cases, it is more convenient to deal with number of moles or molar flow rates rather than conversion.

Membrane reactors and multiple rxns taking place in gas phase are examples.

The main difference in molar flow rates, you have to write the mole balance on each and every species.
Membrane reactors can be used to increase conversion when the rxn is thermodynamically limited as well as to increase the selectivity when multiple rxns are occuring.
A. Membrane reactors
B. Multiple reaction

Liquids: Use concentrations, i.e., $\mathrm{C}_{\mathrm{A}}$

$$
\mathrm{C}_{\mathrm{A}}=\frac{F_{\mathrm{A}}}{v_{0}}
$$

1. For the elementary liquid phase reaction $A \Leftrightarrow>B \quad$ carried out in a CSTR, where $V, v_{0}, C_{A 0}, k$, and $K_{c}$ are given and the feed is pure $A$, the combined mole balance, rate laws, and stoichiometry are:

$$
\begin{gathered}
\tau=\frac{\mathrm{V}}{\mathrm{v}_{\mathrm{o}}}=\frac{\mathrm{C}_{\mathrm{Ao}}-\mathrm{C}_{\mathrm{A}}}{\mathrm{k}\left[\mathrm{C}_{\mathrm{A}}-\frac{\mathrm{C}_{\mathrm{E}}}{\mathrm{~K}_{\mathrm{c}}}\right]} \\
\mathrm{\tau}=\frac{\mathrm{C}_{\mathrm{B}}}{\mathrm{k}\left[\mathrm{C}_{\mathrm{A}}-\frac{\mathrm{C}_{\mathrm{B}}}{\mathrm{~K}_{\mathrm{c}}}\right]}
\end{gathered}
$$

There are two equations, two unknowns, $C_{A}$ and $C_{B}$ Gases: Use Molar Flow Rates, I.E. FI

$$
\begin{gathered}
\nu=p_{0} \frac{F_{T}}{F_{T 0}} \frac{\mathrm{P}}{\mathrm{P}_{0}} \frac{\mathrm{~T}_{0}}{\mathrm{~T}} \quad \mathrm{C}_{\mathrm{A}}=\frac{\mathrm{F}_{\mathrm{A}}}{\nu}=\frac{\mathrm{F}_{\mathrm{A}}}{\nu_{0}} \frac{\mathrm{~F}_{\mathrm{T}}}{\mathrm{~F}_{\mathrm{T}}} \frac{\mathrm{P}}{\mathrm{P}_{0}} \frac{\mathrm{~T}_{0}}{\mathrm{~T}} \\
\mathrm{C}_{\mathrm{A}}=C_{\mathrm{D}} \frac{\mathrm{~F}_{\mathrm{A}}}{\nu}=\left(\frac{\mathrm{F}_{\mathrm{A}}}{\mathrm{~F}_{\mathrm{T}}}\right) \frac{\mathrm{P}}{\mathrm{P}_{0}} \frac{\mathrm{~T}_{0}}{\mathrm{~T}}, \quad \mathrm{C}_{\mathrm{T0}}=\frac{\mathrm{P}_{0}}{\mathrm{RT}_{0}}
\end{gathered}
$$

2. If the above reaction, $A \Leftrightarrow B$,carried out in the gas phase in a PFR, where $V, v_{o}, C_{A 0}, k$, and $K_{c}$ are given and the feed is pure $A$, the combined mole balance, rate laws, and stoichiometry yield, for isothermal operation $\left(T=T_{0}\right)$ and no pressure drop $(\Delta \mathrm{P}=0)$ are:

$$
\begin{gathered}
\frac{d \mathrm{~F}_{\mathrm{A}}}{\mathrm{dV}}=-\mathrm{k}\left[\mathrm{C}_{\mathrm{To}}\left(\frac{\mathrm{~F}_{\mathrm{A}}}{\mathrm{~F}_{\mathrm{T}}}\right)-\frac{\mathrm{C}_{\mathrm{To}_{0}}\left(\frac{\mathrm{~F}_{\mathrm{B}}}{\mathrm{~F}_{\mathrm{T}}}\right)}{\mathrm{K}_{\mathrm{c}}}\right] \\
\frac{\mathrm{d} \mathrm{~F}_{\mathrm{B}}}{\mathrm{dV}}=-\mathrm{k}\left[\mathrm{C}_{\mathrm{To}_{0}}\left(\frac{\mathrm{~F}_{\mathrm{A}}}{\mathrm{~F}_{\mathrm{T}}}\right)-\frac{\mathrm{C}_{\mathrm{To}_{0}}\left(\frac{\mathrm{~F}_{\mathrm{B}}}{\mathrm{~F}_{\mathrm{T}}}\right)}{\mathrm{K}_{\mathrm{c}}}\right] \\
\mathrm{F}_{\mathrm{T}}=\mathrm{F}_{\mathrm{A}}+\mathrm{F}_{\mathrm{B}}
\end{gathered}
$$

## - Microreactors



Are characterized by their high surface area to volume ratios (due to many micro-tubes and channels). Dchannel $=100 \mu \mathrm{~m}$, Lch $=2 \mathrm{~cm}$

Control of heat and mass transfer resistance!!

They are used for highly exothermis rxns, for rxns with toxic or explosive intermediates. ALso,i for the productions of speciality chemicalsi combinatorial chemical screening, chemical sensors.

In modeling, we assume they are PFR. $\mathrm{dFa} / \mathrm{dV}=\mathrm{rA}$


## Membrane Reactors

Membrane reactors can be used to achieve conversions greater than the original equilibrium value. These higher conversions are the result of Le Chatelier's Principle; you can remove one of the reaction products and drive the reaction to the right. To accomplish this, a membrane that is permeable to that reaction product, but is impermeable to all other species, is placed around the reacting mixture.

Example: The following reaction is to be carried out isothermally in a membrane reactor with no pressure drop. The membrane is permeable to Product C, but it is impermeable to all other species.


For membrane reactors, we cannot use conversion. We have to work in terms of the molar flow rates $F_{A}, F_{B}, F_{C}$.

Mole Balances

$$
\begin{aligned}
& \frac{d F_{A}}{d W^{\prime}}=r_{A}^{\prime} \\
& \frac{d F_{B}}{d W^{\prime}}=r_{B}^{\prime}=-r_{A}^{\prime} \\
& \frac{d F_{C}}{d W^{\prime}}=r_{C}^{\prime}-k_{C} C_{C}=-3 r_{A}^{\prime}-k_{C} C_{C}
\end{aligned}
$$

Rate Laws

$$
\begin{aligned}
-r_{A}^{\prime} & =k_{A}\left[c_{A}-\frac{c_{\mathrm{B}} C_{C}^{3}}{k_{\mathrm{C}}}\right] \\
r_{\mathrm{B}} & =-r_{\mathrm{A}} \\
r_{\mathrm{C}} & =-3 r_{\mathrm{A}}
\end{aligned}
$$

Stoichiometry
Isothermal, no pressure drop

$$
\begin{aligned}
& C_{T 0}=\frac{P_{0}}{R_{0}} \\
& C_{A}=C_{T 0} \frac{F_{A}}{F_{T}} \\
& C_{\mathrm{B}}=C_{T 0} \frac{F_{\mathrm{B}}}{F_{\mathrm{T}}} \\
& \mathrm{C}_{\mathrm{C}}=\mathrm{C}_{\mathrm{T0}} \frac{\mathrm{~F}_{\mathrm{C}}}{F_{\mathrm{T}}} \\
& \mathrm{~F}_{\mathrm{T}}=\mathrm{F}_{\mathrm{A}}+\mathrm{F}_{\mathrm{B}}+\mathrm{F}_{\mathrm{C}}
\end{aligned}
$$

Combine Polymath will combine for you
Parameters $\quad \mathrm{C}_{\mathrm{TO}}=0.2 \frac{\mathrm{~mol}}{\mathrm{dm}^{3}}, \mathrm{~F}_{\mathrm{AO}}=10 \frac{\mathrm{~mol}}{\mathrm{~s}}$

$$
\mathrm{k}_{\mathrm{a}}=10 \frac{\mathrm{dm}^{3}}{\mathrm{kgcats}}, \mathrm{k}_{\mathrm{c}}=0.5 \frac{\mathrm{dm}^{3}}{\mathrm{~kg} \mathrm{cats}^{2}}, \mathrm{~K}_{\mathrm{c}}=200 \frac{\mathrm{~mol} \mathrm{l}^{2}}{\mathrm{dm}^{6}}
$$

Solve
Polymath

## 3. Semibatch Reactors

Semibatch reactors can be very effective in maximizing selectivity in liquid phase reactions.


$$
A+B \xrightarrow{k_{D}} D \quad \text { (product) }
$$

$$
A+B \xrightarrow{k_{U}} U \quad \text { (undesired) }
$$

$$
r_{D}=k_{D} \cdot C_{A}^{2} \cdot C_{B}
$$

$$
r_{U}=k_{U} \cdot C_{A} \cdot C_{B}^{2}
$$

$$
\operatorname{Selectivity}(D / U)=\frac{k_{D} \cdot C_{A}}{k_{U} \cdot C_{B}}
$$

The reactant that starts in the reactor is always the limiting reactant

Three Forms of the Mole Balance Applied to Semibatch Reactors


If you have multiple reactions, use concentrations to make mole balances!!

## ODE Solutions to CRE Problems

| Algorithm Steps | Polymath Equations |  |
| :--- | :--- | :--- |
| Mole Balance | $\mathrm{d}(\mathrm{X}) / \mathrm{d}(\mathrm{V})=-\mathrm{rA} / \mathrm{FAO}$ |  |
| Rate Law | $\mathrm{rA}=-\mathrm{k}^{*}\left(\left(\mathrm{CA}^{* *} 2\right)-(\mathrm{CB} / \mathrm{KC})\right)$ |  |
| Stoichiometry | $\mathrm{CA}=(\mathrm{CAO}(1-\mathrm{X})) /(1+\mathrm{eps} * \mathrm{X})$ |  |
|  | $\mathrm{CB}=\left(\mathrm{CAO}{ }^{*} \mathrm{X}\right) /\left(2^{*}(1+\mathrm{eps} * \mathrm{X})\right)$ |  |
| Parameter Evaluation | eps $=-0.5$ | $\mathrm{CAO}=0.2$ |
|  | $\mathrm{FAO}=2$ |  |
|  | $\mathrm{KA}=5$ | $\mathrm{KC}=100$ |
| Initial and Final Values | $\mathrm{X}_{0}=0$ | $\mathrm{~V}_{0}=0$ |

$\frac{d X}{d V}=\frac{-r_{A}}{F_{A 0}}$
$r_{A}=-k\left\{\left[C_{A 0} \cdot \frac{(1-X)}{1+\varepsilon \cdot X}\right]^{2}-\left[\frac{C_{A 0} \cdot X}{2(1+\varepsilon X) \cdot K_{C}}\right]\right\}$
[V, X] = ode45(@vdp1, [0 500], [0]) Matlab solution

## Example: Elementary Irreversible Reaction

Consider the following irreversible elementary reaction

$$
\begin{aligned}
& A+B \rightarrow C+D \\
& -r_{A}=k C_{A} C_{B}
\end{aligned}
$$

The combined mole balance, rate law, and stoichiometry may be written in terms of number of moles, conversion, and/or concentrati

| Conversion | Concentration | Number of Moles |
| :---: | :---: | :---: |
| $\frac{d X}{d t}=\frac{k(1-X)\left(N_{B i}+F_{B 0} t-N_{A 0} X\right)}{V_{0}+v_{0} t}$ | $\frac{d C_{A}}{d t}=r_{A}-C_{A} \frac{v_{0}}{V}$ | $\frac{d N_{A}}{d t}=r_{A} V$ |
|  | $\frac{d C_{B}}{d t}=r_{A}+\left(C_{B 0}-C_{B}\right) \frac{v_{0}}{V}$ | $\frac{d N_{E}}{d t}=F_{A D}+r_{E} V$ |

## Polymath Equations

| Conversion | Concentration | Moles |
| :---: | :---: | :---: |
| $\mathrm{d}(\mathrm{X}) / \mathrm{d}(\mathrm{t})=-\mathrm{ra*} \mathrm{~V} / \mathrm{Nao}$ | $d(C a) / d(t)=r a-(C a * v o) / v$ | $\mathrm{d}(\mathrm{Na}) / \mathrm{d}(\mathrm{t})=\mathrm{ra*} \mathrm{~V}$ |
| $\mathrm{ra}=-\mathrm{k} * \mathrm{Ca} * \mathrm{Cb}$ | $\mathrm{d}(\mathrm{Cb}) / \mathrm{d}(\mathrm{t})=\mathrm{rb}+\left((\mathrm{Cbo}-\mathrm{Cb})^{*} \mathrm{vo}\right) / \mathrm{V}$ | $d(N b) / d(t)=r b * V+F b o$ |
| $\mathrm{Ca}=\mathrm{Nao}{ }^{*}(1-\mathrm{X}) / \mathrm{V}$ | $\mathrm{ra}=-\mathrm{k} * \mathrm{Ca} * \mathrm{Cb}$ | $\mathrm{ra}=-\mathrm{k} * \mathrm{Ca} * \mathrm{Cb}$ |
| $\mathrm{Cb}=(\mathrm{Nbi}+\mathrm{Fbo} * \mathrm{t}-\mathrm{NaO} * \mathrm{X}) / \mathrm{V}$ | $\mathrm{rb}=\mathrm{ra}$ | $\mathrm{rb}=\mathrm{ra}$ |
| $\mathrm{V}=\mathrm{V} \mathrm{o}+\mathrm{v}^{*} \mathrm{t}$ | $\mathrm{V}=\mathrm{V} 0+\mathrm{vo}{ }^{*} \mathrm{t}$ | $v=V_{0}+v_{0}{ }^{*} t$ |
| V O $=100$ | V O $=100$ | V O $=100$ |
| $\mathrm{vo}=2$ | $\mathrm{vo}=2$ | $\mathrm{vo}=2$ |
| $\mathrm{NaO}=100$ | $\mathrm{FbO}=5$ | $\mathrm{Fbo}=5$ |
| $\mathrm{FbO}=5$ | $\mathrm{NaO}=100$ | $\mathrm{Ca}=\mathrm{Na} / \mathrm{V}$ |
| $\mathrm{Nbi}=0$ | $\mathrm{Cbo}=\mathrm{Fbo} / \mathrm{vo}$ | $\mathrm{Cb}=\mathrm{Nb} / \mathrm{V}$ |
| $k=0.1$ | $k=0.01$ | $k=0.01$ |
|  | $\mathrm{Na}=\mathrm{Ca}$ * V |  |
|  | $X=(\mathrm{NaO}-\mathrm{Na}) / \mathrm{NaO}$ |  |

## Equilibrium Conversion in Semibatch Reactors with Reversible

 ReactionsConsider the following reversible reaction:

$$
A+B \Leftrightarrow C+D
$$

Everything is the same as for the irreversible case, except for the rate law

$$
-r_{A}=k_{A}\left[C_{A} C_{B}-\frac{C_{C} C_{D}}{K_{C}}\right]
$$

Where:

$$
\mathrm{C}_{\mathrm{A}}=\frac{N_{\mathrm{A} 0}(1-X)}{V} \quad \mathrm{C}_{\mathrm{B}}=\frac{\left(F_{\mathrm{B} 0} \mathrm{t}-N_{\mathrm{A} 0} X\right)}{V} \quad \mathrm{C}_{\mathrm{C}}=\mathrm{C}_{\mathrm{D}}=\frac{N_{\mathrm{A} 0} X}{V}
$$

At equilibrium, $-r_{A}=0$, then

$$
\begin{aligned}
& K_{\mathrm{C}}=\frac{\mathrm{C}_{\mathrm{Ce}} \mathrm{C}_{\mathrm{De}}}{\mathrm{C}_{\mathrm{Ae}} \mathrm{C}_{\mathrm{Be}}}=\frac{N_{\mathrm{Ce}} N_{\mathrm{De}}}{\mathbb{N}_{\mathrm{Ae}} N_{\mathrm{Be}}} \\
& K_{C}=\frac{N_{A 0} X_{e}^{2}}{\left(1-X_{e}\right)\left(F_{B 0} t-N_{A 0} X_{e}\right)}
\end{aligned}
$$

```
function f=volume(V,x)
CaO=0.2;
Kc=100;
FaO=5;
k=2;
epsilon=-0.5;
ra=k*(((Ca0*(1-x(1))/(1+epsilon*x(1)))^2)-
(Ca0*x(1)/(2*Kc*(1+epsilon*x(1)))));
f(1)=ra/Fa0;
>> [v x]=ode45('volume',[0 500],[0]);
>> plot(V,x)
>> grid
>> xlabel('Volume')
>> ylabel('conversion')
```



```
function f = packedbed(W,x)
alpha = 0.0002;
k = 10;
epsilon = -0.5;
FA0=2.5;
CAO = 0.2;
f = zeros(2,1);
CA = (CAO*(1-x(1))*x(2))/(1 + epsilon*x(1));
ra = k*(CA.^2);
f(1) = ra / FAO;
f(2) = -alpha*(1 + epsilon*x(1))/(2*x(2));
>> [W x]=ode45('packedbed', [0 1000], [0;1]);
>> plot(W,x(:,1))
>> xlabel('W, kg')
>> ylabel('X')
>> plot(W,x(:,2))
>> xlabel('W, kg')
>> ylabel('Y')
```




## Combining mole balances, rate laws and stoichiometry



|  | Batch | CSTR | PFR |
| :---: | :---: | :---: | :---: |
| Mole Balance: | $t=N_{A 0} \int_{0}^{X} \frac{d X}{-r_{A} V}$ | $V=\frac{F_{A 0} X}{-r_{A}}$ | $V=F_{A 0} \int_{0}^{x} \frac{d x}{-r_{A}}$ |
| Rate Law: | $-r_{A}=k C_{A}^{2}$ | $-r_{A}=K_{C}^{2}$ | $-r_{A}=k C_{A}^{2}$ |
| Stoichiometry: | Gas: $\mathrm{V}=\mathrm{V}_{0}$ (e.g., constant volume steel container) | Gas: $T=T_{0}, P=P_{0}$ | Gas: $\mathrm{T}=\mathrm{T}_{0}, \mathrm{P}=\mathrm{P}_{0}$ |
|  |  | Per Mole of A: $\begin{gathered} \mathrm{A} \rightarrow \frac{\mathrm{~B}}{2} \\ 8=1.0\left(\frac{1}{2}-1\right)=-0.5 \end{gathered}$ | Per Mole of A: $\begin{gathered} A \rightarrow \frac{B}{2} \\ 8=1.0\left(\frac{1}{2}-1\right)=-0.5 \end{gathered}$ |
|  | $C_{A}=\frac{N_{A}}{V}=\frac{N_{A 0}(1-X)}{V_{0}}$ | $C_{A}=\frac{F_{A}}{v}=\frac{F_{A 0}(1-X)}{v_{0}(1+X X)}$ | $C_{A}=\frac{F_{A}}{v}=\frac{F_{A 0}(1-X)}{v_{0}(1+Q X)}$ |
|  | $C_{A}=C_{A 0}(1-X)$ | $C_{A}=C_{A 0} \frac{(1-X)}{(1+\varepsilon X)}$ | $C_{A}=C_{A 0} \frac{(1-X)}{(1+\varepsilon X)}$ |
|  | $C_{B}=\frac{N_{B}}{V}=\frac{N_{A O}\left(+\frac{1}{2} x\right)}{V_{0}}$ | $C_{0}=\frac{F_{i}}{v}=\frac{F_{N}\left(+\frac{1}{2} X\right)}{v_{j}(1+e X)}$ | $C_{e}=\frac{F_{8}}{v}=\frac{F_{N}\left(+\frac{1}{2} X\right)}{v_{s}(1+e X)}$ |
|  | $C_{B}=\frac{C_{A O} X}{2}$ | $C_{B}=\frac{C_{A O} X}{2(1+\varepsilon X)}$ | $C_{B}=\frac{C_{A O} X}{2(1+\varepsilon X)}$ |

## Pressure Drop in Packed Bed Reactors

```
Ergun Equation
    \(\frac{d P}{d z}=\frac{-G}{p g_{c} D_{P}}\left(\frac{1-\phi}{\phi^{3}}\right)[\underbrace{\frac{150(1-\phi) \mu}{D_{P}}}+\underbrace{1.75 \mathrm{G}}]\)
    laminar turbulent
\(\mathrm{P}=\) pressure (kPa)
Dp = diameter of particle (m)
\(\Phi=\) porosity \(=\) volume of void \(/\) total bed volume
\(\dot{m}_{0}=\dot{m}(s t-s t)\)
\(\rho_{0} \cdot v_{0}=\rho \cdot v\)
\(1-\Phi=\) volume of solid / total V
\(\mathrm{g}_{\mathrm{C}}=1\) (metric)
\(\mu=\) viscosity of gas (kg / m s)
\(z=\) length down the packed bed ( \(m\) )
\(\mathrm{u}=\) superficial velocity \(=\mathrm{v}_{0}\) (volumetric flow) \(/ \mathrm{A}^{2}\) (cross-area)
\(\rho=\) gas density (kg/m3)
\(G=\rho u=\) superficial mass velocity \(\left(\mathrm{kg} / \mathrm{m}^{2} \mathrm{~s}\right)\)
```

Ergun, S., 1952. Fluid flow through packed columns. Chemical Engineering Progress 48, pp. 89-94.

For gas phase reactions, as the pressure drop increases, the concentration decreases, resulting in a decreased rate of reaction, hence a lower conversion when compared to a reactor without a pressure drop.




4


Effect of presure drop on P ,rate, con'n, and x.

Part 2: Mole Balances in terms of Conc'n \& Molar Flow Rates
In some cases, it is more convenient to deal with number of moles or molar flow rates rather than conversion.

Membrane reactors and multiple rxns taking place in gas phase are examples.
Microreactors with multiple reactions

