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







$$C_{A0} = \frac{Y_{A0}P_0}{RT_0} = \frac{(0.5)(16.4 \text{ atm})}{\left(\frac{0.082 \text{ atm} \cdot \text{m}^3}{\text{ kmol} \cdot \text{K}}\right)(500\text{ K})} = 0.2 \frac{\text{kmol}}{\text{m}^3} = 0.2 \frac{\text{mol}}{\text{dm}^3}$$

$$\frac{\text{Combine}}{-r_A} = \text{kC}_A^2 C_B = \text{kC}_{A0}^3 \frac{(1-X)^2}{(1-0.5X)^2}$$

$$-r_A = \left(10 \frac{\text{dm}^6}{\text{mol}^2 \cdot \text{s}}\right) \left(0.2 \frac{\text{mol}}{\text{dm}^3}\right)^3 \frac{(1-X)^2}{(1-0.5X)^2}$$

$$-r_A = \left(0.08 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}\right) \frac{(1-X)^2}{(1-0.5X)^2}$$

$$\frac{\text{Evaluate}}{-r_A} = \frac{(5 \text{ mol/s})(0.9)[1-0.5(0.9)]^2}{\left(0.8 \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}}\right)(1-0.9)^2}$$

$$\boxed{\forall = 1701 \text{ dm}^3}$$

PFR and Batch Re Elementary Gas Ph PFR	eactors lase Reaction: $2A + B \rightarrow C$
Mole Balance	$V = F_{A0} \int_0^X \frac{dX}{-r_A}$
Rate Law	$-r_{A} = kC_{A}^{2}C_{B}$
<u>Stoichiometry</u>	gas phase, isothermal (T = T_0), no pressure drop (P = P_0), $C_{Ao}=C_{Bo}$ ($\Theta=1$), $v=v_0(1+\epsilon X)$
	$A + \frac{B}{2} \longrightarrow \frac{C}{2}$
	$C_{A} = C_{A0} \frac{(1-X)}{(1+\varepsilon X)}$
	$\varepsilon = y_{A0}\delta = \frac{1}{2}\left(\frac{1}{2} - \frac{1}{2} - 1\right) = -\frac{1}{2}$
	$\mathbf{v} = \mathbf{v}_{\mathrm{o}} \left(1 - \frac{1}{2} \mathbf{X} \right)$
	$C_{\rm B} = \frac{F_{\rm A0}}{v} = \frac{F_{\rm A0}\left(1 - \frac{1}{2}\right)}{v_{\rm o}\left(1 - \frac{1}{2}X\right)} = C_{\rm A0}$
	$C_B = C_{A0}$



Deriving C_A and C_B
Remember that the reaction is:
$$2A + B \rightarrow C$$

For a gas phase system: $C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0(1+\varepsilon X)(P_0/P)(T/T_0)}$
If the conditions are isothermal (T = T₀) and isobaric (P = P₀):
 $C_A = C_{A0} \frac{(1-X)}{(1+\varepsilon X)} \frac{T_0}{T} \frac{P}{P_0} = C_{A0} \frac{(1-X)}{(1+\varepsilon X)}$
We must divide by the stoichiometric coefficient of our basis of calculation yielding:
 $A + \frac{1}{2}B \rightarrow \frac{1}{2}C$

And if the feed is equal molar, then:

$$\varepsilon = y_{A0}\delta = 0.5\left(\frac{1}{2} - \frac{1}{2} - 1\right) = -0.5$$

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

$$C_{A} = C_{A0} \frac{(1-X)}{(1-0.5X)}$$

Similarly for C_B :

$$C_{B} = C_{A0} \frac{\left(\Theta_{B} - \frac{1}{2} X \right)}{(1 + \epsilon X)} = C_{A0} \frac{(1 - 0.5X)}{(1 - 0.5X)} = C_{A0}$$

Batch Reactor Constant Volume, V=Vo and the pressure changes.
$$\underline{Mole Balance}$$
 $t = N_{A0} \int_{0}^{X} \frac{dX}{-r_{A}V} = C_{A0} \int_{0}^{X} \frac{dX}{-r_{A}}$ $\underline{Rate Law}$ $-r_{A} = kC_{A}^{2}C_{B}$ $\underline{Stoichiometry}$ $C_{A} = \frac{N_{A}}{V_{0}} = \frac{N_{A0}}{V_{0}}(1-X)$ $C_{B} = \frac{N_{A0}}{V_{0}} \left(\Theta_{B} - \frac{1}{2}X\right) = C_{A0} \left(1 - \frac{X}{2}\right)$ $P = \frac{N_{T}}{N_{T0}} P_{o} = \frac{C_{T}}{C_{T0}} P_{o}$ $\underline{Combine}$ $-r_{A} = kC_{A0}^{3}(1-X)^{2} \left(1 - \frac{X}{2}\right)$ $t = \frac{1}{kC_{A0}^{2}} \int_{0}^{X} \frac{dX}{(1-X)^{2} \left(1 - \frac{X}{2}\right)}$



$$t = \frac{1}{kC_{A0}^2} \left[\frac{\Delta X_1}{3} (f(X=0) + 4f(X=0.3) + f(X=0.6)) + \frac{\Delta X_2}{3} (f(X=0.6) + 4f(X=0.75) + f(X=0.9)) \right]$$

$$t = 2.5s \left[\frac{(0.3)}{3} [1 + 4(2.4) + 7.81] \right] + \frac{(0.15)}{3} [7.81 + 4(25.6) + 181]$$

$$t = 2.5s \left[\frac{0.3}{3} (18.4) + \frac{0.15}{3} [291] \right] = 2.5s [1.84 + 14.55]$$

$$t = 41s$$

$$P = \frac{N_T}{N_{T0}} P_0 = \frac{(N_{A0} + N_{B0} + \delta N_{A0} X) P_0}{N_{T0}}$$

$$= (1 + y_{A0} \delta X) P_0$$

$$= \left(1 + \left(\frac{1}{2}\right) \left(\frac{-1}{2}\right) (0.9) \right) 16 4$$

$$= 12.7 \alpha t m$$

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 V = V₀)

Gas phase with constant volume $V = V_0$.

$$\frac{1}{V} \cdot \left(\frac{dN_A}{dt}\right) = r_A$$

$$\frac{1}{V} \cdot \left(\frac{dN_A}{dt}\right) = \frac{1}{V_0} \cdot \frac{dN_A}{dt} = \frac{dN_A/V_0}{dt} = \frac{dC_A}{dt} = r_A$$

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

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

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

$$A \rightarrow B$$

$$N_{A0} \cdot \frac{dX}{dt} = -r_A \cdot V_0 \qquad [1]$$

$$-r_A = k \cdot C_A^2 \qquad [2]$$

$$C_A = C_{A0} \cdot (1 - X)$$
 [3]

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

$$\frac{dX}{dt} = k \cdot C_{A0} \cdot (1 - X)^2$$

Rearrange:

$$\frac{dX}{\left(1-X\right)^2} = k \cdot C_{A0} \cdot dx$$

$$\textcircled{0} t = 0; X = 0; T = T_0 \text{ (isothermal)} \rightarrow k \rightarrow \text{ constant}$$
$$\int_0^t t = \frac{1}{k \cdot C_{A0}} \int_0^X \frac{dX}{(1-X)^2} \implies t = \frac{1}{k \cdot C_{A0}} \cdot \left(\frac{X}{1-X}\right)$$

It is important to know the reaction time, t_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 (t_F), heat (t_h) and clean (t_C).

 $t = t_{f} + t_{h} + t_{C} + t_{R}$

[1]

[2]

Volumetric flow rate

Design of Continuous Stirred Tank Reactors

CSTRs are usually used for liquid phase rxns:

$$V = \frac{\overrightarrow{F_{A0}} \cdot X}{(-r_A)_{exit}} = \frac{\overrightarrow{v_0} \cdot C_{A0} \cdot X}{-r_A}$$

(Design Eq'n for CSTR)

Divide by v₀: $\tau = \frac{V}{v_0} = \frac{C_{A0} \cdot X}{-r_A}$

A single CSTR: First order irreversible rxn: $-r_A = k \cdot C_A$ [3] Combine [2], [3] and [4] $C_A = C_{A0} \cdot (1 - X)$ [4] $\tau = \frac{1}{k} \cdot \left(\frac{X}{1 - X} \right)$ [5] $X = \frac{\tau \cdot k}{1 + \tau \cdot k}$ [6] Combine [4] and [6] $C_A = \frac{C_{A0}}{1 + \tau \cdot k}$ rxn Damköhler #, Da: a dimensionless # that for a first order rxn says the degree of conversion that can be achieved in cont. flow reactor.

$$Da = \frac{-r_{A0} \cdot V}{F_{A0}} : \frac{\text{rate of } rxn \text{ of } A}{\text{rate of convective transport of } A|_{t=0}}$$

For a second order rxn:
$$Da = \frac{-r_{A0} \cdot V}{F_{A0}} = \frac{k \cdot C_{A0}^{2} \cdot V}{v_{0} \cdot C_{A0}} = \tau \cdot k \cdot C_{A0}$$
$$Da \le 0.1 \qquad X < 0.10$$
$$Da \ge 10 \qquad X > 0.90$$
$$X = \frac{Da}{1+Da} \qquad \text{First order liq-phase rxn (Eq'n [6])}$$



If both reactors are of equal size, $(\tau_1 = \tau_2 = \tau)$

and operate at the same T ($k_1 = k_2 = k$)

$$C_{A2} = \frac{C_{A0}}{\left(1 + \tau \cdot k\right)^2}$$

for n equal sized CSTR system

$$C_{An} = \frac{C_{A0}}{(1 + \tau \cdot k)^n} = \frac{C_{A0}}{(1 + Da)^n}$$

Substituting for $C_{\mbox{\scriptsize An}}$ in terms of conversion

$$C_{A0} \cdot (1-X) = \frac{C_{A0}}{(1+Da)^n} \implies$$

 $X = 1 - \frac{1}{(1+Da)^n} = 1 - \frac{1}{(1+\tau \cdot k)^n}$



Example: 2^{nd} order rxn, $v = v_0$, $C_A = C_{A0}$ (1-X); $F_{A0} X = v_0 C_{A0} X$ Combine $-r_A = k C_{A2}$ and $V = F_{A0} X / -r_A$

$$V = \frac{F_{A0} \cdot X}{k \cdot C_{A}^{2}} = \frac{v_{0} \cdot C_{A0} \cdot X}{k \cdot C_{A0}^{2} \cdot (1 - X)^{2}}$$

Divide by v₀:

$$\tau = \frac{V}{v_0} = \frac{X}{k \cdot C_{A0} \cdot (1 - X)^2}$$

$$X = \frac{(1 + 2 \cdot \tau \cdot k \cdot C_{A0}) - \sqrt{(1 + 2 \cdot \tau \cdot k \cdot C_{A0})^2 - (2 \cdot \tau \cdot k \cdot C_{A0})^2}}{2 \cdot \tau \cdot k \cdot C_{A0}}$$

$$X = \frac{(1 + 2 \cdot Da) - \sqrt{1 + 4Da}}{2 \cdot Da}$$
Since $\tau \cdot k \cdot C_{A0} = Da$
for a second order rxn.

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

Example: The elementary liquid phase reaction $2A \rightarrow B$ is carried out isothermally in a CSTR. Pure A enters at a volumetric flow
rate of 25 dm³/s and at a concentration of 0.2 mol/dm³.What CSTR volume is necessary to achieve a 90% conversion when k = 10
dm³/(mol*s)?Mole Balance $V = \frac{F_{Ao}X}{-r_a}$ Rate Law $-r_A = kC_A^2$ Stoichiometryliquid phase (v = v_o)
 $F_{Ao} = v_o C_{Ao}$ $F_a = \frac{F_a}{v_o} = \frac{F_{Ao}}{v_o} = \frac{F_{Ao}(1-X)}{v_o}$ $C_A = C_{Ao}(1-X)$

$$\frac{\text{Combine}}{V = \frac{v_o C_{A_o} X}{k C_{A_o}^2 (1 - X)^2} = \frac{v_o X}{k C_{A_o} (1 - X)^2}}$$

$$\frac{\text{Evaluate}}{V = \frac{25 \frac{dm^3}{s} (0.90)}{(10 \frac{dm^3}{mol^3})(0.2 \frac{mol}{dm^3})(1 - 0.9)^2}$$

$$V = 1125 \text{ dm}^3$$
Space Time
$$\tau = \frac{V}{v_o} = \frac{1125 dm^3}{25 \frac{dm^3}{s}} = 45s$$

$2A \rightarrow B$ only A fed $P_0 = 8.2 \text{ atm}$ $T_0 = 500 \text{ K}$ $C_{A0} = 0.2 \text{ mol/dm}$ $k = 0.5 \text{ dm}^3/\text{mol-s} \text{ v}_0 = 2.5 \text{ dm}^3/\text{s}$	$2A \rightarrow B$ only A fed $P_0 = 8.2 \text{ atm}$ $T_0 = 500 \text{ K}$ $C_{A0} = 0.2 \text{ mol/dm}$ $k = 0.5 \text{ dm}^3/\text{mol-s} \text{ V}_0 = 2.5 \text{ dm}^3/\text{s}$	$2A \rightarrow B$ only A fed $P_0 = 8.2 \text{ atm}$ $T_0 = 500 \text{ K}$ $C_{A0} = 0.2 \text{ mol/d}$ $k = 0.5 \text{ dm}^3/\text{mol-s} \text{ v}_0 = 2.5 \text{ dm}^3/\text{s}$
$2A \rightarrow B$ $T_{0} = 500 \text{ K}$ $C_{A0} = 0.2 \text{ mol/dm}$ $k = 0.5 \text{ dm}^{3}/\text{mol-s} $	$2A \rightarrow B$ $T_{0} = 500 \text{ K}$ $C_{A0} = 0.2 \text{ mol/dm}$ $k = 0.5 \text{ dm}^{3}/\text{mol-s} $	$\begin{array}{c c} \mathbf{2A} \longrightarrow \mathbf{B} \\ \hline & & T_{o} = 500 \text{ K} \\ \hline & & K = 0.5 \text{ dm}^3/\text{mol-s} v_{o} = 2.5 \text{ dm}^3/\text{s} \end{array}$
$k = 0.5 \text{ dm}^3/\text{mol-s} v_0 = 2.5 \text{ dm}^3/\text{s}$	$k = 0.5 \text{ dm}^3/\text{mol-s} v_0 = 2.5 \text{ dm}^3/\text{s}$	$k = 0.5 \text{ dm}^3/\text{mol-s} v_0 = 2.5 \text{ dm}^3/\text{s}$

	<u>Batch</u>	<u>CSTR</u>	PFR
Mole Balance:	$t = N_{A0} \int_{0}^{X} \frac{dX}{-r_{A} \vee}$	$\vee = \frac{F_{A0} \times}{-r_A}$	$V = F_{A0} \int_{0}^{X} \frac{dX}{-r_{A}}$
Rate Law:	$-r_A = kC_A^2$	$-r_A = kC_A^2$	$-r_A = kC_A^2$
<u>Stoichiometry :</u>	Gas: V = V ₀ (e.g., constant volume steel container)	Gas: T =T ₀ , P =P ₀	Gas: $T = T_0$, $P = P_0$
		Per Mole of A:	Per Mole of A:
		$A \rightarrow \frac{B}{2}$	$A \rightarrow \frac{B}{2}$
		$\varepsilon = 1.0 \left(\frac{1}{2} - 1 \right) = -0.5$	$\varepsilon = 1.0 \left(\frac{1}{2} - 1\right) = -0.5$
	$C_{A} = \frac{N_{A}}{V} = \frac{N_{A0} \left(1 - X\right)}{V_{0}}$	$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0(1+\varepsilon X)}$	$C_{A} = \frac{F_{A}}{\upsilon} = \frac{F_{A0}(1-\varkappa)}{\upsilon_{0}(1+\varkappa)}$
	$C_{A}=C_{A0}\left(1-X\right)$	$C_A = C_{A0} \frac{(1-X)}{(1+\varepsilon X)}$	$C_A = C_{A0} \frac{(1-X)}{(1+\varepsilon X)}$
	$C_{B} = \frac{N_{B}}{V} = \frac{N_{AD}\left(+\frac{1}{2}X\right)}{V_{D}}$	$C_{\rm B} = \frac{F_{\rm B}}{\upsilon} = \frac{F_{\rm Ao}\left(+\frac{1}{2}X\right)}{\upsilon_{\rm s}\left(1+eX\right)}$	$C_{0} = \frac{F_{0}}{\upsilon} = \frac{F_{ac}\left(+\frac{1}{2}X\right)}{\upsilon_{i}(1+eX)}$
	$C_B = \frac{C_{A0}X}{2}$	$C_{B} = \frac{C_{A0}X}{2(4+a)}$	$C_{B} = \frac{C_{A0}X}{2(4+e^{3})}$

<u>Combine:</u>	$t = \frac{1}{kC_{A0}} \int_{0}^{X} \left[\frac{1}{(1-X)^2} \right] dX$	$V = \frac{F_{A0} \times (1 - 0.5 \times)^2}{k C_{A0}^2 (1 - \times)^2}$	$\label{eq:rescaled_states} V = \frac{F_{AO}}{kC_{AO}^2} \int_0^X \Biggl[\frac{(1-0.5X)^2}{(1-X)^2} \Biggr] dX$
<u>Integrate</u>	$t = \frac{1}{kC_{A0}} \left[\frac{X}{1 - X} \right]$		$ = \frac{F_{A0}}{kC_{A0}^2} \left[2\epsilon (1 + \epsilon) ln(1 - X) + \epsilon^2 X + \frac{(1 + \epsilon)^2 X}{1 - X} \right] $
<u>Evaluate</u>	$kC_{A0} = \left(\frac{0.2 \text{ dm}^3}{\text{mol} \cdot s}\right) \left(\frac{0.5 \text{ mol}}{\text{dm}^3}\right)$ $= 0.1 \text{ s}^{-1}$ $kC_{A0} = 0.1 \text{ sec}^{-1}$	$kC_{A0}^{2} = 0.5 \frac{dm^{3}}{mol \cdot s} \left(0.2 \frac{mol}{dm^{3}} \right)^{2}$ $= 0.02 \frac{mol}{dm^{3} \cdot s}$ $\nabla = \frac{0.5 \frac{mol}{s} (0.9)}{0.02 \frac{mol}{dm^{3} \cdot s}} \frac{(1 - 0.5(0.9))^{2}}{(1 - 0.9)^{2}}$	$F_{A0} = 0.5 \frac{\text{mol}}{\text{s}}$ $kC_{A0}^{2} = 0.02 \frac{\text{mol}}{\text{dm}^{3}\text{s}}$ $\nabla = \frac{5 \frac{\text{mol}}{\text{s}}(9)}{.02 \frac{\text{mol}}{\text{dm}^{3}\text{s}}} \left[2(-5)(1-5)\ln(1-9) + (-5)^{2}(9) + \frac{(1-5)^{2}(9)}{1-9} \right]$
<u>For X = 0.9:</u>	$t = \left(\frac{1}{0.1 \text{ s}^{-1}}\right) \left(\frac{0.9}{1 - 0.9}\right)$	V = 680.6 dm ³	V = 90.7 dm ³
	t = 90s ec	$\tau = \frac{V}{v_0} = 272.3 \text{sec}$	$\tau = \frac{V}{V_0} = 36.3 \sec \theta$

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.)

Equilibrium Conversion, X_e

$$K_{C} = \frac{C_{C}^{c} C_{D}^{d}}{C_{A}^{a} C_{B}^{b}}$$

Calculate Equilibrium Conversion (Xe) for a Constant Volume SystemExample: Determine Xe for a PFR with no pressure drop, $P = P_0$ Given that the system is gas phase and isothermal, determine the reactor
volume when X = 0.8 Xe $\boxed{\texttt{Reaction} \quad Additional Information}$
 $2A \leftrightarrow B \quad C_{A0} = 0.2 \text{ mol/dm}^3$
 $K_C = 100 \text{ dm}^3/\text{mol}$ $2A \leftrightarrow B \quad C_{A0} = 0.2 \text{ mol/dm}^3$
 $K_C = 100 \text{ dm}^3/\text{mol}$ First calculate Xe:
Equilibrium constant Kc is; $K_C = \frac{C_{Be}}{C_{Ae}}$
 $C_{Ae} = C_{A0}(1-X_e)$
 $C_{Be} = C_{A0}(1-X_e)$ $K_C = \frac{Xe(1 + eXe)}{2C_{A0}(1-Xe)^2}$ $X_e = 0.89$
 $X = 0.8X_e = 0.711$

Deriving The Equilibrium Constant (K_c) and Equilibrium Conversion (X_e) for a Non-Constant Volume System:

The reversible reaction:

 $2A \Leftrightarrow B$

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, K_c , for this reaction is:

$$K_{\rm C} = \frac{C_{\rm Be}}{C_{\rm Ae}^2}$$

A is the limiting reactant $\mathsf{A} \Leftrightarrow \mathsf{B/2}$

where
$$C_{Ae}$$
 and C_{Be} are:

$$C_{Ae} = \frac{F_{Ae}}{v_e} = \frac{F_{A0}(1-X_e)}{v_0(1+\varepsilon X_e)} = \frac{C_{A0}(1-X_e)}{(1+\varepsilon X_e)}$$

$$C_{Be} = \frac{F_{Be}}{v_e} = \frac{F_{A0}(X_e/2)}{v_0(1+\varepsilon X_e)} = \frac{C_{A0}(X_e/2)}{(1+\varepsilon X_e)}$$

Substituting for C_{Ae} and C_{Be} gives us:

$$K_{\rm C} = \frac{\left[\frac{C_{\rm A0}(0.5 \times_{\rm e})}{(1 + \varepsilon \times_{\rm e})}\right]}{\left[\frac{C_{\rm A0}^2(1 - \times_{\rm e})^2}{(1 + \varepsilon \times_{\rm e})^2}\right]}$$
$$K_{\rm C} = \frac{\chi_{\rm e}(1 + \varepsilon \times_{\rm e})}{2C_{\rm A0}(1 - \times_{\rm e})^2}$$

Substituting known values (C_{A0} = 0.2 mol/dm³ and K_C = 100 dm³/mol), and realizing that:

$$\varepsilon = y_{A0}\delta = (1.0)\left(\frac{1}{2} - \frac{2}{2}\right) = -0.5$$
$$100 = \frac{X_e(1 - 0.5X_e)}{2(0.2)(1 - X_e)^2}$$

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

Batch Reactor With a Reversible Reaction

The following reaction follows an elementary rate law

$$N_2 + O_2 \xrightarrow{k_1}{k_{-1}} 2NO$$

Initially 77% N₂, 15% O₂, 8% inerts are fed to a batch reactor where 80% of the equilibrium conversion (X_e = 0.02) is reached in 151 μ s. What is the specific reaction rate constant k₁?

Additional Information

$$X_p = 0.02$$
, $V = 0.4 \text{ dm}^3$, $K_C = 0.01$, $P = 20 \text{ atm}$, $T = 2700 \text{ K}$



Combining

$$-r_{A} = k_{1}C_{A}^{2}\left[(1-X)(\Theta_{B}-X) - \frac{4X^{2}}{K_{C}}\right]$$

$$= r_{A}$$

$$C_{A0}\frac{dX}{dt} = -r_{A}$$

$$C_{A0}\frac{dX}{dt} = -r_{A}$$
Rearranging and integrating

$$t = C_{A0}\int_{0}^{x}\frac{dX}{-r_{A}} = \frac{1}{k_{1}C_{A0}}\int_{0}^{x}\frac{dX}{(1-X)(\Theta_{B}-X) - 4X^{2}/K_{C}}$$
Evaluate:
$$C_{A0} = \frac{y_{A0} \cdot P_{0}}{R \cdot T_{0}} = \frac{(0.77) \cdot (20 \text{ atm})}{(0.082\frac{\text{atm} \cdot \text{dm}^{3}}{\text{mol} \cdot \text{K}})(2700 \text{ K})}$$

$$C_{A0} = 6.96 \times 10^{-2} \text{ mol/dm}^{3}$$
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 k1 and substituting for CAO,
$$\Theta_B$$
, t, and Kc gives

$$k_1 = \frac{1}{(151 \times 10^{-6} \text{ s})(0.0696 \text{ mol}/\text{dm}^3)} \times \int_0^{0.016} \frac{\text{dX}}{0.195 - 1.195 \cdot \text{X} - 399 \cdot \text{X}^2}$$
Use Simpson's three point formula to integrate

$$k_1 = 9.51 \times 10^4 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \int_0^{0.016} f(X) \text{dX}$$

$$X_0 = 0 \qquad f(X_0) = 5.128$$

$$X_1 = 0.008 \qquad f(X_1) = 6.25$$

$$X_2 = 0.016 \qquad f(X_2) = 13.56$$
with $\Delta X = 0.016/2 = 0.008$

$$\int_{X_0}^{X_2} f(X) \text{dX} = \frac{\Delta X}{3} [f(X_0) + 4f(X_1) + f(X_2)]$$

$$k_1 = 9.51 \times 10^4 \times \left(\frac{0.008}{3}\right) (5.128 + 4 \times 6.25 + 13.56)$$

$$k_1 = 1.11 \times 10^4 \text{ dm}^3/\text{mol} \cdot \text{s}$$

Tubular Reactors:

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



No radial variation in velocity, conc'n, T or $-r_A$.

Design Eq'n:

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

In the absence of pressure drop or heat exchange, integral form of the design equation is used:

$$V = F_{A0} \cdot \int_{0}^{X} \frac{dX}{-r_{A}}$$

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:

$$F_{A0} \frac{dX}{dW} = -r'_{A}$$

Rate Law

Second order in A and irreversible: $-r_A' = kC_A^2$

Stoichiometry
$$C_A = \frac{F_A}{\upsilon} = C_{A0} \frac{(1-X)}{(1+\varepsilon X)} \frac{P}{P_0} \frac{T_0}{T}$$

Isothermal, $T = T_0$ $C_A = C_{A0} \frac{(1-X)}{(1+\varepsilon X)} \frac{P}{P_0}$
Combine $\frac{dX}{dW} = \frac{kC_{A0}^2}{F_{A0}} \frac{(1-X)^2}{(1+\varepsilon X)^2} \left(\frac{P}{P_0}\right)^2$
Need to find (P/P₀) as a function of W (or V if you have a PFR).



Variable Density

$$\rho = \rho_0 \frac{P}{P_0} \frac{T_0}{T} \frac{F_{T_0}}{F_T}$$

$$\frac{dP}{dz} = \frac{-G}{\rho_0 g_c D_P} \left(\frac{1-\phi}{\phi^3}\right) \left[\frac{150(1-\phi)\mu}{D_P} + 1.75G\right] \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T_0}}$$

$$\beta_0 = \frac{G}{\rho_0 g_c D_P} \left(\frac{1-\phi}{\phi^3}\right) \left[\frac{150(1-\phi)\mu}{D_P} + 1.75G\right]$$
Catalyst Weight
$$W = zA_c \rho_b = zA_c (1-\phi)\rho_c$$

$$\rho_b = bulk density$$

$$\rho_c = solid catalyst density$$

$$\phi = porosity (a.k.a., void fraction)$$

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

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

Then
$$\frac{dP}{dW} = -\frac{\alpha}{2} \frac{P_0}{\left(\frac{P}{P_{P_0}}\right)} \frac{T}{T_0} \frac{F_T}{F_{T_0}}$$
$$-\frac{d\left(\frac{P}{P_0}\right)}{dW} = -\frac{\alpha}{2} \frac{T}{\left(\frac{P}{P_0}\right)} \frac{T}{T_0} \frac{F_T}{F_{T_0}}$$
We will use this form for multiple reactions:
$$\frac{dy}{dW} = -\frac{\alpha}{2y} \frac{T}{T_0} \frac{F_T}{F_{T_0}} \qquad \left(y = \frac{P}{P_0}\right)$$
$$\frac{d(P/P_0)}{dW} = -\frac{\alpha}{2(P/P_0)} \frac{T}{T_0} (1 + \varepsilon X)$$
Since
$$F_T = F_{T_0} + F_{A0} \delta X = F_{T0} \left(1 + \frac{F_{A0}}{F_{T0}} \delta X\right)$$
$$-\frac{F_T}{F_{T0}} = 1 + \varepsilon \cdot X \qquad \left(\varepsilon = y_{A0} \cdot \delta = \frac{F_{A0}}{F_{T0}} \cdot \delta\right)$$

$$\begin{array}{ll} \displaystyle \frac{dy}{dW} = -\frac{\alpha}{2y} \frac{T}{T_0} (1 + eX) & \text{when } \varepsilon < 0; & \Delta P \text{ will be less than } \varepsilon = 0. \\ \text{when } \varepsilon > 0; & \Delta P \text{ will be greater than } \varepsilon = 0. \end{array}$$
Isothermal Operation
$$\begin{array}{ll} \displaystyle \frac{dy}{dW} = -\frac{\alpha}{2y} (1 + eX) \\ \displaystyle \frac{dX}{dW} = \frac{kC_{Ao}^2 (1 - X)^2}{F_{Ao} (1 + \varepsilon X)^2} y^2 \end{array}$$
Notice that
$$\begin{array}{ll} \displaystyle \frac{dX}{dW} = f(X, P) \text{ and } \frac{dP}{dW} = f(X, P) \text{ or } \frac{dy}{dW} = f(y, X) \end{array}$$
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. \end{array}

Analytical Solution
$$\mathbf{A} \rightarrow \mathbf{B}$$
, [e], PFR with $-\mathbf{r}_{A}^{i} = \mathbf{k} \mathbf{C}_{A}^{i}$
 $\frac{dy}{dW} = -\frac{\alpha}{2y}(1 + \varepsilon X)$
 $2y \cdot \frac{dy}{dW} = -\alpha$
 $y = 1$ $(P = P_{0}) @ W = 0$
 $y^{2} = 1 - \alpha \cdot W$
IF $T = T_{0}$ AND $\varepsilon = 0$ $\underline{y = (1 - \alpha W)^{1/2}}$
CAUTION: Never use this form if $\varepsilon \neq 0$
For $\varepsilon = 0$ $C_{A} = C_{A0}(1 - X)y = C_{A0}(1 - X)(1 - \alpha W)^{1/2}$

<u>Solve</u>

$$-r'_{A} = kC^{2}_{A} = kC^{2}_{A0}(1-X)^{2}(1-\alpha W)$$

$$F_{A0} \frac{dX}{dW} = -r'_{A}$$

$$\frac{dX}{dW} = \frac{kC^{2}_{A0}}{F_{A0}}(1-X)^{2}(1-\alpha W)$$

$$\boxed{\frac{X}{1-X} = \frac{kC^{2}_{A0}}{F_{A0}}\left[W - \frac{\alpha W^{2}}{2}\right]}$$

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



Pressure Drop in Pipes:

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

$$\frac{dP}{dL} = -G \cdot \frac{du}{dL} - \frac{2 \cdot f \cdot G^2}{g \cdot D}$$

Where

G = ρ u (g/cm³s) = mass velocity is constant along L.

u = average velocity of gas, cm/s.

f = fanning friction factor

f = fnc (Re, pipe roughness

$$\frac{P}{P_0} = \left[1 - \frac{4 \cdot f \cdot G^2 \cdot V}{\rho_0 \cdot P_0 \cdot A_C \cdot D}\right] = (1 - \alpha_p V)^{1/2}$$

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Optimum Particle Diameter

$$A \to B$$

- $r_A = kC_{A0}(1 - X)y, \quad y = \frac{P}{P_0}$
$$\frac{dy}{dw} = -\frac{\alpha}{2y}(1 + \varepsilon X)$$

as α increases the pressure drop increases

$$\alpha = \frac{2G}{A_{c}\rho_{c}P_{0}\rho_{0}D_{p}\phi^{3}} \left[\frac{150(1-\phi)\mu}{D_{p}} + 1.75G\right]$$

Laminar Flow, Fix $P_{0},\,\rho_{0},\,\Phi$

$$\rho_0 = P_0(MW)/RT_0$$
$$\rho_0 P_0 \sim P_0^2$$











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

$$\alpha = \frac{2G}{A_c \rho_o \rho_c g_c D_P \phi P_o} \left[\frac{150 \mu (1-\phi)}{D_P} + 1.75G \right]$$

Turbulent Flow

 $\alpha \sim \frac{G^2}{A_c D_P P_0^2}$

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.

$$\alpha_2 = \alpha_1 \left(\frac{G_2}{G_1}\right)^2 \left(\frac{A_{c1}}{A_{c2}}\right) \left(\frac{D_{P1}}{D_{P2}}\right) \left(\frac{P_{o1}}{P_{o2}}\right)^2$$

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

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

Laminar Flow

$$\alpha \sim \frac{G}{A_c D_P^2} , \quad G = \frac{\dot{m}}{A_c}$$
$$\alpha_2 = \alpha_1 \left(\frac{D_{P1}}{D_{P2}}\right)^2 \left(\frac{A_{c1}}{A_{c2}}\right)^2$$



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 reactorsB. Multiple reactionLiquids: Use concentrations, i.e., C_A

$$C_A = \frac{F_A}{r_o}$$

1. For the elementary liquid phase reaction $A \le B$ carried out in a CSTR, where V, v_o, C_{Ao}, k, and K_c are given and the feed is pure A, the combined mole balance, rate laws, and stoichiometry are:

$$\tau = \frac{V}{v_o} = \frac{C_{Ao} - C_A}{k \left[C_A - \frac{C_B}{K_c} \right]}$$
$$\tau = \frac{C_B}{k \left[C_A - \frac{C_B}{K_c} \right]}$$

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

$$\begin{split} \nu &= \nu_0 \frac{F_T}{F_{T0}} \frac{P}{P_0} \frac{T_0}{T} & C_A &= \frac{F_A}{\nu} = \frac{F_A}{F_0} \frac{F_{T0}}{F_T} \frac{P}{P_0} \frac{T_0}{T} \\ C_A &= C_T \frac{F_A}{\nu} = \left(\frac{F_A}{F_T}\right) \frac{P}{P_0} \frac{T_0}{T} , \quad C_{T0} = \frac{P_0}{RT_0} \end{split}$$

2. If the above reaction, $A \le B$, carried out in the gas phase in a PFR, where V, v_o, C_{Ao}, k , and K_c are given and the feed is pure A, the combined mole balance, rate laws, and stoichiometry yield, for isothermal operation (T=T_o) and no pressure drop (ΔP =0) are:

$$\frac{\mathbf{d}\mathbf{F}_{A}}{\mathbf{d}\mathbf{V}} = -\mathbf{k} \begin{bmatrix} \mathbf{C}_{To} \left(\frac{\mathbf{F}_{A}}{\mathbf{F}_{T}}\right) - \frac{\mathbf{C}_{To} \left(\frac{\mathbf{F}_{B}}{\mathbf{F}_{T}}\right)}{\mathbf{K}_{c}} \end{bmatrix}$$
$$\frac{\mathbf{d}\mathbf{F}_{B}}{\mathbf{d}\mathbf{V}} = -\mathbf{k} \begin{bmatrix} \mathbf{C}_{To} \left(\frac{\mathbf{F}_{A}}{\mathbf{F}_{T}}\right) - \frac{\mathbf{C}_{To} \left(\frac{\mathbf{F}_{B}}{\mathbf{F}_{T}}\right)}{\mathbf{K}_{c}} \end{bmatrix}$$
$$\mathbf{F}_{T} = \mathbf{F}_{A} + \mathbf{F}_{B}$$





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 $\frac{dF_A}{dW} = r'_A$
 $\frac{dF_B}{dW} = r'_B = -r'_A$
 $\frac{dF_C}{dW} = r'_C - \kappa_C C_C = -3r'_A - \kappa_C C_C$ Rate Laws $-r'_A = \kappa_A \left[C_A - \frac{C_B C_C^3}{\kappa_C} \right]$
 $r_B = -r_A$
 $r_C = -3r_A$







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Example: Elementary Irreversible Reaction

Consider the following irreversible elementary reaction

$$A + B \rightarrow C + D$$

$$-r_A = kC_A C_B$$

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

$\frac{\mathrm{dX}}{\mathrm{dt}} = \frac{\mathrm{k}(1-\mathrm{X})(\mathrm{N}_{\mathrm{Bi}}+\mathrm{F}_{\mathrm{B0}}\mathrm{t}-\mathrm{N}_{\mathrm{A0}}\mathrm{X})}{\mathrm{V}_{\mathrm{0}}+\mathrm{v}_{\mathrm{0}}\mathrm{t}}$	$\frac{dC_A}{dt} = r_A - C_A \frac{\upsilon_0}{V}$	$\frac{dN_{A}}{dt} = r_{A}V$
<u>-</u>	$\frac{\mathrm{dC}_{B}}{\mathrm{dt}} = r_{A} + (C_{B0} - C_{B})\frac{v_{0}}{V}$	$\frac{\mathrm{d}N_{\mathrm{B}}}{\mathrm{d}t} = F_{\mathrm{Ao}} + r_{\mathrm{B}}V$

Conversion	Concentration	Moles
d(X)/d(t) = -ra*V/Nao	d(Ca)/d(t) = ra - (Ca*vo)/V	d(Na)/d(t) = ra*V
ra = -k*Ca*Cb	d(Cb)/d(t) = rb + ((Cbo-Cb)*vo)/V	d(Nb)/d(t) = rb*V + Fbc
$Ca = Nao^*(1 - X)/V$	ra = -k*Ca*Cb	ra = -k*Ca*Cb
Cb = (Nbi + Fbo*t - Nao*X)/V	rb = ra	rb = ra
V = Vo + vo*t	V = Vo + vo*t	V = Vo + vo*t
Vo = 100	Vo = 100	Vo = 100
vo = 2	vo = 2	vo = 2
Nao = 100	Fbo = 5	Fbo = 5
Fbo = 5	Nao = 100	Ca = Na/V
Nbi = 0	Cbo = Fbo/vo	Cb = Nb/V
k = 0.1	k = 0.01	k = 0.01
	Na = Ca*V	
	X = (Nao-Na)/Nao	

Equilibrium Conversion in Semibatch Reactors with Reversible Reactions

Consider 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:

$$C_{A} = \frac{N_{A0}(1-X)}{V} \qquad C_{B} = \frac{(F_{B0}t - N_{A0}X)}{V} \qquad C_{C} = C_{D} = \frac{N_{A0}X}{V}$$

At equilibrium, -r_A=0, then $K_{C} = \frac{C_{Ce}C_{De}}{C_{Ae}C_{Be}} = \frac{N_{Ce}N_{De}}{N_{Ae}N_{Be}}$

$$K_{C} = \frac{N_{A0} X_{e}^{2}}{(1 - X_{e})(F_{B0}t - N_{A0} X_{e})}$$

```
function f=volume(V,x)
Ca0=0.2;
Kc=100;
Fa0=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;
CA0 = 0.2;
f = zeros(2,1);
CA = (CA0*(1-x(1))*x(2))/(1 + epsilon*x(1));
ra = k*(CA.^{2});
f(1) = ra / FA0;
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')
```





	Batch	CSTR	PFR
Mole Balance:	$t = N_{A0} \int_{0}^{X} \frac{dX}{-r_{A} \vee}$	$\vee = \frac{F_{A0} \times}{-r_A}$	$V = F_{A0} \int_{0}^{X} \frac{dX}{-r_{A}}$
Rate Law:	$-r_A = kC_A^2$	$-r_A = kC_A^2$	$-r_A = kC_A^2$
Stoichiometry :	Gas: V = V ₀ (e.g., constant volume steel container)	Gas: T =T ₀ , P =P ₀	Gas: $T = T_0$, $P = P_0$
		Per Mole of A:	Per Mole of A:
		$A \rightarrow \frac{B}{2}$	$A \rightarrow \frac{B}{2}$
		$\varepsilon = 1.0 \left(\frac{1}{2} - 1\right) = -0.5$	$\varepsilon = 1.0 \left(\frac{1}{2} - 1\right) = -0.5$
	$C_{A} = \frac{N_{A}}{V} = \frac{N_{A0}(1-X)}{V_{0}}$	$C_{A} = \frac{F_{A}}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_{0}(1+\varepsilon X)}$	$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0(1+\varepsilon X)}$
	$C_{A} = C_{A0}(1-X)$	$C_A = C_{A0} \frac{(1-X)}{(1+sX)}$	$C_A = C_{A0} \frac{(1-X)}{(1+eX)}$
	$C_{\mathbf{B}} = \frac{N_{\mathbf{B}}}{V} = \frac{N_{\mathbf{A}0} \left(+ \frac{1}{2} X \right)}{V_{0}}$	$C_{\oplus} = \frac{F_{\oplus}}{\upsilon} = \frac{F_{Ae}\left(+\frac{1}{2}\mathbf{X}\right)}{\upsilon_{p}(\mathbf{i} + e\mathbf{X})}$	$C_{\pm} = \frac{F_{\pm}}{\upsilon} = \frac{F_{Av}\left(+\frac{1}{2}X\right)}{\upsilon_{p}(1+eX)}$
	$C_{\theta} = \frac{C_{A0}X}{2}$	$C_{B} = \frac{C_{A0}X}{2(1+sX)}$	$C_{B} = \frac{C_{A0} \times}{2(1 + \epsilon \times)}$





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