Reaction 1

First semester 2025-2026

د.رياض الشوابكة

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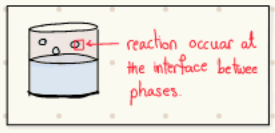
Madar Team

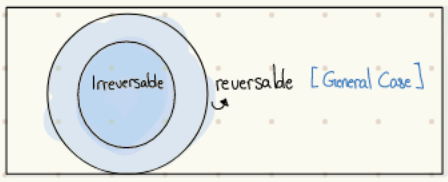
Reactions

- Homogenous Reaction — "one phase"
- Heterogenous Reaction — "multipul phase"



Reactions

- Irreversible
- Reversable



* Depend on k_f and k_B $\quad A + B \rightleftharpoons C + D$ reversable $\quad k_{eq} = \frac{k_f}{k_B} \approx \boxed{1}$

$A + B \longrightarrow C + D$ Irreversable

* Rate law $\quad aA + bB \rightleftharpoons cC + dD$

$$-\frac{1}{a}\frac{dN_A}{dt} = -\frac{1}{b}\frac{dN_B}{dt} = \frac{1}{c}\frac{dN_C}{dt} = \frac{1}{d}\frac{dN_D}{dt}$$

$-r_A \Rightarrow$ Rate of disappearance of num of mole A

$-r_B \Rightarrow$ Rate of disappearance of num of mole B

$r_C \Rightarrow$ Rate of appearance of num of mole C

$r_D \Rightarrow$ Rate of appearance of num of mole D

- The rate of chem reaction with respect to species i

$$r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of fluid})\,(\text{time})}$$

- The rate of reaction that relates $-r_i$ to species concentration

$$-r_A = k_f(T)\, f(C_A, C_B, C_C, C_D, \ldots)$$

* Irreversable $\quad -r_A = k_f(T)(C_A, C_B)$

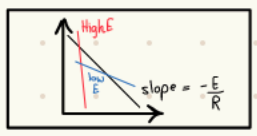
* k_f reaction rate constant. → not constant but is not function of concentration.

$k_f(T) = A e^{-E/RT}$

T: [K] R: 8.314 J/mol.K E: Activating energy J/mol

$k_f(T) = A e^{-E/RT}$

$\ln[k_f] = \underbrace{\ln A}_{\text{intercept}} \underbrace{-\frac{E}{R}}_{\text{slope}} \frac{1}{T}$



Case 1: Irreversable homogenous reaction :-

$$aA + bB \xrightarrow{k_f} cC + dD$$

$$r_A = -k_f C_A^a C_B^b$$

$$r_B = -\frac{b}{a} k_f C_A^a C_B^b$$

① $A + 2B \rightarrow C$ $\quad r_B = -2k_f C_A C_B^2$

$F + R \rightarrow C$ $\quad r_R = -k_f C_F C_D$

$r_B > r_R$

rate ↑ → Production ↑ ✓

② k_f → function of activating energy

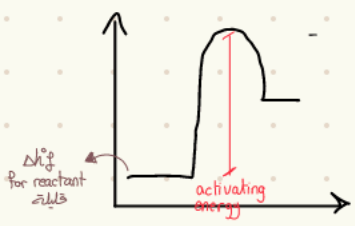
↳ activating energy ↑ → cost ↑ ✗

* rxn [1] $\quad$ rxn [2]

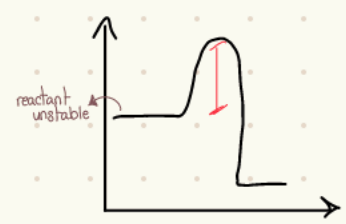
$A + 2B \rightarrow C$ ✓ $\quad F + R \rightarrow C$

activating energy >> activating energy ✓

} Over all cost اکثر اقل
عشان اخر اقرر احسن rxn .



Endothermic	Exothermic
Safty ↑	safty ↓
need energy	excess energy can be used
Activating energy ↑	· Activating energy

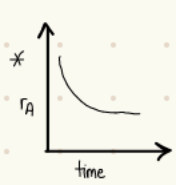


Case 2: Reversable homogenous reaction :-

$$aA + bB \underset{k_B}{\overset{k_{eq}}{\rightleftharpoons}} cC + dD \qquad * \; k_{eq} = \frac{k_f}{k_B} = \frac{C_C^c \; C_D^d}{C_A^a \; C_B^b}$$

$$r_A = -k_f C_A^a C_B^b + k_B C_D^d C_C^c$$

$$r_D = +k_f C_A^a C_B^b - k_B C_D^d C_C^c$$

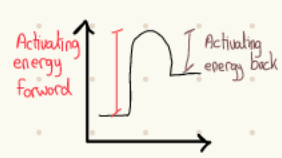


10 → 8 → 6 → 3 → 3

5 m, 10 m, very long time, ∞

↑ reasistance time

↑↑ Flow rate reactant



$\Delta H_{rxn} = E_{af} - E_{aB}$

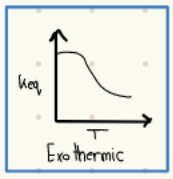
$$* \; k_f = A_f e^{-E_{af}/RT}$$

$$k_B = A_B e^{-E_{aB}/RT}$$

$$k_{eq} = \frac{k_f}{k_B} = \frac{A_f e^{-E_{af}/RT}}{A_B e^{-E_{aB}/RT}}$$

$$k_{eq} = \frac{A_f}{A_B} e^{-\frac{E_{af}}{RT} + \frac{E_{aB}}{RT}} \longrightarrow \Delta H_{rxn} = E_{af} - E_{aB}$$

$$k_{eq} = \frac{A_f}{A_B} e^{-\frac{\Delta H_{rxn}}{RT}}$$

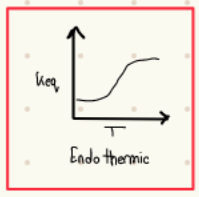


* ΔH_{rxn} → negative

$$k_{eq} = \frac{A_f}{A_B} e^{\frac{\Delta H_{rxn}}{RT}} \Rightarrow \uparrow Temp \; , \downarrow k_{eq}$$

energy between bonds unstable $\xrightarrow[\text{taking out energy}]{}$ stable

* Rate ↑ → k_{eq} ↑ → Temp ↓ [exothermic]



* ΔH_{rxn} → +

$$k_{eq} = \frac{A_f}{A_B} e^{-\frac{\Delta H_{rxn}}{RT}}$$

* k_{eq} ↑ , Temp ↑

$$* \; K_{eq}(T) = K_{eq}(T_1) \exp\left[\frac{\Delta H^\circ_{Rx}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

→ need ref point.

Example 2.2 Reversible reaction

Consider the dehydrogenation reaction of benzene to produce Heptalene. What is the net rate of reaction?

$$2C_6H_6 \underset{k_{-B}}{\overset{k_B}{\rightleftharpoons}} C_{12}H_{10} + H_2$$

$$2B \underset{k_B}{\overset{k_f}{\rightleftharpoons}} D + H_2$$

$r_{B\,forward} = -k_f C_B^2$

$r_{B\,Back} = k_B C_a C_D$

$r_{B\,net} = r_{B\,forward} + r_{B\,Back}$

$r_{B\,net} = k_B C_a C_D - k_f C_B^2$

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Reaction order :-

① $-r_A = k C_A^a C_B^b$

↳ for elementary rxn

order in A ⇒ a
order in B ⇒ b
over all order ⇒ a+b

② $-r_A = \dfrac{k C_A}{1 + k' C_B}$ ⇒

- Low C_B: n = 1 (w.r.t. A)
- High C_B: $n_A = 1$, $n_B = -1$ (*apparent* orders)

→ خارج تستخدمه براكشن ١

Units of reaction constant :-

↳ depent on reaction order

$[k] = \dfrac{[\text{Concentration}]^{1-n}}{\text{time}}$

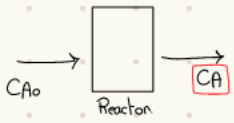
n: over all reaction order

Zero order → $r_A = -k$ $\quad [k] = \dfrac{[mol/L]^{1-0}}{s} = \dfrac{mol}{L \cdot s}$

First order → $r_A = -kC_A$ $\quad [k] = \dfrac{[mol/L]^{1-1}}{s} = s^{-1}$

Second order → $r_A = -kC_A^2$ $\quad [k] = \dfrac{[mol/L]^{1-2}}{s} = \dfrac{L}{mol \cdot s}$

Third order → $r_A = -kC_A^3$ $\quad [k] = \dfrac{[mol/L]^{1-3}}{s} = \dfrac{[L/mol]^2}{s}$



Key reactant

$aA + bB \rightleftharpoons cC + dD$

Key reactant ⇒ A $\quad$ ↑ Rate $\quad$ key → limiting reactant.

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

Reaction conversion

Flow out , flowin على فرق

$A + \frac{b}{a}B \rightarrow \frac{c}{a}C$

$N_{consumed\,A} = N_{A_0} - N_A$
N_{A_0}: initally moles
N_A : moles after reaction

$N_{produced\,C} = N_C^\circ + N_C$
N_C° = initally moles
N_C = moles After reaction

* X :- ratio of the Nconsumed to N_A°

$X = \dfrac{N_{consumed}}{N_{A_0}}$ $\quad [0, 1]$

Species	*Initially* (mol)	*Change* (mol)	*Remaining* (mol)
A	N_{A0}	$-(N_{A0}X)$	$N_A = N_{A0} - N_{A0}X$
B	N_{B0}	$-\frac{b}{a}(N_{A0}X)$	$N_B = N_{B0} - \frac{b}{a}N_{A0}X$
C	N_{C0}	$\frac{c}{a}(N_{A0}X)$	$N_C = N_{C0} + \frac{c}{a}N_{A0}X$
D	N_{D0}	$\frac{d}{a}(N_{A0}X)$	$N_D = N_{D0} + \frac{d}{a}N_{A0}X$
I (inerts)	N_{I0}	–	$N_I = N_{I0}$
Totals	N_{T0}		$N_T = N_{T0} + \underbrace{\left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)}_{\delta} N_{A0}X$

Extent of reaction

$\xi = \dfrac{N_i - N_{i0}}{\nu_i}$ $\quad \left[0, \dfrac{n_A^\circ}{a}\right]$ $\quad X = \dfrac{N_i - N_{i0}}{N_{i0}}$

$X N_i^\circ = N_i - N_{i0}$

$\xi = \dfrac{X N_i^\circ}{\nu_i}$

* Conversion ⇒ (مش) Exent of reaction
* if we have more than one reaction ⇒ we use extend of reaction → $N_A = N_A^\circ - \xi_1 - \xi_2$

The general mole balance equations:-

In − out + Generation = Accumilation.

$-0 - F_j + G_j = \dfrac{dN_j}{dt}$ $\quad$ [mole / time]

$G_j = \int r_j \, dV$ → constant volume → $r_j \cdot V$

* Design → Time
  ↳ Volume

Batch reactor:

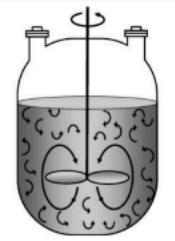
$\cancel{F_{j0}} - \cancel{F_j} + \int r_j \, dV = \dfrac{dN_j}{dt}$

no flow in and out.

$\int r_j \, dV = \dfrac{dN_j}{dt}$

constant volume

$r_j V = \dfrac{dN_j}{dt}$



if it's first order rxn. $r = -kC_A$

$-kC_A V = \dfrac{dN_j}{dt}$

$\dfrac{\text{mole}}{\text{Volume}} = C_A \rightarrow C_A V \rightarrow N_i$

$\int_{t_0}^{t} dt = \int_{n_0}^{n_i} \dfrac{dN_i}{-N_i k}$

$t = \dfrac{-1}{k} \ln N_i \Big]_{n_0}^{n_i}$ ⇒ السالب موجود التكامل ⇒ لازم الجواب يكون (N)

- moles → $\dfrac{dN_i}{dt} = V r_i$
- Concentrations → $\dfrac{d\left[\frac{N_i}{V}\right]}{dt} = r_i$ → $\dfrac{dC_{Ai}}{dt} = r_A$
- Extend of reaction → $\left[\dfrac{dN_i}{dt} = V r_i\right] \times \dfrac{1}{\nu_i}$ → $\dfrac{d\xi}{dt} = \dfrac{V r_i}{\nu_i}$
- Conversion → $\left[\dfrac{dN_i}{dt} = V r_i\right] \times \dfrac{1}{N_0}$ → $\dfrac{dX}{dt} = \dfrac{V r_i}{N_0}$

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CSTR

$$F_{j0} - F_j + G_j = \frac{dN_j}{dt}$$

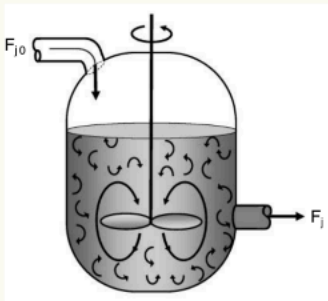
Constant volume [rV]

steady state
volume flowrate in = out

$$F_{j0} - F_j + rV = 0$$

$\rightarrow V$ ✓
$\rightarrow + X$

F = mole flow Rate $\rightarrow \frac{mole}{volume} \times \frac{volume}{time} \rightarrow v_0 C_A$



* Perfect mixing

$$rV = v_0 [C_A - C_{A0}]$$

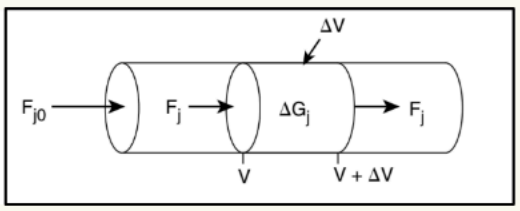
$$V = \frac{v_0 [C_A - C_{A0}]}{r}$$

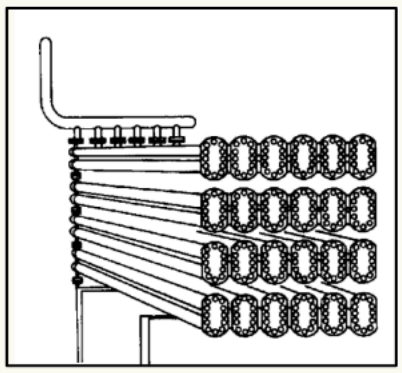
v_0 : Constant

$\rightarrow$ time ✓ $\rightarrow v_0 = \frac{V}{t}$
$\rightarrow$ Volume ✓

* if $\Delta C_A \Rightarrow$ constant and V constant and I want to ↑ yield $\Rightarrow$ ↑ volume flowrate

Tubular Reactor [PFR]





* perfect unmixed
* ↓D ↓mixing

* Assume → number of tubes $\left[\frac{\text{molar flow Rate}}{\text{number of tube}}\right]$

↳ مثلا عندي 60 L
اذا طلع معاي
العرض من جميع الانابيب
من منطقي ⇐ new Assume
num, < num₂

$$F_{j0}\Big|_V - F_j\Big|_{V+\Delta V} + G_j = \frac{dN_j}{dt} \quad 0$$

G_j ↳ constant volume

$$F_{j0}\Big|_V - F_j\Big|_{V+\Delta V} = r\,\Delta V$$

$$\frac{F_{j0}\Big|_V - F_j\Big|_{V+\Delta V}}{\Delta V} = r$$

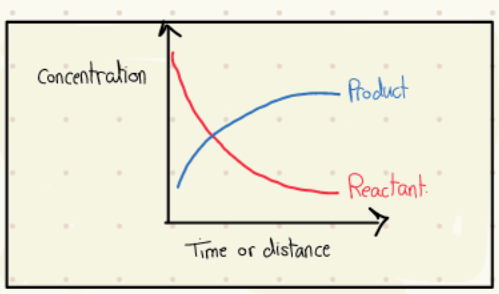
$$\frac{dF_j}{dV} = r$$

$$\int \frac{dF_j}{r} = \int dV$$

* Catcalyst [Hetrogenous rxn] Generation = $r'_A \Delta W = \frac{\text{mole A}}{\text{time [mass of catalyst]}} \times$ mass catalyst.

$$\frac{dF_A}{dW} = r'_A \rightarrow W = \int \frac{dF_A}{r'_A}$$

* For Batch and continuous systems:

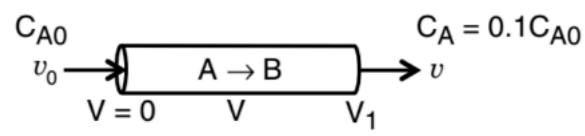


Example 2.5 Sizing of reactors

The bellow reaction is first order in A, $-r_A = k\,C_A$, and is carried out in a tubular reactor in which the volumetric flowrate, $v = 10\ \mathrm{L/min}$, is constant, i.e., $v_o = v$. What will be the volume of this reactor needed to reduce the initial concentration to 10%?

$k = 0.23\ \mathrm{min}^{-1}$

$$A \longrightarrow B$$



Solution

$$F_{j0}\Big|_{V} - F_j\Big|_{V+\Delta V} + G_j = \frac{dN_j}{dt}$$

G_j → constant volume

$$F_{j0}\Big|_{V} - F_j\Big|_{V+\Delta V} = r\,\Delta V$$

$$\frac{F_{j0}\Big|_{V} - F_j\Big|_{V+\Delta V}}{\Delta V} = r$$

$$\frac{dF_j}{dV} = r$$

$$\int dF_j = \int r\,dV$$

$$\int dF_j = \int -k\,C_A\,dV$$

$$\frac{\dot V}{-k}\int_{C_{A0}}^{C_A}\frac{dC_A}{C_A} = \int dV \Rightarrow F = \dot V C_A$$

$\dot V$ → constant

$$\frac{\dot V}{-k}\ln\frac{C_A}{C_{A0}} = V$$

$$C_A = 10\%\,C_{A0}$$

$$\frac{\dot V}{-k}\ln\frac{0.01\,C_{A0}}{C_{A0}} = V$$

$$\frac{-10}{0.23}\ln 0.01 = 200\,L$$

• Topic 3: Stoichiometry in Liquid and gas system:

• Liquid systems:

* $V_o = V$ if I don't have packing bed

* $C_A = \frac{F_A}{V}$ A: key reactant

$$X = \frac{F_{A0} - F_A}{F_{A0}}$$

$$F_A = -X F_{A0} + F_{A0}$$

$$F_A = F_{A0}(1 - X)$$

$$C_A = \frac{F_{A0}(1-X)}{V} = C_{A0}(1-X)$$

$$C_B = C_B^\circ - \frac{b}{a}X C_{A0}^\circ$$

$$C_B = C_B^\circ \times \frac{C_{A0}^\circ}{C_{A0}^\circ} - \frac{b}{a}X C_{A0}^\circ$$

$$\Theta_B = \frac{C_B^\circ}{C_{A0}^\circ}$$

$$C_B = \Theta_B C_{A0}^\circ - \frac{b}{a}X C_{A0}^\circ$$

$$C_B = C_{A0}^\circ\left[\Theta_B - \frac{b}{a}X\right]$$

$$\therefore \Theta_i = \frac{C_i^\circ}{C_{A0}^\circ} = \frac{F_i^\circ}{F_{A0}^\circ} = \frac{y_i^\circ}{y_{A0}^\circ}$$

* $aA + bB \rightarrow cC + dD$

$$F_A = F_{A0}^\circ - X F_{A0}^\circ \rightarrow F_A = F_{A0}^\circ(1-X)$$

$$F_B = F_B^\circ - \frac{b}{a}F_{A0}^\circ X \rightarrow F_B = F_{A0}^\circ\left(\Theta_B - \frac{b}{a}X\right)$$

$$F_C = F_C^\circ + \frac{c}{a}F_{A0}^\circ X \rightarrow F_C = F_{A0}^\circ\left(\Theta_C - \frac{c}{a}X\right)$$

$$F_D = F_d^\circ + \frac{d}{a}F_{A0}^\circ X \rightarrow F_D = F_{A0}^\circ\left(\Theta_D - \frac{d}{a}X\right)$$

$$F_I = F_{A0}\Theta_I$$ » inert

$$F_T = F_{T0} + \delta F_{A0} X$$

Example: Liquid Systems

Consider the liquid phase reaction bellow; what is the concentration of each species in term of conversion

$$NaOH + \frac{1}{3}(C_{17}H_{35}COO)_3C_3H_5 \longrightarrow C_{17}H_{35}COONa + \frac{1}{3}C_3H_5(OH)_3$$

$$A + \frac{1}{3}B \longrightarrow C + \frac{1}{3}D$$

$$C_A = C_{A0}^\circ - C_{A0}^\circ X \rightarrow C_A = C_{A0}^\circ(1-X)$$

$$C_B = C_B^\circ - \tfrac{1}{3}C_{A0}^\circ X \rightarrow C_B = C_{A0}^\circ\left(\Theta_B - \tfrac{1}{3}X\right)$$

$$C_C = C_C^\circ + C_{A0}^\circ X \rightarrow C_C = C_{A0}^\circ(\Theta_C + X)$$

$$C_D = C_D^\circ + \tfrac{1}{3}C_{A0}^\circ X \rightarrow C_D = C_{A0}^\circ\left(\Theta_D + \tfrac{1}{3}X\right)$$

$$C_I = C_{A0}^\circ\Theta_I$$

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- For Gas system:

$* \; V_i \neq V_o \xrightarrow{?}$ Compersable change with Pand T.

$\hookrightarrow V_i = \frac{F}{F^o} \frac{P_o}{P} \frac{T}{T_o} (V_o)$

$$\frac{P_o V_o = n_o R T_o}{P_i V_i = n_i R T_i}$$

$$\frac{P_o}{P_i} \frac{V_o}{V_i} = \frac{n_o}{n_i} \frac{T_o}{T_i}$$

$$\left(\frac{P_o}{P_i}\right)\left(\frac{n_i}{n_o}\right)\left(\frac{T_i}{T_o}\right) V_o = V_i \; \#$$

$$* \; C_A = \frac{F_A}{V} = F_A \left(\frac{P_i}{P_o}\right) \left(\frac{F_T^o}{F_{Ti}}\right)\left(\frac{T_o}{T_i}\right)\left(\frac{1}{V_o}\right)$$

$$C_A = C_T^o \frac{F_A}{F_T} \left(\frac{P_i}{P}\right)\left(\frac{T_o}{T_i}\right) \; \#$$

$$C_B = C_T^o \frac{F_B}{F_T} \frac{P_i}{P} \frac{T_o}{T_i} \; \#$$

$$* \; F_T = F_T^o + \delta X F_{A^o}$$

$$V_i = \frac{F}{F^o} \frac{P_o}{P} \frac{T}{T_o} (V_o)$$

$$V_i = \frac{F_T^o + \delta X F_{A^o}}{F_T^o} \frac{P_o}{P} \frac{T}{T_o} (V_o)$$

$$V_i = \left(1 + \delta X \frac{F_A^o}{F_T^o}\right) \frac{P_o}{P} \frac{T}{T_o} V_o$$

$$* \; \frac{F_A^o}{F_T^o} = y_A^o \qquad * \; \delta y_{A^o} = \varepsilon$$

$$V_i = (1 + \varepsilon X) \frac{P_o}{P} \frac{T}{T_o} (V_o) \; \#$$

$$* \; C_A = \frac{F_A}{V}$$

- $F_A = F_A^o (1 - X)$
- $V_i = (1 + \varepsilon X) \frac{P_o}{P} \frac{T}{T_o} (V_o)$

$$C_A = \frac{F_A^o (1 - X)}{(1 + \varepsilon X) \frac{P_o}{P} \frac{T}{T_o} (V_o)}$$

$$C_B = \frac{F_A^o \left(\Theta_B - X \frac{b}{a}\right)}{(1 + \varepsilon X) \frac{P_o}{P} \frac{T}{T_o} (V_o)}$$

if $A + B \rightarrow$ Product.

$r_A = -k C_A C_B$

$$r_A = -k \frac{F_A^o (1 - X)}{(1 + \varepsilon X) \frac{P_o}{P} \frac{T}{T_o} (V_o)} \cdot \frac{F_A^o \left(\Theta_B - X \frac{b}{a}\right)}{(1 + \varepsilon X) \frac{P_o}{P} \frac{T}{T_o} (V_o)} \qquad \frac{F_A^o}{V^o} = C_A$$

$$r_A = -k \, C_{A_o}^2 \left[\frac{(1 - X)}{1 + X\varepsilon \; \frac{P_o}{P} \frac{T}{T_o}} \cdot \frac{\left(\Theta_B - X \frac{b}{a}\right)}{(1 + X\varepsilon) \frac{P_o}{P} \frac{T}{T_o}} \right] \; \#$$

Example:

Calculate the equilibrium conversion (X_{ef}) for gas phase reaction in a flow reactor

Consider the following elementary reaction $2A \Leftrightarrow B$ (reversable)
Where K_C=20 dm³/mol and C_{A0}=0.2 mol/dm³.

Calculate the equilibrium conversion for both a batch reactor (X_{eb}) and a flow reactor (X_{ef}).

* mole Balance

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

* Rate law

at equilibrium: $r_B = r_f$

$$k_f C_A^2 = C_B k_B$$

$$\therefore \frac{k_f}{k_B} = k_{eq}$$

$$\therefore r_{net} = r_f + r_B$$

$$r_{net} = -k_f C_A^2 + k_B C_B$$

$$r_{net} = -k_f C_A^2 + \frac{k_f}{k_{eq}} C_B$$

$$\# \; r_{net} = k_f \left[C_A^2 + \frac{C_B}{K_{eq}} \right]$$

* stoichiometry

Species	Feed	change	Remaining
A	N_A°	$-XN_{A0}$	$N_A = N_{A0}(1-X)$
B	0	$+\frac{1}{2}XN_A^\circ$	$N_B = 0 + N_A^\circ X \frac{1}{2}$
	$N_T^\circ = N_A^\circ$		$N_T = N_A^\circ - N_A^\circ X \frac{1}{2}$

$$* \; C_A = \frac{N_A}{V} = \frac{N_A^\circ (1-X)}{V(1+\varepsilon X)}$$

$$C_A = C_A^\circ \frac{(1-X)}{(1+\varepsilon X)}$$

$$* \; C_B = \frac{N_A^\circ \frac{1}{2} X}{V(1+\varepsilon V)} = \frac{C_A^\circ X}{2(1+\varepsilon V)}$$

$$* \; r = -k_f \left[\left(C_A^\circ \frac{(1-X)}{(1+\varepsilon X)} \right)^2 - \frac{\frac{C_A^\circ X}{2(1+\varepsilon V)}}{20} \right]$$

$$r = -k_f \left[C_A^{\circ 2} \frac{(1-X)^2}{(1+\varepsilon X)^2} - \frac{C_A^\circ X}{40(1+\varepsilon V)} \right]$$

at equilibrum $r = 0$

$$\frac{C_A^\circ X}{K_c (1+\varepsilon V)} = C_A^{\circ 2} \frac{(1-X)^2}{(1+\varepsilon X)^2}$$

$$K_c C_A^\circ = \frac{X(1+\varepsilon X)}{(1-X)^2}$$

$$X = 0.7$$

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- Liquid Phase Undergraduate Laboratory Experiment

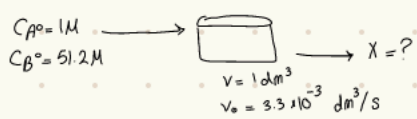
$$(CH_2CO)_2O + H_2O \rightarrow 2CH_3COOH$$
$$A + B \rightarrow 2C$$

Feed

Volumetric flow rate	v_0 = 0.0033 dm³/s
Acetic Anhydride	7.8% (1M)
Water	92.2% (51.2M)
Elementary with k'	$1.95 \times 10^{-4}\ dm^3/(mol.s)$

Case I	CSTR	V = 1 dm³
Case II	PFR	V = 0.311 dm³

① CSTR



* mol Balance $F_{j0} - F_j + G_j = \frac{dN_j}{dt}$

Constant volume (rV) — steady state volume flowrate in = out

$$F_{j0} - F_j + rV = 0 \longrightarrow V = \frac{F_j - F_{j0}}{r}$$

* Rate law ① elementary ② irreversable $r_A = -k_A C_A C_B$

* Stoichiomentary

	Fed	change	Remaining
A	F_{A0}	$-XF_{A0}$	$F_A = F_{A0}(1-X)$
B	F_{B0}	$-XF_{A0}$	$F_B = F_{B0} - F_{A0}X$
C	0	$+XF_{A0}\,2$	$F = 0 + 2F_{A0}X$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{V_0} = C_{A0}[1-X]$$

$$C_B = \frac{F_B}{V} = \frac{F_{B0} - F_{A0}(X)}{V_0} = C_{A0}(\Theta_B - X)$$

$$\Theta_B = \frac{51.2}{1} = 51.2 \rightarrow C_B = C_{A0}(51.2 - X)$$

G maximum value 1

$C_B \approx C_{A0}(51.2)$ Assumption

$C_B \approx C_{B0}$

* $r_A = -k_A C_A C_B$

$r_A = -k_A C_{A0}(1-X) C_{B0}$

* combine step rate as function of conversion

$$V = \frac{F_j - F_{j0}}{r} \qquad \frac{F_{A0}(1-X) - F_{A0}}{-K(1-X)C_{A0}}$$

$$V = \frac{F_j - F_{j0}}{-k_A C_{A0}(1-X) C_{B0}}$$

$$= \frac{V}{v} = \frac{C_{A0}(-X)}{-k C_{A0}(1-X) C_{B0}}$$

$$\frac{1}{3.3\times10^{-3}} = \frac{1(-X)}{-1.95\times10^{-4}(1)(1-X)\,51.2}$$

$X = 0.75$

② PFR

* mole Balance $\frac{dF_j}{dV} = r$

$$\int \frac{dF_j}{r} = \int dV$$

* Rate law $r_A = -k_A C_A C_B$

* Stoichiomentary

	Fed	change	Remaining
A	F_{A0}	$-XF_{A0}$	$F_A = F_{A0}(1-X)$
B	F_{B0}	$-XF_{A0}$	$F_B = F_{B0} - F_{A0}X$
C	0	$+XF_{A0}\,2$	$F = 0 + 2F_{A0}X$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{V_0} = C_{A0}[1-X]$$

$$C_B = \frac{F_B}{V} = \frac{F_{B0} - F_{A0}(X)}{V_0} = C_{A0}(\Theta_B - X)$$

$$\Theta_B = \frac{51.2}{1} = 51.2 \rightarrow C_B = C_{A0}(51.2 - X)$$

G maximum value 1

$C_B \approx C_{A0}(51.2)$ Assumption

$C_B \approx C_{B0}$

* $r_A = -k_A C_A C_B$

$r_A = -k_A C_{A0}(1-X) C_{B0}$

* combine step

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

$$\frac{dX}{dV} = \frac{k_A C_{A0} C_{B0}(1-X)}{F_{A0}}$$

$$\frac{dX}{k_A C_{A0} C_{B0}(1-X)} = \frac{dV}{C_{A0}}$$

$$\frac{1}{k_A C_{A0} C_{B0}} \ln 1-X = -\frac{0.311}{1}$$

$$\frac{1}{0.0033(1.95\times10^{-4})(1)(51.2)} \ln 1-X = -0.311$$

$X = 0.64$

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Example 2

- Gas Phase: PFR and Batch Calculation

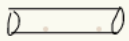
$$2NOCl \rightarrow 2NO + Cl_2$$
$$2A \rightarrow 2B + C$$

Pure NOCl fed with $C_{NOCl,0}$ = 0.2 mol/dm³ follows an elementary rate law with k = 0.29 dm³/(mol.s)

Case I PFR with v_0 = 10 dm³/s
Find space time, τ with X = 0.9
Find reactor volume, V for X = 0.9

Case II Batch constant volume
Find the time, t, necessary to achieve 90% conversion. Compare τ and t.

① Case 1:



$C_{A0} = 0.2$
$\dot{v} = 10$
$X = 0.9$
$k = 0.29$

* mole balance:

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

* Rate law → Irreversable

$$r_A = -k C_A^2$$

* Stoichiomentary $A \longrightarrow B + \frac{1}{2}C$

A	F_{A0}	$-F_{A0} X$	$F_A = F_{A0}(1-X)$
B	0	$+ F_{A0} X$	$F_B = F_{A0}(\Theta_B + X)$
C	0	$+ F_{A0} \frac{1}{2} X$	$F_C = F_{A0}(\Theta_C + \frac{1}{2}X)$

$$C_A = \frac{F_A}{V} = \frac{F_{A0}(1-X)}{V(1+\varepsilon X)}$$ isobaric, isothermal

$$C_A = \frac{F_A}{V} = \frac{F_{A0}(1-X)}{V(1+\varepsilon X)}$$

$$C_A = \frac{C_{A0}(1-X)}{1+\varepsilon X} \qquad \varepsilon = y_{A0}\,\delta$$

$$\delta = \frac{1}{2} + 1 - 1 = \frac{1}{2}$$

$$r_A = -k C_A^2 \rightarrow -k\left[\frac{C_{A0}(1-X)}{1+\varepsilon X}\right]^2$$

* Combine step:

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

$$\frac{dX}{dV} = \frac{k\left[\frac{C_{A0}(1-X)}{1+\varepsilon X}\right]^2}{F_{A0}}$$

$$\frac{dX}{dV} = \frac{k C_{A0}^2 (1-X)^2}{F_{A0}(1+\varepsilon X)^2}$$

$$\frac{dX}{dV} = \frac{k C_{A0}^2 (1-X)^2}{C_{A0}\dot{v}(1+\varepsilon X)^2}$$

$$\frac{dX(1+\frac{1}{2}X)^2}{(1-X)} = \frac{k C_{A0}^{\cancel{2}}\, dV}{C_{A0}\dot{v}} = \frac{k V C_{A0}}{\dot{v}} = \frac{k \tau C_{A0}}{} = \int_0^X \frac{(1+\varepsilon X)^2}{(1-X)^2}$$

$k \tau C_{A0} = 17.0211$

$\tau = 293.46$ sec

$V = 293.46 \times 10 = 2934.6$ L

Case 2:

$X = 0.9$

$C_{A0} = 0.2$
$\dot{v} = 10$
$X = 0.9$
$k = 0.29$

* mole Balance

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

* Stoichiomentary

A	F_{A0}	$-F_{A0} X$	$F_A = F_{A0}(1-X)$
B	0	$+ F_{A0} X$	$F_B = F_{A0}(\Theta_B + X)$
C	0	$+ F_{A0} \frac{1}{2} X$	$F_C = F_{A0}(\Theta_C + \frac{1}{2}X)$

$$C_A = \frac{F_A}{V} = \frac{F_{A0}(1-X)}{V(1+\varepsilon X)}$$ isobaric, isothermal, constant volume

$$C_A = \frac{F_A}{V} = \frac{F_{A0}(1-X)}{V}$$

$$C_A = C_{A0}(1-X)$$

$$r_A = -k C_A^2 \rightarrow -k\left[C_{A0}(1-X)\right]^2$$

* Combine step:

$$\frac{dX}{dt} = \frac{-rV}{N_{A0}} = \frac{-r}{C_{A0}}$$

$$\frac{dX}{dt} = \frac{k\left[C_{A0}(1-X)\right]^2}{C_{A0}}$$

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

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

$$9 = k C_{A0}\, t$$

$$t = 155 \text{ s}$$

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* Topic 4

Example

The formation of ammonia is to be carried out isothermally at 227°C in packed bed reactor and with a pressure of 16.4 atm. This is an isobaric (constant pressure) flow system with equimolar feeds of N_2 & H_2. Assume the gas mixture behaves like an ideal gas.

$$H_2 + \tfrac{1}{3}N_2 \rightarrow \tfrac{2}{3}NH_3$$

What are the concentrations of H_2, N_2, and NH_3 when H_2 is 60% consumed?

$y = 0.5$

$$A + \tfrac{1}{3}B \rightarrow \tfrac{2}{3}C$$

* mole Balance

$$\int \frac{dF_i}{r} = \int dV$$

* rate law $\quad r_A = -k C_A C_B^{1/3}$

* Stoichiomentary

A	F_A°	$-X F_A^\circ$	$F_A = F_A^\circ(1-X)$
B	F_A°	$-X F_A^\circ 1/3$	$F_B = F_A^\circ(1-X/3)$
C	0	$+X F_A^\circ 2/3$	$F_C = X F_A^\circ 2/3$

$$C_A = \frac{F_A^\circ(1-X)}{V} = \frac{C_A^\circ(1-X)}{(1+\varepsilon X)} \qquad C_C = \frac{C_A^\circ X\, 2/3}{1+\varepsilon X}$$

$$C_B = \frac{F_A^\circ(1-X/3)}{V} = \frac{C_A^\circ(1-X/3)}{(1+\varepsilon X)}$$

$C_A^\circ \Rightarrow ?$

$$PV = N_T^\circ RT$$

$$\frac{16.4}{500 \times 0.082} = C_T^\circ$$

$C_T^\circ = 0.4 \quad C_A^\circ = 0.2$

$$\varepsilon = \delta y_A$$

$$0.5[2/3 - 1/3 - 1] = -1/3$$

$$C_A = \frac{C_A^\circ(1-X)}{(1+\varepsilon X)} = \frac{0.2[1-0.6)}{(1-1/3(0.6))} = 0.1$$

$$C_B = \frac{C_A^\circ(1-X/3)}{(1+\varepsilon X)} = 0.2\,\frac{(1-(0.6)1/3)}{1-1/3(0.6)} = 0.2$$

$$C_C = \frac{C_A^\circ X\, 2/3}{1+\varepsilon X} = \frac{0.2 \times 0.6 \times 2/3}{1-1/3(0.6)} = 0.1$$

* Damköhler Number : "Da"

$$Da = \frac{\text{Reaction rate}}{\text{Diffusion rate}} = \frac{\text{Diffusion Time}}{\text{Reation Time}} = \frac{-r_{A0} V}{F_{A0}} = k C_0^{n-1} \tau$$

n: reaction order

$1° \rightarrow Da = k C_0^{0} \tau$

$2° \rightarrow Da = k C_0^{1} \tau$

$Da \uparrow \rightarrow X \uparrow \rightarrow$ yield $\downarrow$ ☹

$Da \downarrow \rightarrow X \downarrow$ ☺

Example

Consider the following second order reaction takes place in a tubular reactor at isothermal condition. What will be the volume of this reactor if (a) is a liquid phase (b) gas phase reaction is considered.

$$2A \rightarrow B$$

- liquid system :-

* mole Balance

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

* Rate law :

$$r = -k A^2$$

* Stoichiomentary

A	F_{A0}	$-X F_{A0}$	$F_A = F_A^\circ (1-X)$
B	0	$+X F_{A0} \frac{1}{2}$	$F_B = F_A^\circ \frac{1}{2} X$

$$C_A = \frac{F_A^\circ (1-X)}{V}$$

$$C_A = C_A^\circ (1-X)$$

$$r = -k C_A^{\circ 2} (1-X)^2$$

$$V = F_{A0} \int_0^X \frac{dX}{-r_A} \rightarrow V = F_{A0} \int \frac{dX}{k C_A^{\circ 2} (1-X)^2}$$

$$V = F_A^\circ \frac{1}{k C_A^{\circ 2}} \left[\frac{X}{1-X} \right]$$

$$V = \underline{C_{A0} v} \frac{1}{k C_A^{\circ 2}} \left[\frac{X}{1-X} \right]$$

$$X = \frac{\tau k C_A^\circ}{1 + \tau k C_A^\circ}$$

$\Rightarrow X = 1 \hookrightarrow$ maximum ?

$\hookrightarrow \frac{\infty}{1+\infty} = \frac{\infty}{\infty} = 1$

$\tau k C_A = \infty \quad Da = \infty$

① $\tau = \frac{V}{V_0} = \infty \rightarrow V_0 \downarrow\downarrow \rightarrow$ yield $\downarrow$ ☹

$\rightarrow V = \infty \rightarrow \uparrow$ cost Ⓐ

② $C_{A0} = \infty$

- Gas system

* mole Balance

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

* Rate law :

$$r = -k A^2$$

* Stoichiomentary isothermal, isobaric

A	F_{A0}	$-X F_{A0}$	$F_A = F_A^\circ (1-X)$
B	0	$+X F_{A0} \frac{1}{2}$	$F_B = F_A^\circ \frac{1}{2} X$

$$C_A = \frac{F_A}{V} = \frac{F_A^\circ (1-X)}{V_0 (1+\varepsilon X)} = C_A^\circ \frac{(1-X)}{1+\varepsilon X}$$

$$r = -k \frac{C_A^{\circ 2} (1-X)^2}{(1+\varepsilon X)^2}$$

$$V = F_{A0} \frac{(1+\varepsilon X)^2}{-k C_{A0}^2 (1-X)^2} dx$$

$$V = \frac{V_0}{k C_A^\circ} \left[2\varepsilon(1+\varepsilon) \ln[1-X] + \varepsilon^2 X + \frac{(1+\varepsilon)^2 X}{1-X} \right]$$

if $X = 1 \rightarrow$ $\frac{V_0}{k C_A^\circ} \left[2\varepsilon(1+\varepsilon) \ln[1-X] + \varepsilon^2 X + \frac{(1+\varepsilon)^2 X}{\text{zero}} \right]$ ∞

$\hookrightarrow \frac{V_0}{k C_A^\circ} [\infty] = \infty$

$\hookrightarrow V = \infty$ Ⓐ

لازم اقلل من هاد الـ Term عشان يصير عندي Balance

* $V_0 \downarrow\downarrow$
* $C_A^\circ \uparrow\uparrow$

or * $(1+\varepsilon) \downarrow$? $\rightarrow \varepsilon = y_A \delta$

* $y_A \downarrow \rightarrow \frac{C_A}{C_A + \text{other}} \uparrow$

* بقدر $X \uparrow$ بدون ما $\downarrow$ yield بطريق اكثر لما يكون الـ rxn gasphase

The **reversible gas-phase decomposition of nitrogen tetroxide,** N_2O_4**, to nitrogen dioxide** NO_2 is to be carried out **isothermally** at 340 **K** and a pressure of 202.6 kPa **(2 atm)** [This pressure is for the **inlet feed**]. The **concentration equilibrium constant,** $K_c = 0.1$ mol/L.

$$N_2O_4 \rightleftharpoons 2NO_2$$

2] Cal the eq concentration of N_2O_4 in a constant vol Batch:

$A \rightarrow 2B$

A	C_{A0}	XC_{A0}	$C_A = C_{A0}(1-X)$
B	0	$2XC_{A0}$	$C_B = \cancel{C_{B0}} + 2XC_{A0}$ (zero)

$* \; PV = n_T RT$

$202.6 \; V = n_T \, 340 \, (8.314)$

$C_T^0 = 0.071 \; \frac{mol}{m^3} = C_{A0}$

$$K_c = \frac{C_{Beq}^2}{C_{Aeq}} = \frac{(2X_{eq}\overset{0.071}{C_{A0}})^2}{\underset{0.071}{C_{A0}}(1-X)_{eq}} = 0.1$$

$X_{eq} \Rightarrow 0.44$

$C_{Beq} = 2[0.44][0.071] = 0.062 \; \frac{mol}{m^3}$

B] Calculat C_{Beq} in flow reactor:

A	F_{A0}	$F_A = F_{A0}(1-X)$
B	0	$F_B = 2XF_{A0}$

$C_{A0} = \frac{F_{A0}}{v_0}$

$C_A = \frac{F_{A0}}{v_0(1+\varepsilon X)} = C_{A0}\frac{(1-X)}{(1+\varepsilon X)}$

$C_B = \frac{2C_{A0}X}{1+\varepsilon X}$

$\varepsilon = y_{A0}\delta = 1(1) = 1$

$$K_c = \frac{\left[\frac{2C_{A0}X}{1+\varepsilon X}\right]^2}{C_{A0}\frac{(1-X)}{(1+\varepsilon X)}} = \frac{\left[\frac{2(0.071)X}{1+X}\right]^2}{(0.071)\frac{(1-X)}{(1+X)}} = 0.1$$

$X_{eq} = 0.51$

$C_{Beq} = \frac{2 \times 0.071 \times 0.51}{1+0.51} = 0.047$

C] what will be the rate law for Batch (constant vol) and (continous reator)

$r_A = r_f + r_B$

$-k_f(C_A) + k_B C_B^2$

$-k_f\left[C_A - \frac{1}{K_c}C_B^2\right]$

for Batch

$-k_f\left[C_{A0}(1-X) - \frac{4C_{A0}^2X^2}{K_c}\right]$

for continous

$-k_f\left[\frac{C_A(1-X)}{1+\varepsilon X} - \frac{4C_{A0}^2X^2}{K_c(1+\varepsilon X)}\right]$

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D] The volume of CSTR achieve 80% of eq conversion

if $F_A = 3$ mol/min $X_e = 0.5$

* $X = 0.8 \times 0.5 = \boxed{0.4}$

$$V = \frac{F_A \; X}{r_A} =$$

for continous

$$-k_f \left[\frac{C_A \cdot (1-X)}{1+\epsilon X} - \frac{4 \, C_{A0}^2 \, X^2}{k_c \, (1+\epsilon X)} \right]$$

$$-0.5 \left[\frac{0.072 \, (1-0.4)}{1+0.4} - \frac{4 \times 0.072^2 \times 0.4^2}{0.1 \, (1+0.4)} \right]$$

$$r_A = -6.9 \times 10^{-3}$$

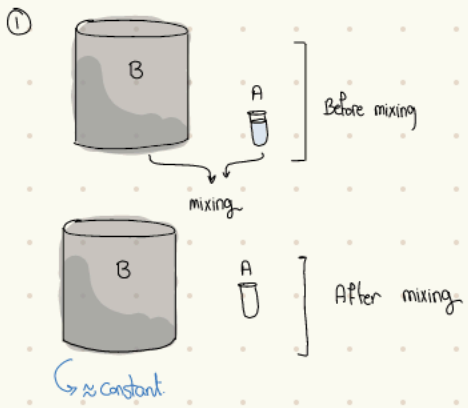
$$V = \frac{3 \times 0.4}{6.9 \times 10^{-3}} = \boxed{171.4 \; L}$$

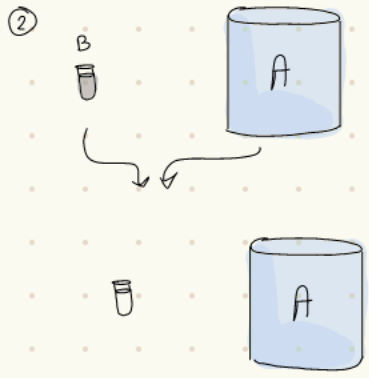
Topic 5:

Determination rate order and constant

- Method of Excess
- Method of half lives
- Integral Method
- Differential Method

* method of excess





$r = -k C_A^a \underbrace{C_B^b}_{\text{constant}}$

$r = {}'k C_A^a$

↳ rate depent only on A

$r = -k \underbrace{C_A^a}_{\text{constant}} C_B^b$

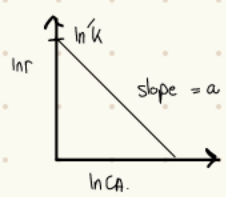
$r = -{}'k C_B^b$

↳ rate depent only on B

* note $C_A + C_B \rightarrow$ initial consentrations

$* \; r = {}'k C_A^a$

$\ln r = \ln {}'k + a \ln C_A$



Example

Given the following data for variation of concentration of species with the rate of their reaction. Determine the order of reaction using the initial rate method.

A+ B+ 2C → D + 2E

Experiment	[A] mol dm^{-3}	[B] mol dm^{-3}	[C] mol dm^{-3}	Rate mol dm^{-3} s^{-1}
1	0.1	0.5	0.25	0.1
2	0.2	0.5	0.25	0.2
3	0.1	1.0	0.25	0.4
4	0.1	0.5	0.5	0.1

- $r = -k C_A^a C_B^b C_C^c$
- from rxn 1-2

$r_1 \Rightarrow (0.1)^a \cancel{(0.5)^b} \cancel{(0.25)^c} \cancel{k} = 0.1$

$r_2 \Rightarrow (0.2)^a \cancel{(0.5)^b} \cancel{(0.25)^c} \cancel{k} = 0.2$

$\left[\frac{0.1}{0.2}\right]^a = \frac{0.1}{0.2}$ $\boxed{\alpha = 1}$

- from rxn 1-4

$r_1 \Rightarrow \cancel{(0.1)^a} \cancel{(0.5)^b} (0.25)^c \cancel{k} = 0.1$

$r_4 \Rightarrow \cancel{(0.1)^a} \cancel{(0.5)^b} (0.5)^c \cancel{k} = 0.1$

$\left[\frac{0.25}{0.5}\right]^c = 1$ $\boxed{c = 0}$

- from rxn 1,3

$r_1 \Rightarrow \cancel{(0.1)^a} (0.5)^b \cancel{(0.25)^c} \cancel{k} = 0.1$

$r_3 \Rightarrow \cancel{(0.1)^a} (0.1)^b \cancel{(0.25)^c} \cancel{k} = 0.4$

$\left[\frac{0.5}{1.0}\right]^b = \left[\frac{.1}{.4}\right]$ $\boxed{b = 2}$

$r = -k C_A C_B^2$

The rxn → 3rd order.

MADAR

* method of half-lifes

$t_{1/2}$ → time required for the concentration of reactant to decrease to half of its initial value.

zero order

$r_A = -kC_A^0$

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

$dC_A = -k\,dt$

$C_{A2} - C_{A1} = -kt$

$C_{A2} = \frac{1}{2}C_{A1}$ at $t_{1/2}$

$\frac{1}{2}C_{A1} - C_{A1} = -k\,t_{1/2}$

$\frac{\frac{1}{2}C_{A1}}{k} = t_{1/2}$

* ↑↑

first order

$r_A = -kC_A^1$

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

$\frac{dC_A}{C_A} = -k\,dt$

$\ln C_{A2} - \ln C_{A1} = -kt$

$C_{A2} = \frac{1}{2}C_{A1}$ at $t_{1/2}$

$\ln \frac{0.5C_{A1}}{C_{A1}} = -k\,t_{1/2}$

$\frac{0.693}{k} = t_{1/2}$

* $t_{1/2}$ don't depent on C_A^0

sec order

$r_A = -kC_A^2$

$\frac{dC_A}{C_A^2} = -k\,dt$

$C_{A1}^{-1} - C_{A2}^{-1} = -k\,t$

$C_{A2} = \frac{1}{2}C_{A1}$ at $t_{1/2}$

$\frac{1}{C_{A1}} - \frac{2}{C_{A1}} = -k\,t_{1/2}$

$\frac{1}{kC_{A1}} = t_{1/2}$

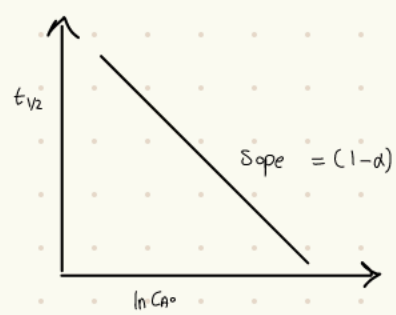
* ↑↓

We then use the definition of half-life, $t = t_{1/2}$ when $C_A = 1/2C_{A0}$

$$t_{1/2} = \frac{2^{\alpha-1} - 1}{k\,(\alpha - 1)} \frac{1}{C_{A0}^{\alpha-1}}$$

sec order * $t_{1/2} = \frac{2^1 - 1}{k} \frac{1}{C_A^0} = \frac{1}{C_A^0 k}$ #

zero order * $t_{1/2} = \frac{2^{-1} - 1}{k(-1)} \frac{1}{C_A^{0-1}} = \frac{1}{2k} C_A^0$ #



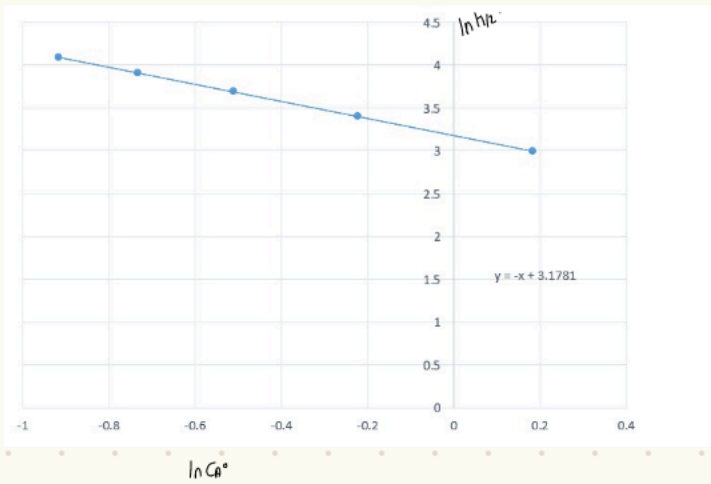
$$\ln t_{1/2} = \ln \frac{2^{\alpha-1} - 1}{k\,(\alpha - 1)} + (1 - \alpha) \ln C_{A0}$$

Example

Based on the following concentration data as a function of time, determine the behavior of the half-life as the reaction progresses. Use this information to determine if the following reaction is 0 order, 1 order, or 2 order in A. Also, use the data to estimate the rate constant for the reaction.

time (s)	[A] (M)
0	1.200
10	0.800
20	0.600 $= C_{A0}/2$
30	0.480
40	0.400
50	0.343
60	0.300
70	0.267
80	0.240
90	0.218
100	0.200

$t_{1/2}$	20-0	30: 40-10	40: 60-20	50: 80-30	60
C_{A0}	1.2	0.8	0.6	0.48	0.4
$\ln C_{A0}$	0.18	-0.22	-0.5	-0.73	-0.9
$\ln t_{1/2}$	2.9	3.4	3.6	3.9	4.1



$y = -X + 3.1781$

slope $= -1$

$-1 = 1 - \alpha$

$\alpha = 2$ sec order.

$* \ \frac{1}{k C_{A0}} = t_{1/2}$

$\frac{1}{0.8 \ (30)} = 0.0417$

$\frac{M^{1-2}}{s} \rightarrow \boxed{\frac{M^{1-n}}{s}}$ #

* Integral method

* بنتوقع ال order
وبعمل Data ال fit
ازا طلع liner ✓

zero order

$r_A = -kC_A^0$

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

$dC_A = -k\,dt$

$C_{A_2} - C_{A1} = -kt$

$C_A = C_A^0 - kt$

first order

$r_A = -kC_A^1$

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

$\frac{dC_A}{C_A} = -k\,dt$

$\ln C_{A_2} - \ln C_{A1} = -kt$

$\ln \frac{C_A}{C_A^0} = -kt$

$\ln \frac{C_A^0}{C_A} = kt$

sec order

$r_A = -kC_A^2$

$\frac{dC_A}{C_A^2} = -k\,dt$

$C_{A_1}^{-1} - C_{A_2}^{-1} = -k\,t$

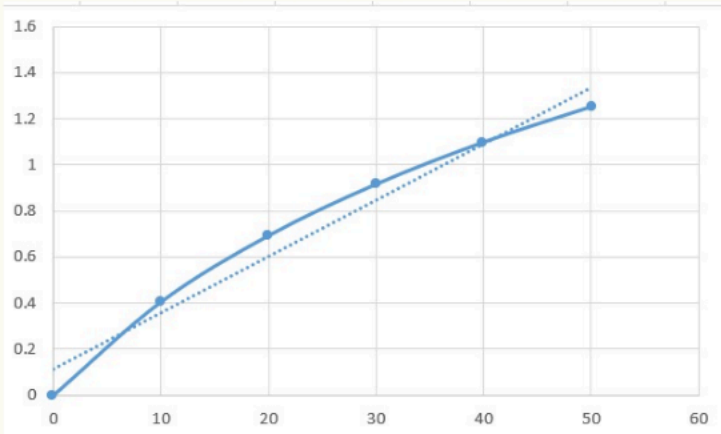
$\frac{1}{C_A} = kt + \frac{1}{C_{A0}}$

time (s)	[A] (M)
0	1.200
10	0.800
20	0.600
30	0.480
40	0.400
50	0.343
60	0.300
70	0.267
80	0.240
90	0.218
100	0.200

* Assume first order: »

$\ln \frac{C_A^0}{C_A} = kt$

time	[A]	ln [A1]/[A]
0	1.2	0
10	0.8	0.405465
20	0.6	0.693147
30	0.48	0.916291
40	0.4	1.098612
50	0.343	1.252346



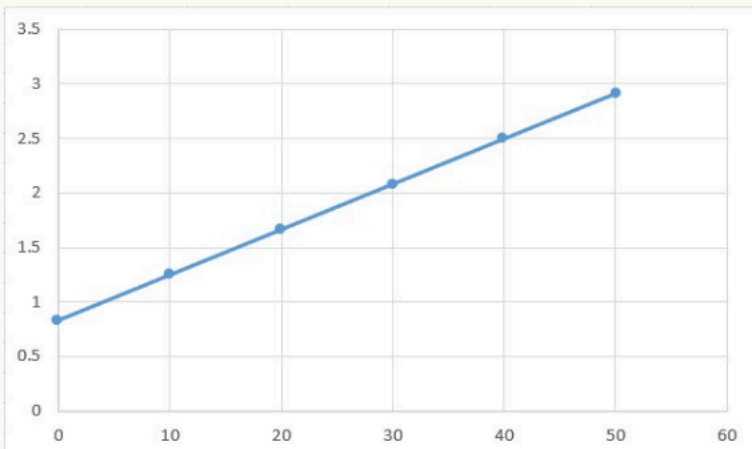
not liner X

The order ≠ 1 ✗

* Assum the order = 2

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

time	[A]	1/[A]
0	1.2	0.833333
10	0.8	1.25
20	0.6	1.666667
30	0.48	2.083333
40	0.4	2.5
50	0.343	2.915452



liner ✓

The order = 2

* zero → not liner
first → ~
sec → ~
Thirsd → ~
⋮ ⋮

} The rxn not elementary

* Differential method

① $-\frac{dC_A}{dt} = k_A C_A^{\alpha}$

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

↳ the slope.

Example

Liquid phase reaction between trimethylamine(A) and n-propyl bromide (B) was studied by Winkler & Hinshelwood. The results at 139.4 C are shown below. Initial solutions of A and B in benzene is 0.1 molar each, were mixed and placed in constant temperature bath. After certain times, they were cooled to stop the reaction. Determine the first order and second order specific rates, k1 and k2, assuming the reaction is irreversible. Use integration and differential methods.

A + B → Pr - Iuel.

Run	t, min	x (%)
1	13	11.2
2	34	25.7
3	59	36.7
4	120	55.2

integral method

* assume first order.

first order

$r_A = -kC_A^1$

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

$\frac{dC_A}{C_A} = -k\,dt$

$\ln C_{A_2} - \ln C_{A_1} = -kt$

$\ln \frac{C_A}{C_A^\circ} = -kt$

$\ln \frac{C_A^\circ}{C_A} = kt$

$X = 11.2 = \frac{0.1 - C_A}{0.1} \times 100$ at time 13 min.

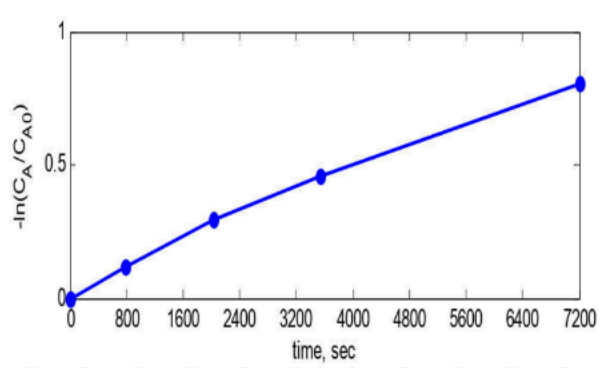
$C_A = 0.0888$

$\Rightarrow \ln \frac{0.1}{0.888} = k(13)$

$k = 9.137 \times 10^{-3} \frac{M^{n-1}}{min} = \boxed{1.52 \times 10^{-4}\ s^{-1}}$

If you repeat for four of the runs:

Run	t, sec	$k_1 \times 10^{-4}$ (s^{-1})
1	780	1.54
2	2040	1.46
3	3540	1.30
4	7200	1.12



* sec order: $2A \rightarrow$ Product.

$$r_A = -kC_A^2$$

$$\frac{dC_A}{C_A^2} = -k\,dt$$

$$C_{A_1}^{-1} - C_{A_2}^{-1} = -k\,t$$

$$\frac{1}{C_A} = kt + \frac{1}{C_{A_0}}$$

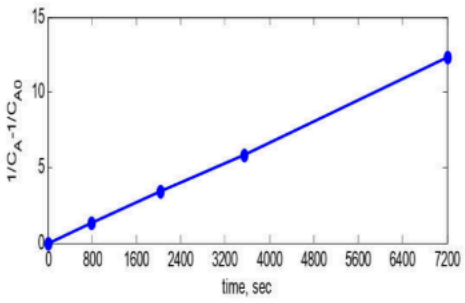
$$X = 11.2 = \frac{0.1 - C_A}{0.1} \times 100$$ at time 13 min.

$$C_A = 0.0888$$

$$\frac{1}{0.0888} = k(13) + \frac{1}{0.1} = 1.62 \times 10^{-3} \frac{L}{gmol \cdot \boxed{s}}$$

If you repeat for four of the runs:

Run	t, sec	$k_1 \times 10^{-4}$ (s^{-1})	$k_2 \times 10^{-3}$ (L/mol s)
1	780	1.54	1.63
2	2040	1.46	1.70
3	3540	1.30	1.64
4	7200	1.12	1.71



So, it is SECOND ORDER

Example 5–2 Integral Method of CRE Data Analysis

Use the integral method to confirm that the reaction is second order wrt triphenyl methyl chloride as described in Example 5-1 and to calculate the specific reaction rate k'

$$\text{Trityl (A)} + \text{Methanol (B)} \rightarrow \text{Products}$$

Example 5–1 Determining the Rate Law

The reaction of triphenyl methyl chloride (trityl) (A) and methanol (B)

$$(C_6H_5)_3CCl + CH_3OH \rightarrow (C_6H_5)_3C\overset{\overset{\displaystyle 0}{\|}}{C}H_3 + HCl$$

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

was carried out in a solution of benzene and pyridine at 25°C. Pyridine reacts with HCl that then precipitates as pyridine hydrochloride thereby making the reaction irreversible.

The concentration-time data in Table E5-1.1 was obtained in a batch reactor

TABLE E5-1.1. RAW DATA

Time (min)	0	50	100	150	200	250	300
Concentration of A (mol/dm³) × 10³	50	38	30.6	25.6	22.2	19.5	17.4

(At $t = 0$, $C_A = 0.05\ M$)

The initial concentration of methanol was 0.5 mol/dm³.

* $A + B \rightarrow$ Product

* Rate law $= C_A^{\alpha} C_B^{\beta}(-k) = r_A$.

Bc $C_A \ll C_B$ Assume $C_{B0} \approx C_B$ constant.

$\hookrightarrow r_A = -k' C_A^{\alpha}$

sec order

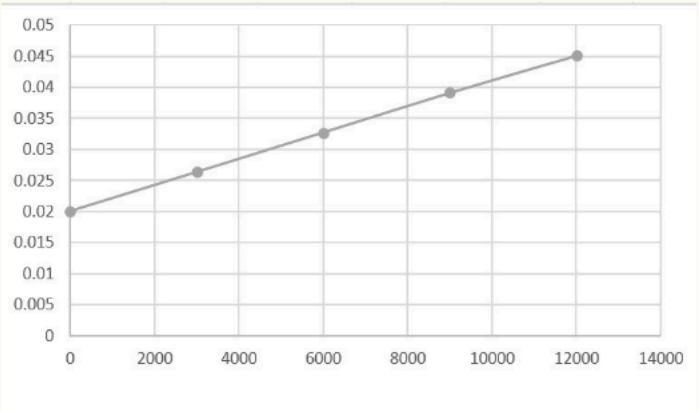
$r_A = -kC_A^2$

$\frac{dC_A}{C_A^2} = -k\,dt$

$C_{A_1}^{-1} - C_{A_2}^{-1} = -k\,t$

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

ca	time (s)	1/ca
50	0	0.02
38	3000	0.026316
30.6	6000	0.03268
25.6	9000	0.039063
22.2	12000	0.045045



Liner ✓ The rxn → 2nd order.

or

	ca	time (s)	1/ca	k
0	50	0	0.02	#DIV/0!
50	38	3000	0.026316	0.000126
100	30.6	6000	0.03268	0.000127
150	25.6	9000	0.039063	0.000127
200	22.2	12000	0.045045	0.000125

k values are equal ≈ ✓
The rxn is sec order ✓

$k' = \frac{k}{C_B}$ $\quad 0.0013 \times 0.05 \times 10^3$

$= 0.065\ \frac{1}{sM}$

$$* \quad r_A = -k\, C_A\, C_B$$

$$C_A = C_A^\circ (1-X)$$

$$C_B = C_A^\circ (\Theta_B - X)$$

$$r_A = -k\, C_A (1-X)\, C_A^\circ (\Theta_B - X)$$

$$\frac{dC_A}{dt} = \cancel{C_A^\circ} \frac{dX}{dt} = -\, k\, \cancel{C_A^\circ} (1-X)\, C_A^\circ (\Theta_B - X)$$

$$\frac{dX}{dt} = -k (1-X)\, C_A^\circ (\Theta_B - X) \quad \#$$

Topic 6: comparison between reactors

Batch reactor:

$$\cancel{F_{A0}} - \cancel{F_A} + rV = \frac{dN_A}{dt}$$

$$rV = \frac{dN_A}{dt}$$

$$N_A = (1-X)N_{A0}$$

$$rV\,dt = d(1-X)N_{A0}$$

$$\int dt = \int N_{A0}\frac{dX}{rV}$$

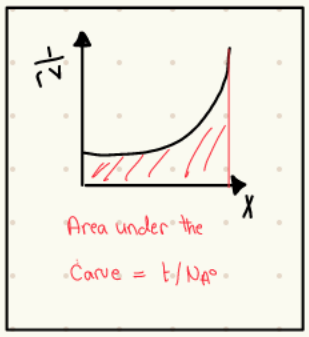
$$t = C_{A0}\int_0^{X_0}\frac{dX}{r}$$

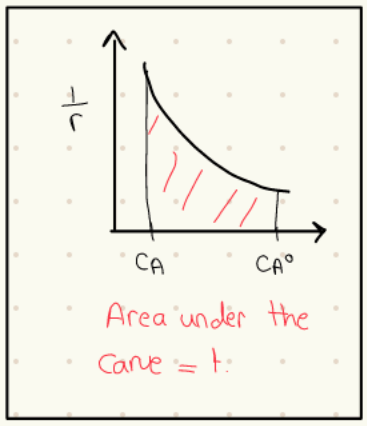
$$X = \frac{C_{A0}-C_A}{C_{A0}}$$

$$X = 1 - \frac{C_A}{C_{A0}}$$

$$dX = \cancel{dX}_{0} - \frac{dC_A}{C_{A0}}$$

$$t = -\int\frac{dC_A}{r}$$





Continuous Reactor CSTR:-

$$F_{A0} - F_A + rV = \cancel{\frac{dN_A}{dt}}^{\,0}$$

$$F_{A0} - (F_{A0} - F_{A0}X) = rV$$

$$F_{A0}X = Vr$$

$$\frac{X}{r} = \frac{V}{F_{A0}}$$

Plug flow Reactor PFR

$$F_{A0} - F_A + rV = \cancel{\frac{dN_A}{dt}}$$

$$F_{j0}\big|_V - F_j\big|_{V+\Delta V} = r\,\Delta V$$

$$\frac{F_{j0}\big|_V - F_j\big|_{V+\Delta V}}{\Delta V} = r$$

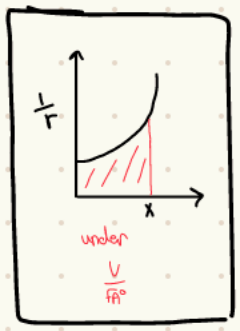
$$\frac{dF_j}{dV} = r$$

$$\int\frac{dF_j}{r} = \int dV$$

$$\frac{F_{A0}(1-X)}{r} = V$$

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

$$\frac{dX}{r} = \frac{V}{F_{A0}}$$



* Space - Time: $\tau = \frac{V}{V_0}$ [time]

Tubular < cstR < Batch

* Space - velocity: $S = \frac{\dot{V}}{V} = \frac{1}{\tau}$ [Time^{-1}]

* LHSV $= \frac{V_0|_{liq}}{V}$

* GHSV $= \frac{V_0|_{STP}}{V}$

* Reactors in series

1- CSTR

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

$V = V_1 + V_2$

$V = \frac{F_{A0} X_1}{r_{A1}} + \frac{F_{A0}(X_2 - X_1)}{r_{A2}}$

$r_{A1} \neq r_{A2}$

Example 6.1 CSTRs in series

For the two CSTRs in series, 40% conversion is achieved in the first reactor. What is the volume of each of the two reactors necessary to achieve 80% overall conversion of the entering species A?

X	0.0	0.1	0.2	0.4	0.6	0.7	0.8
$(F_{A0}/-r_A)(m^3)$	0.89	1.09	1.33	2.05	3.54	5.06	8.0

Solution

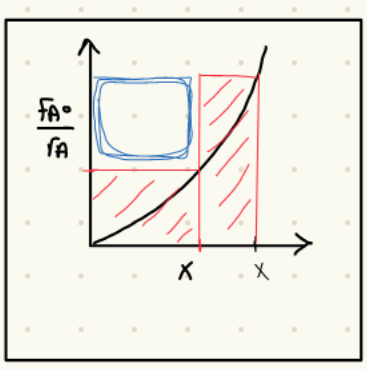
$X_1 = 0.4 \qquad X_2 = 0.8$

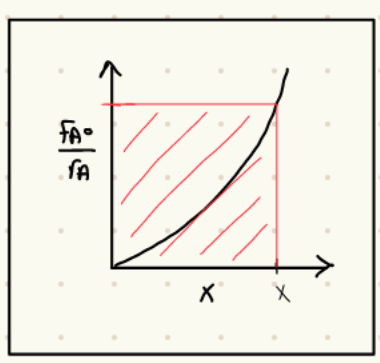
$V = \frac{F_{A0} X_1}{r_{A1}} + \frac{F_{A0}(X_2 - X_1)}{r_{A2}}$

$V = 2.05 \times 0.4 + 8 \times (0.8 - 0.4) = 4.02\ m^3$

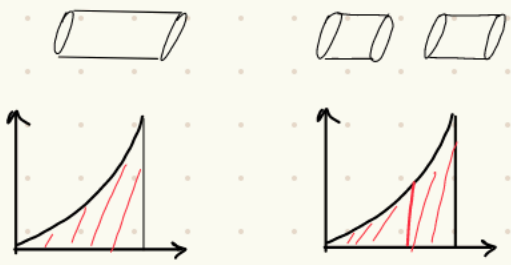
* if I have one reactor

$V = 0.8 \times 8 = 6.4\ m^3$





- PFR

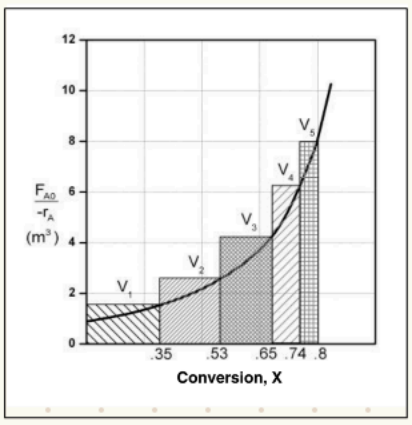


V = V

* اهم Reactor هو أول واحد لاحه Ca↑ ← Ra↑

* ليش بستخدم اكثر من PFR بدل واحد PFR ؟ 1 ΔP اقل.
2 Cost
3 Geometry Point view

* one PFR can be modeled by large number of CSTR.



Example 2–6 Sizing Plug-Flow Reactors in Series

Using either the data in Table 2-3 or Figure 2-2, calculate the reactor volumes V_1 and V_2 for the plug-flow sequence shown in Figure 2-7 when the intermediate conversion is 40% and the final conversion is 80%. The entering molar flow rate is the same as in the previous examples, 0.4 mol/s.

Solution

TABLE 2-3 PROCESSED DATA –2

X	0.0	0.1	0.2	0.4	0.6	0.7	0.8
$[F_{A0}/-r_A](m^3)$	0.89	1.08	1.33	2.05	3.54	5.06	8.0

* Simpson's rule

$$\int_a^b f(x)\,dx = S_n$$

$$S_n = \frac{\Delta x}{3}\left[f(x_0) + 4f(x_1) + f(x_2)\right]$$

* $\frac{F_{A0}}{r}\,dX = V$

① $\Delta X = \frac{0.4 - 0}{2} = \boxed{0.2}$

$X_1 = 0 \quad X_2 = 0.2 \quad X_3 = 0.4$

$\frac{0.2}{3}\left[0.89 + 4[1.33] + 2.05\right] = 0.551\ m^3$

② $\frac{F_{A0}}{r}\,dX = V$

$\Delta X = \frac{0.8 - 0.4}{2} = \boxed{0.2}$

$X_1 = 0.4 \quad X_2 = 0.6 \quad X_3 = 0.8$

$V_2 = \frac{0.2}{3}\left[2.05 + 4(3.54) + 8\right] = 1.614\ m^3$

$V = V_1 + V_2 = 2.165\ m^3$

if I have one reactor.

$0 \longrightarrow 0.8$

$\Delta X = \frac{0.8}{2} = \boxed{0.4}$

$\frac{0.4}{3}\left[0.89 + 4(2.05) + 8\right] = 2.2\ m^3$ #

MADAR

Example: Consider the liquid phase reaction;

A → Products

which is to take place in a PFR. The following data was obtained in a batch reactor.

X	0	0.4	0.8
$-r_A$(mol/dm^{3}s)	0.01	0.008	0.002

If the molar feed of A to the PFR is 2 mol/s, what PFR volume is necessary to achieve 80 % conversion under identical conditions as those under which the batch data was obtained?

$V = \int_0 \frac{F_{A0}}{r} dx$

* $\Delta X = \frac{0.8 - 0}{2} = \boxed{0.4}$

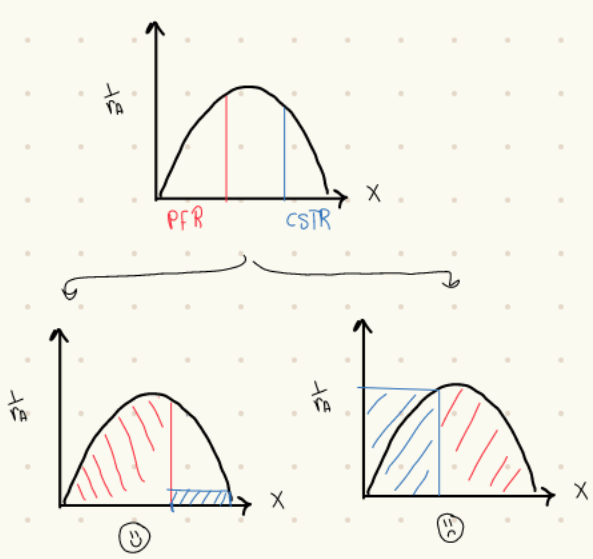
* $X_1 = 0 \quad X_2 = 0.4 \quad X_3 = 0.8$

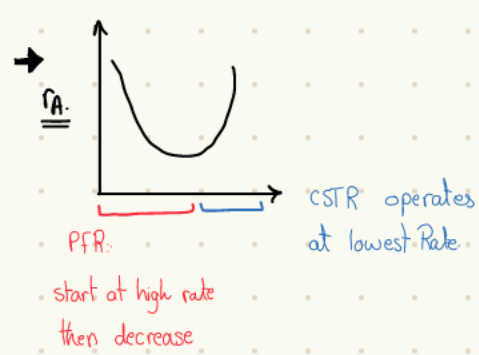
$1/r \Rightarrow 100 \quad 125 \quad 500$

* $V = 2\left[\frac{0.4}{3}\left[100 + 4(125) + 500\right]\right]$

$V = 293 \ dm^3$.

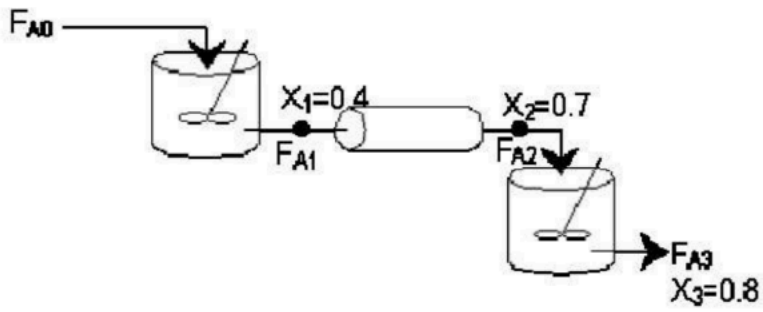
* Combination of CSTR's and PFR's in Series.



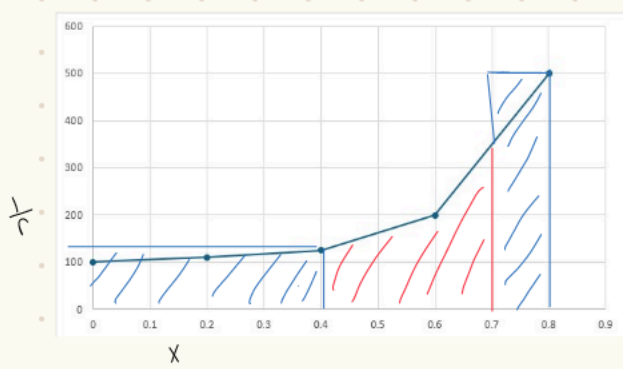


Reactors in Series: CSTR – PFR – CSTR

Using the data in the table, calculate the reactor volumes V_1, V_2 and V_3 for the CSTR/PFR/CSTR reactors in series sequence along with the corresponding conversion.



X	0	0.2	0.4	0.6	0.8
$-r_A\left(\frac{mol}{dm^3 \bullet s}\right)$	0.010	0.0091	0.008	0.005	0.002
$(1/-r_A)\left(\frac{dm^3 \bullet s}{mol}\right)$	100	110	125	200	500
$F_{A0}/-r_A\ (dm^3)$	200	220	250	400	1000



* V_1 CSTR

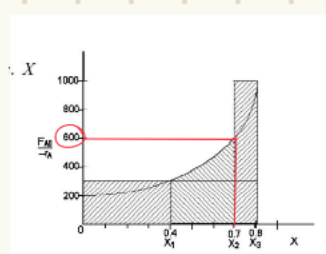
$$V_1 = \frac{F_{A0}\ X}{r} \rightarrow 250 \times 0.4 = 100\ dm^3$$

* V_2 PFR $0.4 \rightarrow 0.7$

$$\Delta X = \frac{0.7 - 0.4}{2} = 0.15$$

$X_1 = 0.4$ $\quad X_2 = 0.55$ $\quad X_3 = 0.7$

$\hookrightarrow 250$ $\quad \hookrightarrow 370$ $\quad \hookrightarrow 600$



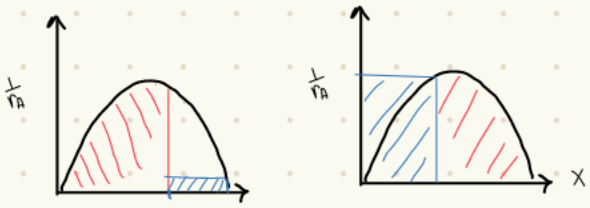
$$V_2 = \frac{0.15}{3}\left[250 + 4[370] + 600\right] = 116.5\ dm^3$$

* V_3 CSTR

$$V_3 = \frac{F_{A0}\ X}{r} = 1000 \times [0.8 - 0.7] = 100$$

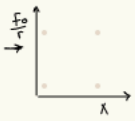
* Total volume $\Rightarrow 316.5\ dm^3$

* Is There any diffrent between CSTR - PFR , PFR - CSTR ?



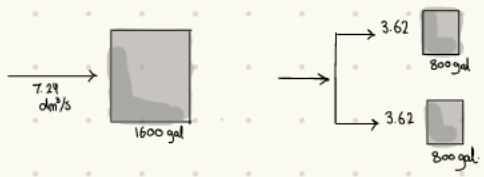
$$V_1 + V_2 \neq V_1^* + V_2^*$$

* Leven spiel plot



* Topic 7:

Performance of isothermal parallel CSTR:



* $V_1 = V_2 = V_3$
* $X_1 = X_2 = X_3$
* $r_{A1} = r_{A2} = r_{A3}$
* $V_i = \frac{F_{A0} X_i}{r_{Ai}}$

* $V_i = \frac{V}{n} \rightarrow \frac{1600}{2} = 800$
* $F_{A0i} = \frac{F_{A0}}{n} \rightarrow \frac{7.24}{2} = 3.62$

- The X from one reactor = The overall X from all reactors.

Performance of PFRs in Parallel:

* $V_1 = V_2 = V_3$
* $X_1 = X_2 = X_3$

* $V_i = \frac{V}{n}$
* $F_{A0i} = \frac{F_{A0}}{n}$

* L↓, X↓, yield↑.

* Pressure Drop in PFRs

* $C_A = \frac{F_A}{V}$
* $V = V_0 (1+\varepsilon X) \frac{T}{T_0} \frac{P_0}{P}$
* $C_A = \frac{F_A}{V_0 (1+\varepsilon X) \frac{T}{T_0} \frac{P_0}{P}}$

if I have a sec order rxn.

$r = -k C_a^2$

$r = -k \frac{C_{a_0}^2 (1-X)^2}{(1+\varepsilon X)^2} \frac{P^2}{P_0^2} \frac{T_0^2}{T^2}$

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

$F_A = F_A^0 - F_A^0 X$

$$\frac{F_A^0 \, dX}{dW_A} = k \frac{C_{a_0}^2 (1-X)^2}{(1+\varepsilon X)^2} \frac{P^2}{P_0^2} \frac{T_0^2}{T^2}$$

isotherm

$\frac{dX}{dW} = f(X, P)$

need to find relation between $\frac{P}{P_0}$ with W or V of PFRs.

* ergun equation

Ergun Equation is used here

$$\frac{dP}{dW} = -\frac{\beta_0}{A_c(1-\phi)\rho_c}\frac{P_0}{P}\left(\frac{T}{T_0}\right)\frac{F_T}{F_{T0}} \times \frac{2}{2} \times \frac{P_0}{P_0}$$

Or by substituting $\frac{F_T}{F_{T0}} = 1 + \varepsilon X$ to get

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

$p \to \frac{P}{P_0}$, $p \to \frac{P}{P_0}$

Where $\alpha = \frac{2\beta_0}{A_c \rho_c (1-\phi) P_0}$ and $\beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_P \phi^3}\left[\frac{150(1-\phi)\mu}{D_P} + 1.75G\right]$ $\left(\text{e.g., } \frac{\text{kPa}}{\text{m}}, \frac{\text{atm}}{\text{ft}}\right)$

Notation of Ergun's equation

P = pressure, lb_f/ft^2 or (kPa)

ϕ = porosity = $\frac{\text{volume of void}}{\text{total bed volume}}$ = void fraction

$1-\phi = \frac{\text{volume of solid}}{\text{total bed volume}}$ → solid fraction.

$g_c = 32.174\ \text{lb}_m \cdot \text{ft/s}^2 \cdot \text{lb}_f$ (conversion factor)

$= 4.17 \times 10^8\ \text{lb}_m \cdot \text{ft/h}^2 \cdot \text{lb}_f$

(Recall that for the metric system $g_c = 1.0$)

D_P = diameter of particle in the bed, ft or (m)

μ = viscosity of gas passing through the bed, $\text{lb}_m/\text{ft} \cdot \text{h}$ or $(\text{kg/m} \cdot \text{s})$

z = length down the packed bed of pipe, ft or (m)

u = superficial velocity = volumetric flow rate ÷ cross-sectional area of pipe, ft/h or (m/s)

ρ = gas density, lb_m/ft^3 or (kg/m^3)

$G = \rho u$ = superficial mass velocity, $(\text{lb}_m/\text{ft}^2 \cdot \text{h})$ or $(\text{kg/m}^2 \cdot \text{s})$

* Catalyst weight $W = z A_c \rho_b = z A_c (1-\phi)\rho_c$

* Assume $\frac{F}{F_0} = 1$, isotherm.

$1 + \varepsilon X$

$$\frac{dp}{dW} = -\frac{\alpha}{2p}$$

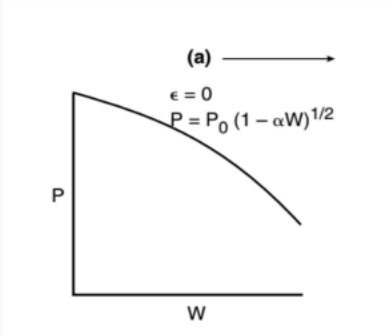
$$2p\,dp = -\alpha\,dW$$

$$p^2 + C = -\alpha W$$

at $W = 0$, $P_0 = P$ $\boxed{p = 1}$

$$1 + C = 0$$

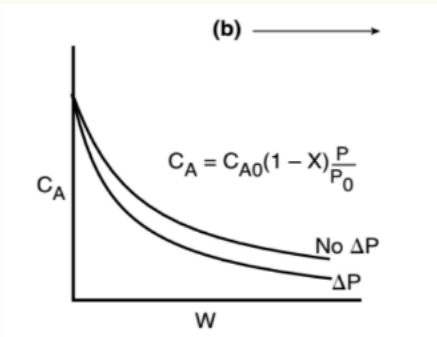
$\boxed{C = -1}$ → $p^2 = 1 - \alpha W$



$$y^2 = 1 - \alpha W$$

$$P = P_0 (1 - \alpha W)$$

$\uparrow W \longrightarrow \downarrow y, \downarrow P$



$$C_A = C_A^\circ (1 - X) \frac{P}{P_0} \cancel{\frac{T_0}{T}} \cancel{\frac{1}{1+\epsilon X}}$$

$$C_A = C_A^\circ (1 - X) \frac{P}{P_0}$$

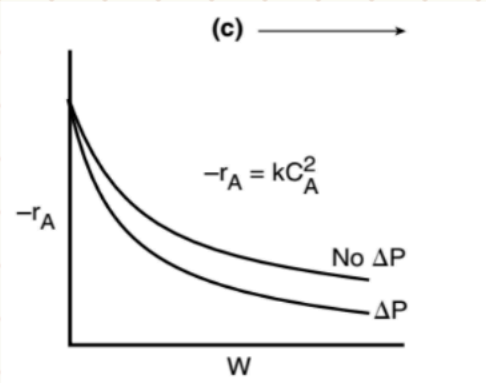
$C_A \uparrow, y \uparrow$

$* \uparrow W, \downarrow P, y \downarrow$

$PV = nRT$

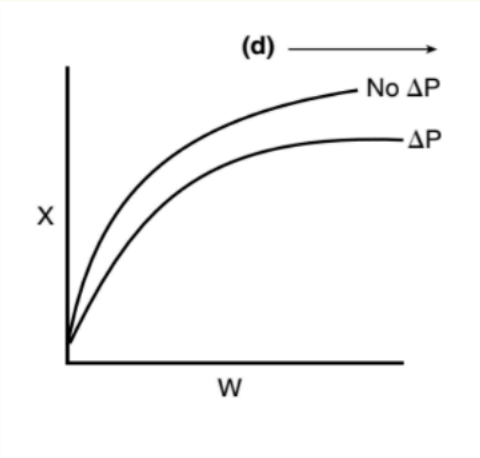
$\downarrow P \left(\frac{1}{C_A}\right) \uparrow = \text{constant}$

$\uparrow P, C_A \uparrow$

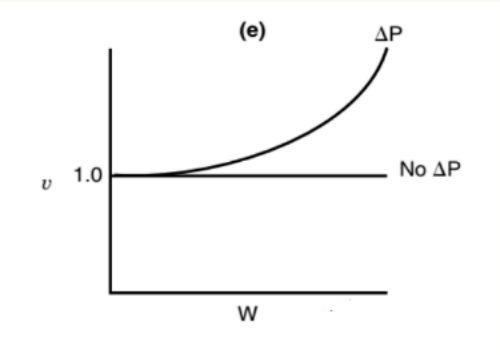


$* \; C_A \uparrow, -r_A \uparrow$

$* \; \uparrow W \; \downarrow y \; \downarrow C_A \; \downarrow -r_A$



no $\Delta P \longrightarrow -r_A \uparrow \longrightarrow X \uparrow$



Topic 8: Pressure Drop in reactors:

$\boxed{\text{Gas}}$ $2A \longrightarrow B + C$ in BFR

* $F_{A0}\dfrac{dX_A}{dW} = -r_A$

* $-r_A = kC_A^2$

A	F_{A0}	$-XF_{A0}$	$F_A = F_{A0} - XF_{A0}$
B	0	$+\frac{1}{2}XF_{A0}$	$F_B = \frac{1}{2}XF_{A0}$

* $C_A = \dfrac{F_A}{v} = \dfrac{C_{A0}(1-X)}{1+\varepsilon X_A}\dfrac{P}{P_0}$

$$F_{A0}\frac{dX_A}{dW} = -k\frac{C_{A0}^2(1-X)^2}{(1+\varepsilon X_A)^2}\left(\frac{P}{P_0}\right)^2$$

$$\frac{dX_A}{dW} = \frac{-k}{F_{A0}}\frac{C_{A0}^2(1-X)^2}{(1+\varepsilon X_A)^2}\left(\frac{P}{P_0}\right)^2 \rightarrow f(P, X_A)$$

$$\frac{dP}{dW} = \frac{\alpha}{2}\cancel{\frac{T}{T_0}}\frac{P_0}{P/P_0}(1+\cancel{\varepsilon X_A}) = \frac{2\beta_0}{A_c\rho_c(1-\phi)P_0}$$

$$\frac{P}{P_0} = \sqrt{1-\alpha W}$$

$$\frac{dX_A}{dW} = \frac{-k}{F_{A0}}\frac{C_{A0}^2(1-X)^2}{(1+\varepsilon X_A)^2}(1-\alpha W)$$

$$\int_0^{X_A}\frac{F_{A0}}{C_{A0}^2 k}\frac{(1+\cancel{\varepsilon X_A})^2}{(1-X_A)^2} = \int_0^W (1-\alpha W)\,dW$$

$$\rightarrow \frac{F_{A0}}{kC_{A0}^2}\int_0^{X_A}\frac{dX_A}{(1-X_A)^2} = \int_0^W (1-\alpha W)dW$$

Solve for X_A

$$\rightarrow \left(\frac{X_A}{1-X_A}\right) = W\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{\upsilon_0}\right)$$

$$\rightarrow X_A = W\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{\upsilon_0}\right) - W\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{\upsilon_0}\right)X_A$$

$$\rightarrow X_A + W\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{\upsilon_0}\right)X_A = W\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{\upsilon_0}\right)$$

$$\boxed{\rightarrow X_A = \frac{\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{\upsilon_0}\right)}{1+\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{\upsilon_0}\right)}}$$

$X_A \overset{?}{=} 0$

$\left[1-\frac{\alpha W}{2}\right]\left[\frac{kC_{A0}}{V_0}\right] \rightarrow C_{A0} = 0$, $\dot{V} = \infty$ مستحيل

* even if $W = 0$ $X_A \neq 0$.

$$\boxed{\rightarrow W = \frac{1-\sqrt{1-\left(\frac{2\upsilon_0\alpha}{kC_{A0}}\right)\left(\frac{X_A}{1-X_A}\right)}}{\alpha}}$$

if $X = 0$

$$\boxed{\rightarrow W = \frac{1-\sqrt{1-\left(\frac{2\upsilon_0\alpha}{kC_{A0}}\right)\left(\frac{X_A}{1-X_A}\right)}}{\alpha}}$$

$W = \frac{1-1}{\alpha} = 0$

if $X = 0$, $W = 0$.

Example 8.2 Calculating Pressure Drop in a Packed Bed

Plot the pressure drop in a 60-ft length of 1½-inch schedule 40 pipe packed with catalyst pellets ¼ inch in diameter. There is 104.4 lb_m/h of gas passing through the bed. The temperature is constant along the length of pipe at 260°C. The void fraction is 45% and the properties of the gas are similar to those of air at this temperature. The entering pressure is 10 atm.

1½-inch schedule 40 pipe ⇨ $A_c = 0.01414\ ft^2$

Ergun Equation is used here

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

Or by substituting $\frac{F_T}{F_{T0}} = 1 + \varepsilon X$ to get

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

Where $\alpha = \frac{2\beta_0}{A_c\rho_c(1-\phi)P_0}$ and $\beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_P \phi^3}\left[\frac{150(1-\phi)\mu}{D_P} + 1.75G\right]$ $\left(\text{e.g., } \frac{kPa}{m}, \frac{atm}{ft}\right)$

* $G = \frac{\dot{m}}{A_c} = \frac{104.4\ lbm/h}{0.01414\ ft^2} = 7383.3\ \frac{lbm}{h \cdot ft^2}$
* $\phi = 0.45$
* $\rho = 0.413\ lbm/ft^3$
* $\mu = 0.0673\ lbm/ft.h$
* $D_p = 1/4\ in = 0.0208$
* $g_c = 4.17 \times 10^8$

$\beta_0 = 164.1\ \frac{lbf}{ft^3} \longrightarrow 0.0775\ \frac{atm}{ft}$

$$\frac{P}{P_0}^2 = 1 - \frac{2\beta_0 L}{P_0}$$

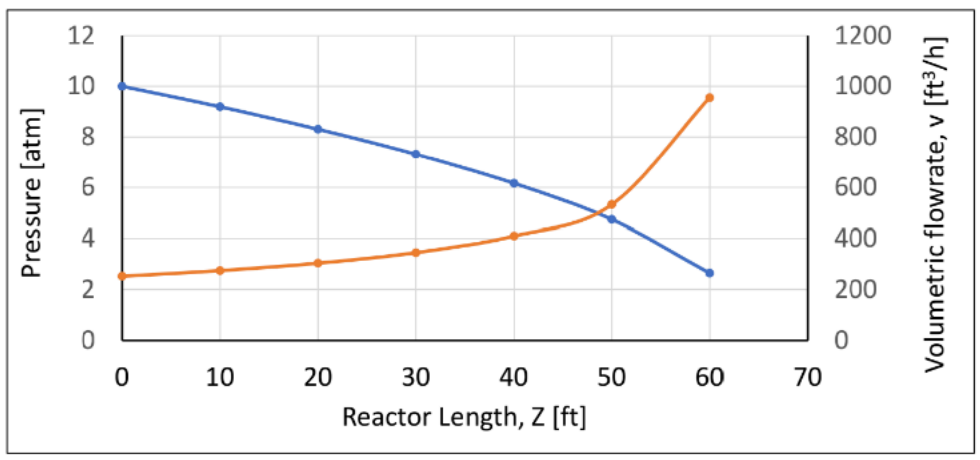
$$\frac{P}{P_0}^2 = 1 - \frac{2[0.0775]60}{10}$$

$$\frac{P}{P_0} = 0.26$$

$P = P_0 \times 0.26$

$V = V_0 \frac{P_0}{P}$

z (ft)	0	10	20	30	40	50	60
p/po	1.00	0.92	0.83	0.73	0.62	0.47	0.26
p	10.00	9.19	8.31	7.31	6.16	4.74	2.65
v (ft3/h)	252.80	275.01	304.34	345.62	410.10	532.95	955.49



Example 1: Gas Phase Reaction in PBR for δ=0

Gas Phase reaction in PBR with δ = 0 (Analytical Solution)

$$A + B \rightarrow 2C$$

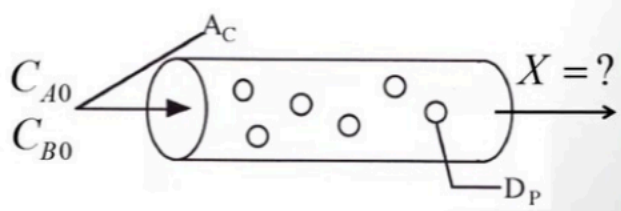
Equimolar feed of A and B and:

$k_A = 1.5 dm^6/mol/kg/min$

$\alpha = 0.0099\ kg^{-1}$

Find X at 100 kg

$$C_{A0} = C_{B0}$$



$C_A^\circ = 0.2 \qquad F_{A0} = 2$

$\delta = 2 - 1 - 1 = 0$

$$F_A^\circ \frac{dX}{dW} = -r_A$$

$$r_A = -k C_A C_B$$

A	F_A°	$-X F_A^\circ$	$F_A^\circ(1-X)$
B	F_B°	$-X F_A^\circ$	$F_B^\circ - F_A^\circ X$
C	0	$+2X F_A^\circ$	$+2F_A^\circ X$

$$C_A = \frac{F_A^\circ(1-X)}{(1+\cancel{\varepsilon}^{\,0} X)\frac{P_0}{P}\frac{T}{\cancel{T_0}}(v_0)}$$

$\varepsilon = 0$; isothermal

$$C_A = C_A^\circ (1-X)\frac{P}{P_0}$$

$$C_B = C_A^\circ (1-X)\frac{P}{P_0} \qquad C_A^\circ = C_B^\circ$$

$$r_A = -k\left[C_A^\circ(1-X)\frac{P}{P_0}\right]^2$$

$$F_A^\circ \frac{dX}{dW} = -k\left[C_A^\circ(1-X)\frac{P}{P_0}\right]^2 \rightarrow F(X, P)$$

$$\frac{P}{P_0} = \sqrt{1-\alpha W}$$

$$F_A^\circ \frac{dX}{dW} = -k\left[C_A^\circ(1-X)\frac{\sqrt{1-\alpha W}}{2}\right]^2$$

$$\int \frac{dX}{1-X} = \int -k C_A^{\circ 2}(1-X)^2 (1-\alpha W)\, dW$$

$W = 0 \quad X = 0 \qquad W = W \quad X = X$

$$\frac{X}{1-X} = \frac{k C_{A0}^2}{F_A^\circ}\left[W - \alpha\frac{W^2}{2}\right]$$

$$\frac{X}{1-X} = \frac{1.5\,(2)^2}{F_A}\left[100 - 0.0099\,\frac{100^2}{2}\right] \qquad X = 0.6$$

Example 4–5 Effect of Pressure Drop on the Conversion Profile

Reconsider the packed bed in Example 4-4 for the case where a second-order reaction

$$2A \rightarrow B + C$$

is taking place in 20 meters of a $1\frac{1}{2}$ schedule 40 pipe packed with catalyst. The flow and packed-bed conditions in the example remain the same except that they are converted to SI units; that is, P_0 = 10 atm = 1013 kPa, and

Entering volumetric flow rate: v_0 = 7.15 m³/h (252 ft³/h)
Catalyst pellet size: D_p = 0.006 m (ca. $\frac{1}{4}$-inch)
Solid catalyst density: ρ_c = 1923 kg/m³ (120 lb/ft³)
Cross-sectional area of $1\frac{1}{2}$-in. schedule 40 pipe: A_C = 0.0013 m²
Pressure drop parameter: β_0 = 25.8 kPa/m
Reactor length: L = 20 m

We will change the particle size to learn its effect on the conversion profile. However, we will assume that the specific reaction rate, k, is unaffected by particle size, an assumption we know from Chapter 12 is valid only for small particles.

(a) First, calculate the conversion in the absence of pressure drop.
(b) Next, calculate the conversion accounting for pressure drop.
(c) Finally, determine how your answer to (b) would change if the catalyst particle diameter were doubled.

The entering concentration of A is 0.1 kmol/m³ and the specific reaction rate is

$$k = \frac{12\,\text{m}^6}{\text{kmol}\cdot\text{kg cat}\cdot\text{h}}$$

2-1-1 = 0 = Z.

* $r = -k C_A^2$
* $F_{A0} \frac{dX}{dW} = -r$

* A	F_{A0}	$-X F_{A0}$	$C_A = C_{A0}(1-X)$
B	0	$+\frac{1}{2} X F_{A0}$	
C	0	$+\frac{1}{2} X F_{A0}$	

* $F_{A0} \frac{dX}{dW} = -k C_A^2$

$$\frac{F_{A0}\, dX}{C_{A0}^2 (1-X)^2} = -k\, dW$$

- $W = z A_c \rho_b = z A_c (1-\phi)\rho_c$

$20 \times 0.0013 \times (1-45)(1923) = 27.5$ kg.

$\boxed{X = 0.82}$ 2

* $C_A = C_{A0}(1-X)\frac{P}{P_0}$

$$\alpha = \frac{2\beta_0}{P_0 A_c \rho_B}$$

$$\frac{2\,[25.8]\,\frac{kPa}{m}}{1013\,kPa\,[0.0013]\,m^2\,1058\,\frac{kg}{m^3}} = 0.037\ kg^{-1}$$

$$\rightarrow X_A = \frac{\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{v_0}\right)}{1+\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{v_0}\right)}$$

$X = 0.69$

$$\beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_P \phi^3}\left[\frac{150(1-\phi)\mu}{D_P} + 1.75G\right] \quad \left(\text{e.g., } \frac{\text{kPa}}{\text{m}}, \frac{\text{atm}}{\text{ft}}\right)$$

2

$\beta_0 \rightarrow \frac{1}{2}\beta_0$

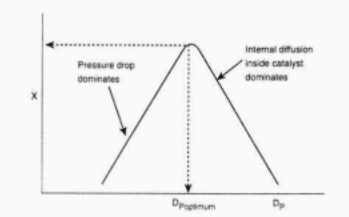
$$\frac{1}{2}\alpha = \frac{2\beta_0 \frac{1}{2}}{P_0 A_c \rho_B}$$

$0.037\ kg^{-1} \times \frac{1}{2} = 0.0185\ kg^{-1}$

$$\rightarrow X_A = \frac{\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{v_0}\right)}{1+\left(1-\frac{\alpha W}{2}\right)\left(\frac{kC_{A0}}{v_0}\right)}$$

$X = 0.774$

↑D, ↓ΔP, ↑r_a, ↑X.



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Topic 9: multiple reactions.

① Parallel reactions

$$A \xrightarrow{k_1} B$$
$$A \xrightarrow{k_2} C$$

② Series reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

③ Independnt reactions $A + B \xrightarrow{k_1} C$

$D + E \xrightarrow{k_2} M$

④ Complex reactions. $A + B \rightarrow C + D$

$A + C \rightarrow E$

$E \rightarrow G$

* Desired and undesired rxn's

* $A \xrightarrow{k_D} D$

  $A \xrightarrow{k_U} U$

* $A \xrightarrow{k_D} D \xrightarrow{k_U} U$

* $Y_D = \frac{r_D}{-r_A}$ [Instantanous]

* $\tilde{Y}_D = \frac{N_D}{N_{A0} - N_A}$ or $\frac{F_D}{F_{A0} - F_A}$ [over all]

* $S_{D/U} = \frac{\text{rate of formation } D}{\text{rate of formation } U}$ [Instantanous]

* $\tilde{S}_{D/U} = \frac{\text{Exit flow rate of } D}{\text{Exit flow rate of } U}$ [over all]

∴ For CSTR $\tilde{Y} = Y$, $S_{D/U} = \tilde{S}_{D/U}$

* $A \rightarrow D$ $\quad r_D = k_D C_A^{\alpha_1}$

  $A \rightarrow U$ $\quad r_U = k_U C_A^{\alpha_2}$

  $-r_A = r_D + r_U$

  $-r_A = k_D C_A^{\alpha_1} + k_U C_A^{\alpha_2}$

$$S_{D/U} = \frac{k_D C_A^{\alpha_1}}{k_U C_A^{\alpha_2}}$$

- Case 1:- $\alpha_1 > \alpha_2$

  ↳ Batch, PFR

  $S_{D/U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$

  $S_{D/U} = C_A^{\oplus}$ ↑↑ maximum $S_{D/U}$, keeping C_A as high as possible during rxn.

- Case 2:- $\alpha_1 < \alpha_2$

  ↳ CSTR

  $S_{D/U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$

  $S_{D/U} = C_A^{\ominus}$ ↑↓

- Case 3:- $E_D > E_U$

  $k_D = A_D e^{-E_D/RT}$

  $k_U = A_U e^{-E_U/RT}$

  $\frac{k_D}{k_U} = \frac{A_D}{A_U} \frac{e^{-E_D/RT}}{e^{-E_U/RT}} \rightarrow \frac{A_D}{A_U} e^{-\frac{[E_D - E_U]}{RT}}$

  $E_D > E_U \rightarrow e^{\frac{\oplus}{T}} \Rightarrow$ ↑ $S_{D/U}$, ↑T.

  * keep Temp as high as possible

- Case 4:- $E_D < E_U$ $\quad E_U > E_D \rightarrow e^{\frac{\oplus}{T}} \Rightarrow$ ↑ $S_{D/U}$, ↓T.

EXAMPLE 9.1

The following reactions are observed when an olefin is epoxidized with oxygen:

$$\text{alkene} + O_2 \Longrightarrow \text{epoxide}$$
$$\text{epoxide} + O_2 \Longrightarrow CO_2 + H_2O$$
$$\text{alkene} + O_2 \Longrightarrow CO_2 + H_2O$$

Calculate the maximum epoxide selectivity assuming an excess of dioxygen.

$A + O \rightarrow \boxed{E}\ D$

$E + O \rightarrow CD$

$A + O \rightarrow CD$

$$r_A = -k_1 C_A C_o - k_3 C_A C_o \quad \rightarrow \quad -r_A = k_1 C_A C_o + k_3 C_A C_o$$

$$r_E = k_1 C_A C_o - k_2 C_{EB} C_o$$

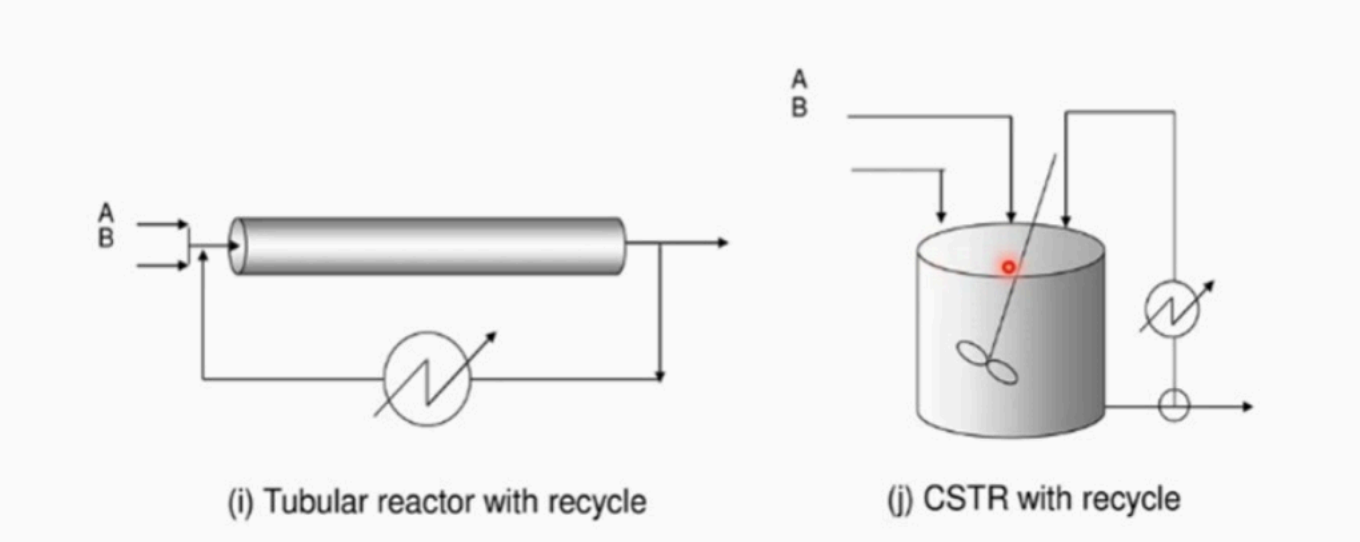
$$r_{CD} = k_3 C_A C_o + k_2 C_{EB} C_o$$

$$S_{DM} = \frac{k_1 C_A C_o - k_2 C_{EB} C_o}{k_3 C_A C_o + k_2 C_{EB} C_o}$$

$$\text{yield} = \frac{r_D}{-r_A} = \frac{k_1 C_A C_o - k_2 C_{EB} C_o}{k_1 C_A C_o + k_3 C_A C_o}$$

* Criteria for selection: 1) Safety
2) selectivity
3) yield
4) Temp control
5) cost.

*

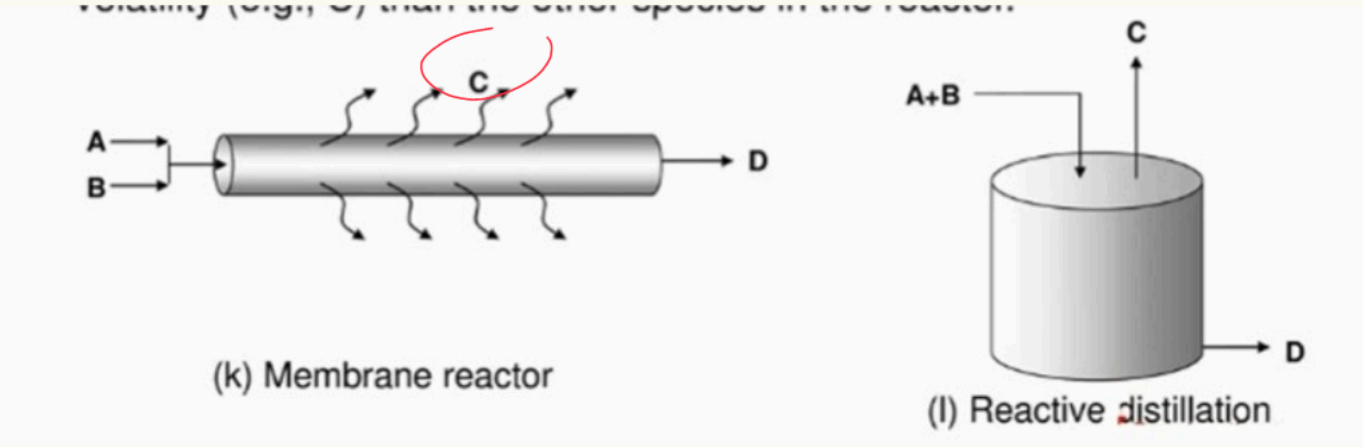


(i) Tubular reactor with recycle (j) CSTR with recycle

* recyle → ① Dilute the inlet stream
② Cooling

* used for highly exo reaction.

*



(k) Membrane reactor (l) Reactive distillation

* for reversible rxn
* $A + B \rightleftharpoons C + D$

C: high volatility.

Example 8–2 Choice of Reactor and Conditions to Minimize Unwanted Products

For the parallel reactions

$$A + B \longrightarrow D: \qquad r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}$$

$$A + B \longrightarrow U: \qquad r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

consider all possible combinations of reaction orders and select the reaction scheme that will maximize $S_{D/U}$.

$A + B \rightarrow D$

$A + B \rightarrow U$

$r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}$

$r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$

$$* \quad S_{D/U} = \frac{k_1 C_A^{\alpha_1} C_B^{\beta_1}}{k_2 C_A^{\alpha_2} C_B^{\beta_2}} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2}$$

- Case 1: $\alpha_1 > \alpha_2 \quad \beta_1 > \beta_2$

$$S_{D/U} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2 \oplus} C_B^{\beta_1 - \beta_2 \oplus}$$

$S_{D/U} \uparrow \rightarrow C_A \uparrow \; C_B \uparrow$

* Batch, PFR

- Case 2: $\alpha_1 > \alpha_2 \quad \beta_1 < \beta_2$

$$S_{D/U} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2 \oplus} C_B^{\beta_1 - \beta_2 \ominus}$$

$\uparrow S_{D/U} \rightarrow \uparrow C_A \; \downarrow C_B$

* Semi Batch reactor [B slowly feed to A]
* membrane/Tuber reactor with side stream
* CSTR in series with small B in feed

- Case 3: $\alpha_1 < \alpha_2 \quad \beta_1 < \beta_2$

$$S_{D/U} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2 \ominus} C_B^{\beta_1 - \beta_2 \ominus}$$

$\uparrow S_{D/U} \rightarrow C_A \downarrow \; C_B \downarrow$

* CSTR
* Tubular with large recycle ratio
* feed Diluted with inert

- Case 4: $\alpha_1 < \alpha_2 \quad \beta_1 > \beta_2$

$$S_{D/U} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2 \ominus} C_B^{\beta_1 - \beta_2 \oplus}$$

* Semi Batch reactor [A slowly feed to B]
* membrane/Tuber reactor with side stream
* CSTR in series with small A in feed

* Design of a Batch reactor for series of rxn's

$A \rightarrow B \rightarrow C$

- Consider the following reaction scheme:
  - $A \xrightarrow{k_1} B \xrightarrow{k_2} C$
    - If: both reactions are elementary AND
    - If: $k_1 = 0.06\ min^{-1}$, $k_2 = 0.04\ min^{-1}$, $C_{AO} = 2.0\ mol/L$
- Determine the concentrations of A, B and C vs. t

* $\frac{dN_i}{dt} = r_i V$

* $\frac{dC_i}{dt} = r_i$

* A :- $r_A = -k_1 C_A$

$$\frac{dC_A}{dt} = -k_1 C_A \longrightarrow \frac{dC_A}{C_A} = -k\, dt \longrightarrow C_A = C_A^\circ \exp[-k_1 t]$$

* B :- $r_B = k_1 C_A - k_2 C_B$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \longrightarrow \frac{dC_B}{dt} = k_1 C_A^\circ \exp[-k_1 t] - k_2 C_B \quad \Rightarrow \text{integrating factor} = \exp[k_2 t]$$

$$\left[\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} \exp[-k_1 t]\right] \times \exp[k_2 t]$$

$$\underbrace{\exp[k_2 t]\frac{dC_B}{dt} + k_2 C_B \exp[k_2 t]} = k_1 C_{A0} \exp[-k_1 t] \exp[k_2 t]$$

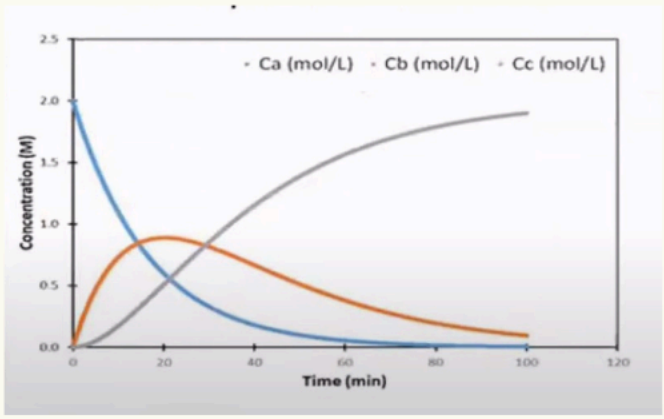
$$\frac{d\,[C_B \exp[k_2 t]]}{dt} = k_1 C_A^\circ \exp[-k_1 t] \exp[k_2 t]$$

$$d\,C_B \exp[k_2 t] = k_1 C_A^\circ \exp[(k_2 - k_1)t] \Big|_0^t$$

$$C_B \exp[k_2 t] = \frac{k_1 C_{A0}}{k_2 - k_1} \exp[(k_2 - k_1)t] - 1$$

$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} \frac{[\exp[(k_2 - k_1)t] - 1]}{\exp[k_2 t]}$$

$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} \exp[-k_1 t] - \exp[-k_2 t]$$



MAX B

$$\frac{dC_B}{dt} = 0$$

$$0 = k_1 C_A - k_2 C_B$$

$$0 = k_1 C_A^\circ \exp[-k_1 t] - k_2 \frac{k_1 C_{A0}}{k_2 - k_1} \exp[-k_1 t] - \exp[-k_2 t]$$

$$\cancel{k_1 C_A^\circ} \exp[-k_1 t] = k_2 \frac{\cancel{k_1 C_{A0}}}{k_2 - k_1} \exp[-k_1 t] - \exp[-k_2 t]$$

$$1 = \frac{k_2}{k_2 - k_1}\left[1 - \frac{\exp[-k_2 t]}{\exp[k_1 t]}\right]$$

$$\frac{k_2}{k_2}(1) - \frac{k_2 - k_1}{k_2} = \exp[(k_1 - k_2)t]$$

$$\frac{k_1}{k_2} = \exp[(k_1 - k_2)t]$$

$$t_{max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

$t_{max} = 20.3\ min$

$C_B = 0.89$

$C_A = 0.59$

$C_C = 0.52$

* C : $r_C = k_2 C_B$

$$\frac{dC_C}{dt} = k_2 C_B \longrightarrow dC_C = \int_0^t \frac{k_2 k_1}{k_2 - k_1} C_A^\circ [\exp[-k_1 t] - \exp[-k_2 t]]\, dt$$

$$C_C = \frac{k_2 k_1 C_A^\circ}{k_2 - k_1}\left[\frac{-1}{k_1}\exp[-k_1 t] - \frac{1}{k_2}\exp[-k_2 t]\right]\Big|_0^t$$

$$C_C = \frac{k_2 k_1 C_{A0}}{k_2 - k_1}\left[\frac{1 - \exp[-k_1 t]}{k_1} - \frac{1 - \exp[-k_2 t]}{k_2}\right]$$

$$Y = \frac{r_D}{-r_A} = \frac{k_1 C_A - k_2 C_B}{k_1 C_A} = 1 - \left(\frac{k_2}{k_1}\right)\left(\frac{C_B}{C_A}\right)$$

* $k_1 \uparrow$, $C_{B\,max} \uparrow$

$\hookrightarrow k_1 = k_0 \exp\left[-\frac{E_A}{RT}\right]$

Evaluate: Substituting for $C_{A0} = 2$ mol/dm^3, $k_1 = 0.5\text{h}^{-1}$, and $k_2 = 0.2\text{h}^{-1}$ the concentrations as a function of time are

$$C_A = C_A^\circ \exp[-k_1 t]$$

$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1}\left(\exp[-k_1 t] - \exp[-k_2 t]\right)$$

$$C_C = \frac{k_2 k_1 C_{A0}}{k_2 - k_1}\left[\frac{1 - \exp[-k_1 t]}{k_1} - \frac{1 - \exp[-k_2 t]}{k_2}\right]$$

$$\frac{dC_B}{dt} = k_1 C_A^\circ \exp[-k_1 t] - k_2 C_B \rightarrow \text{integrating factor} = \exp[k_2 t]$$

* t_{Bmax} :- $0 = k_1 C_A^\circ \exp[-k_1 t] - k_2 \frac{k_1 C_{A0}}{k_2 - k_1}\left[\exp[-k_1 t] - \exp[-k_2 t]\right]$

* $\boxed{t_{Bmax} = 3.05\ h}$

$C_A = 0.435$

$C_{Bmax} = 1.1$

$C_C = 0.48$

$$\tilde{Y} = \frac{F_B}{F_A^\circ - F_A} = \frac{(C_B)\cancel{v}}{(C_A^\circ - C_A)\cancel{v}} \quad \frac{1.1}{2 - 0.44} = 0.705.$$

$$\tilde{S}_{D/U} = \frac{C_B}{C_C} = \frac{1.1}{0.48} = 2.3$$

- Find the instantaneous and overall selectivity for the formation of B if:
  - $A \rightarrow B$; $k_1 = 0.022\ s^{-1}$
  - $A \rightarrow C$; $k_2 = 0.014\ s^{-1}$

- Assume that initially the ideal, 3.0 L batch reactor only contains a 2.0 M solution of A

$$A \begin{matrix} \nearrow B \\ \searrow C \end{matrix}$$

$$r_B = C_A k_1$$

$$-r_A = C_A k_1 + C_A k_2$$

$$r_C = C_A k_2$$

$$\frac{dC_i}{dt} = r_i$$

$$\frac{dC_A}{dt} = (C_A k_1 + C_A k_2) -$$

$$\frac{dC_A}{C_A k_1 + C_A k_2} = 1\, dt$$

$$\frac{dC_A}{C_A (k_1 + k_2)} = dt$$

$$\frac{1}{k_1 + k_2} \ln \frac{C_A}{C_A^\circ} = t$$

$$\ln \frac{C_A}{C_A^\circ} = -t(k_1 + k_2)$$

$$C_A = C_A^\circ \exp[-t(k_1 + k_2)] \quad \#$$

$$\frac{dC_B}{dt} = r_B$$

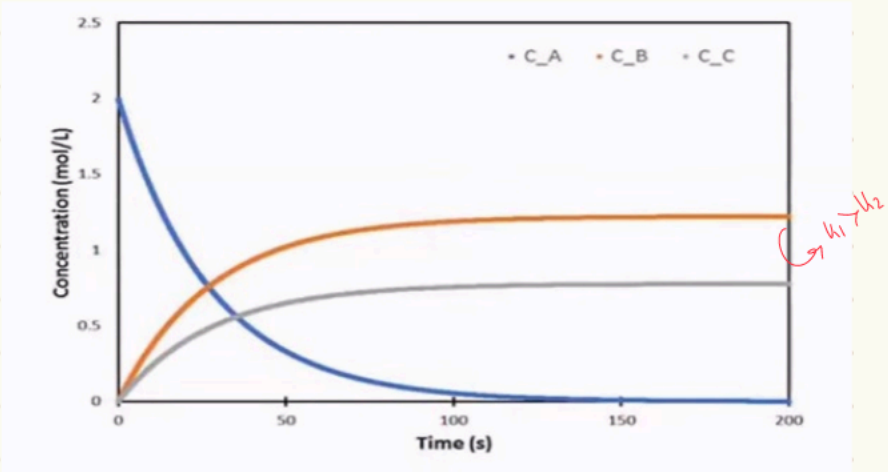
$$\frac{dC_B}{dt} = k_1 C_A$$

$$\frac{dC_B}{dt} = k_1 C_A^\circ \exp[-t(k_1 + k_2)]$$

$$C_B = \frac{-k_1 C_A^\circ}{k_1 + k_2} e[-(k_1 + k_2)t] \Big|_0^t$$

$$C_B = \frac{-k_1 C_A^\circ}{k_1 + k_2} [1 - \exp -(k_1 + k_2)t] \quad \#$$

$$C_C = \frac{-k_2 C_A^\circ}{k_1 + k_2} [1 - \exp -(k_1 + k_2)t] \quad \#$$



$$S_{D/U} = \frac{C_A k_1}{C_A k_2} = \frac{r_D}{r_U} = \frac{0.022}{0.014} = 1.57 \quad \#$$

$$\tilde{S}_{D/U} = \frac{C_B}{C_C} = \frac{\frac{-k_1 C_A^\circ}{k_1 + k_2} [1 - \exp -(k_1 + k_2)t]}{\frac{-k_2 C_A^\circ}{k_1 + k_2} [1 - \exp -(k_1 + k_2)t]}$$

$$\frac{C_B}{C_C} = \frac{k_1}{k_2} = 1.57 \quad \#$$

Design of a plug flow reactor (PFR) for a series of reactions

The bellow elementary liquid-phase series reaction is carried out in a

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$A \rightarrow B \rightarrow C$$

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

$$-r_A = k_1 C_A$$

$$r_B = k_1 C_A - k_2 C_B$$

$$r_C = k_2 C_B$$

$$* \; v_0 \frac{dC_A}{dW} = -k_1 C_A$$

$$* \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \frac{-k}{v_0} dW$$

$$\ln \frac{C_A}{C_{A0}} = \frac{-k}{v_0} W$$

$$C_A = C_{A0} \exp[-k_1 \tau] \; \#$$

$\frac{W}{v_0} = \tau$ space time related to mass of packing.

$$v_0 \frac{dC_B}{dW} = r_B$$

$$v_0 \frac{dC_B}{dW} = k_1 C_A - k_2 C_B$$

$$C_B = k_1 C_{A0} \frac{e^{-k_1 \tau} - e^{-k_2 \tau}}{k_2 - k_1} \; \#$$

maximum B $\frac{dC_B}{d\tau} = 0$

$$\tau_{obt} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

$$X_{obt} = \frac{C_{A0} - C_A}{C_{A0}} = 1 - e^{-k_1 \tau_{obt}}$$

Design of an isothermal, isobaric plug flow reactor (PFR) for a general multiple reactions

Consider the following parallel reactions:

$$\text{Reaction 1:} \quad A \xrightarrow{k_1} B \qquad -r_{1A} = k_{1A}C_A$$

$$\text{Reaction 2:} \quad 2A \xrightarrow{k_2} C \qquad -r_{2A} = k_{2A}C_A^2$$

① $A \longrightarrow B$

$2A \longrightarrow C$

$-r_A = k_1 C_A + k_2 C_A^2$

$r_B = k_1 C_A$

$r_C = \frac{1}{2} k_2 C_A^2$

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

$\frac{dF_A}{dV} = -k_1 C_A - k_2 C_A^2$

$\frac{dF_B}{dV} = k_1 C_A$

$\frac{dF_C}{dV} = \frac{1}{2} k_2 C_A^2$

$C_j = C_{T0} \frac{F_j}{F_T} \frac{P}{P_0} \frac{T_0}{T}$

isobaric isothermal

$C_A = C_{T0} \frac{F_A}{F_T}$

$C_B = C_{T0} \frac{F_B}{F_T}$

$C_C = C_{T0} \frac{F_C}{F_T}$

$F_T = F_A + F_B + F_C$

$\frac{dF_A}{dV} = -k_1 C_A - k_2 C_A^2 \rightarrow \frac{dF_A}{dt} = -k_1 C_{A0} \frac{F_A}{F_T} - k_2 \left[C_{A0} \frac{F_A}{F_T}\right]^2$

$\frac{dF_B}{dV} = k_1 C_A \longrightarrow \frac{dF_B}{dt} = k_1 C_{A0} \frac{F_A}{F_T}$

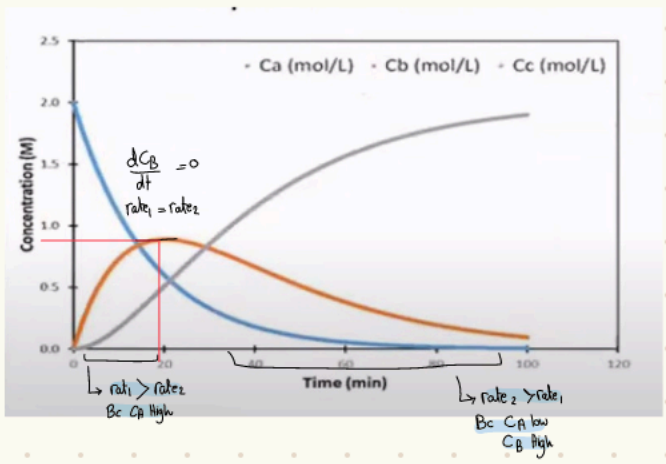
$\frac{dF_C}{dV} = \frac{1}{2} k_2 C_A^2 \longrightarrow \frac{dF_C}{dt} = \frac{1}{2} k_2 \left[C_{A0} \frac{F_A}{F_T}\right]^2$

$F_T = F_A + F_B + F_C$

Topic 1:

* $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

maximum B = optimum time



* Volume
* Volumetric flow rate
* τ optimum $= \frac{V}{\dot{V}}$

$A + 2B \rightarrow C + D$

$2D + 3A \rightarrow C + E$

$B + 2C \rightarrow D + F$

$r_{D1} = k_{D1} C_A C_B^2$

$r_{E2} = k_{f2} C_A C_B \rightarrow r_{D2} = -2k_2 C_D C_A$

$r_{f3} = k_{f3} C_B C_C \rightarrow r_{D3} = k_{f3} C_B C_C^2$

A) $S_{D/E} = \frac{r_D}{r_E} = \frac{k_{D1} C_A C_B^2 - k_2 2 C_D C_A + k_{f3} C_B C_C^2}{k_2 C_A C_D}$

$\frac{r_D}{r_E} = \frac{k_{D1}}{k_2} \frac{C_B^2}{C_D} - 2 + \frac{k_{f3}}{k_2} \frac{C_B}{C_A} \frac{C_C^2}{C_D}$

High conc. of B, low conc A.

$A \rightarrow \boxed{B}$

* PFR

* $A + 2B \rightleftharpoons C$

$\frac{dF_A}{dV} = r_A \qquad -r_A = k_f \left[C_A C_B^2 - \frac{C_C}{K_{eq}} \right]$

$\frac{r_A}{-1} = \frac{r_B}{-2} = \frac{r_C}{+1}$

$\frac{dF_B}{dV} = r_B \qquad r_B = -2k_f \left[C_A C_B^2 - \frac{C_C}{K_{eq}} \right]$

$\frac{dF_C}{dV} = r_C \qquad r_C = k_f \left[C_A C_B^2 - \frac{C_C}{K_{eq}} \right]$

$C_A = C_T^\circ \frac{F_A}{F_T} \frac{P}{P_0} \frac{T_0}{T}$

$C_B = C_T^\circ \frac{F_B}{F_T} \frac{P}{P_0} \frac{T_0}{T}$

$C_C = C_T^\circ \frac{F_C}{F_T} \frac{P}{P_0} \frac{T_0}{T}$

$\frac{dF_A}{dV} = -k_f \left[C_T^\circ \frac{F_A}{F_T} \cancel{\frac{P}{P_0}} \cancel{\frac{T_0}{T}} \times \left(C_T^\circ \frac{F_B}{F_T} \cancel{\frac{P}{P_0}} \cancel{\frac{T_0}{T}} \right)^2 - \frac{C_T^\circ \frac{F_C}{F_T} \cancel{\frac{P}{P_0}} \cancel{\frac{T_0}{T}}}{K_{eq}} \right]$

4 unknown = 4 eq ✓

$\frac{dF_B}{dV} = -2k_f \left[C_T^\circ \frac{F_A}{F_T} \cancel{\frac{P}{P_0}} \cancel{\frac{T_0}{T}} \times \left(C_T^\circ \frac{F_B}{F_T} \cancel{\frac{P}{P_0}} \cancel{\frac{T_0}{T}} \right)^2 - \frac{C_T^\circ \frac{F_C}{F_T} \cancel{\frac{P}{P_0}} \cancel{\frac{T_0}{T}}}{K_{eq}} \right]$

$\frac{dF_C}{dV} = k_f \left[C_T^\circ \frac{F_A}{F_T} \cancel{\frac{P}{P_0}} \cancel{\frac{T_0}{T}} \times \left(C_T^\circ \frac{F_B}{F_T} \cancel{\frac{P}{P_0}} \cancel{\frac{T_0}{T}} \right)^2 - \frac{C_T^\circ \frac{F_C}{F_T} \cancel{\frac{P}{P_0}} \cancel{\frac{T_0}{T}}}{K_{eq}} \right]$

$F_T = F_A + F_B + F_C$

for packed bed reactor → pressure drope → $\frac{dP}{dW} = \frac{\beta_0}{A_c (1-\phi) \rho_c} \frac{P_0}{P} \frac{F_T}{F_{T0}}$

Example 11.1 Multiple Gas-Phase Reactions in a PBR

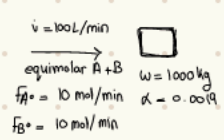
The following complex gas-phase elementary reactions take place isothermally in a PBR. The feed is equimolar in A and B with $F_{A0} = 10$ mol/min and the volumetric flow rate is 100 L/min. The catalyst weight is 1,000 kg, the pressure drop is $\alpha = 0.0019\ kg^{-1}$, and the total entering concentration is $C_{T0} = 0.2\ mol/L$.

$$(1) \qquad A + 2B \rightarrow C \qquad -r'_{1A} = k_{1A} C_A C_B^2$$

$$(2) \qquad 2A + 3C \rightarrow D \qquad -r'_{2C} = k_{2C} C_A^2 C_C^3$$

$$k_{1A} = 100\left(\frac{dm^9}{mol^2 \cdot kg\text{-cat} \cdot min}\right) \text{ and } k_{2C} = 1{,}500\left(\frac{dm^{15}}{mol^4 \cdot kg\text{-cat} \cdot min}\right)$$

Show how the values of F_A, F_B, F_C, F_D, y, and $S_{C/D}$ varies with catalyst weight, W



$A + 2B \rightarrow C$

$2A + 3C \rightarrow D$

$r_A = -k_1 C_A C_B^2 - \frac{2}{3} k_2 C_A^2 C_C^3$

$r_B = -2k_1 C_A C_B^2$

$r_C = +k_1 C_A C_B^2 - k_2 C_A^2 C_C^3$

$r_D = \frac{+1}{3} k_2 C_A^2 C_C^3$

$C_A = \overset{0.2}{\cancel{C_{T0}}} \frac{F_A}{F_T} \frac{P}{\cancel{P_0}} \frac{\cancel{T_0}}{T}$

$C_B = \overset{0.2}{\cancel{C_{T0}}} \frac{F_B}{F_T} \frac{P}{\cancel{P_0}} \frac{\cancel{T_0}}{T}$

$C_C = \overset{0.2}{\cancel{C_{T0}}} \frac{F_C}{F_T} \frac{P}{\cancel{P_0}} \frac{\cancel{T_0}}{T}$

$C_D = \underset{0.2}{\cancel{C_{T0}}} \frac{F_C}{F_T} \frac{P}{\cancel{P_0}} \frac{\cancel{T_0}}{T}$

$r_A = -k_1 \left[0.2 \frac{F_A}{F_T} P\right]\left[0.2 \frac{F_B}{F_T} P\right]^2 - 2/3 \left[0.2 \frac{F_A}{F_T} P\right]^2 \left[0.2 \frac{F_C}{F_T} P\right]^3 k_2$

$r_B = -2k_1 \left[0.2 \frac{F_A}{F_T} P\right]\left[0.2 \frac{F_B}{F_T} P\right]^2$

$r_C = \left[0.2 \frac{F_A}{F_T} P\right]\left[0.2 \frac{F_B}{F_T} P\right]^2 - k_2 \left[0.2 \frac{F_A}{F_T} P\right]^2 \left[0.2 \frac{F_C}{F_T} P\right]^3$

$r_D = 1/3\, k_2 \left[0.2 \frac{F_A}{F_T} P\right]^2 \left[0.2 \frac{F_C}{F_T} P\right]^3$

$\frac{dF_A}{dW} = r_A = -k_1 \left[0.2 \frac{F_A}{F_T} P\right]\left[0.2 \frac{F_B}{F_T} P\right]^2 - 2/3 \left[0.2 \frac{F_A}{F_T} P\right]^2 \left[0.2 \frac{F_C}{F_T} P\right]^3 k_2$

$\frac{dF_B}{dW} = r_B = -2k_1 \left[0.2 \frac{F_A}{F_T} P\right]\left[0.2 \frac{F_B}{F_T} P\right]^2$

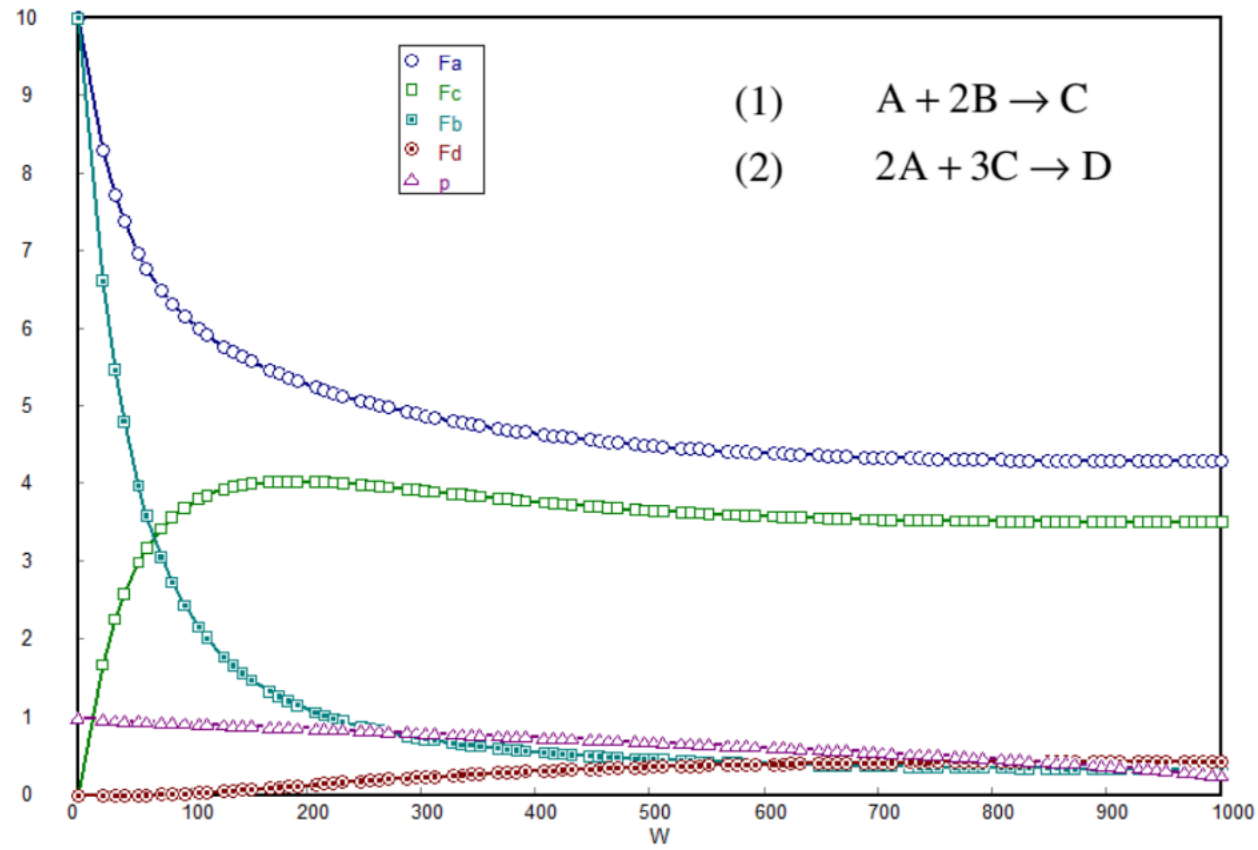
$\frac{dF_C}{dW} = r_C = \left[0.2 \frac{F_A}{F_T} P\right]\left[0.2 \frac{F_B}{F_T} P\right]^2 - k_2 \left[0.2 \frac{F_A}{F_T} P\right]^2 \left[0.2 \frac{F_C}{F_T} P\right]^3$

$\frac{dF_D}{dW} = r_D = 1/3\, k_2 \left[0.2 \frac{F_A}{F_T} P\right]^2 \left[0.2 \frac{F_C}{F_T} P\right]^3$

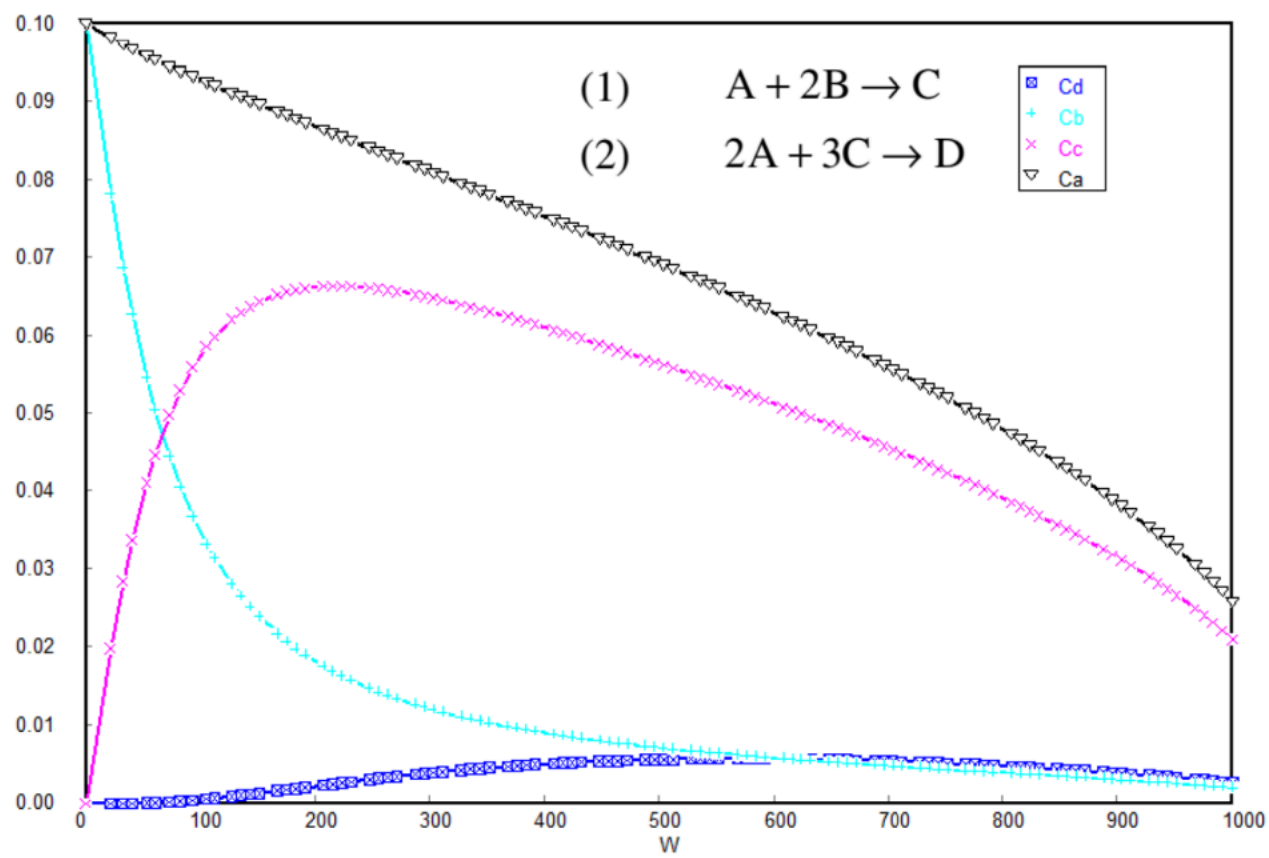
① $\frac{dP}{dW} = -\frac{\alpha}{2P} \frac{F_T}{F_{T0}}$

② $F_T = F_A + F_B + F_C + F_D$

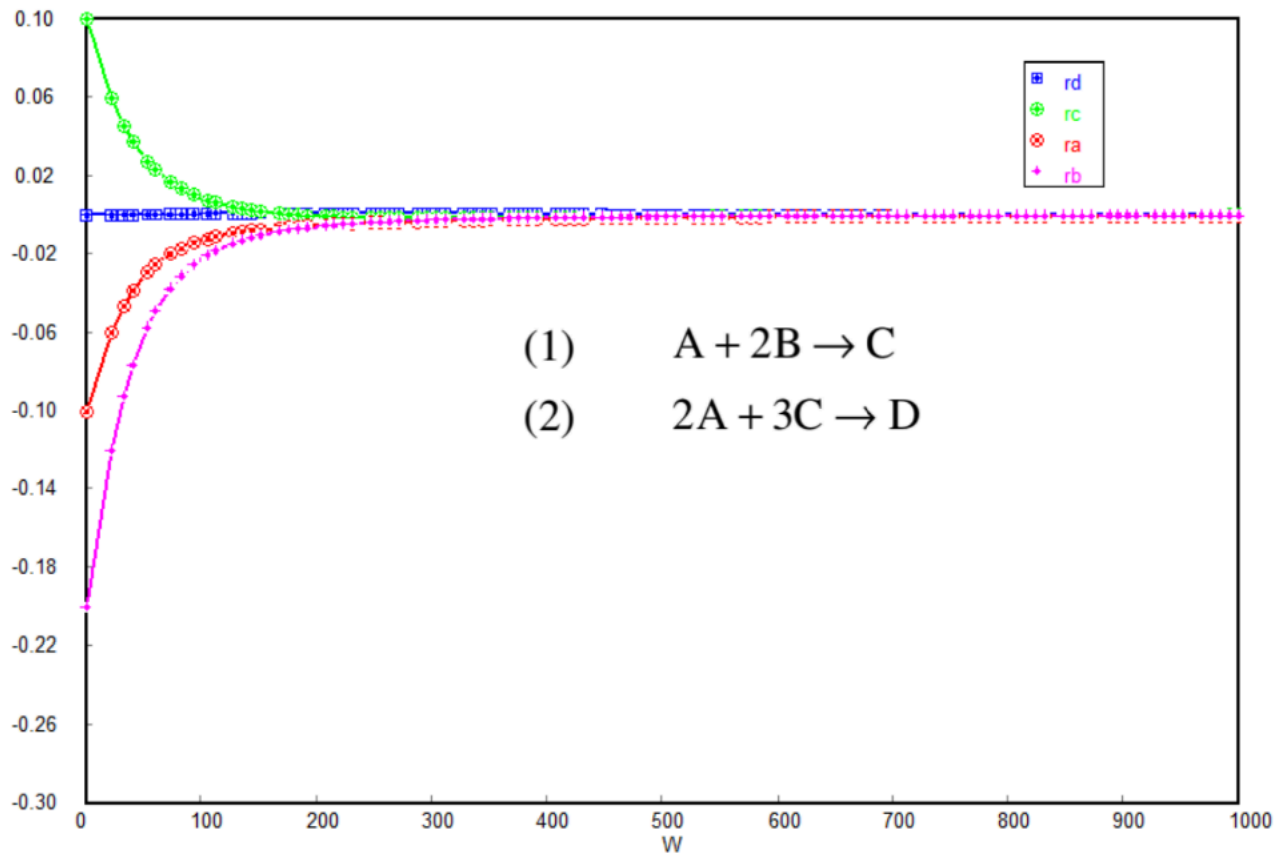
Variation of molar flowrates and pressure drop with weight of catalyst



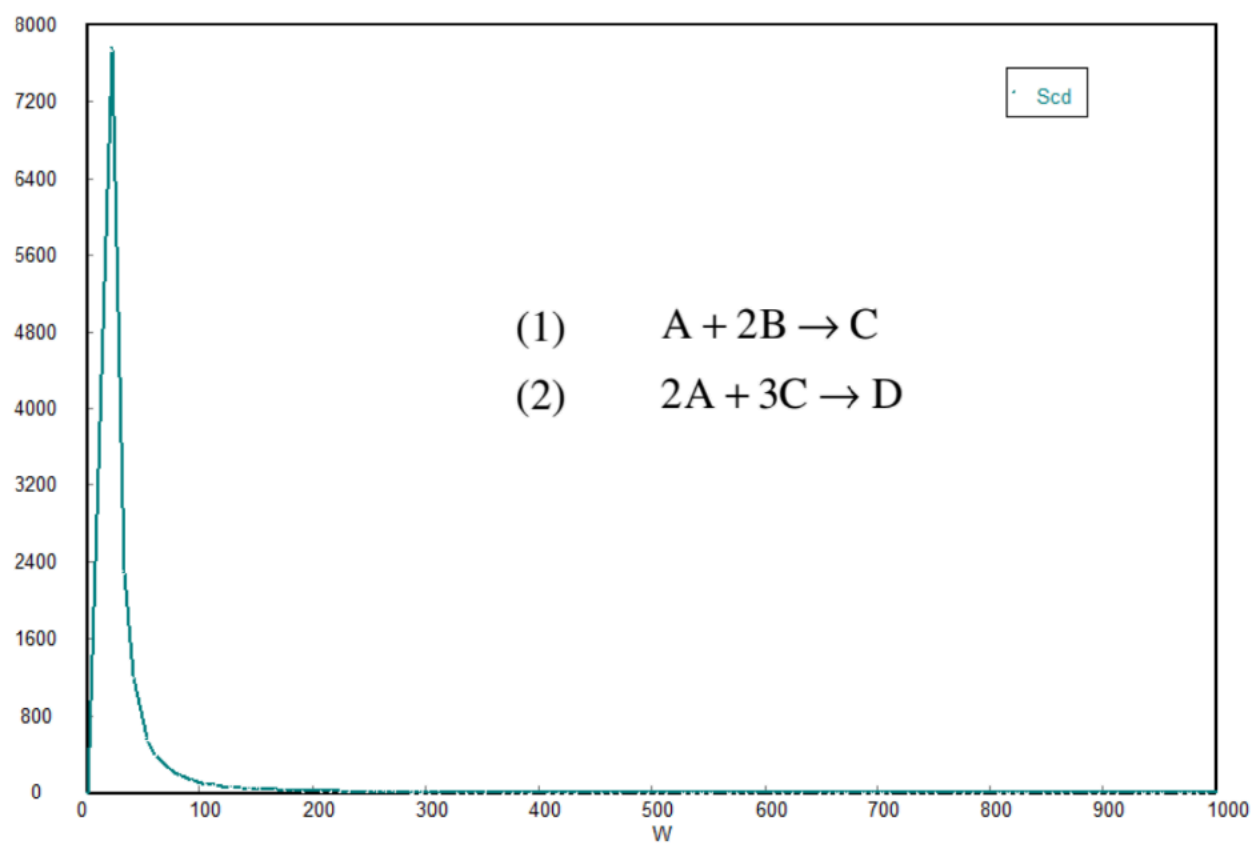
Variation of concentrations with weight of catalyst



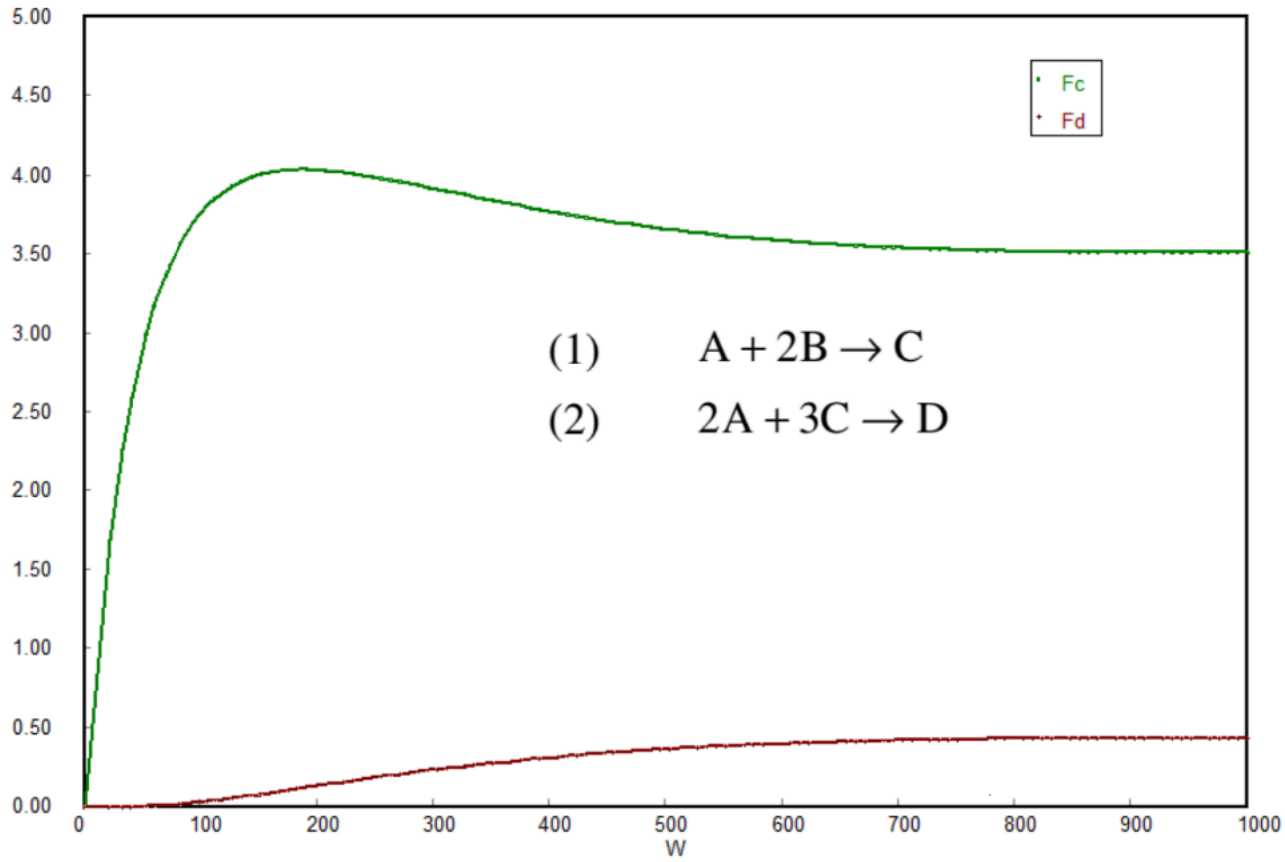
Variation of reaction rates with weight of catalyst



Variation of reaction selectivity with weight of catalyst



Variation of flowrate of desired *C* and non-desired *D* with weight of catalyst

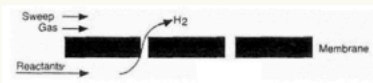


✯ membrane Reactor:

↳ some of Product Diffuse Out

or some of Reactant Diffuse in

- increase ↑ X (when rxn thermodynamically limited)



$$CH_4 + H_2O \leftrightarrow 3H_2 + CO$$

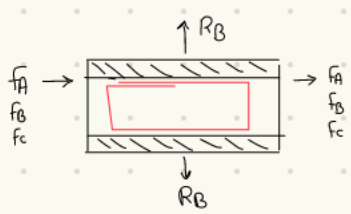
eq rxn → shift rxn to the product.

- ↑ S_D

$$CH_4 + \frac{1}{2}O_2 \leftrightarrow 2H_2 + CO$$

$$CH_4 + 2O_2 \leftrightarrow 2H_2O + CO_2$$

- Pure product



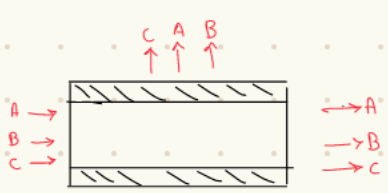
In − out − Out by diffusion + gen = Acc

$$F_B\big|_V - F_B\big|_{V+\Delta V} - R_B\Delta V + r_B\Delta V = 0$$

$$-\frac{\left[F_B\big|_{V+\Delta V} - F_B\big|_V\right]}{\Delta V} - \frac{R_B\Delta V}{\Delta V} + \frac{r_B\Delta V}{\Delta V} = 0$$

$$\frac{dF_B}{dV} = -R_B + r_B$$

✯ we Don't use X in membrane Reactors-



$$X = \frac{F_{A0} - F_A}{F_{A0}}$$

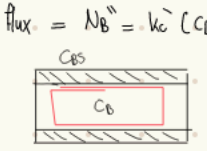
→ A dec → by rxn
↳ Diffusion

$$F_B = F_{A0}(\Theta_B + \nu_B X)$$

✯ Rate of Diffusion R_B.

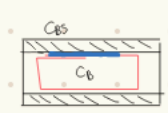
depent on Concentration profile

molar flux $= N_B'' = k_c'(C_B - C_{BS})$



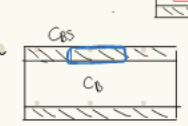
k_c → all Resistance

* tube side D_{BR}



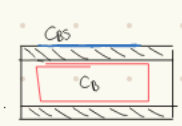
* membrane tself

D_{eff}



* the shell

D_{BS}



$R_B = N_B''\,a$

↳ area of the wall

$$a = \frac{\text{Area}}{\text{Volume}} = \frac{\pi DL}{\frac{\pi D^2 L}{4}} = \frac{4}{D}$$

$R_B = k_c\, a\,[C_B - C_{BS}]$

Assume gas flow very fast $C_{BS} = 0$

$R_B = k_c\, a\, C_B$

Consider the following dehydrogenation reaction : $A \rightleftharpoons B + C$

which is to be carried out, isothermally, in a catalytic membrane reactor (CMR). The equilibrium constant for this reaction is quite small at 227°C (K_c = 0.05 mol/l). The membrane is permeable to B – which is H_2 – but not to A and C. Pure gaseous A enters the reactor at 8.2 atm and 227°C at a rate of 10 mol/min.

Consider the rate of diffusion of B out of the reactor per unit volume of reactor, R_B, to be proportional to the concentration of B (i.e. $R_B = k_c C_B$, where k_c represents the overall mass transfer coefficient). The reactor volume is 400 liters. The specific reaction rate, k, and the transport coefficient, k_c, are:

$k = 0.7\ \text{min}^{-1}$ and $k_c = 0.2\ \text{min}^{-1}$.

(a) Perform differential mole balances on A, B, and C to arrive at a set of coupled differential equations to solve.

(b) Plot the molar flow rates of each species as a function of the reactor volume.

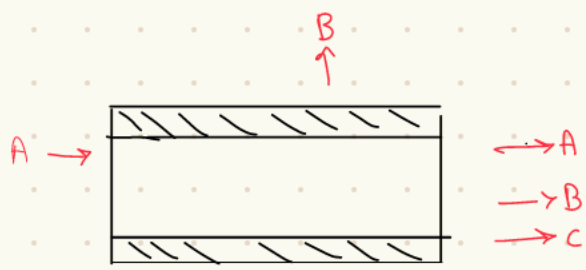
(c) Calculate the conversion at the exit of the reactor.

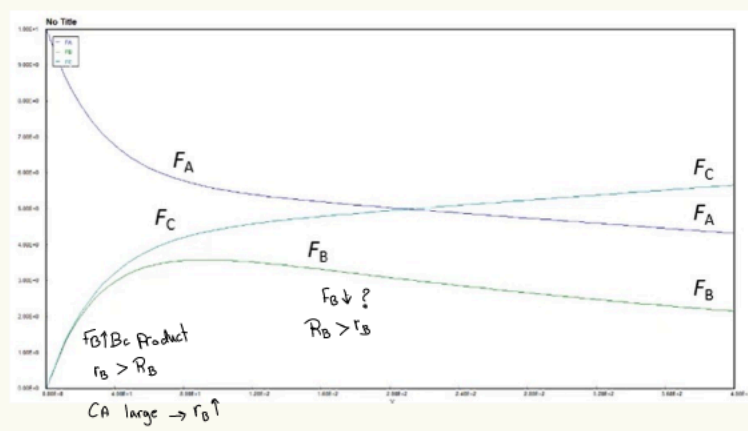
a] mole Balance

$$\frac{dF_B}{dV} = -R_B + r_B$$

$$\frac{dF_A}{dV} = -\cancel{R_A} + r_A$$

$$\frac{dF_C}{dV} = -\cancel{R_C} + r_C$$





C_A large $\rightarrow r_B \uparrow$

C_B small $\rightarrow R_B \downarrow$

* Rate law

$A \rightleftharpoons B + C$

$r_f = k_f C_A$

$r_B = k_B C_B C_C$

$$r_A = -k_f\left(C_A - \frac{C_B C_C}{K_c}\right)$$

$$r_B = k_f\left(C_A - \frac{C_B C_C}{K_c}\right)$$

$$r_C = k_f\left(C_A - \frac{C_B C_C}{K_c}\right)$$

* Concentration

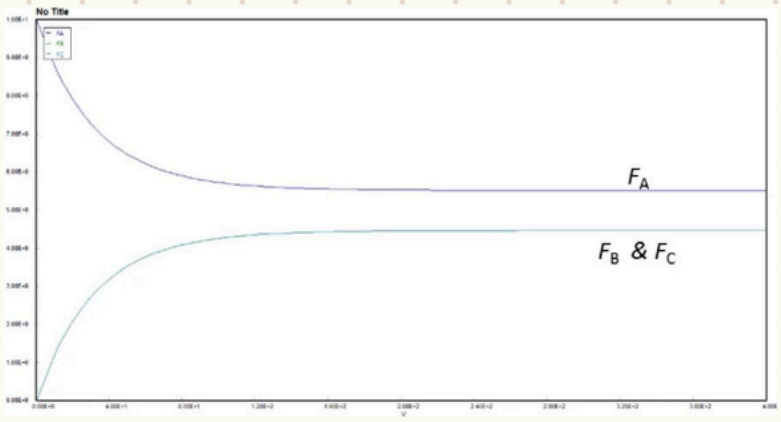
$$C_i = \frac{f_i}{v} = \frac{f_i}{v_0}\frac{F_T^\circ}{F_T}\frac{P}{P_0}\frac{T_0}{T}$$

$$C_i = C_T^\circ \frac{f_i}{F_T}$$

$$C_A = C_T^\circ \frac{F_A}{F_T}$$

$$C_B = C_T^\circ \frac{F_B}{F_T}$$

$$C_C = C_T^\circ \frac{F_C}{F_T}$$



* $F_T = F_A + F_B + F$

* $C_T^\circ \Rightarrow PV = nRT$

$$\frac{P}{RT} = \frac{n}{V}$$

$$\frac{8.2 \times 10^5}{(227+273)(8.314)} = 197.25\ \frac{mol}{m^3}$$

TABLE 6-2. SUMMARY OF RELATIONSHIP FOR MULTIPLE REACTIONS OCCURRING IN A PFR

Mole balances:	$\frac{dF_j}{dV} = r_j$	(6-26)
Rates:		
Relative rates:	$\frac{r_{iA}}{-a_i} = \frac{r_{iB}}{-b_i} = \frac{r_{iC}}{c_i} = \frac{r_{iD}}{d_i}$	(6-16)
Rate laws:	$r_{ij} = k_{ij} f_i(C_1, C_j, C_n)$	
Net laws:	$r_j = \sum_{i=1}^{q} r_{ij}$	(6-17)
Stoichiometry:		
(gas phase)	$C_j = C_{T0} \frac{F_j}{F_T} \frac{P}{P_0} \frac{T_0}{T}$	(3-42)
	$F_T = \sum_{j=1}^{n} F_j$	(6-20)
(liquid phase)	$C_j = \frac{F_j}{v_0}$	(6-19)

* CSTR $F_{j0} - F_j = -r_j V$

$$M + H \longrightarrow X + \cancel{X_e} \qquad -r_{M_1} = k_1 C_H^{1/2} C_M$$
$$X + H \longrightarrow T + \cancel{X_e} \qquad r_{2T} = k_2 C_H^{1/2} C_X$$

$$r_M = -k_1 C_H^{1/2} C_M$$
$$r_H = -k_1 C_H^{1/2} C_M - k_2 C_H^{1/2} C_X$$
$$r_X = -k_2 C_H^{1/2} C_X + k_1 C_H^{1/2} C_M$$
$$r_T = k_2 C_H^{1/2} C_X$$
$$r_{Xe} = k_2 C_H^{1/2} C_X + k_1 C_H^{1/2} C_M$$

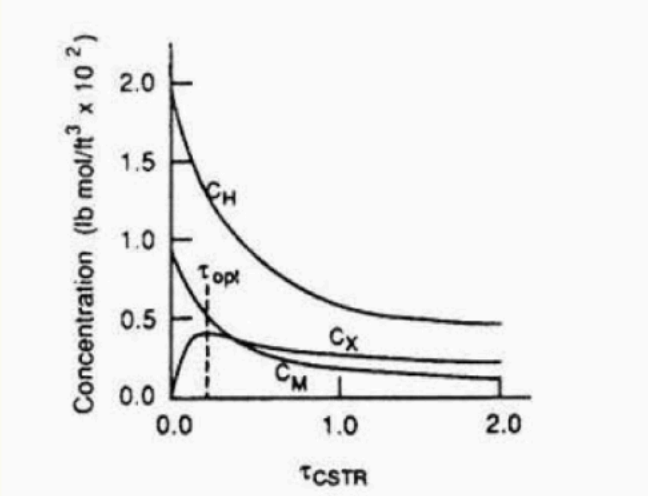
$$v_0 (C_{H0} - C_H) = r_H V \rightarrow (C_{H0} - C_H) = [+k_1 C_H^{1/2} C_M + k_2 C_H^{1/2} C_X]\tau$$
$$v_0 (C_{M0} - C_M) = r_M V \rightarrow (C_{M0} - C_M) = [+k_1 C_H^{1/2} C_M]\tau$$
$$v_0 (C_{X0} - C_X) = r_X V_X \rightarrow (\overset{0}{\cancel{C_{X0}}} + C_X) = [-k_2 C_H^{1/2} C_X + k_1 C_H^{1/2} C_M]\tau$$
$$v_0 (C_{T0} - C_T) = r_T V \rightarrow (\overset{0}{\cancel{C_{T0}}} + C_T) = [k_2 C_H^{1/2} C_X]\tau$$
$$v_0 (C_{Xe0} - C_{Xe}) = r_{Xe} V \rightarrow (\overset{0}{\cancel{C_{Xe0}}} + C_{Xe}) = [k_2 C_H^{1/2} C_X + k_1 C_H^{1/2} C_M]\tau$$

$$f(C_H) = [+k_1 C_H^{1/2} C_M + k_2 C_H^{1/2} C_X]\tau - (C_{H0} - C_H)$$
$$f(C_M) = [+k_1 C_H^{1/2} C_M]\tau - (C_{M0} - C_M)$$
$$f(X) = [-k_2 C_H^{1/2} C_X + k_1 C_H^{1/2} C_M]\tau - (\overset{0}{\cancel{C_{X0}}} + C_X)$$
$$f(T) = [k_2 C_H^{1/2} C_X]\tau - (\overset{0}{\cancel{C_{T0}}} + C_T)$$
$$f(Xe) = [k_2 C_H^{1/2} C_X + k_1 C_H^{1/2} C_M]\tau - (\overset{0}{\cancel{C_{Xe0}}} + C_{Xe})$$

$v = 476$ $\qquad C_{T0} = \frac{P_0}{R T_0} = 0.032$

$V = 238$

$\tau = 0.5$



Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	Ch	0.0089436	4.638E-13	0
2	Cm	0.0029085	1.222E-13	0
3	Cx	0.0031266	-2.196E-13	0

Example 11.3 Multiple liquid-Phase Reactions in a CSTR

The following complex liquid-phase elementary reactions take place isothermally in a 2,500 L CSTR. The feed is equimolar in A and B with F_{A0}= 200 mol/min and the volumetric flow rate is 100 L/min. The total entering concentration is $C_{T0} = 0.2\ mol/L$.

$$(1) \quad A + 2B \rightarrow C \qquad -r'_{1A} = k_{1A} C_A C_B^2$$

$$(2) \quad 2A + 3C \rightarrow D \qquad -r'_{2C} = k_{2C} C_A^2 C_C^3$$

$$k_{1A} = 10\left(\frac{dm^3}{mol}\right)^2 \Big/ min \text{ and } k_{2C} = 15\left(\frac{dm^3}{mol}\right)^4 \Big/ min$$

Find the concentrations of A, B, C, and D exiting the reactor, along with the exiting overall selectivity, $S_{C/D}$.

$A + 2B \rightarrow C \qquad -r_{1A} = k_1 C_A C_B^2$

$2A + 3C \rightarrow D \qquad -r_2 C = k_2 C_A^2 C_c^3$

$\frac{r_{A1}}{-1} = \frac{r_{B1}}{-2} = \frac{r_{C1}}{1}$

$r_A = -k_1 C_A C_B^2$

$r_B = -\frac{1}{2} k_1 C_A C_B^2$

$r_C = k_1 C_A C_B^2$

$\frac{r_A}{-2} = \frac{r_C}{-3} = \frac{r_D}{1}$

$r_C = k_2 C_A^2 C_c^3$

$r_A = -\frac{2}{3} k_2 C_A^2 C_c^3$

$r_D = -\frac{1}{3} k_2 C_A^2 C_c^3$

$v_0 = 100\ dm^3/min$

$k_{1A} = 10\ (dm^3/mol)^2/min$

$k_{2C} = 15\ (dm^3/mol)^4/min$

$V = 2,500\ dm^3$

$C_{A0} = 2.0\ mol/dm^3$

$C_{B0} = 2.0\ mol/dm^3$

$* r_A = -k_1 C_A C_B^2 - \frac{2}{3} k_2 C_A^2 C_c^3$

$* r_B = -\frac{1}{2} k_1 C_A C_B^2$

$* r_C = k_1 C_A C_B^2 + k_2 C_A^2 C_c^3$

$* r_D = -\frac{1}{3} k_2 C_A^2 C_c^3$

$F_{j0} - F_j = -r_j V$

$v\,[C_{j0} - C_j] = -r_j V$

$* [C_{A0} - C_A] = [k_1 C_A C_B^2 + \frac{2}{3} k_2 C_A^2 C_c^3]\tau$

$* [C_{B0} - C_B] = [\frac{1}{2} k_1 C_A C_B^2]\tau$

$* [\cancel{C_{C0}}^{\text{zero}} + C_C] = [k_1 C_A C_B^2 + k_2 C_A^2 C_c^3]\tau$

$* [\cancel{C_{D0}}^{\text{zero}} + C_D] = [-\frac{1}{3} k_2 C_A^2 C_c^3]\tau$

$* F(C_A) = [k_1 C_A C_B^2 + \frac{2}{3} k_2 C_A^2 C_c^3]\tau - [C_{A0} - C_A]$

$* F(C_B) = [\frac{1}{2} k_1 C_A C_B^2]\tau - [C_{B0} - C_B]$

$* F(C_C) = [k_1 C_A C_B^2 + k_2 C_A^2 C_c^3]\tau - C_C$

$* F(C_D) = [-\frac{1}{3} k_2 C_A^2 C_c^3]\tau - C_D$

Nonlinear equations

1 f(Ca) = v*Cao-v*Ca+ra*V = 0
2 f(Cb) = v*Cbo-v*Cb+rb*V = 0
3 f(Cc) = -v*Cc+rc*V = 0
4 f(Cd) = -v*Cd+rd*V = 0

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	Ca	0.5326529	-3.979E-13	2.
2	Cb	0.0848008	8.527E-14	1.
3	Cc	0.1929784	-7.354E-13	1.
4	Cd	0.2548737	2.345E-13	0.1

Results

$* S_{D/U} = \frac{0.19}{0.25} = 0.76$

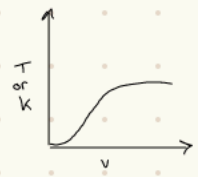
* Adiabatic, nonisothermal $X = 70\%$ Volume = ? PFR:-

$A \longrightarrow B$

① $\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$

② $r_A = -k C_A$

↳ not constant → T not constant.



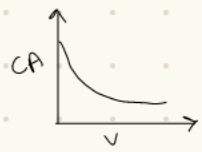
* $k = k_1 \exp\left[\frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T}\right]\right]$

$r_A = -k_1 \exp\left[\frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T}\right]\right] C_A$

③ $C_A = C_{A0}(1-X)$

$r_A = -k_1 \exp\left[\frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T}\right]\right] C_{A0}(1-X)$

$\frac{dX}{dV} = \frac{k_1 \exp\left[\frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T}\right]\right] C_{A0}(1-X)}{F_{A0}}$



system

open: mass ✓, Heat ✓

close: mass ✗, Heat ✓

$Acc = \dot{Q} - \dot{W} + \sum E_i F_i \Big|_{in} - \sum E_i F_i \Big|_{out}$ [J/s]

steady state = 0

↳ for open system.

* $E_i = U_i$ + ~~Potential energy~~ + ~~kinetic energy~~ + ~~other energies~~.

$E_i = U_i$ [internal energy]

* $H_i = U_i + PV_i$

* $\frac{dE}{dt} = \dot{Q} - \dot{W}_s + \sum H_i F_i \Big|_{in} - \sum H_i F_i \Big|_{out}$

* $Q = UA\,\Delta T_{lm}$

* W → shaft work

↳ Flow work → work $= \sum F_i P V_i$

F_i: mole flow rate

V_i: molar volume

$\frac{mol}{s} \Big| \frac{N}{m^2} \Big| \frac{m^3}{mol} = \frac{N\,m}{s} = \frac{J}{s}$ ✓

$F_i = F_{A0}(\Theta_i + \nu_i X)$, $\Theta_i = \frac{F_{i0}}{F_{A0}}$

$\sum H_i F_i = \sum H_i F_{i0} + \sum F_{A0} X \nu_i H_i$

$= \sum H_i F_{i0} + F_{A0} X \underbrace{\sum \nu_i H_i}_{\text{Heat of Rxn}}$

* $\sum F_{i0} H_i^\circ - \sum H_i F_i^\circ - F_{A0} X \sum \nu_i H_i$

$\sum F_i^\circ (H_i^\circ - H_i) - F_{A0} X\, \Delta H_{rxn}(T)$

$Q - W_s + F_{A0} \sum \Theta_i (H_i^\circ - H_i) - \Delta H_{RX} F_{A0} X = 0$ → I can use it with phase change reactor

* ΔH_{rxn}?

$aA + bB \rightarrow cC + dD$

$\Delta H_{rxn} = \frac{d}{a} H_D + \frac{c}{a} H_C - \frac{b}{a} H_B - H_A$

$\Delta H_{rxn}(T) = \left[\frac{d}{a} H_D^\circ + \frac{c}{a} H_C^\circ - \frac{b}{a} H_B^\circ - H_A^\circ\right] + \left[\frac{d}{a} C_{pD} + \frac{c}{a} C_{pC} - \frac{b}{a} C_{pB} - C_{pA}\right](T - T_R)$

* Case 1:- Adiabatic $Q=0$

$$X = \frac{\sum C_p \Theta_i (T-T_0)}{-\Delta H_{rxn}}$$

$$T = T_0 + \frac{-\Delta H_{rxn} X}{\sum \Theta C_{pi}}$$

* Case 2: Variation of temp with conversion for adiabatic T.R:-

$$* \cancel{\frac{dE}{dt}} = -C_p \Theta_i (T-T_0) - \Delta H_{rxn} X$$

$$0 = -C_p \Theta_i (T-T_0) - X \Delta H_{rxn}^\circ + \Delta C_p (T-T_R) X$$

$$0 = -C_p \Theta_i (T-T_0) - X H_{rxn}^\circ - \Delta C_p T X + \Delta C_p T_R X$$

$$+C_p \Theta_i T + \Delta C_p T X = +T_0 C_p \Theta_i - X H_{rxn}^\circ + \Delta C_p T_r X$$

$$T(X \Delta C_p + C_p \Theta_i) = -T_0 C_p \Theta_i - X H_{rxn}^\circ + \Delta C_p T_r X$$

$$T = \frac{-T_0 C_p \Theta_i - X H_{rxn}^\circ + \Delta C_p T_r X}{(X \Delta C_p + C_p \Theta_i)}$$

* Case 3: CSTR with Heat exchange :-

$$\underbrace{\cancel{\frac{dE}{dt}}}_{0} = \dot{Q} - \underbrace{\cancel{\dot{W}_s}}_{0} + \sum H_i F_i \Big|_{in} - \sum H_i F_i \Big|_{out}$$

$$0 = \dot{Q} + \sum H_i F_i \Big|_{in} - \sum H_i F_i \Big|_{out}$$

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

$$0 = -C_p \Theta_i (T-T_0) - X H_{rxn}^\circ - \Delta C_p T X + \Delta C_p T_R X + UA(T_a - T)$$

$$X = \frac{\frac{UA}{F_{A0}}(T-T_a) + \sum \Theta_i C_{pi} (T-T_0)}{-\Delta H_{rxn}^\circ}$$

* Case 4:- Batch and semi-batch, unsteady state CSTR:-

$Acc \neq 0.$

* Batch $F_{in}, F_{out} = 0$

$$\frac{dT}{dt} = \frac{(-r_A V)(-\Delta H_{rxn}) - UA(T-T_A)}{\sum N_i C_{pi}}$$

* semi-batch, unsteady state CSTR

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \sum_{i=1}^{n} F_{i0} C_{P_i}(T - T_{i0}) + [-\Delta H_{Rx}(T)](-r_A V)}{\sum_{i=1}^{n} N_i C_{P_i}}$$

* Case 5:- PFR, PBR with Q:

$$\frac{dT}{dV} = \frac{(\text{Heat "generated"}) - (\text{Heat "removed"})}{\sum F_i C_{P_i}} = \frac{Q_g - Q_r}{\sum F_i C_{P_i}}$$

PFR in terms of conversion

$$\frac{dT}{dV} = \frac{\overbrace{r_A \Delta H_{Rx}(T)}^{Q_g} - \overbrace{Ua(T - T_a)}^{Q_r}}{F_{A0}\left(\sum \Theta_i C_{P_i} + \Delta C_P X\right)} = \frac{Q_g - Q_r}{F_{A0}\left(\sum \Theta_i C_{P_i} + \Delta C_P X\right)}$$

PBR in terms of conversion

$$\frac{dT}{dW} = \frac{r'_A \Delta H_{Rx}(T) - \frac{Ua}{\rho_b}(T - T_a)}{F_{A0}\left(\sum \Theta_i C_{P_i} + \Delta C_P X\right)}$$

$$Q - W_s + F_{A0} \sum \Theta_i (H_i^\circ - H_i) - \Delta H_{Rx} F_{A0} X = 0$$

*Case 1:- Adiabatic $Q=0$

$$\cancel{Q} - \cancel{W_s} + F_{A0} \sum \Theta_i (H_i^\circ - H_i) - \Delta H_{Rx} F_{A0} X = 0$$

$H = C_p \Delta T$ *$C_p \rightarrow$ constant

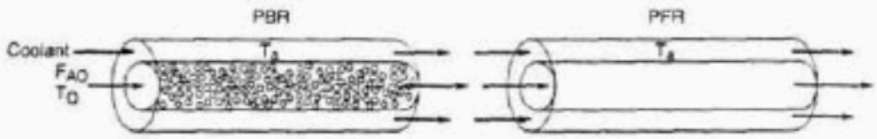
$$F_{A0} \sum \Theta_i C_p (T - T_0) + F_{A0} X \Delta H_{rxn} = 0$$

$$X = \frac{\sum C_p \Theta_i (T - T_0)}{-\Delta H_{rxn}} \qquad T = T_0 + \frac{-\Delta H_{rxn} X}{\sum \Theta C_{pi}}$$

* exo Temp↑, X↑
* endo Temp↓, X↓

TABLE 8-1. ENERGY BALANCES OF COMMON REACTORS (CONTINUED)

3. **PFR/PBR with heat exchange**



3A. **PBR in terms of conversion**

$$\frac{dT}{dW} = \frac{\frac{Ua}{\rho_B}(T_a - T) + r'_A\,\Delta H_{Rx}(T)}{F_{A0}(\Sigma\Theta_i C_{P_i} + \Delta C_P X)} \tag{T8-1.D}$$

3B. **PFR in terms of conversion**

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + r_A \Delta H_{Rx}(T)}{F_{A0}(\Sigma\Theta_i C_P + \Delta C_P X)} \tag{T8-1.E}$$

3C. **PBR in terms of molar flow rates**

$$\frac{dT}{dW} = \frac{\frac{Ua}{\rho_B}(T_a - T) + r'_A\,\Delta H_{Rx}(T)}{\Sigma F_i C_{P_i}} \tag{T8-1.F}$$

3D. **PFR in terms of molar flow rates**

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + r_A \Delta H_{Rx}(T)}{\Sigma F_i C_{P_i}} \tag{T8-1.G}$$

4. **Batch**

$$\frac{dT}{dt} = \frac{(-r_A V)(-\Delta H_{Rx}) - UA(T - T_a)}{\Sigma N_i C_{P_i}} \tag{T8-1.H}$$

5. **For Semibatch or unsteady CSTR**

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_s - \sum_{i=1}^{n} F_{i0}(C_{P_i}(T - T_{i0}) + [-\Delta H_{Rx}(T)](-r_A V))}{\sum_{i=1}^{n} N_i C_{P_i}} \tag{T8-1.I}$$

6. **For multiple reactions in a PFR**

$$\frac{dT}{dV} = \frac{Ua(T_a - T) + \Sigma r_{ij}\Delta H_{Rxij}}{\Sigma F_i C_{P_i}} \tag{T8-1.J}$$

TABLE 8-1. ENERGY BALANCES OF COMMON REACTORS (CONTINUED)

7. **For a variable coolant temperature, T_a**

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_c C_{P_c}} \tag{T8-1.K}$$

These are the equations that we will use to solve reaction engineering problems with heat effects.

[**Nomenclature:** U = overall heat-transfer coefficient, (J/m^2 • s • K); A = CSTR heat-exchange area, (m^2); a = PFR heat-exchange area per volume of reactor, (m^2/m^3); C_{P_i} = mean heat capacity of species i, (J/mol/K); C_{P_c} = the heat capacity of the coolant, (J/kg/K), $\dot{m}_c$ = coolant flow rate, (kg/s); ΔH_{Rx} = heat of reaction, (J/mol); $\Delta H^\circ_{Rx} = \left(\frac{d}{a}H^\circ_D + \frac{c}{a}H^\circ_C - \frac{b}{a}H^\circ_B - H^\circ_A\right)$ J/molA; ΔH_{Rxij} = heat of reaction wrt species j in reaction i, (J/mol); $\dot{Q}$ = heat added to the reactor, (J/s); and $\Delta C_P = \left(\frac{d}{a}C_{P_D} + \frac{c}{a}C_{P_C} - \frac{b}{a}C_{P_B} - C_{P_A}\right)$ (J/molA • K). All other symbols are as defined in

* Calculate ΔH_{rxn} for : at 150 C.

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

$$C_{P_{H_2}} = 6.992 \text{ cal/mol } H_2 \cdot K$$
$$C_{P_{N_2}} = 6.984 \text{ cal/mol } N_2 \cdot K$$
$$C_{P_{NH_3}} = 8.92 \text{ cal/mol } NH_3 \cdot K$$

The enthalpies of formation at 25°C are

$$H^\circ_{NH_3}(T_R) = -11{,}020 \frac{\text{cal}}{\text{mol } NH_3}, \quad H^\circ_{H_2} = 0, \text{ and } H^\circ_{N_2} = 0$$

$$\Delta H_{rxn} = \Delta H_{rxn}^\circ + \Delta C_p (T - T_R)$$

$$\Delta H_{rxn}^\circ = 0 - 0 + 2[-11020] = -22040 \text{ cal/mol } N_2$$

$$\Delta C_p = -6.984 - 3(6.992) + 2[8.92] = -10.12 \text{ cal/mol } N_2 \cdot K$$

$$\Delta H_{rxn} = -22040 - 10.12[423 - 298] = -23310 \text{ cal/} N_2 \text{ mol}$$

$$\Delta H_{rxn} \text{ based on } H_2 \text{ :- } \frac{-23310 \text{ cal}}{\text{mol } N_2} \left| \frac{\text{mol } N_2}{3 \text{ mol } H_2} \right. = -7770 \text{ cal/} H_2 \text{ mol}$$

Example 8–3 Liquid-Phase Isomerization of Normal Butane

Normal butane, C_4H_{10}, is to be isomerized to isobutane in a plug-flow reactor. Isobutane is a valuable product that is used in the manufacture of gasoline additives. For example, isobutane can be further reacted to form iso-octane. The 2004 selling price of *n*-butane was 72 cents per gallon, while the price of isobutane was 89 cents per gallon.

The reaction is to be carried out adiabatically in the liquid phase under high pressure using essentially trace amounts of a liquid catalyst which gives a specific reaction rate of 31.1 h^{-1} at 360 K. Calculate the PFR and CSTR volumes necessary to process 100,000 gal/day (163 kmol/h) at 70% conversion of a mixture 90 mol % *n*-butane and 10 mol % *i*-pentane, which is considered an inert. The feed enters at 330 K.

Temp feed

Additional information:

$\Delta H_{Rx} = -6900$ J/mol · butane, Activation energy = 65.7 kJ/mol

$K_C = 3.03$ at 60°C, $C_{A0} = 9.3$ kmol/dm³ = 9.3 kmol/m³

Butane	*i*-Pentane
$C_{P_{n\text{-}B}} = 141$ J/mol · K	$C_{P_{i\text{-}P}} = 161$ J/mol · K

$C_{P_{i\text{-}B}} = 141$ J/mol · K = 141 kJ/kmol · K

2] $A \rightleftharpoons B$ $\qquad T_0 = 330$

① $F_{A0}\frac{dX}{dV} = -r_A$

② $r_A = k\left[C_A - \frac{C_B}{K_c}\right] \rightarrow C_A = \frac{C_B}{K_c}$

$C_A = C_A^\circ(1-X)$

$C_B = XC_A^\circ$

at eq $\rightarrow r_A = 0$

$C_A = \frac{C_B}{K_c}$

$C_A^\circ(1-X_{eq}) = \frac{XC_A^\circ}{K_c}$

$X_{eq} = \frac{K_c}{1+K_c}$ #

$K_c = K_{c1}\exp\left[\frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T}\right]\right] \rightarrow K_c = 3.03\exp\left[\frac{65700}{8.31}\left[\frac{1}{333} - \frac{1}{T}\right]\right]$

$T = T_0 + \frac{-\Delta H_{rx} X}{\Sigma\Theta C_{pi}}$ $\rightarrow$ Adiabatic

* $T = 330 + \frac{6900}{159}X \rightarrow T = 330 + 43.4X$ >> Linear ☺ #

$\Sigma\Theta C_{pi} = 141 + 161\left[\frac{0.1}{0.9}\right] = 159$

Nonlinear equations

1 f(T) = Kc/(1+Kc)-Xe = 0

Explicit equations

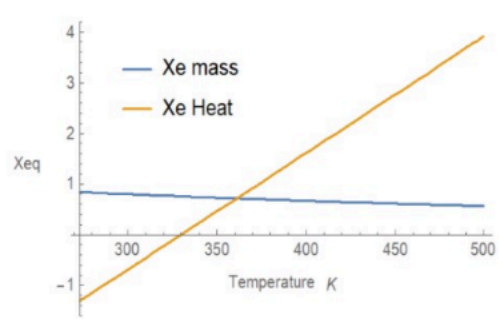
1 Kc = 3.03*exp(-830.3*(T-333)/(333*T))

2 Xe = (T-330)/(43.3)

Calculated values of NLE variables

	Variable	Value	f(x)	Initial Guess
1	T	360.923	-3.331E-16	400. (300. < T < 500.)

	Variable	Value
1	Kc	2.498424
2	Xe	0.714157



$* \; V = \int \frac{F_{A0}}{-r_A} \, dX$ → $\frac{F_{A0}}{-r_A}$ vs X

a. Volume of PFR at 95% of equilibrium conversion

$X = 0.95\, X_e = 0.95(0.714) = 0.68$

$T = 330 + 43.4X$ ⇨ $k = 31.1 \exp\left[7906\left(\frac{T-360}{360T}\right)\right](h^{-1})$ ⇨ $K_C = 3.03 \exp\left[-830.3\left(\frac{T-333}{333T}\right)\right]$

⇨ $-r_A = kC_{A0}\left[1-\left(1+\frac{1}{K_C}\right)X\right]$

X	T (K)	k (h^{-1})	K_C	X_e	$-r_A$(kmol/m^3·h) T, C_{A0}, k_c	$\frac{F_{A0}}{-r_A}$ (m^3)
0	330	4.22	3.1	0.76	39.2	3.74
0.2	338.7	7.76	2.9	0.74	52.8	2.78
0.4	347.3	14.02	2.73	0.73	58.6	2.50
0.6	356.0	24.27	2.57	0.72	37.7	3.88
0.65	358.1	27.74	2.54	0.718	24.5	5.99
0.7	360.3	31.67	2.5	0.715	6.2	23.29

E8-3.1 was constructed. For example, at $X = 0.2$.

(a) $T = 330 + 43.4(0.2) = 338.6$ K

(b) $k = 31.1 \exp\left[7906\left(\frac{338.6-360}{(360)(338.6)}\right)\right] = 31.1 \exp(-1.388) = 7.76 \text{ h}^{-1}$

(c) $K_C = 3.03 \exp\left[-830.3\left(\frac{338.6-333}{(333)(338.6)}\right)\right] = 3.03e^{-0.0412} = 2.9$

(d) $X_e = \frac{2.9}{1+2.9} = 0.74$

(e) $-r_A = \left(\frac{7.76}{\text{h}}\right)(9.3)\frac{\text{mol}}{\text{dm}^3}\left[1-\left(1+\frac{1}{2.9}\right)(0.2)\right] = 52.8 \frac{\text{mol}}{\text{dm}^3\cdot\text{h}} = 52.8 \frac{\text{kmo}}{\text{m}^3\cdot}$

(f) $\frac{F_{A0}}{-r_A} = \frac{(0.9 \text{ mol butane/mol total})(163. \text{ kmol total/h})}{52.8 \frac{\text{kmol}}{\text{m}^3\cdot\text{h}}} = 2.78 \text{ m}^3$

$0 \to 0.7$

$\Delta X = \frac{0-0.7}{5} =$ 5 بين 0 و 0.7 بخطوة زوجي

$0 \to 0.6$

$\Delta X = \frac{0.6}{3}$ → عن طريق الـ Simpson 3/8

$\frac{3}{8}\Delta X\left[f_0 + 3f_1 + 3f_2 + f_3\right]$

$X_0 = 0$ $X_1 = 0.2$ $X_2 = 0.4$ $X_3 = 0.6$

3.74 2.78 2.5 3.88

$V = 1.7595$

$0.6 \to 0.7$

$\Delta X = \frac{0.6-0.7}{2} = 0.05$

$X_1 = 0.6$ $X_2 = 0.65$ $X_3 = 0.7$

3.88 5.99 23.29

$\frac{\Delta X}{3}\left[f_0 + 4f_1 + f_2\right]$

$\frac{0.05}{3}\left[3.88 + 4 \times 5.99 + 23.29\right] = 0.952$

$V = 2.6 \text{ m}^3$

$X = 0.68$ ← $0.95\, X_{eq}$

$\Delta X = \frac{0.68}{2} = 0.34$

$X_0 = 0$ $X_2 = 0.34$ $X_3 = 0.68$

$\frac{0.34}{3}\left[3.73457 + 4 \times 2.49036 + 10.394\right]$

$V = 2.7$

X	T	K	KC	ra	fa/-ra
0	330	4.22383	3.09947	39.2817	3.73457
0.34	344.756	11.7771	2.78303	58.9071	2.49036
0.68	359.512	30.1866	2.52108	14.1139	10.394
2.7302					

$\Delta X = 0.17$

$X_1 = 0$ $X_2 = 0.17$ $X_3 = 0.34$ $X_4 = 0.51$ $X_3 = 0.68$

◆ الصيغة العامة

$$\int_a^b f(x)\,dx \approx \frac{h}{3}\left[f(x_0) + 4f(x_1) + 2f(x_2) + 4f(x_3) + \cdots + 2f(x_{n-2}) + 4f(x_{n-1}) + f(x_n)\right]$$

X	T	K	KC	ra	fa/-ra
0	330	4.22383	3.09947	39.2817	3.73457
0.17	337.378	7.13251	2.93353	51.2118	2.86457
0.34	344.756	11.7771	2.78303	58.9071	2.49036
0.51	352.134	19.0418	2.64608	52.6418	2.78676
0.68	359.512	30.1866	2.52108	14.1139	10.394
2.36383					

* CSTR

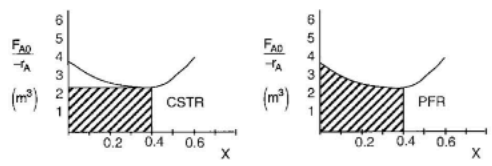
$$V = \frac{F_{A0} \cdot X}{-r_A}$$

X	T	K	KC	ra	fa/-ra
0.4	347.36	13.9862	2.73323	59.0074	2.48613
0.7	360.38	31.8286	2.5071	6.15479	23.8351

$V = 1\ m^3$ at $X = 0.4$

$V = 17 m^3$ at $X = 0.7$

Comparison between size of CSTR and PFR for the given rate of isomerization of n-butane



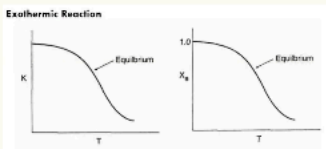
We see that the CSTR volume (1 m³) to achieve 40% conversion in this adiabatic reaction is less than the PFR volume (1.15 m³).

Topic 13:

* X_{eq} ⇒ highest X can achieved

* $A + B \rightleftharpoons C + D + \text{Heat}\uparrow$

shift to the left
$X\downarrow$ $K_c\downarrow$



* $A + B + \text{Heat}\uparrow \rightleftharpoons C + D$

shift to the Right
$X\uparrow$ $K_c\uparrow$

* Adipatic equilibrium conversions.

- $X_{eq} \rightarrow \boxed{K_c}$

$$A \rightleftharpoons B$$

$$K_c = \frac{C_B}{C_A}$$

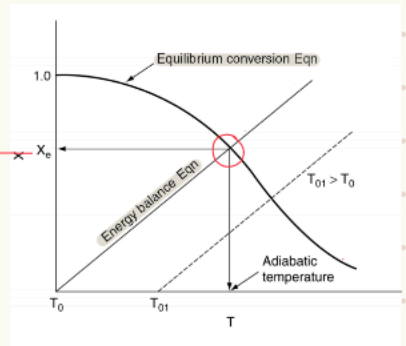
$$K_c = \frac{X_{eq}\, C_A^{\circ}}{C_A^{\circ}(1 - X_{eq})}$$

$$K_c = \frac{X_{eq}}{1 - X_{eq}}$$

$$K_c - X_{eq} K_c = X_{eq}$$

$$\frac{K_c}{1 + K_c} = X_{eq}$$ # → Function of T.

$$X = \frac{\sum C_p\, \Theta_i\, (T - T_0)}{-\Delta H_{rxn}}$$ # energy balance Function of T.

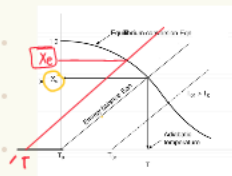


* How we can $X_{eq}\uparrow$?

① change the Reactor

② Add heat exchanger exo therm → cooler

③ Change the Feed Temp.



Example 13.1: Adiabatic Equilibrium Temperature

For the elementary liquid-phase reaction takes place in an adiabatic CSTR, determine the adiabatic equilibrium temperature and conversion when pure A is fed to the reactor at a temperature of 300 K. What is the CSTR volume necessary to achieve 90% of the adiabatic equilibrium conversion for $v_o = 5\ L/min$?

$$A \rightleftharpoons B$$

$$\frac{K_c}{1+K_c} = X_{eq}$$

$$\Delta H_{rxn}(T) = \left[\frac{d}{a}H_D^\circ + \frac{c}{a}H_C^\circ - \frac{b}{a}H_B^\circ - H_A^\circ\right] + \left[\frac{d}{a}C_{pd} + \frac{c}{a}C_{pc} - \cancel{\frac{b}{a}C_{pb}}^{\,0} - C_{pa}\right](T - T_R)$$

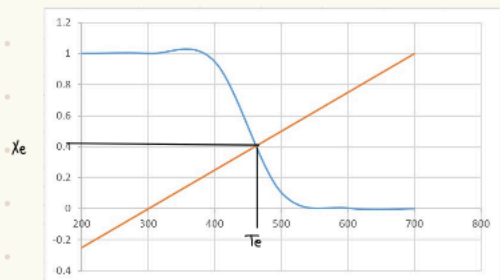
$$\Delta H_{rxn} = -60 \times 10^3 + 40 \times 10^3 = -20 \times 10^3$$

$$K_c = K_{c1} \exp\left[\frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T}\right]\right]$$

$$K_c = 100\,000 \exp\left[\frac{-20 \times 10^3}{1.987}\left[\frac{1}{298} - \frac{1}{T}\right]\right] \qquad \boxed{R = cal/K}$$

$$X = \frac{\sum C_p \Theta_i (T - T_0)}{-\Delta H_{rxn}}$$

$$X = \frac{50}{+20 \times 10^3}(T - 300) = 2.5 \times 10^{-3}(T - 300)$$



$T_e = 470$

$X_e = 0.42$

$* \ 90\% \ X_e = 0.42$

$$\boxed{X = 0.378}$$

$$X = \frac{\sum C_p \Theta_i (T - T_0)}{-\Delta H_{rxn}}$$

$$0.378 = \frac{50}{+20 \times 10^3}(T - 300)$$

$$T = 451.2\ K$$

$$* \quad V = \frac{v_o C_A^\circ X}{r}$$

$$r_A = k_f\left[C_A - \frac{C_B}{K_c}\right]$$

$$k_f = 10^{-3} \exp\left[\frac{10^4}{1.987}\left[\frac{1}{298} - \frac{1}{451.2}\right]\right] = 0.31$$

$$K_c = 1.05$$

$$C_A = C_A^\circ(1 - X)$$

$$C_B = X C_A^\circ$$

$$r_A = 0.31\left[(1 - 0.378) - \frac{0.378}{1.05}\right] = 0.681$$

$$V = \frac{0.378 \times 5}{0.681} = 23\ dm^3$$

Solution

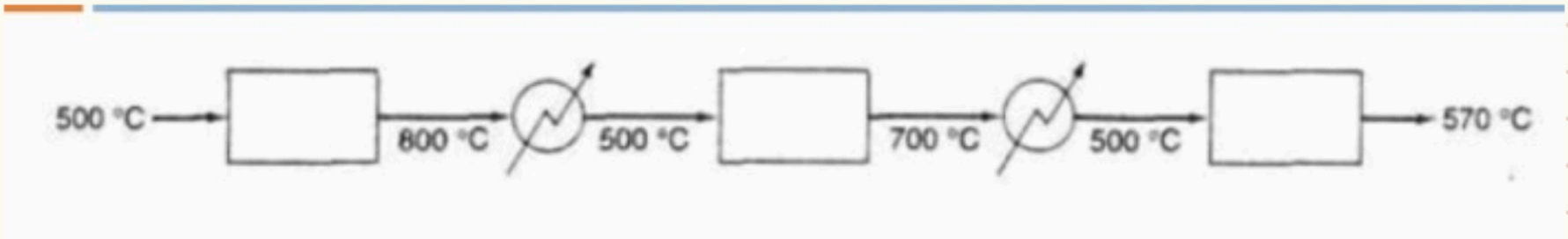
$$A \rightleftharpoons B$$

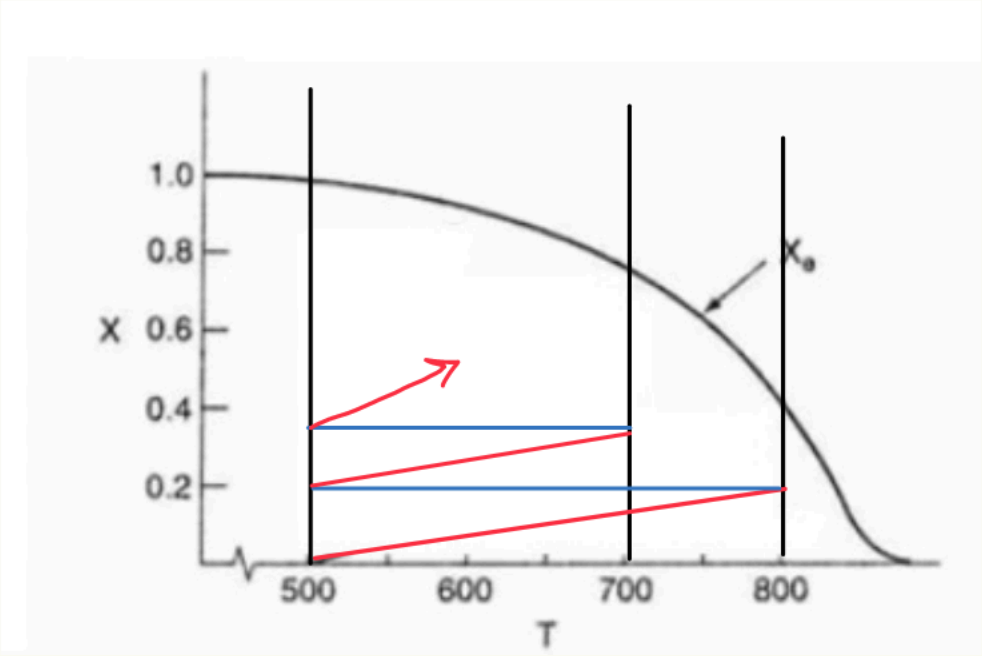
$$H_A^\circ(298\ K) = -40{,}000\ cal/mol \qquad H_B^\circ(298\ K) = -60{,}000\ cal/mol$$

$$C_{P_A} = 50\ cal/mol \cdot K \qquad C_{P_B} = 50\ cal/mol \cdot K$$

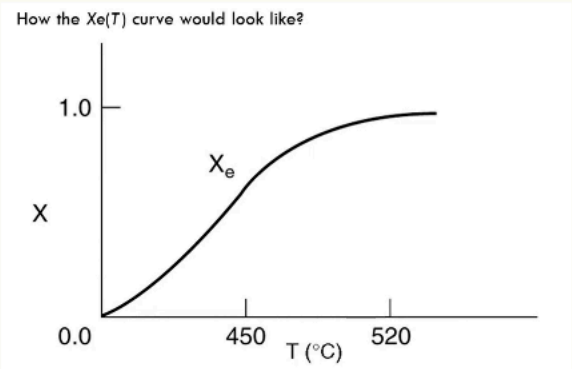
$$K_e = 100{,}000 \text{ at } 298\ K,\ k = 10^{-3}\exp\left(\frac{E}{R}\left(\frac{1}{298} - \frac{1}{T}\right)\right)\min^{-1} \text{ with } E = 10{,}000\ \frac{cal}{mol}$$

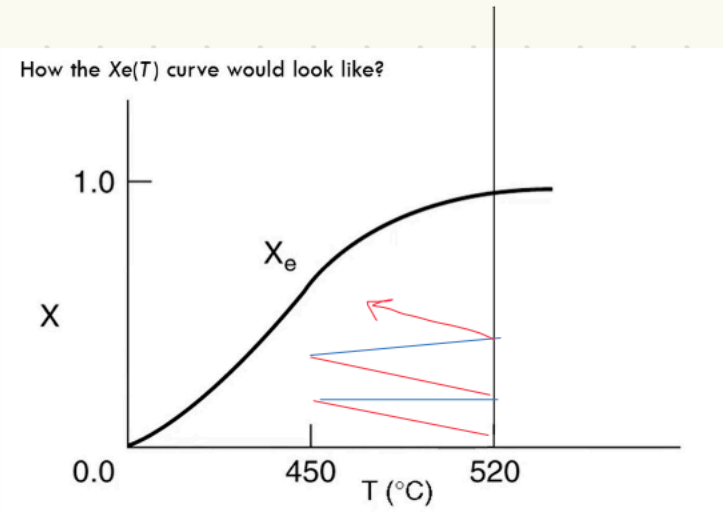
* Interstage cooling or Heating





* endothermic





* CSTR (well mixed)

with heat effect → to calculate Q → to ↓ Temp.
→ to calculate T → at given Q.

$$0 = \dot{Q} - \dot{W}_s - \Delta H$$

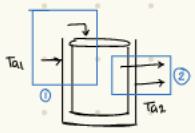
$$\dot{Q} - \dot{W}_s = F_{A0} \sum \Theta_i C_p (T - T_0) + F_{A0} X \, \Delta H_{rxn}(T)$$

$$F_{A0} X = -r_A V \rightarrow \text{D. eq.}$$

$$\dot{Q} - \dot{W}_s = F_{A0} \sum \Theta_i C_p (T - T_0) + (-r_A) V \, \Delta H_{rxn}(T)$$

$$Q = UA \, \Delta T_{lm}$$

$$\Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln(\Delta T_1 / \Delta T_2)}$$



* high rate flow coolant

$T_{a1} \approx T_{a2} \rightarrow T_a$

$Q = UA(T_a - T)$ Q from reactor

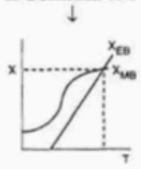
$Q_c = \dot{m}_c C_{pc} (T_{a2} - T_{a1})$ Q transferred from coolant

$\dot{m}_c$ ✓
T_{a1} ✓ } How to calculate T_{a2} → from Q (heat transfer into the coolent)

* $Q_{reactor} = -Q_{coolent}$

* $T_{a2} = T - (T - T_{a1}) \exp\left[\frac{-UA}{\dot{m}_c C_p}\right]$

Ways to specify the sizing of a CSTR

A	B	C
Specify X Find V and T ↓ Calculate T From Eqn. (8-56) ↓ Calculate k $k = Ae^{-E/RT}$	Specify T Find X and V ↓ Calculate X From Eqn. (8-55) ↓ Calculate k $k = Ae^{-E/RT}$	Specify V Find X and T ↓ Use Eqn. (8-55) to plot X_{EB} vs. T ↓ Solve Eqn. (8-53) for $X_{MB} = f(T)$ to find X_{MB} vs. T (e.g., $X_{MB} = \frac{\tau A \exp[-E/(RT)]}{1 + \tau A \exp[-E/(RT)]}$)
(e.g., $-r_A = kC_{A0}(1 - X)$)	(e.g., $-r_A = kC_{A0}(1 - X)$)	
↓ Calculate $-r_A(X,T)$ ↓ Calculate V $V = \frac{F_{A0}X}{-r_A}$	↓ Calculate $-r_A(X,T)$ ↓ Calculate V $V = \frac{F_{A0}X}{-r_A}$	↓ Plot X_{EB} and X_{MB} as a function of T ↓ 

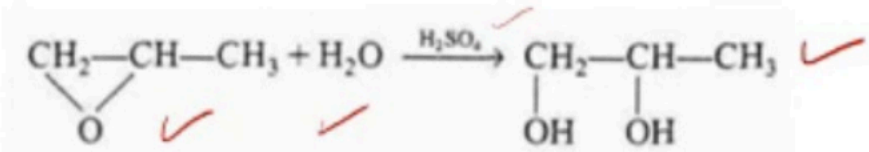
X_{MB} = conversion calculated from the mole balance
X_{EB} = conversion calculated from the energy balance

Case 1:- $X \xrightarrow{E.B} T \rightarrow k \longrightarrow r_A \xrightarrow{M.B} V$

Case 2:- $T \xrightarrow{E.B} X$, $T \rightarrow k$ } $r_A \xrightarrow{M.B} V$

Case 3:- V solved EB, MB eq.

Propylene glycol is produced by the hydrolysis of propylene oxide:



Over 800 million pounds of propylene glycol were produced in 2004 and the selling price was approximately $0.68 per pound. Propylene glycol makes up about 25% of the major derivatives of propylene oxide. The reaction takes place readily at room temperature when catalyzed by sulfuric acid.

You are the engineer in charge of an adiabatic CSTR producing propylene glycol by this method. Unfortunately, the reactor is beginning to leak, and you must replace it; you told your boss several times that sulfuric acid was corrosive and that mild steel was a poor material for construction. There is a nice-looking overflow CSTR of 300-gal capacity standing idle; it is glass-lined; and you would like to use it.

Thermo data (from Handbook of Chemistry & Physics):

Prop.\Species	MeOH (M)	PO (A)	H_2O (B)	PG (C)
$\Delta H^\circ_{f,i}$ (528°R) [Btu/lbmol]		-66,600	-123,000	-226,000
$C_{p,i}$ [Btu/lbmol·°F]	19.5	35	18	46

* $A + B \rightarrow C$

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

* $-r_A = kC_A$

* $C_A = C_{A0}(1-X)$

* $V = \frac{v_0 X}{k(1-X)} \rightarrow \tau = \frac{X}{k(1-X)}$ $\quad \tau k = \frac{X}{1-X}$

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

$\frac{1+\tau k}{\tau k} = \frac{1}{X} \quad \boxed{X = \frac{\tau k}{1+\tau k} \ \#} \rightarrow X, T$ unknown

$\tau = V/v = 40.1 / 326.34 = 0.12$

$k = 16.96 \times 10^{12} \exp -32400/RT$

$\Delta H_{rxn}(T_R) = +666\times10^2 + 123\times10^3 - 226\times10^3 =$

$\Delta C_p = -35 - 18 + 46 = -7$ Btu/lbmol.F°

$\Delta H_{rxn}(T) = -36400 - 7(T - 528_R)$

$\Sigma \Theta_i C_{pi}$

$1(35) + (19.5)_m \frac{71.87}{43.04} + (18)_B \frac{802.8}{43.04} + (46)_c \frac{0}{43.04} \leftarrow F_{c0}$

$\Sigma \Theta_i C_{pi} = 403.3$

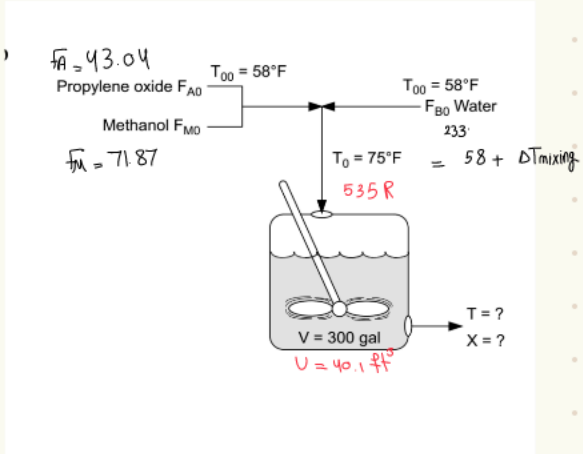
* $Q - \cancel{W_s}^{0} = F_{A0} \Sigma \Theta_i C_p (T - T_0) + F_{A0} X \Delta H_{rxn}(T)$

1. Can you use a CSTR as a replacement for the leaking one if it will be operated adiabatically? If so, what will be the conversion of propylene oxide to glycol? heat generated

* mixing Point

$v_0 = v_{0A} + v_{0B} + v_{0M}$

$46.62 + 46.62 + 233.1 = 326.34$

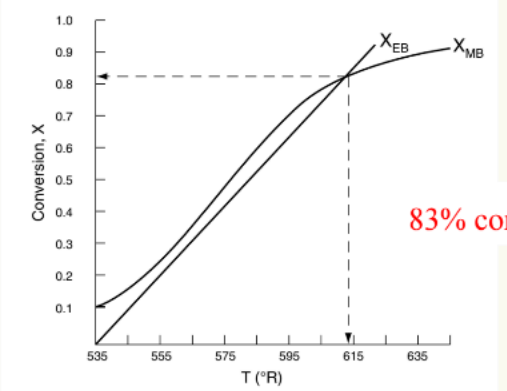


a] Adiabatic

$\frac{\cancel{Q} + F_{A0} \Sigma \Theta_i C_p (T - T_0)}{-\Delta H_{rxn} F_{A0}} = X$

$X = \frac{403.3 \times (T - 535)}{36400 - 7(T - 528_R)}$ ——— ②

$X = \frac{0.12 [16.96 \times 10^2 \exp -32400/1.987T]}{1 + 0.12 [16.96 \times 10^2 \exp -32400/1.987T]}$ ——— ①



83% conversion and 613 R. > 584 ⓗ

Propylene oxide is a rather low-boiling-point substance. With the mixture you are using, you feel that you cannot exceed an operating temperature of 125 F, or you will lose too much oxide by vaporization through the vent system. 584.67 R

2. If a cooling coil with 40 ft^2 surface is used to remove the excess heat using a large amount of cooling-water flow rate at temperature of 85 °F can be maintained. A typical overall heat-transfer coefficient for such a coil is 100 Btu/h. ft^2.F. Will the reactor satisfy the previous constraint of 125 °F maximum temperature if the cooling coil is used?

$$X Q - \cancel{W_s}^{0} = F_{A0} \sum \Theta_i C_p (T - T_0) + F_{A0} X \Delta H_{rxn}(T)$$

$$Q = UA(T_a - T) \rightarrow \frac{100\ \text{BTU}}{\text{h.ft}^2\text{F}} \times 40\ \text{ft}^2 \times (545 - T)$$

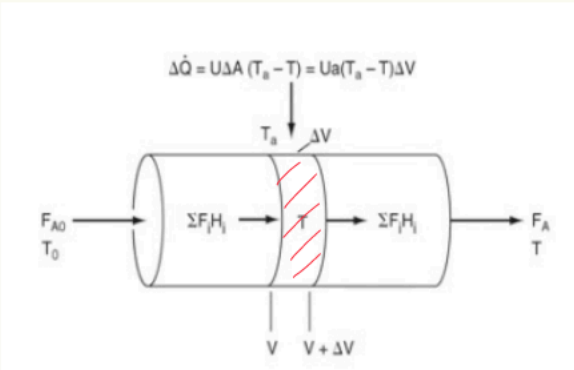
$$X = \frac{Q - F_{A0} \sum \Theta_i C_p (T - T_0)}{F_{A0}\ \Delta H_{rxn}}$$

$$X = \frac{100 \times 40\,(545 - T) - 43.04\,(403.3)\,(T - 535)}{43.04\,(-36400 - 7(T - 528))} \quad \text{— ②}$$

$T = 564$. $X = 0.36$ → lower X.

$\hookrightarrow 564 < 584$ ✓

$$X = \frac{0.12\,[16.96 \times 10^{12} \exp -32400/1.987T]}{1 + 0.12\,[16.96 \times 10^{12} \exp -32400/1.987\,T]} \quad \text{— ①}$$



energy balance :-

in − out = $\frac{dE}{dt}$

$\Sigma F_i \Delta H\big|_V - \Sigma F_i \Delta H\big|_{V+\Delta V} + \Delta Q = 0$ → steady state

$-\left(\Sigma F_i \Delta H\big|_{V+\Delta V} - \Sigma F_i H_i\big|_V\right) + Ua(T_a - T)\Delta V = 0$

$-\frac{d\Sigma F_i H_i}{dV} + Ua(T_a - T) = 0.$

$\frac{d F_i H_i}{dV} \longrightarrow F_i \frac{dH_i}{dV} + H_i \frac{dF_i}{dV}$

$\frac{dF_i}{dV} = r_i \longrightarrow \frac{dF_i}{dV} = \nu_i \cdot r_A$ $\boxed{\frac{r_A}{-1} = \frac{r_i}{\nu_i}}$

$dH_i = C_{pi}\, dT$

$* \Sigma F_i C_{pi} \frac{dT}{dV} + H_i \nu_i (-r_A)$

$-\Sigma\left(F_i C_{pi} \frac{dT}{dV} + H_i \nu_i (-r_A)\right) + Ua(T_a - T) = 0.$

$-\frac{dT}{dV} \Sigma F_i C_{pi} + r_A \Sigma H_i \nu_i$

↳ H_{RXN}

$r_A \Delta H_{rxn} - \frac{dT}{dV} \Sigma F_i C_{pi} + Ua(T_a - T) = 0$

$-\frac{r_A - \Delta H_{RXN} + Ua(T_a - T)}{\Sigma F_i C_{pi}} = \frac{dT}{dV}$

* exothermic, with cooling :

$-r_A - \Delta H_{RXN}$ ⇒ Heat Generated (+)(+)

$T_a < T$ $Ua(T_a - T)$ ⇒ Q Heat Removed ⊖

* endothermic with heating

$-r_A - \Delta H_{RXN}$ ⇒ Heat Absorbed (+)(−)

$T_a > T$ $Ua(T_a - T)$ ⇒ Q Heat transfer ⊕

- Coolent , heating mediums :-
- T_a → constant → when it does not ?

$m_c C_{pc}(T_{a1} - T_{a0}) = Q$ $\frac{Q}{m_c C_{pc}} = \Delta T$

when = 0 ?

* heat capacity >> heat transfer ⇝ $\Delta T = 0$

↳ m_c ↑↑

- if T_a not constant :-

Case A :- Co current :-

in − out = $\cancel{acc}$

$0 = \Delta Q + m_c H\big|_V - m_c H_c\big|_{V+\Delta V}$

$0 = Ua(T - T_a)\Delta V - \left(m_c H_c\big|_{V+\Delta V} - m_c \Delta H_c\big|_V\right) = 0$

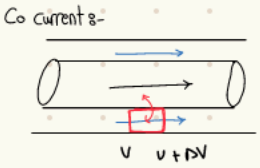
$0 = Ua(T - T_a) - \frac{d(m_c H_c)}{dV}$ (constant) $dH = C_p\, dT_a$

$0 = Ua(T - T_a) - m_c C_p \frac{dT_a}{dV}$

$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{m_c C_{pc}}$

@ $V = 0$ $T_a = T_{a0}$. ✓

* Co current :-

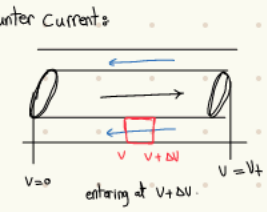


Case B :- Counter current :-

$0 = Ua(T - T_a)\Delta V + \left(m_c H_c\big|_{V+\Delta V} - m_c \Delta H_c\big|_V\right) = 0$

$\frac{Ua(T_a - T)}{m_c C_p} = \frac{dT_a}{dV}$

* Counter current :



Example 14.2: Isomerization of an exothermic reaction of n-butane to i-butane in non-isothermal, non-adiabatic PFR

The isomerization of n-butane is an elementary, reversible and exothermic reaction that is carried out in the liquid phase PFR under high pressure using essentially trace amounts of a liquid catalyst. It gives a specific reaction rate of 31.1 h^{-1} at 360 K. The feed enters the reactor at 305 K. The coolant media enters at 315 K with $\dot{m}_c = 500\ kg/h$ and heat capacity of $C_{pc} = 28\ kJ/kg.K$.

$$n\text{-}C_4H_{10} \rightleftharpoons i\text{-}C_4H_{10}$$

dditional information:

$\Delta H_{Rx} = -34{,}500$ kJ/kmol $\qquad Ua = 5{,}000$ kJ/m³·h·K.

$C_{A0} = 1.86$ kmol/m³ $\qquad F_{A0} = 14.7$ kmol A/h

Butane: $C_{P_{n\text{-}B}} = 141$ J/mol·K

i-Pentane: $C_{P_{i\text{-}P}} = 161$ J/mol·K

$C_{P_{i\text{-}B}} = 141$ J/mol·K = 141 kJ/kmol·K

$A \rightleftharpoons B$

$k = 31.1$ at 360k $\qquad k_c = 3.03 \exp\left[-830.3\left[\frac{T-333}{333T}\right]\right] \qquad F_{A0} = 14.67$

$T_0 = 305$

$T_{a1} = 315 \quad \dot{m}_c = 500, \ C_{pc} = 28.$

$U_a = 5000$

① $\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$

$-r_A = -k\left[C_A - \frac{C_B}{k_c}\right]$

$* \ C_A = C_{A0}(1-X)$

$* \ C_B = C_{A0} \cdot X.$

$-r_A = k C_{A0}\left[1 - \left[1 + \frac{1}{k_c}\right] X\right]$

$* \ k_c = 3.03 \exp\left[-830.3\left[\frac{T-333}{333T}\right]\right]$

$* \ k = 31.1 \exp\left[7906\left[\frac{T-360}{360T}\right]\right]$

① $X_{eq} = \frac{k_c}{1+k_c}$

$* \ k_c = 3.03 \exp\left[-830.3\left[\frac{T-333}{333T}\right]\right]$

② $\frac{dT}{dV} = \frac{r_A \Delta H_{rxn} - U_a(T - T_a)}{F_{A0} \sum \Theta_i C_{pi}}$

$$\frac{k C_{A0}\left[1 - \left[1 + \frac{1}{k_c}\right] X\right] - 5000(T - T_a)}{14.67}$$

$\frac{dT_a}{dV} = \frac{U_a(T - T_a)}{\dot{m}_c C_p} \longrightarrow \frac{5000(T - T_a)}{5000(28)}$

Differential equations

1 d(Ta)/d(V) = Ua*(T-Ta)/m/Cpc
2 d(X)/d(V) = -ra/Fa0
3 d(T)/d(V) = ((ra*deltaH)-Ua*(T-Ta))/Cpo/Fa0

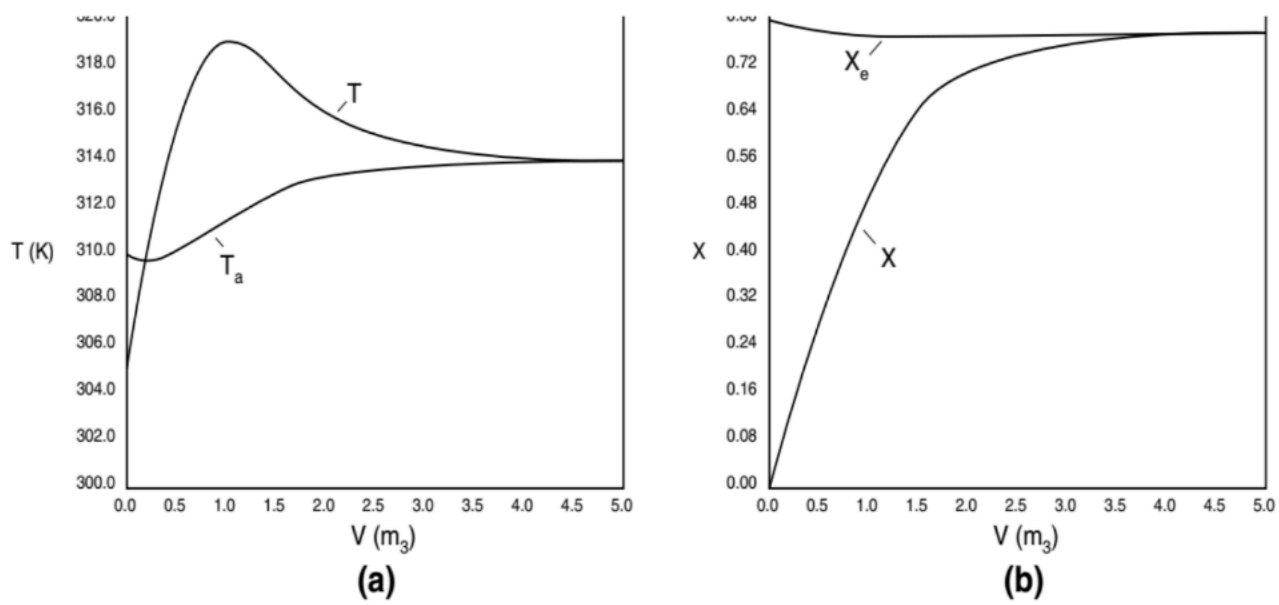
Explicit equations

1 Cpc = 28
2 m = 500
3 Ua = 5000
4 Ca0 = 1.86
5 Fa0 = 0.9*163*.1
6 deltaH = -34500
7 k = 31.1*exp((7906)*(T-360)/(T*360))
8 Kc = 3.03*exp((deltaH/8.314)*((T-333)/(T*333)))
9 Xe = Kc/(1+Kc)
10 ra = -k*Ca0*(1-(1+1/Kc)*X)
11 Cpo = 159
12 rate = -ra

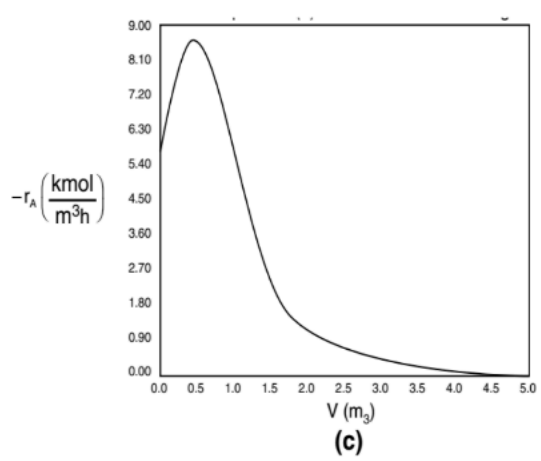
Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	Ca0	1.86	1.86	1.86	1.86
2	Cpc	28.	28.	28.	28.
3	Cpo	159.	159.	159.	159.
4	deltaH	-3.45E+04	-3.45E+04	-3.45E+04	-3.45E+04
5	Fa0	14.67	14.67	14.67	14.67
6	k	0.5927441	0.5927441	63.21931	6.80861
7	Kc	9.512006	0.8200563	9.512006	2.641246
8	m	500.	500.	500.	500.
9	ra	-1.102504	-24.31058	-0.1181808	-0.1181808
10	rate	1.102504	0.1181808	24.31058	0.1181808
11	T	305.	305.	372.0171	336.7102
12	Ta	315.	314.5286	335.6949	335.6949
13	Ua	5000.	5000.	5000.	5000.
14	V	0	0	5.	5.
15	X	0	0	0.7185996	0.7185996
16	Xe	0.9048707	0.4505664	0.9048707	0.7253687

Variation of T and X vs V in exothermic, non-isothermal, non-adiabatic isomerization reaction with co-current heat exchange



Effect of reactor volume on rate of isomerization of n-butane in exothermic, non-isothermal, non-adiabatic reaction with co-current heat exchange



Topic 15 : $\boxed{\text{unsteady state}}$

$\hookrightarrow \frac{dE}{dt} \neq 0$

* Energy Balanc on Batch Reactor adipatic

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

* $X = \frac{\sum \Theta_i C_{pi} (T - T_0)}{-\Delta H_{rxn}}$ or $T = T_0 + \frac{[-\Delta H_{rxn}(T_r)] X}{\sum \Theta_i C_{pi} + X_b C_p}$

* Energy Balanc on Batch Reactor Heat Exchanger

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

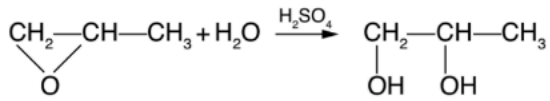
* $\frac{dT}{dt} = \frac{\dot{Q}_g - \dot{Q}_r}{N_{A0} C_{ps}}$

* $\dot{Q}_r = m_c C_{pc} \left[(T - T_a) \left[1 - \exp\left[\frac{-UA}{m_c C_p} \right] \right] \right]$

* $\dot{Q}_g = (-r_A V)(-\Delta H_{rxn})$

Example 15.1 Unsteady state batch reactor with heat exchange

Suppose a batch reactor is used for the production of propylene glycol from hydrolysis of propylene oxide according



$$A + B \longrightarrow C$$

The reactor is charged with 4 L of ethylene oxide, 4 L of methanol, and 10 L of water containing 0.1 wt % H_2SO_4. The concentration of pure ethylene oxide and methanol are 13.7 mol/L and 24.7 mol/L respectively. The initial temperature of all materials after mixing is 286 K (13˚C).

If the reactor temperature increases above 350 K (77˚C), a secondary, more exothermic reaction will take over, causing runaway and subsequent explosion. The coolant enters at 290 K (17˚C) and the flow rate through the exchanger is 10 g/s.

$$\Delta H_{R_X} = -20{,}202 \text{ cal/mol}, \; C_{P_A} = 35 \text{ cal/mol/K}, \; C_{P_B} = 18 \text{ cal/mol/K},$$
$$C_{P_C} = 46 \text{ cal/mol/K, and } C_{P_M} = 19.5 \text{ cal/mol/K}.$$

$A + B \rightarrow C$

$V_A = 4L$

$V_M = 4L$

$V_W = 10L$

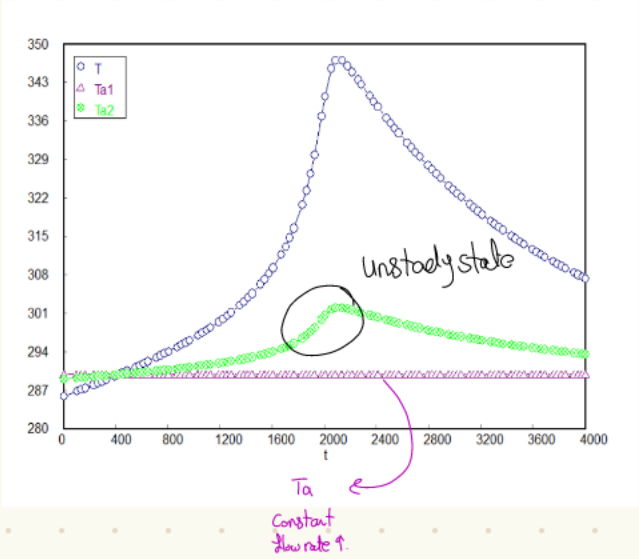
$C_{A^\circ} = 13.7$

$C_{M^\circ} = 24.7$

$T_0 = 287K$

$F_a = 10 g/s \quad T_a = 290$

$UA = 10$



* number of mols.

$13.7 \frac{mol}{L} \times 4 = N_{A_0} = 54.8$

$24.7 \frac{mol}{L} \times 4 = N_{M_0} = 98.8$

$55.55 \frac{mol}{L} \times 10 = N_{B_0} = 555 \qquad C_{water} = \frac{1000\ g}{L} \text{ Density} \times \frac{mol}{18g} \text{ molar mass} = 55.55$

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

$-r_A = C_{A0}\, k\, (1-X)$

$k = 4.71 \times 10^9 \exp\left[\left[\frac{E}{R}\right]\frac{1}{T}\right]$

* $\frac{dT}{dt} = \frac{Q_g - Q_r}{N_{A0} \cdot C_{ps}} \qquad Q_r = m_c C_{pc}\left[(T - T_a)\left[1 - \exp\left[\frac{-UA}{m_c C_p}\right]\right]\right]$

$Q_g = (-r_A V)(-\Delta H_{rxn})$

$C_{ps} \Rightarrow \sum C_p \Theta_i = 35 + 18\left[\frac{555}{54.8}\right] + 19.5\left[\frac{98.8}{54.8}\right] = 252.5$

Sol by Polymath

Differential equations

1 d(T)/d(t) = (Qg-Qr)/Cps/Nao
2 d(X)/d(t) = k*(1-X)

Explicit equations

1 UA = 10
2 DeltaH = -20202
3 Ta1 = 290
4 Cpc = 4.18
5 Cps = 252.5
6 mc = 10
7 k = .000273*exp(9059*(1/297-1/T))
8 Ta2 = T-(T-Ta1)*exp(-UA/mc/Cpc)
9 Qr = mc*Cpc*(T-Ta1)*(1-exp(-UA/mc/Cpc))
10 Nao = 54.8
11 Qg = Nao* k*(1-X)*(-DeltaH)
12 DeltaQ = Qr-Qg

Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	Cpc	4.18	4.18	4.18	4.18
2	Cps	252.5	252.5	252.5	252.5
3	DeltaH	-2.02E+04	-2.02E+04	-2.02E+04	-2.02E+04
4	DeltaQ	-129.0831	-1911.68	458.3634	155.5053
5	k	8.446E-05	8.446E-05	0.0224452	0.0007724
6	mc	10.	10.	10.	10.
7	Nao	54.8	54.8	54.8	54.8
8	Qg	93.50797	0.0004292	2329.262	0.0004292
9	Qr	-35.57509	-35.57509	508.6372	155.5058
10	T	286.	286.	347.1903	307.4848
11	t	0	0	4000.	4000.
12	Ta1	290.	290.	290.	290.
13	Ta2	289.1489	289.1489	302.1684	293.7202
14	UA	10.	10.	10.	10.
15	X	0	0	0.9999995	0.9999995

MADAR

Topic 16 :-

- unstady state CSTR :-

* $\frac{dN_A}{dt} = F_{A0} - F_A + r_A V$

$\rightarrow \neq 0.$

* $\frac{dC_A}{dt} = \frac{(C_A^\circ - C_A)\dot{v}}{V} + r_A.$

$N_A = C_A V$

$F_A = C_A \dot{v}$

* $\frac{dT}{dt} = \frac{\dot{Q}_g - \dot{Q}_r}{\sum N C_p} \longrightarrow \dot{Q}_g = r_A V (\Delta H_{rxn})$

$\dot{Q}_r = F_{A0} \sum \Theta_i C_{pi} (T - T_0) + \dot{m}_c C_{pc} (T - T_{a1}) \left[1 - \exp\left[\frac{-UA}{\dot{m}_c C_{pc}}\right]\right]$

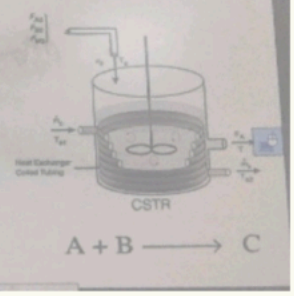
* $T_{a2} = T - (T - T_{a1}) \exp\left[\frac{-UA}{\dot{m}_c C_p}\right]$

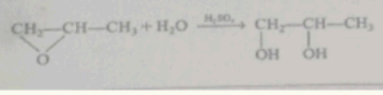
Example 16.1 Startup of CSTR

Consider the production of propylene glycol (C) in a CSTR with a heat exchanger. Initially, there is only water, $C_{wi} = 3.45$ lb-mol/ft^3, at $Ti = 75$F and 0.1 wt % H_2SO_4 in the 500-gallon reactor. The feed stream consists of 80 lb-mol/h of propylene oxide (A), 1000 lb-mol/h of water (B) containing 0.1 wt % H_2SO_4, and 100 lb-mol/h of methanol (M).

The water coolant flows through the heat exchanger at a rate of 5 lbm/s (1000 b-mol/h). The molar densities of pure propylene oxide (A), water (B), and methanol (M) are A_0 0.923 lb-mol/ft^3, B_0 3.45 lb-mol/ft^3, and M_0 1.54 lb-mol/ft^3, respectively.

Plot T and C_A as a function of time for this reactor





$A + B \longrightarrow C$

$A + B \longrightarrow C$

$\frac{dC_A}{dt} = \frac{(C_A^\circ - C_A)\dot{v}}{V} + r_A.$

$\frac{dC_B}{dt} = \frac{(C_B^\circ - C_B)\dot{v}}{V} + r_B.$

$\frac{dC_C}{dt} = \frac{(C_C^\circ - C_C)\dot{v}}{V} + r_C.$

$\frac{dC_M}{dt} = \frac{(C_M^\circ - C_M)\dot{v}}{V} + r_M.$

* $r_A = -k C_A^2 (1 - X)$
* $r_B = -k C_A^2 (1 - X)$
* $r_C = k C_A^2 (1 - X)$

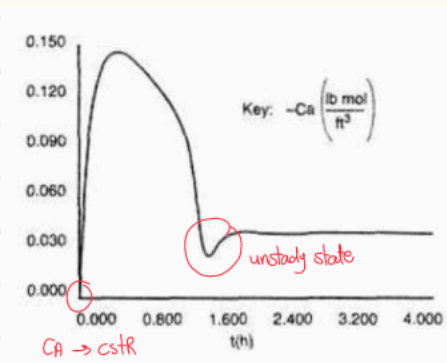


Figure E9-5.1 Propylene oxide concentration as a function of time.

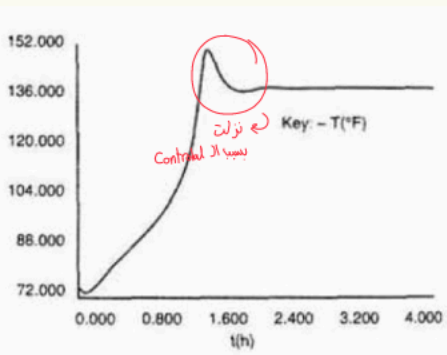


Figure E9-5.2 Temperature–time trajectory for CSTR startup.

* $\frac{dT}{dt} = \frac{\dot{Q}_g - \dot{Q}_r}{\sum N C_p} \longrightarrow \dot{Q}_g = r_A V (\Delta H_{rxn})$

$\dot{Q}_r = F_{A0} \sum \Theta_i C_{pi} (T - T_0) + \dot{m}_c C_{pc} (T - T_{a1}) \left[1 - \exp\left[\frac{-UA}{\dot{m}_c C_{pc}}\right]\right]$

$\sum N_i C_{pi} = C_{pA} N_A + C_{pB} N_B + C_{pC} N_C + C_{pM} N_M$

$\sum \Theta_i C_{pi} = \Theta_A C_{pA} + \Theta_B C_{pB} + \Theta_C C_{pC} + \Theta_M C_{pM}$

- PFR unsteady state:

$$\frac{\partial C_i}{\partial t} = r_i - \frac{\partial f_i}{\partial v}$$

$$U_a (T_a - T) - \left[\Sigma F_i C_{pi}\right] \frac{\partial T}{\partial v} + (-r_A)(-\Delta H_{rxn}) = \Sigma [F_i C_{pi}] \frac{\partial T}{\partial t}$$

Co Current: $\frac{\partial T_a}{\partial v} = \frac{U_a (T - T_a)}{\dot{m} C_p}$

Counter current: $\frac{\partial T_a}{\partial v} = \frac{U_a (T_a - T)}{\dot{m} C_p}$

Non-isothermal Multiple Reactions for Batch and semi-batch reactors

$$\boxed{\frac{dT}{dt} = \frac{\dot{m}_c C_{P_c} (T_{a1} - T)[1 - \exp(-UA / \dot{m}_c C_{P_c})] + \sum_{i=1}^{q} r_{ij}\, V\, \Delta H_{Rxij}(T) - \sum_{j=1}^{m} F_{j0} C_{Pj} (T - T_0)}{\sum_{j=1}^{m} N_{j0} C_{Pj}}}$$

For large coolant flow rates

$$\boxed{\frac{dT}{dt} = \frac{V \sum_{i=1}^{q} r_{ij}\, \Delta H_{Rxij} - UA(T - T_a) - \sum_{j=1}^{m} F_{j0} C_{P_j} (T - T_0)}{\sum_{j=1}^{m} N_j C_{P_j}}}$$