Chapter 4 Isothermal Reactor Design

4.1 Design Structure for Isothermal Reactors

Fig. 4-1
Fig. 4-2

1. mole balance (design eq.)
2. rate law $(-r_A = f(C_A, C_B, \cdots))$
3. stoichiometry ($C_j = h(x)$)
4. combine ($3 + 2 \longrightarrow -r_A = g(x) \xrightarrow{\text{代入}}$ design eq.)

4.2 Scale-up of BR Data to CSTR Design (Liquid-phase)

laboratory exp. $\xrightarrow{\text{scale up}}$ pilot-plant or full-scale

need
- chemical kinetics
- transport limitations

kinetics can be analyzed with lab-scale BR.

4.2.1 Batch operation

Const-V

mol bal. $\frac{1}{\underset{\text{Const}}{V}}\left(\frac{dN_A}{dt}\right) = r_A$

$$\Longrightarrow \frac{dC_A}{dt} = r_A \quad \text{or} \quad -\frac{dC_A}{dt} = -r_A$$

rate law consider $A \longrightarrow B$

$$-r_A = kC_A^2$$

combine rate laws and mol. bal.

$$-\frac{dC_A}{dt} = kC_A^2$$

$$-\frac{1}{k}\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2} = \int_0^t dt$$

$$\frac{1}{k}\left(\frac{1}{C_A} - \frac{1}{C_{A0}}\right) = t$$

time needed to reduce from C_{A0} to C_A

total cycle time for batch operation

$$t_t = t_f + t_e + t_c + t_R$$

fill empty clean reaction time

Estimation of t_R for a given conversion

mol. bal. $N_{A0}\frac{dX}{dt} = -r_A \cdot V$

rate law $-r_A = k\,C_A$ (1st order) $-r_A = k\,C_A^2$ (2nd order)

Stoichiometry $(V=V_0)$ $C_A = N_A/V_0 = C_{A0}(1-X)$

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

integrate $t = \frac{1}{k}\ln\frac{1}{1-X}$ $t = \frac{X}{k\,C_{A0}(1-X)}$

to achieve 90% conv.

$$t_R = \frac{1}{k}\ln\frac{1}{1-0.9} = \frac{2.3}{k}$$

$$t_R = \frac{0.9}{k\,C_{A0}(1-0.9)} = \frac{9}{k\,C_{A0}}$$

if $k = 10^{-4}\,s^{-1}$ if $k\,C_{A0} = 10^{-3}\,s^{-1}$

$\Rightarrow t_R = 6.4\,h$ $\Longrightarrow t_R = 2.5\,h$

tk dimensionless tkC_{A0} dimensionless

其值可反應出該BR system的conversion.

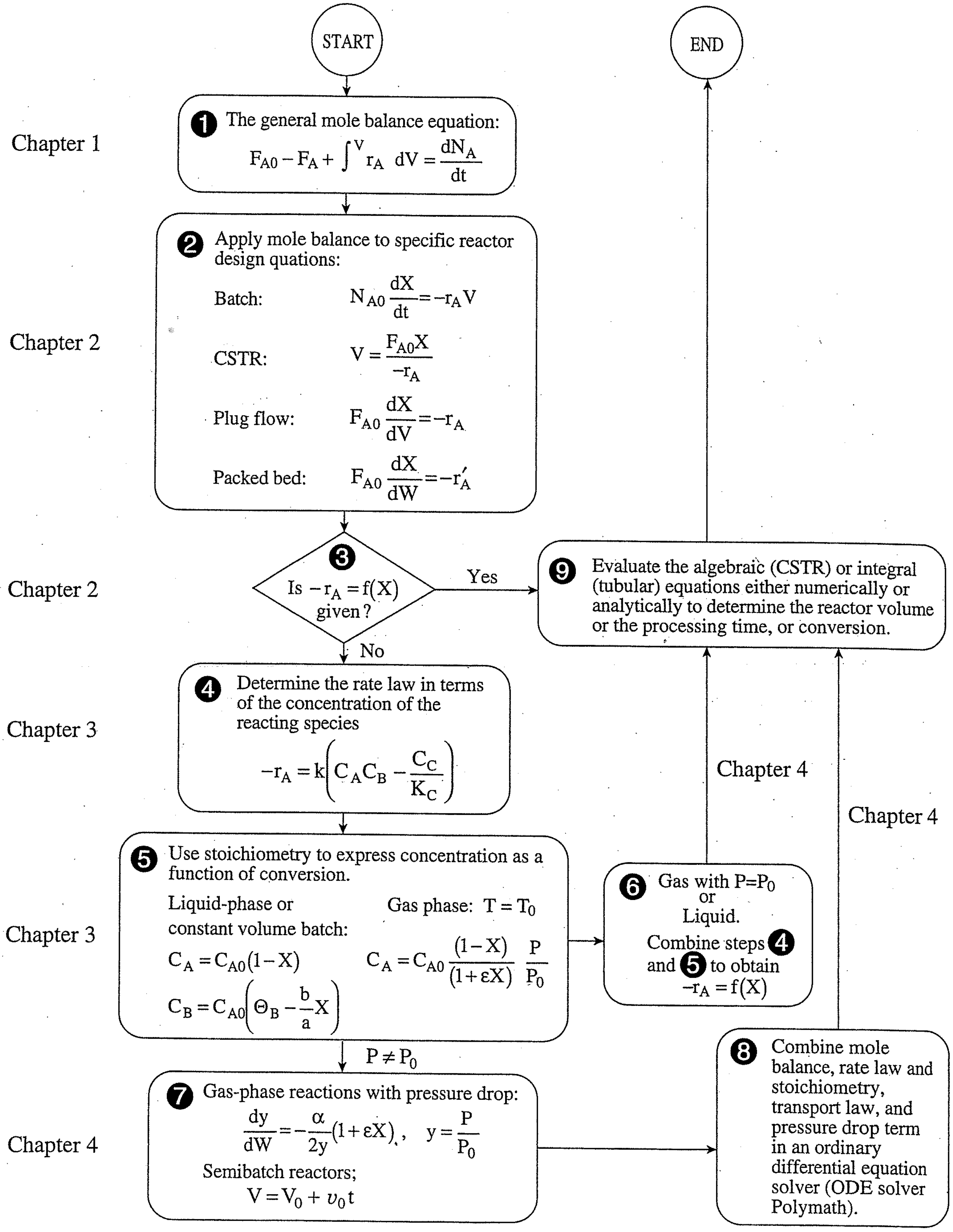


Figure 4-1 Isothermal reaction design algorithm for conversion.

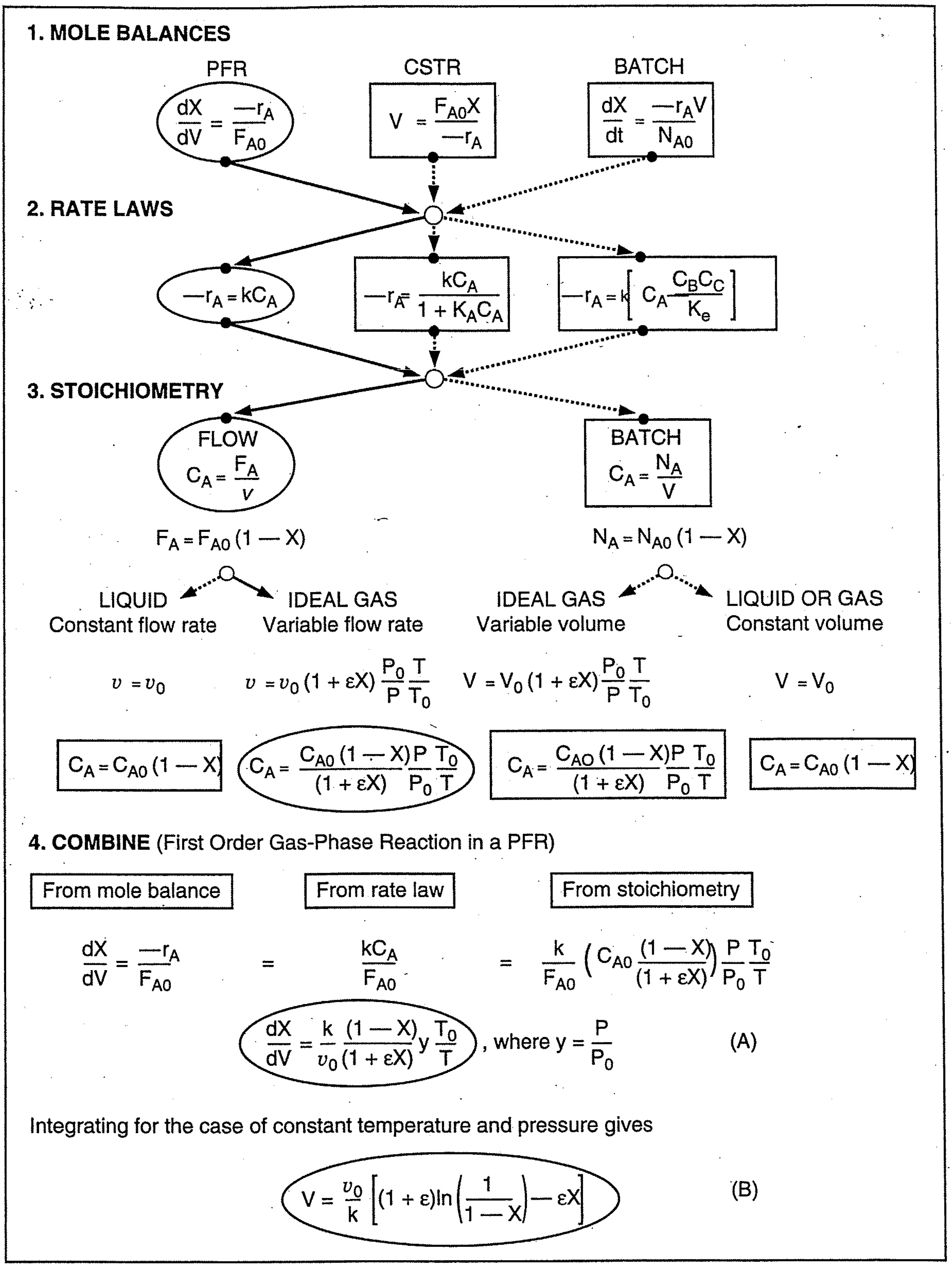
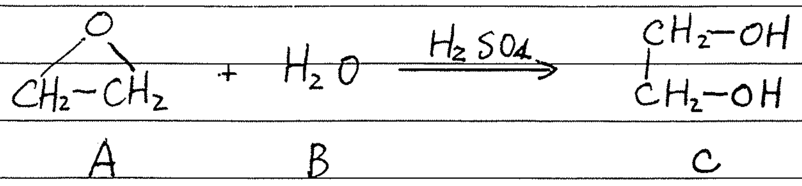


Figure 4-2 Algorithm for isothermal reactors.

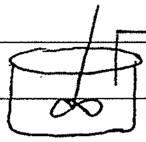
Ex 4-1

ethylene glycol to be produced 200×10^6 pounds per year in a CSTR at 55°C



1st-order in A

need to determine rate const. in a BR



500 mL, 2M of A (2 $kmol/m^3$)

500 mL water (B)

data : time (min)	Conc. of C ($kmol/m^3$)
0.0	0
⋮	⋮
0.2	0.467
⋮	⋮

Sol.: 1. mol bal. $\frac{1}{V}\frac{dN_A}{dt} = r_A$

2. rate law $-r_A = k\,C_A$ $\quad$ ($\because C_B \approx C_{B0}$, water in large excess)

3. stoichiometry.

	A	+	B	$\longrightarrow$	C
$t=0$	N_{A0}		$N_{B0}=\Theta_B N_{A0}$		0
time t	$N_{A0}-N_{A0}X$		$N_{A0}(\Theta_B - X)$		$N_{A0}X$
Conc.	$C_{A0}(1-X)$		$C_{A0}(\overset{\text{large}}{\Theta_B} - X) \approx C_{B0}$		$C_{A0}X$

$$C_A = N_A / V_0 \implies \frac{1}{V}\frac{dN_A}{dt} = \frac{dC_A}{dt}$$

4. combine

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

$$\Rightarrow -\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^t k\,dt$$

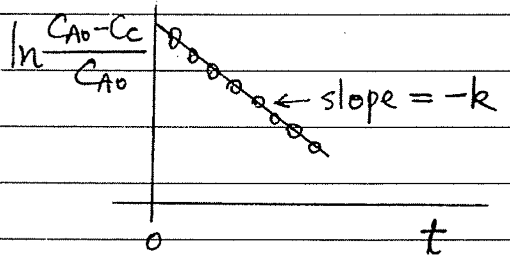
5. integrate

$$\ln\frac{C_{A0}}{C_A} = kt \quad \Rightarrow \quad C_A = C_{A0}e^{-kt}$$

Conc. of C, $N_C = N_{A0}X = N_{A0} - N_A$

$$C_C = \frac{N_C}{V_0} = C_{A0} - C_A = C_{A0}(1 - e^{-kt})$$

$$\Rightarrow \ln\frac{C_{A0} - C_C}{C_{A0}} = -kt$$



use decade method

$\Rightarrow k = 0.311\ \text{min}^{-1}$

$$\therefore \boxed{-r_A = (0.311\ \text{min}^{-1})C_A}$$

4.2.2 Design of CSTRs (大部份為 liq.-phase rxns)

$$V = \frac{F_{A0}\overset{F_{A0}-F_A}{X}}{(-r_A)_{exit}} = v_0\left(\frac{C_{A0} - C_A}{-r_A}\right) \quad \text{at } v = v_0$$

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

Consider 1st-order

$$\tau = \frac{C_{A0} - C_A}{kC_A}$$

$$\Rightarrow C_A = \frac{C_{A0}}{1 + \tau k}$$

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

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

τk : Damköhler number of 1st order rxn in flow reactor

1st order irrev. rxn

$$Da = \frac{-r_{A0}V}{F_{A0}} = \frac{\text{rxn rate of A at entrance}}{\text{Convective rate of A}} = \frac{kC_{A0}V}{v_0 C_{A0}} = \tau k$$

2nd order irrev. rxn

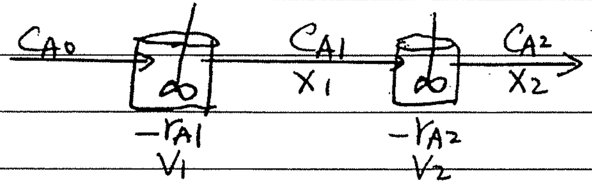
$$Da = \frac{kC_{A0}^2 \cdot V}{v_0 C_{A0}} = \tau k C_{A0}$$

Da is dimensionless, give a quick estimate of conversion

$Da < 0.1$, usually $X < 10\%$

$Da > 10$, usually $X > 90\%$

CSTRs in series



1st-order rxn

$v = v_0$

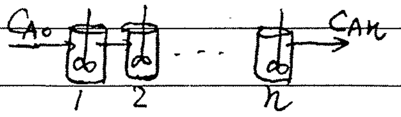
$$C_{A1} = \frac{C_{A0}}{1+\tau_1 k_1}$$

$$V_2 = \frac{F_{A1}-F_{A2}}{-r_{A2}} = \frac{v_0(C_{A1}-C_{A2})}{k_2 C_{A2}}$$

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

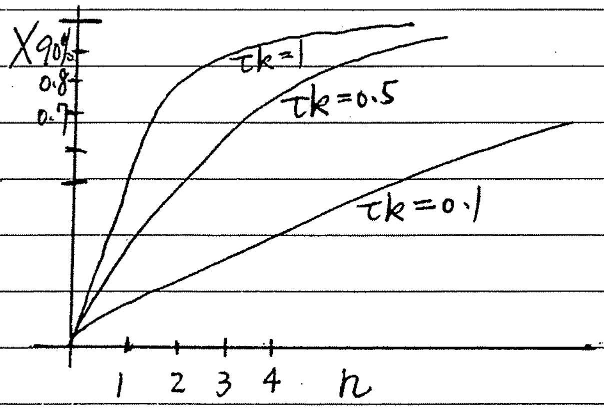
n equal-sized CSTRs $(\tau_1 = \tau_2 \dots = \tau_n = \tau)$

operating at same T $(k_1 = k_2 \dots = k_n = k)$

∴ 

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

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



$D_a \geq 1$

90% achieved in 2-3 reactors

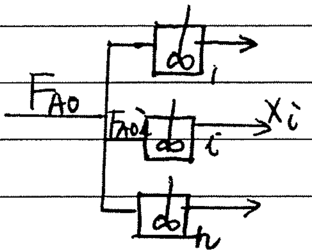
再增加 reactor no. 效率低

$D_a \approx 0.1$

conv. 隨 n↑ 持續提升.

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

CSTRs in Parallel



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

$F_{A0i} = F_{A0}/n$

$$V_i = F_{A0i}\left(\frac{X_i}{-r_{Ai}}\right) \underset{\text{same condition}}{\Longrightarrow} \begin{matrix} X_1 = X_2 = \dots = X \\ -r_{A1} = -r_{A2} \dots = -r_A \end{matrix}$$

且 $\frac{V}{n} = \frac{F_{A0}}{n}\left(\frac{X_i}{-r_{Ai}}\right)$

$$\Longrightarrow V = F_{A0}\left(\frac{X_i}{-r_{Ai}}\right) = \frac{F_{A0}X}{-r_A}$$

∴ parallel 的效果, 與 one stream (F_{A0}) to one large reactor (V) 一樣.

A 2nd-order rxn in a CSTR

$$V = \frac{F_{A0}X}{kC_A^2}$$

$$v = v_0 \text{ and } F_{A0}X = v_0(C_{A0} - C_A)$$

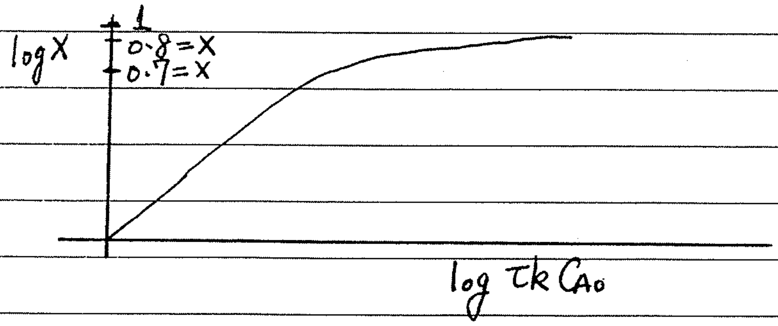
$$\Rightarrow \tau = \frac{V}{v_0} = \frac{C_{A0} - C_A}{kC_A^2}$$

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

二次方程 for X

$$\Rightarrow X = \frac{(1 + 2\tau k C_{A0}) - \sqrt{1 + 4\tau k C_{A0}}}{2\tau k C_{A0}}$$

$$= \frac{(1 + 2Da) - \sqrt{1 + 4Da}}{2Da}$$



at high conv.

X: 0.7 ⟶ 0.85

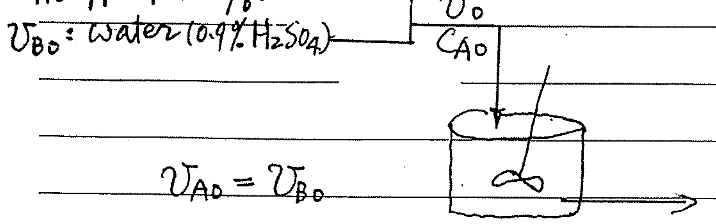
$\tau k C_{A0}$ 約增加10倍

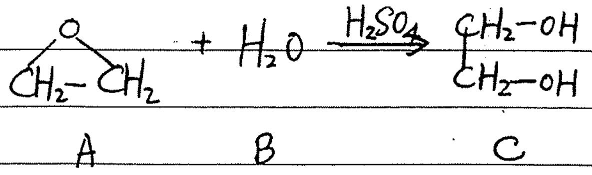
i.e. reactor size 10倍

∵ rxn在lowest conc. 進行

∴ high conv.時, rate很低

Ex. 4-2 Producing 200 million Pounds per year in a CSTR





2×10^8 lb/yr

1) conv. = 80%, reactor size = ?

rate law: Ex 4-2

2) 800-gal reactors in parallel, to achieve 80% conv., how many?

$k = 0.311 \text{ min}^{-1}$

3) 〃 in series 〃

NO. 4-8
DATE

Sol.

1)
$$F_C = 2\times10^8 \frac{lb}{yr} \times \frac{1\ yr}{365\ days} \times \frac{1\ days}{24\ h} \times \frac{1\ h}{60\,min} \times \frac{1\ lbmol}{62\ lb}$$
$$= 6.137 \frac{lbmol}{min}$$

Design eq.

$$V = F_{A0}X/-r_A \quad , \quad F_{A0}X = F_C$$
$$\Longrightarrow F_{A0} = \frac{F_C}{X} = \frac{6.137}{0.8} = 7.67 \frac{lbmol}{min}$$

Rate law

$$-r_A = kC_A$$

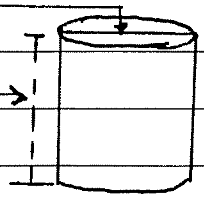
Stoichiometry: liq phase $v = v_0$
$$C_A = C_{A0}(1-X)$$

Combine

$$V = \frac{F_{A0}X}{kC_{A0}(1-X)} = \frac{v_0 X}{k(1-X)}$$
$$v_{A0} = F_{A0}/C_{A01} = 7.67\ (lbmol/min)/1\ (lbmol/ft^3) = 7.67 \frac{ft^3}{min}$$
$$= v_{B0}$$
$$v_0 = v_{A0} + v_{B0} = 15.34 \frac{ft^3}{min}$$
$$\therefore V = \frac{(15.34)(0.8)}{(0.311)(1-0.8)} = 197.3\ ft^3 \quad ※$$

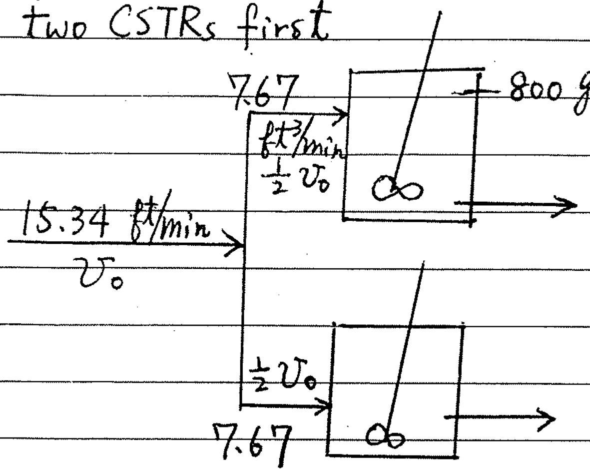
if diameter = 5 ft

⟹ 10 ft tall is necessary



2) parallel CSTRs

try two CSTRs first



$$800\ gal = 800\,gal \times \frac{1\ ft^3}{7.48\ gal} = 107\ ft^3$$

1st order rxn & const-v in CSTR

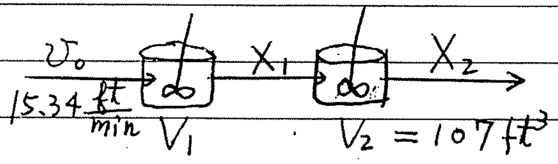
$$X = \frac{\tau k}{1+\tau k}$$

$$\tau = \frac{107}{7.67} = 13.95\ min \quad \therefore\ \tau k = Da = (13.95\ min) \times 0.311\ min^{-1} = 4.34$$

$$\Rightarrow\ X = \frac{4.34}{1+4.34} = 0.81 > 0.8$$

∴ two CSTRs in parallel is enough

3) CSTRs in series



$$V_1 = \frac{F_{A0}X_1}{-r_{A1}} = \frac{F_{A0}X_1}{kC_{A0}(1-X_1)} \qquad V_2 = \frac{F_{A0}(X_2-X_1)}{-r_{A2}} = \frac{v_0(X_2-X_1)}{k(1-X_2)}$$

$$V_1 = \frac{v_0X_1}{k(1-X_1)} \Rightarrow X_1 = 0.684 \qquad \Rightarrow X_2 = 0.9$$

or

∴ $\boxed{\text{two CSTRs enough}}$

$$X_2 = 1 - \frac{1}{(1+\underset{\uparrow}{\tau} k)^{n \leftarrow 2}} = 0.9$$

$\llcorner\ V/v_0 = (107)/(15.34) = 6.97\ min$

for rxn order >0, $\boxed{\text{two CSTRs in Series > in parallel}}$ in conv.

4.3 Tubular Reactors (大部份為 gas-phase rxns)

Design equation

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

integral form $$V = F_{A0}\int_0^X \frac{dX}{-r_A}$$ in the absence of pressure drop or heat exchange

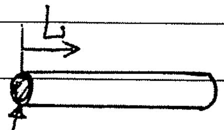
for a 2nd-order rxn

$$V = F_{A0}\int_0^X \frac{dX}{kC_A^2}$$

at constant T and P

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

$$\therefore V = \frac{F_{A0}}{kC_{A0}^2}\int_0^X \frac{(1+\varepsilon X)^2}{(1-X)^2}dX$$

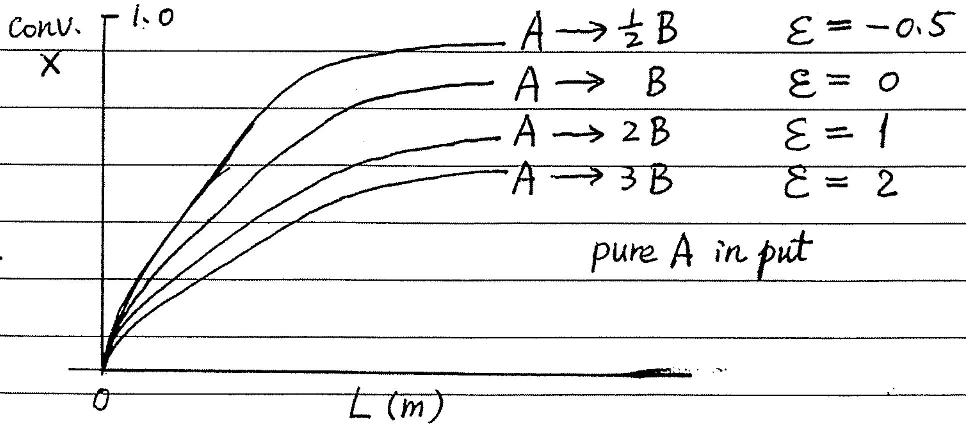


$$V = \frac{v_0}{kC_{A0}}\left[2\varepsilon(1+\varepsilon)\ln(1-X) + \varepsilon^2 X + \frac{(1+\varepsilon)^2 X}{1-X}\right]$$

or

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

$k = 5.0\ \frac{dm^3}{mol\cdot s}$
$A_c = 1.0\ dm^2$
$C_{A0} = 0.2\ \frac{mol}{dm^3}$
$v_0 = 1\ \frac{dm^3}{s}$



Ex. Neglecting v change

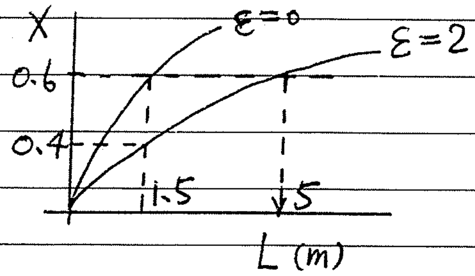
gas-phase cracking rxn in a PFR

$$A \longrightarrow 2B + C \qquad \text{2nd order}$$

$X=0.6$ what error will result if v change is neglected $\downarrow$ $\varepsilon = 0$

Sol.

$$\varepsilon = y_{A0}\cdot\delta = (1)(1+2-1) = 2$$



若 neglect v change,
僅用 1.5 m reactor
$\Longrightarrow X = 0.4$ only

Ex 4-3 Produce 300 million pounds per year in PFR

$$\underset{C_2H_6}{A} \xrightarrow[6\,atm]{1100\,K} \underset{C_2H_4}{B} + \underset{H_2}{C}$$

$\llcorner$ need 300×10^6 lb/yr

$-r_A = kC_A$, $k = 0.072\ s^{-1}$ at 1000 K

if $X = 80\%$ activation $E = 82$ kcal/mol

determine the PFR volume.

Sol.

$$F_B = 300\times10^6\ \frac{lb}{yr}\times\frac{1\ yr}{365\ days}\times\frac{1\ day}{24\ h}\times\frac{1\ h}{3600\ s}\times\frac{1\ lbmol}{28\ lb}$$
$$= 0.340\ \frac{lbmol}{s}$$

$$F_B = F_{A0}X \Longrightarrow F_{A0} = 0.34/0.8 = 0.425\ lbmol/s$$

design eq.	rate law	stoichiometry
$V = F_{A0}\int_0^X \frac{dX}{-r_A}$	$-r_A = kC_A$	$v = v_0(1+\varepsilon X)$ $C_A = C_{A0}\frac{1-X}{1+\varepsilon X}$ $C_B = C_C = \frac{C_{A0}X}{1+\varepsilon X}$

Combine

$$V = \frac{F_{A0}}{kC_{A0}}\int_0^X \frac{(1+\varepsilon X)dX}{(1-X)} = \frac{F_{A0}}{kC_{A0}}\left[(1+\varepsilon)\ln\frac{1}{1-X} - \varepsilon X\right]$$

need parameters

$$C_{A0} = y_{A0}C_{T0} = \frac{y_{A0}P_0}{RT_0} = 1\cdot\frac{6\text{ atm}}{0.73\,(ft^3 atm/lbm\cdot R)\times 1980R}$$

$$= 0.00415\,\frac{lbmol}{ft^3}$$

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

need k at 1100 K

$$\ln k_1 = \ln A - \frac{E}{R}\left(\frac{1}{T_1}\right)$$

$$\ln k_2 = \ln A - \frac{E}{R}\left(\frac{1}{T_2}\right)$$

$$\Rightarrow k_2 = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right]$$

其中 $k_1 = 0.072\ s^{-1}$, $T_1 = 1000K$, $T_2 = 1100K$

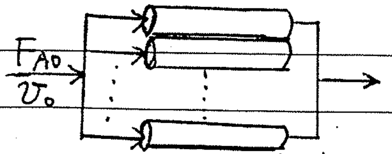
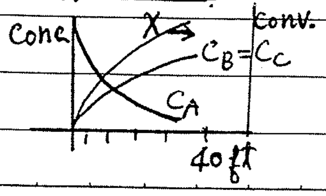
$E = 82\ kcal/mol$, $R = 1.987\times10^{-3}\ kcal/mol\cdot K$

$$\Rightarrow k_2 = 3.07\,s^{-1}$$

将 parameters 代入

$$\Rightarrow V = 33.36\,ft^3\left[2\ln\left(\frac{1}{1-X}\right) - X\right]$$

for $X = 0.8$ $\quad V = 80.7\ ft^3$

若使用 2-in #80 pipes in paralle, Number of pipes necessary ?
(40 ft)



$A_c = 0.0205\ ft^2$ for a 2-in #80

$$V = 80.7\,ft^3 = n\,(0.0205)(40)$$

$$\Rightarrow n = 98.4 \approx 100$$

4.4 Pressure Drop in Reactors

liquid-phase concentration 幾乎不受 Pressure 影响,
$\therefore$ 所以僅討論 gas-phase 的 pressure effect

4.4.1 Pressure Drop and the Rate Law

for ideal gases

$$C_i = \frac{F_i}{v} = \frac{F_{A0}(\Theta_i + \nu_i X)}{v_0(1+\varepsilon X)(P_0/P)(T/T_0)}$$

isothermal

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

P/P_0 is a func. of V or W (catalyst)

$\therefore$ differential form of the design eq must be used

for example : a 2nd-order rxn in a packed-bed reactor

$$A \longrightarrow B$$

the mol. balance

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

rate law

$$-r_A' = k\,C_A^2$$

stoichiometry

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

Combine (assume $T = T_0$)

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

$$\frac{dX}{dW} = \frac{kC_{A0}}{v_0}\left(\frac{1-X}{1+\varepsilon X}\right)^2\left(\frac{P}{P_0}\right)^2$$

$\therefore \frac{dX}{dW} = F_1(X,P)$ need to find : pressure drop 與 W 之 関联, 才能 solve the eq.

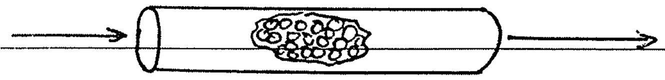
4.4.2 Flow Through a Packed Bed

$\boxed{\text{Ergun equation}}$

$$\underset{\substack{\uparrow\\ \text{pipe length}}}{\frac{dP}{dZ}} = -\frac{G}{\underset{\substack{\uparrow\\ \text{gas density}}}{\rho}\, g_c \underset{\substack{\nwarrow\\ \text{particle diameter}}}{D_p}}\left(\frac{1-\overset{\substack{\text{void fraction}\\ \downarrow}}{\phi}}{\phi^3}\right)\left[\frac{150(1-\phi)\overset{\substack{\text{gas viscosity}\\ \downarrow}}{\mu}}{D_p} + 1.75G\right]$$

u = superficial velocity $= \frac{v}{A_c}$ 未考慮 solid 存在

$G = \rho u$ = superficial mass velocity $= \frac{\rho v}{A_c}$



Ergun eq. 中, 僅 ρ 與 P 有関 $\Rightarrow$ find $\rho = \text{func.}(P)$

$\dot{m}_0 = \dot{m}$ steady state $\therefore$ const. mass flow rate

$\rho_0 v_0 = \rho v$

$\Rightarrow \rho = \rho_0 \frac{v_0}{v} = \rho_0\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)\left(\frac{F_{T0}}{F_T}\right)$ 代入 Ergun eq.

$$\boxed{\frac{dP}{dZ} = -\underset{\uparrow}{\beta_0}\left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)\left(\frac{F_T}{F_{T0}}\right)}$$

$$\frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3}\left[\frac{150(1-\phi)\mu}{D_p} + 1.75G\right]$$

W should replace Z

$$W = \underbrace{(A_c \cdot Z)}_{\text{Vol. of reactor}} \cdot \underbrace{(1-\phi)}_{\text{fraction of solid}} \cdot \overset{\text{Cat. density}}{\rho_c}$$

$$\therefore \quad \frac{dP}{dW} = -\frac{\beta_0}{A_c(1-\phi)\rho_c}\left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)\overbrace{\left(\frac{F_T}{F_{T0}}\right)}^{1+\varepsilon X}$$

$$\Longrightarrow \boxed{\frac{dP}{dW} = -\frac{\alpha}{2}\frac{T}{T_0}\frac{P_0}{P/P_0}(1+\varepsilon X)}, \quad \alpha = \frac{2\beta_0}{A_c\rho_c(1-\phi)P_0}$$

$$\left.\begin{aligned} \frac{dP}{dW} &= F_2(X,P) \\ \frac{dX}{dW} &= F_1(X,P) \end{aligned}\right\} \text{Solved numerically}$$

if $\varepsilon = 0$ or $\varepsilon X \ll 1$ and isothermal

$$\frac{dP}{dW} = -\frac{\alpha P_0}{2(P/P_0)} \quad \text{with } P = P_0 \text{ at } W = 0$$

$$\xrightarrow{\text{integration}} \quad (P/P_0)^2 = 1 - \alpha W$$

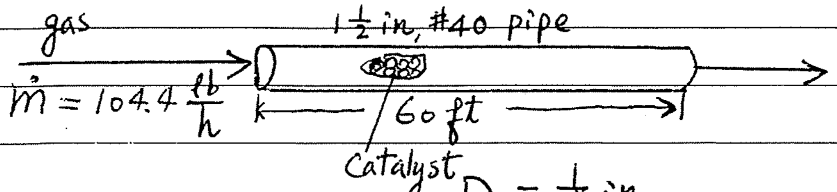
$$\text{or} \quad \boxed{P/P_0 = (1-\alpha W)^{1/2}}$$

$$P/P_0 = \left(1 - \frac{2\beta_0 Z}{P_0}\right)^{1/2} \quad \text{is also true}$$

$$\overset{y_{A0}\delta}{\varepsilon}\chi \ll 1$$

1. χ is low
2. $\delta = 0$
3. A is diluted

Ex 4-4 pressure drop in a packed bed without rxn



$D_p = \frac{1}{4}$ in

$P_0 = 10$ atm

ϕ = void fraction = 45%

$T = T_0 = 260°C$

gas similar to air

find the pressure drop

Sol.

need P vs. z

$$\Longrightarrow \frac{P}{P_0} = \left(1 - \frac{2\beta_0 L}{P_0}\right)^{1/2} \text{ ------- } (*)$$

其中 $$\beta_0 = \frac{G(1-\phi)}{g_c \rho_0 D_p \phi^3}\left[\frac{150(1-\phi)\mu}{D_p} + 1.75\,G\right]$$

$1\frac{1}{2}$-in #40 pipe, $A_c = 0.01414\ ft^2$

$$\Longrightarrow G = \frac{\dot{m}}{A_c} = 7383.3\ \frac{lb}{h \cdot ft^2}$$

air at 260°C and 10 atm

$\mu = 0.0673\ lb/ft \cdot h$

$\rho_0 = 0.413\ lb/ft^3$

$D_p = \frac{1}{4}\ in = 0.0208\ ft$

$g_c = 4.17 \times 10^8\ \frac{lb \cdot ft}{lb_f \cdot h^2}$

$\beta_0 = 0.0775\ \frac{atm}{ft}$

代入 (*)

$$\frac{P}{P_0} = 0.265 \Longrightarrow P = 2.65\ atm$$

$\therefore$ pressure drop $= \Delta P = P_0 - P = 7.35$ atm

Reaction with Pressure Drop

example :

$$A \xrightarrow{cat.} B$$ 2nd order rxn, gas phase carried out in a packed bed

mole bal. $F_{A0}\frac{dX}{dW} = -r_A'$

Rate law $-r_A' = kC_A^2$

Stoichiometry $\varepsilon = 0$ $C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0(1+\underset{\substack{\downarrow\\0}}{\varepsilon}X)\frac{P_0}{P}\underset{\substack{\downarrow\\1}}{\frac{T}{T_0}}}$

$$C_A = C_{A0}(1-X)\frac{P}{P_0}$$
$$= C_{A0}(1-X)(1-\alpha W)^{1/2}$$

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

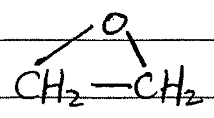
$$\Longrightarrow \frac{v_0}{kC_{A0}}\frac{dX}{(1-X)^2} = (1-\alpha W)dW$$, $X=0$ when $W=0$

$$\Longrightarrow \frac{v_0}{kC_{A0}}\left(\frac{X}{1-X}\right) = W\left(1-\frac{\alpha W}{2}\right)$$

$$X = \frac{\frac{kC_{A0}W}{v_0}\left[1-\frac{\alpha W}{2}\right]}{1+\frac{kC_{A0}W}{v_0}\left[1-\frac{\alpha W}{2}\right]} \qquad W = \frac{1-\{1-[(2v_0\alpha)/kC_{A0}][X/(1-X)]\}^{1/2}}{\alpha}$$

$\alpha = 0$ when $\Delta p = 0$

Ex. 4-6 Calculating X in a reactor with pressure drop

$$C_2H_4 + \frac{1}{2}O_2 \xrightarrow{cat.}$$ 

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

$-r_A' = kP_A^{1/3}P_B^{2/3}$ performed in a PBR

参考課本

$$\boxed{X = \frac{\qquad}{1+\frac{kC_{A0}W}{v_0}\left(1-\frac{\alpha W}{2}\right)}} \tag{4-38}$$

P. 4-18

Solving for the catalyst weight, we have

ght
for
der
'FR
ΔP

$$\boxed{W = \frac{1-\{1-[(2v_0\alpha)/kC_{A0}][X/(1-X)]\}^{1/2}}{\alpha}} \tag{4-39}$$

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

ble
ner
or
its.

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: $\rho_c = 1923$ kg/m³ (120 lb$_m$/ft³)
Cross-sectional area of $1\frac{1}{2}$-in. schedule 40 pipe: $A_C = 0.0013$ m²
Pressure drop parameter: $\beta_0 = 25.8$ 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

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

P. 4-19

Solution

Using Equation (4-38)

$$X = \frac{\dfrac{kC_{A0}W}{v_0}\left(1-\dfrac{\alpha W}{2}\right)}{1+\dfrac{kC_{A0}W}{v_0}\left(1-\dfrac{\alpha W}{2}\right)} \tag{4-38}$$

For the bulk catalyst density,

$$\rho_b = \rho_c(1-\phi) = (1923)(1-0.45) = 1058 \text{ kg/m}^3$$

The weight of catalyst in the 20 m of $1\frac{1}{2}$-in. schedule 40 pipe is

$$W = A_c\rho_b L = (0.0013 \text{ m}^2)\left(1058 \ \frac{\text{kg}}{\text{m}^3}\right)(20 \ \text{m})$$

$$W = 27.5 \text{ kg}$$

$$\frac{kC_{A0}W}{v_0} = \frac{12\text{m}^6}{\text{kmol}\cdot\text{kg cat}\cdot\text{h}}\cdot 0.1\frac{\text{kmol}}{\text{m}^3}\cdot\frac{27.5 \ \text{kg}}{7.15 \ \text{m}^3/\text{h}} = 4.6$$

(a) First calculate the conversion for $\Delta P = 0$ (i.e., $\alpha = 0$)

$$X = \frac{\dfrac{kC_{A0}W}{v_0}}{1+\dfrac{kC_{A0}W}{v_0}} = \frac{4.6}{1+4.6} = 0.82 \tag{E4-5.1}$$

$$\boxed{X = 0.82}$$

(b) Next, we calculate the conversion with pressure drop. Recalling Equation (4-29) and substituting the bulk density $\rho_b = (1-\phi)\,\rho_c = 1058 \text{ kg/m}^3$

$$\alpha = \frac{2\beta_0}{P_0A_c\rho_b} = \frac{2\left(25.8 \ \dfrac{\text{kPa}}{\text{m}}\right)}{(1013 \ \text{kPa})(0.0013\text{m}^2)\left(1058\dfrac{\text{kg}}{\text{m}^3}\right)} \tag{E4-5.2}$$

$$= 0.037 \text{ kg}^{-1}$$

then

$$\left(1-\frac{\alpha W}{2}\right) = 1-\frac{(0.037)(27.5)}{2} = 0.49 \tag{E4-5.3}$$

$$X = \frac{\dfrac{kC_{A0}W}{v_0}\left(1-\dfrac{\alpha W}{2}\right)}{1+\dfrac{kC_{A0}W}{v_0}\left(1-\dfrac{\alpha W}{2}\right)} = \frac{(4.6)(0.49)}{1+(4.6)(0.49)} = \frac{2.36}{3.26} \qquad \text{(E4-5.4)}$$

$$\boxed{X = 0.693}$$

We see the predicted conversion dropped from 82.2% to 69.3% because of pressure drop. It would be not only embarrassing but also an economic disaster if we had neglected pressure drop and the actual conversion had turned out to be significantly smaller.

(c) *Robert the Worrier* wonders: *What if* we increase the catalyst size by a factor of 2? We see from Equation (E4-4.5) that the second term in the Ergun equation is dominant; that is,

$$1.75G >> \frac{150(1-\phi)\mu}{D_p} \qquad \text{(E4-5.5)}$$

Therefore from Equation (4-25)

$$\beta_0 = \frac{G(1-\phi)}{\rho_0 g_c D_p \phi^3}\left[\frac{150(1-\phi)\mu}{D_p} + 1.75G\right]$$

we have

$$\beta_0 = \frac{1.75G^2(1-\phi)}{\rho_0 g_c D_p \phi^3} \qquad \text{(E4-5.6)}$$

We see for the conditions given by Equation (E4-4.4) that the pressure drop parameter varies inversely with the particle diameter

$$\beta_0 \sim \frac{1}{D_P}$$

and thus

$$\alpha \sim \frac{1}{D_P}$$

For Case 2, $D_{P_2} = 2D_{P_1}$

$$\alpha_2 = \alpha_1 \frac{D_{P_1}}{D_{P_2}} = (0.037\ \text{kg}^{-1})\frac{1}{2} \qquad \text{(E4-5.7)}$$

$$= 0.0185\ \text{kg}^{-1}$$

Substituting this new value of α in Equation (E4-5.4)

$$X_2 = \frac{(4.6)\left(1 - \frac{0.0185(27.5)}{2}\right)}{1 + (4.6)\left(1 - \frac{0.0185(27.5)}{2}\right)} = \frac{3.43}{4.43}$$

$$X = 0.774$$

By increasing the particle diameter we decrease the pressure drop parameter and thus increase the reaction rate and the conversion. However, Chapters 10 and 12 explain that when interparticle diffusion effects are important in the catalyst pellet, this increase in conversion with increasing particle size will not always be the case. For larger particles, it takes a longer time for a given number of reactant and product molecules to diffuse in and out of the catalyst particle where they undergo reaction (see Figure 10-6). Consequently, the specific reaction rate decreases with increasing particle size $k \sim 1/D_P$ [see Equation (12-35)], which in turn decreases the conversion. At small particle diameters, the rate constant, k, is large, and at its maximum value, but the pressure drop is also large, resulting in a low rate of reaction. At large particle diameters, the pressure drop is small, but so is the rate constant, k, and the rate of reaction, resulting in low conversion. Thus, we see a low conversion at both large and small particle diameters with an optimum in between. This optimum is shown in Figure E4-5.1. See Problem P4-23.

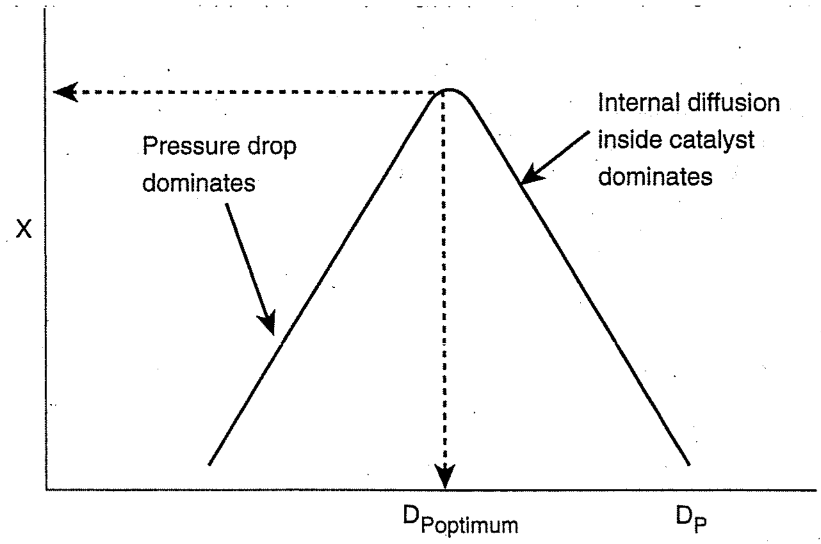


Figure E4-5.1 Finding the optimum particle diameter.

If pressure drop is to be minimized, *why not pack the catalyst into a larger diameter tube* to decrease the superficial velocity, G, thereby reducing ΔP? There are two reasons for *not* increasing the tube diameter: (1) There is an increased chance the gas could channel and bypass most of the catalyst, resulting in little conversion (see Figures 13-2 and 13-10); (2) the ratio of the heat-transfer surface area to reactor volume (catalyst weight) will be decreased, thereby making heat transfer more difficult for highly exothermic and endo-

4.4.4 Pressure drop in Pipes without packing

$$\frac{dP}{dL} = -\underset{\rho\cdot U\,\left[\frac{g}{cm^2\cdot s}\right]}{G}\,\frac{d\overset{\text{gas vel.}}{U}}{dL} - \frac{2\overset{\text{Fanning friction factor}}{f}\,G^2}{\rho\,\underset{\text{pipe diameter}}{D}}$$

$U = G/\rho$, G is constant along the pipe

and $\rho = \rho_0\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)\left(\frac{F_{T0}}{F_T}\right)$

assume $T = T_0$ and $\varepsilon = 0$

$$\Longrightarrow \rho_0\frac{P}{P_0}\frac{dP}{dL} - G^2\frac{dP}{P\,dL} + \frac{2fG^2}{D} = 0$$

integrating with $P = P_0$ when $L = 0$

$$\Longrightarrow \frac{P_0^2 - P^2}{2} = G^2\frac{P_0}{\rho_0}\left[2f\frac{L}{D} + \underset{\text{small } \because P \approx P_0}{\cancel{\ln\frac{P_0}{P}}}\right]$$

$$\Longrightarrow \frac{P_0^2 - P^2}{2} = 2fG^2\frac{P_0}{\rho_0}\frac{L}{D} \qquad L = V/A_c$$

$$\Longrightarrow \boxed{\frac{P}{P_0} = (1 - \alpha_p V)^{1/2}}, \text{ where } \alpha_p = \frac{4fG^2}{A_c\,\rho_0\,P_0\,D}$$

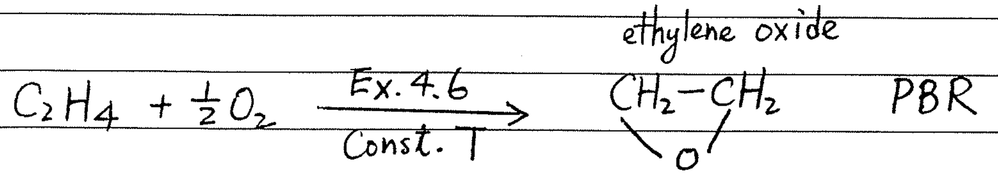
Ex flow in a 1000-ft $1\frac{1}{2}$-in #40 pipe

$$\Rightarrow \alpha_p = 0.0118, \quad \frac{\Delta P}{P_0} < 10\%$$

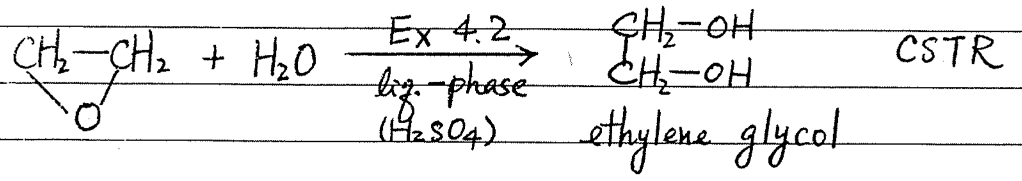
4.5 Synthesizing a Chemical Plant

ethane ethylene

$$C_2H_6 \xrightarrow[\text{Const. T, P}]{\text{Ex 4.4}} C_2H_4 + H_2 \qquad \text{PFR}$$


ethylene oxide

$$C_2H_4 + \tfrac{1}{2}O_2 \xrightarrow[\text{Const. T}]{\text{Ex. 4.6}} \underset{\diagdown O \diagup}{CH_2-CH_2} \qquad \text{PBR}$$



$$\underset{\diagdown O \diagup}{CH_2-CH_2} + H_2O \xrightarrow[\substack{\text{liq.-phase} \\ (H_2SO_4)}]{\text{Ex 4.2}} \begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix} \qquad \text{CSTR}$$

ethylene glycol

Figure 4-11 shows a chemical plant producing 200×10^6 lb/yr (0.102 lbmol/s) ethylene glycol from 402×10^6 lb/yr ethane

Separators are needed after rxns

Profit from a chemical plant

= value of products − cost of reactants − operating costs − separation costs

包含 energy, labor, overhead 管理費, depreciation (折舊)

$$\therefore \text{profit} = \left(\frac{\$0.38}{lb} \times 200\times10^6 \frac{lb}{yr}\right) - \left(\frac{\$0.04}{lb} \times 402\times10^6 \frac{lb}{yr}\right)$$

$$- \left(\frac{\$0.043}{lb} \times 2.26\times10^6 \frac{lb}{yr}\right) - \$8{,}000{,}000/yr$$

ethylene glycol

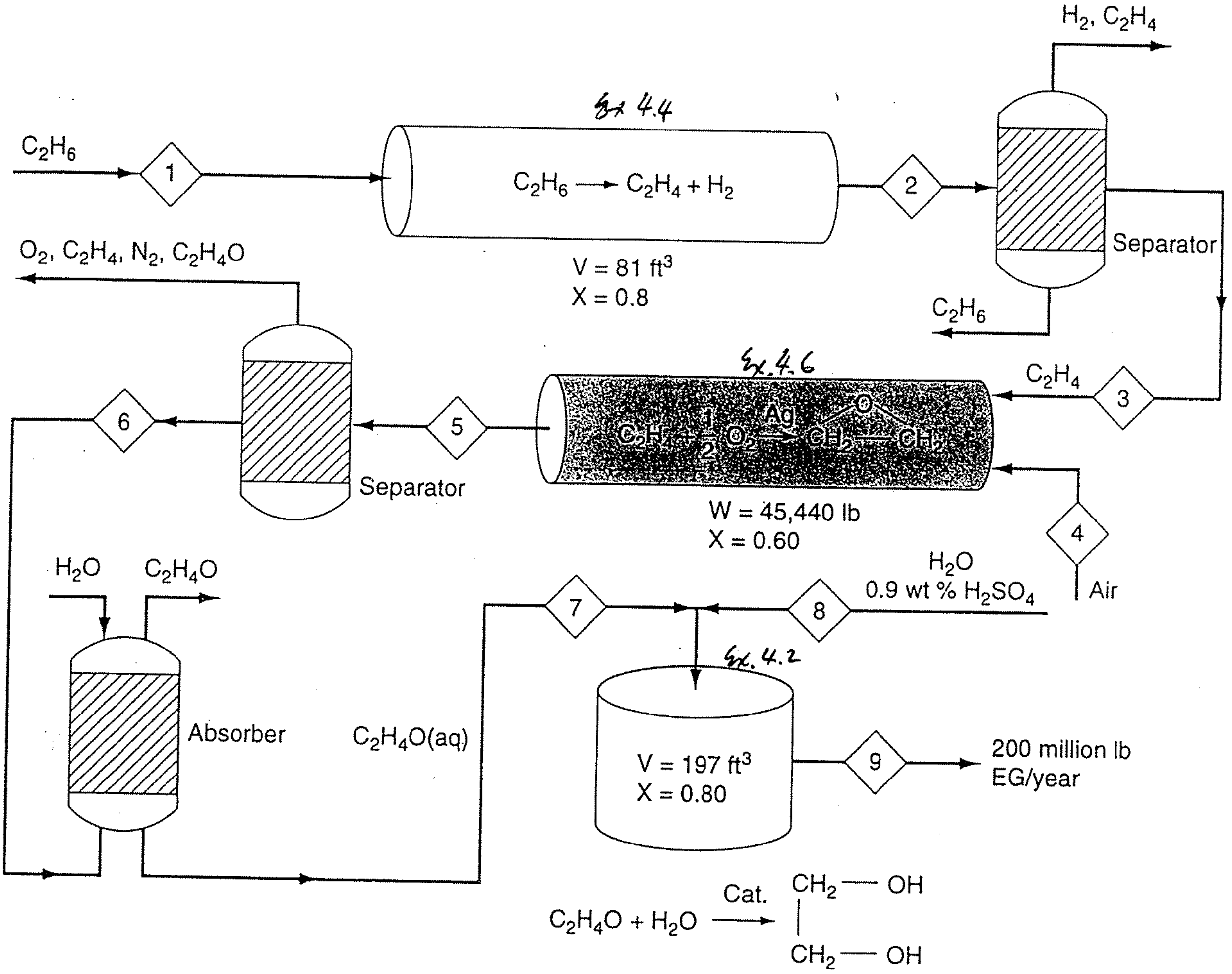
H_2SO_4

ethane

operating cost

$$= \$52 \text{ million}/yr$$

Figure 4-11 Production of ethylene glycol



Stream	Component[a]	Flow rate (lb mol/s)	Stream	Component[a]	Flow rate (lb mol/s)
1	C_2H_6	0.425	6	EO	0.150
2	C_2H_4	0.340	7	EO	0.128
3	C_2H_4	0.300	8	H_2O	0.44
4	Air	0.714	9	EG	0.104
5	EO	0.180			

[a] EG, ethylene glycol; EO, ethylene oxide.

4.6 Using C_A (liquid) and F_A (gas) in the Mole Balances and Rate Laws

membrane reactors and multiple rxns in gas phase → molar rate

liquid phase rxns → Concentration

与 conversion 不同之處是使用 C_j or F_j 時, 須針对 each species 做 mol. bal.

4.6.1 CSTR, PFR, PBR and BR

$$aA + bB \longrightarrow cC + dD$$

Liquid-phase : mole balance in terms of concentration

BR	$\dfrac{dC_A}{dt} = r_A$	$\dfrac{dC_B}{dt} = \dfrac{b}{a} r_A$
CSTR	$V = \dfrac{v_0 (C_{A0} - C_A)}{-r_A}$	$V = \dfrac{v_0 (C_{B0} - C_B)}{-\frac{b}{a} r_A}$
PFR	$v_0 \dfrac{dC_A}{dV} = r_A$	$v_0 \dfrac{dC_B}{dV} = \dfrac{b}{a} r_A$
PBR	$v_0 \dfrac{dC_A}{dW} = r_A'$	$v_0 \dfrac{dC_B}{dW} = \dfrac{b}{a} r_A'$

Gas-phase : algorithm using F_j
(computational procedure)

Mole balance

BR	CSTR	PFR
$\frac{dN_A}{dt} = r_A V$	$V = \frac{F_{A0} - F_A}{-r_A}$	$\frac{dF_A}{dV} = r_A$
$\frac{dN_B}{dt} = r_B V$	$V = \frac{F_{B0} - F_B}{-r_B}$	$\frac{dF_B}{dV} = r_B$
⋮	⋮	⋮

Rate law

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

Stoichiometry

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

$$C_j = C_{T0} \frac{F_j}{F_T} \frac{P}{P_0} \frac{T_0}{T} \,, \quad F_T = F_A + F_B + F_C + F_D + F_I$$

Combine : isothermal with no ΔP

$$\frac{dF_A}{dV} = -k_A C_{T0}^{\alpha+\beta} \left(\frac{F_A}{F_T}\right)^{\alpha} \left(\frac{F_B}{F_T}\right)^{\beta}$$

$$\frac{dF_B}{dV} = -\frac{b}{a} \quad 〃$$

$$\frac{dF_C}{dV} = \frac{c}{a} \quad 〃$$

$$\frac{dF_D}{dV} = \frac{d}{a} \quad 〃$$

Solve : using ODE solver

Ex,

gas-phase elementary rxn

$$A \rightleftharpoons 2B \quad , \quad k_A = 2.7\ \text{min}^{-1}$$

$$K_c = 1.2\ \text{mol/dm}^3, \quad F_{A0} = 10\ \text{mol/min}$$

$T = T_0 = 500\text{K}$, $P = P_0 = 4.1\ \text{atm}$ in a 100-dm^3 PFR

determine the molar flow rates

Sol.

mol. bal. $\quad \dfrac{dF_A}{dV} = r_A \ , \quad \dfrac{dF_B}{dV} = r_B$

rate law $\quad -r_A = k_A\left(C_A - \dfrac{C_B^2}{K_C}\right)$

stoichiometry

$$C_{T0} = \frac{P_0}{RT_0} = \frac{4.1\ \text{atm}}{\left(0.082\ \frac{\text{dm}^3\text{atm}}{\text{mol}\cdot\text{K}}\right)(500\text{K})} = 0.1\ \frac{\text{mol}}{\text{dm}^3}$$

$$r_B = 2(-r_A)$$

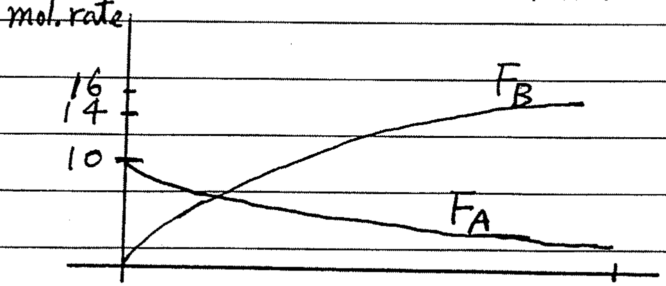
$$F_B = 2(F_{A0} - F_A)$$

$$F_T = F_A + F_B = 2F_{A0} - F_A$$

$$C_A = C_{T0}\frac{F_A}{(2F_{A0} - F_A)} \ , \quad C_B = C_{T0}\frac{F_B}{(2F_{A0} - F_A)} = C_{T0}\frac{2(F_{A0} - F_A)}{2F_{A0} - F_A}$$

Combine

$$\frac{dF_A}{dV} = r_A = -\underset{\underset{2.7\ \text{min}^{-1}}{\uparrow}}{k_A}\left[C_A - C_B^2/\underset{\underset{1.2\ \text{mol/dm}^3}{\uparrow}}{K_c}\right]$$



equilibrium

$$K_c = \frac{C_{Be}^2}{C_{Ae}} \Longrightarrow 1.2 = \frac{C_{T0}^2\,\dfrac{4(F_{A0} - F_{Ae})^2}{(2F_{A0} - F_{Ae})^2}}{C_{T0}\,\dfrac{F_{Ae}}{(2F_{A0} - F_{Ae})}} \Longrightarrow \begin{array}{l} F_{Ae} = 1.34\ \dfrac{\text{mol}}{\text{min}} \\ F_{Be} = 17.32\ \dfrac{\text{mol}}{\text{min}} \end{array}$$

4.8 Microreactors

Advantages of microreactors

Microreactors are emerging as a new technology in CRE. Microreactors are characterized by their high surface area-to-volume ratios in their microstructured regions that contain tubes or channels. A typical channel width might be 100 μm with a length of 20,000 μm (2 cm). The resulting high surface area-to-volume ratio (ca. 10,000 m^2/m^3) reduces or even eliminates heat and mass transfer resistances often found in larger reactors. Consequently, surface-catalyzed reactions can be greatly facilitated, hot spots in highly exothermic reactions can be eliminated, and in many cases highly exothermic reactions can be carried out isothermally. These features provide the opportunity for microreactors to be used to study the intrinsic kinetics of reactions. Another advantage of microreactors is their use in the production of toxic or explosive intermediates where a leak or microexplosion for a single unit will do minimal damage because of the small quantities of material involved. Other advantages include shorter residence times and narrower residence time distributions.

Figure 4-12 shows (a) a microreactor with heat exchanger and (b) a microplant with reactor, valves, and mixers. Heat, Q, is added or taken away by the fluid flowing perpendicular to the reaction channels as shown in Figure 4-12(a). Production in microreactor systems can be increased simply by adding more units in parallel. For example, the catalyzed reaction

$$R-CH_2OH + {}^1\!/_2O_2 \xrightarrow[Ag]{} R-CHO + H_2O$$

required only 32 microreaction systems in parallel to produce 2000 tons/yr of acetate!

Because of the good contact between fluid and catalyst, the input rate can be high.

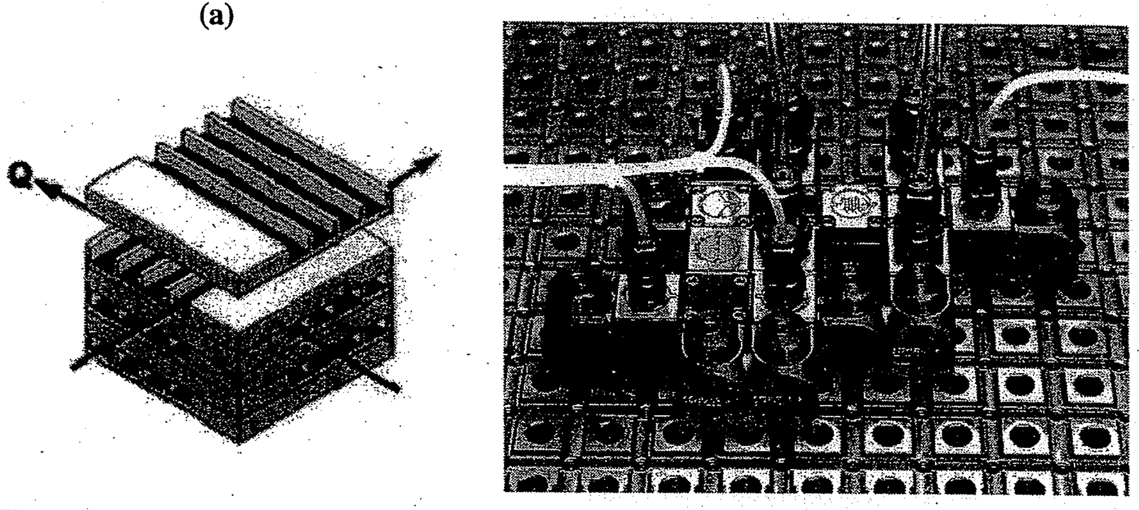


Figure 4-12 Microreactor (a) and Microplant (b). Courtesy of Ehrfeld, Hessel, and Löwe, *Microreactors: New Technology for Modern Chemistry* (Wiley-VCH, 2000).

Microreactors are also used for the production of specialty chemicals, combinatorial chemical screening, lab-on-a-chip, and chemical sensors. In modeling microreactors, we will assume they are either in plug flow for which the mole balance is

$$\frac{dF_A}{dV} = r_A \tag{1-12}$$

or in laminar flow, in which case we will use the segregation model discussed in Chapter 13. For the plug-flow case, the algorithm is described in Figure 4-11.

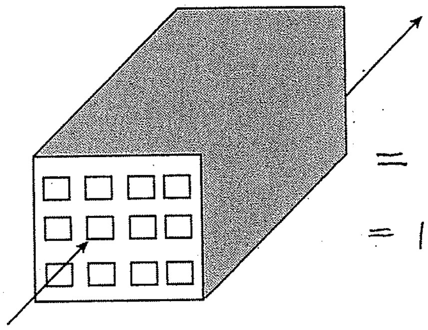
Example 4–7 Gas-Phase Reaction in a Microreactor—Molar Flow Rates

The gas-phase reaction

$$2\text{NOCl} \longrightarrow 2\text{NO} + \text{Cl}_2$$

is carried out at 425°C and 1641 kPa (16.2 atm). Pure NOCl is to be fed, and the reaction follows an elementary rate law.[8] It is desired to produce 20 tons of NO per year in a microreactor system using a bank of ten microreactors in parallel. Each microreactor has 100 channels with each channel 0.2 mm square and 250 mm in length.

$100 \frac{\text{channels}}{\text{reactor}} \times 10 \text{ reactors}$
$= 1000 \text{ channels}$



Each channel

$(0.2\text{ mm})^2 \times 250\text{ mm}$
$= 10\text{ mm}^3 \times \frac{1\text{ dm}^3}{10^6\text{ mm}^3}$
$= 10^{-5}\text{ dm}^3$

Plot the molar flow rates as a function of volume down the length of the reactor. The volume of each channel is 10^{-5} dm^3.

Additional Information

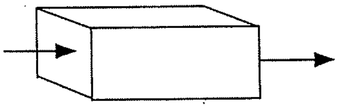
To produce 20 tons per year of NO at 85% conversion would require a feed rate of 0.0226 mol/s of NOCl, or 2.26×10^{-5} mol/s per channel. The rate constant is

$$k = 0.29 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at 500 K with } E = 24 \frac{\text{kcal}}{\text{mol}}$$

Solution

For one channel,

Find V.

$F_{A0} = \frac{22.6\ \mu\text{mol}}{\text{s}}$  $F_B = \frac{19.2\ \mu\text{mol}}{\text{s}}$, $X = 0.85$, $V = ?$

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[8] J. B. Butt, *Reaction Kinetics and Reactor Design*, 2nd ed. (New York: Marcel Dekker, 2001), p. 153.

Although this particular problem could be solved using conversion, we shall illustrate how it can also be solved using molar flow rates as the variable in the mole balance. We first write the reaction in symbolic form and then divide by the stoichiometric coefficient of the limiting reactant, NOCl.

$$2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}_2$$

$$2\text{A} \rightarrow 2\text{B} + \text{C}$$

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

llowing the Algorithm

1. Mole balances on species A, B, and C:

$$\frac{dF_A}{dV} = r_A \quad \text{(E4-7.1)}$$

$$\frac{dF_B}{dV} = r_B \quad \text{(E4-7.2)}$$

$$\frac{dF_C}{dV} = r_C \quad \text{(E4-7.3)}$$

2. Rate law:

$$-r_A = kC_A^2, \quad k = 0.29 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \text{ at } 500 \text{ K} \quad \text{(E4-7.4)}$$

3. Stoichiometry: Gas phase with $T = T_0$ and $P = P_0$, then $v = v_0 \dfrac{F_T}{F_{T0}}$

a. Relative rates

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

$$r_B = -r_A$$

$$r_C = -\tfrac{1}{2} r_A$$

b. Concentration

Applying Equation (3-42) to species A, B, and C, the concentrations are

$$C_A = C_{T0}\frac{F_A}{F_T}, \quad C_B = C_{T0}\frac{F_B}{F_T}, \quad C_C = C_{T0}\frac{F_C}{F_T} \quad \text{(E4-7.5)}$$

$$\text{with } F_T = F_A + F_B + F_C$$

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4. **Combine:** the rate law in terms of molar flow rates is

$$-r_A = kC_{T0}^2\left(\frac{F_A}{F_T}\right)^2$$

combining all

$$\frac{dF_A}{dV} = -kC_{T0}^2\left(\frac{F_A}{F_T}\right)^2 \qquad \text{(E4-7.6)}$$

$$\frac{dF_B}{dV} = kC_{T0}^2\left(\frac{F_A}{F_T}\right)^2 \qquad \text{(E4-7.7)}$$

$$\frac{dF_C}{dV} = \frac{k}{2}C_{T0}^2\left(\frac{F_A}{F_T}\right)^2 \qquad \text{(E4-7.8)}$$

5. **Evaluate:**

$$C_{T0} = \frac{P_0}{RT_0} = \frac{(1641 \text{ kPa})}{\left(8.314\,\frac{\text{kPa}\cdot\text{dm}^3}{\text{mol}\cdot\text{K}}\right)698 \text{ K}} = 0.286\frac{\text{mol}}{\text{dm}^3} = \frac{0.286 \text{ mmol}}{\text{cm}^3}$$

When using Polymath or another ODE solver, one does not have to actually combine the mole balances, rate laws, and stoichiometry as was done in the combine step in previous examples in this chapter. The ODE solver will do that for you. Thanks, ODE solver! The Polymath Program and output are shown in Table E4-7.1 and Figure E4-7.1.

TABLE E4-7.1. POLYMATH PROGRAM

ODE REPORT (RKF45)

```
Differential equations as entered by the user
 [1]  d(Fa)/d(V) = ra
 [2]  d(Fb)/d(V) = rb
 [3]  d(Fc)/d(V) = rc

Explicit equations as entered by the user
 [1]  T = 698
 [2]  Cto = 1641/8.314/T
 [3]  E = 24000
 [4]  Ft = Fa+Fb+Fc
 [5]  Ca = Cto*Fa/Ft
 [6]  k = 0.29*exp(E/1.987*(1/500-1/T))
 [7]  Fao = 0.0000226
 [8]  vo = Fao/Cto

 [9]  Tau = V/vo
 [10] ra = -k*Ca^2
 [11] X = 1-Fa/Fao
 [12] rb = -ra
 [13] rc = -ra/2
 [14] rateA = -ra
```

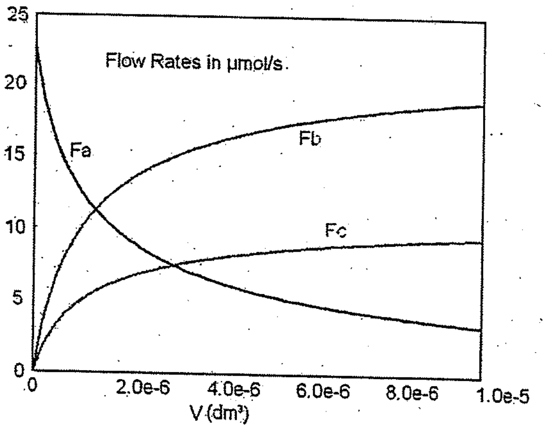


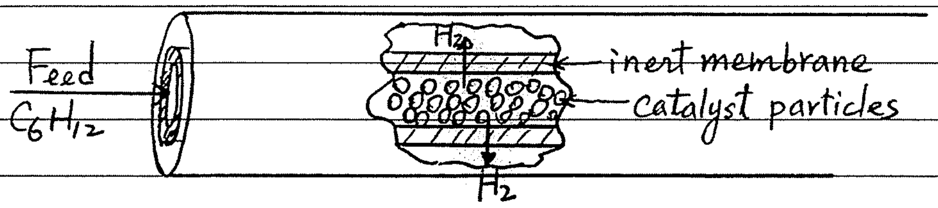
Figure E4-7.1 Profiles of microreactor molar flow rates.

4.6.2 Membrane Reactors

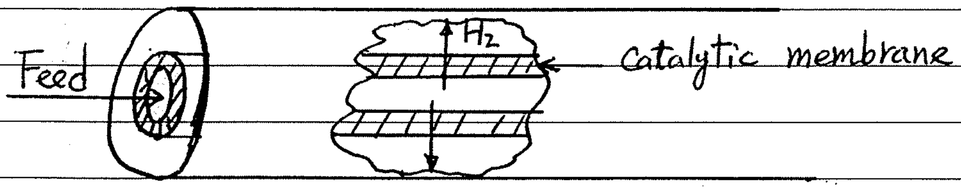
Catalytic membrane reactors can be used to increase the yield of highly reversible rxns

e.g.

$$C_6H_{12} \rightleftharpoons C_6H_6 + 3H_2$$



inert membrane reactor with catalyst pellets on the feed side
IMRCF



catalytic membrane reactor
CMR

H_2 can diffuse through the membrane, but C_6H_{12}, C_6H_6 cannot.

由於 C_{H_2} 很小，反應可持續進行(即使 K_c 很小)

Ex. 4-10 Membrane Reactor for Dehydrogenation

e.g. $C_4H_{10} \rightleftharpoons C_4H_8 + H_2$

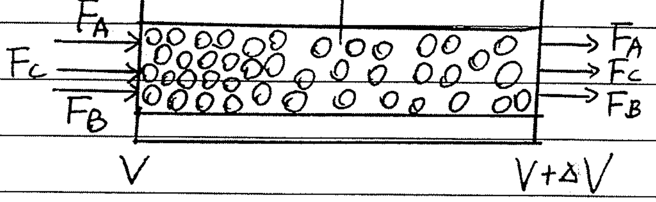
$C_3H_8 \rightleftharpoons C_3H_6 + H_2$

$$A \overset{k}{\rightleftharpoons} B + C \qquad \begin{aligned} k &= 0.7\ \text{min}^{-1} \\ K_c &= 0.05\ \frac{\text{mol}}{\text{dm}^3}\ \text{at } 227^\circ\text{C} \end{aligned}$$

rxn in an IMRCF with pure A input, only B is permeable.
$F_{A0} = 10$ mol/min, $P = P_0 = 8.2$ atm, $T = T_0 = 227^\circ$C

find molar rate vs. V

$R_B = k_c C_B = (0.2\ \text{min}^{-1}) \cdot C_B$



Sol.

$$-r_A = -r_A' \cdot \overset{1.5\ \frac{g}{cm^3}}{\rho_b}$$

mol. bal.

$$F_A\big|_V - F_A\big|_{V+\Delta V} + r_A \Delta V = 0 \xrightarrow{\Delta V \to 0} \frac{dF_A}{dV} = r_A$$

$$F_B\big|_V - F_B\big|_{V+\Delta V} - R_B \cdot \Delta V + r_B \Delta V = 0 \Longrightarrow \frac{dF_B}{dV} = r_B - R_B$$

rate law

$$-r_A = k\left(C_A - \frac{C_B C_C}{K_C}\right), \quad r_B = -r_A, \quad r_C = -r_A$$

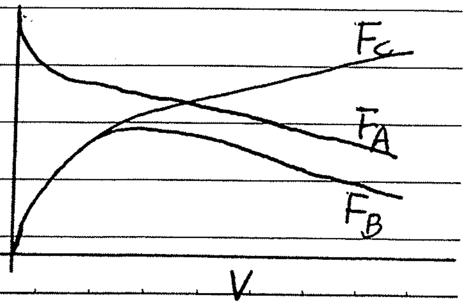
$$R_B = k_c C_B$$

Stoichiometry

$$C_A = C_{T0}\frac{F_A}{F_T}, \quad C_B = C_{T0}\frac{F_B}{F_T}, \quad C_C = C_{T0}\frac{F_C}{F_T}, \quad F_T = F_A + F_B + F_C$$

Combine

$$\left.\begin{aligned} dF_A/dV &= r_A \\ dF_B/dV &= -r_A - k_c \overset{\boxed{P_0/RT_0}}{C_{T0}}\left(\frac{F_B}{F_T}\right) \\ dF_C/dV &= -r_A \\ -r_A &= k\,C_{T0}\left[(F_A/F_T) - \frac{C_{T0}}{K_C}\left(\frac{F_B}{F_T}\right)\left(\frac{F_C}{F_T}\right)\right] \\ F_T &= F_A + F_B + F_C \end{aligned}\right\} \xrightarrow[\substack{V = 0 \\ F_A = F_{A0} \\ F_B = F_C = 0}]{\text{POLYMATH}}$$

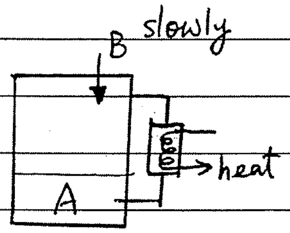


4.7 Unsteady-state Operation of Reactors

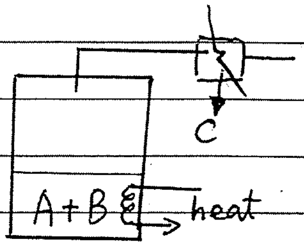
unsteady operation
1. batch reactor
2. startup of a CSTR
3. semibatch reactors

$A + B \longrightarrow C + D$

a.



b.



* 避免 high C_B 而有 side rxn

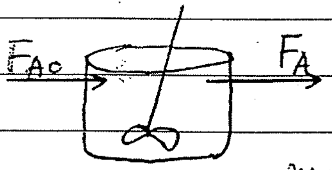
* rxn is highly exothermic

* B is gas

* remove products 以 增加 conv. 和 C_A, C_B

* 例子: reactive distillation 如酯化反應時去除水份.

4.7.1 Startup of a CSTR



want to determine the time necessary for steady state

mole balance $F_{A0} - F_A + r_A V = \frac{dN_A}{dt}$

for liq.-phase, $v = v_0$, $V = V_0$, $\tau = V_0/v_0$

$$\Longrightarrow C_{A0} - C_A + r_A \tau = \tau \frac{dC_A}{dt}$$

1st order, $-r_A = k C_A \Longrightarrow \frac{dC_A}{dt} + \frac{1+\tau k}{\tau} C_A = \frac{C_{A0}}{\tau}$ —— (*)

at stedy state, $\frac{dC_A}{dt} = 0 \Longrightarrow C_{AS} = \frac{C_{A0}}{1+\tau k}$

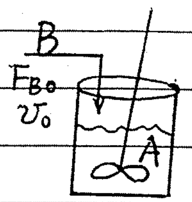
solve (*) $\Longrightarrow C_A = \frac{C_{A0}}{1+\tau k}\left\{1 - \exp\left[-(1+\tau k)\frac{t}{\tau}\right]\right\}$ $C_A = 0$, at $t = 0$

to reach $C_A = 99\% C_{AS} \longrightarrow \boxed{t_s = 4.6 \frac{\tau}{1+\tau k}}$

$\therefore t_s = 4.6\tau$ for slow rxn ; $t_s = \frac{4.6}{k}$ for rapid rxn

大部份 1st order systems, steady state reached in 3-4 τ

4.7.2 Semibatch Reactors



elementary rxn in liq. phase : $A + B \longrightarrow C$

balance on A : in − out + generation = acc.

$$0 - 0 + r_A \cdot V(t) = \frac{dN_A}{dt}$$

Equations in terms of concentration

$$r_A V = \frac{d(C_A V)}{dt} = \frac{V\,dC_A}{dt} + C_A\frac{dV}{dt} \qquad \text{——— } (*)$$

mass balance $\underset{\text{in}}{\rho_0 v_0} - \underset{\text{out}}{0} + \underset{\text{gen.}}{0} = \underset{\text{acc.}}{\frac{d(\rho V)}{dt}}$

similar densities for liqs, $\rho = \rho_0$

$$\therefore \frac{dV}{dt} = v_0 , \qquad V = V_0 \text{ at } t = 0$$

$$\Longrightarrow V = V_0 + v_0 t \qquad \text{代入 } (*)$$

$$r_A V = \frac{V\,dC_A}{dt} + v_0 C_A$$

$$\Longrightarrow \boxed{\frac{dC_A}{dt} = r_A - \frac{v_0}{V}C_A} \text{ - - - diluting effect}$$

balance on B ; $\frac{dN_B}{dt} = r_B V + \underset{\substack{\uparrow \\ v_0 C_{B0}}}{F_{B0}} = \frac{d(C_B V)}{dt} = C_B \underbrace{\frac{dV}{dt}}_{\substack{\uparrow \\ v_0}} + V\frac{dC_B}{dt}$

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

adding effect

Ex 4-11

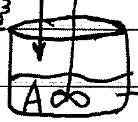
elementary rxn

$$CNBr + CH_3NH_2 \longrightarrow CH_3Br + NCNH_2$$

$C_{B0} = 0.025 \frac{mol}{dm^3}$ A B

$-r_A = k C_A C_B$

$v_0 = 0.05 \frac{dm^3}{s}$



$V_0 = 5\ dm^3,\ C_{A0} = 0.05\ mol/dm^3$

k: $2.2\ dm^3/s.mol$

Sol.

$$\frac{dC_A}{dt} = -kC_AC_B - \frac{v_0}{V}C_A \quad , \quad V = V_0 + v_0 t$$

$$\frac{dC_B}{dt} = -kC_AC_B + \frac{v_0}{V}(C_{B0} - C_B)$$

Similarly for C and D from mol. bal.

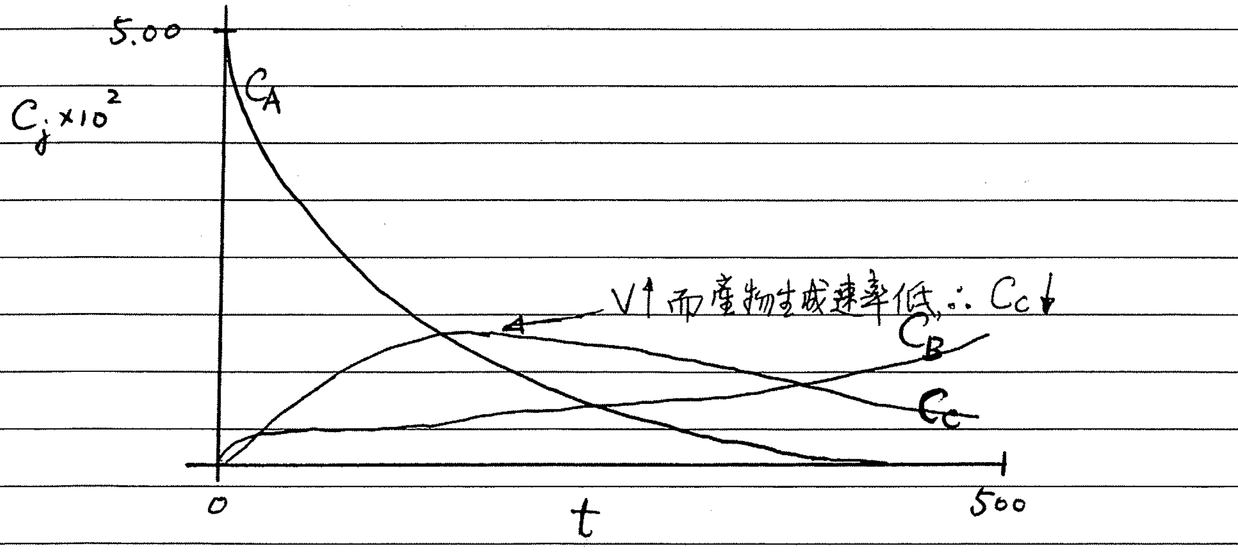
$$\frac{dC_C}{dt} = kC_AC_B - \frac{v_0 C_C}{V}$$

$$\frac{dC_D}{dt} = kC_AC_B - \frac{v_0 C_D}{V}$$

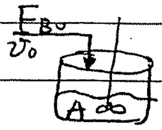
POLYMATH →

$t = 0,\ C_A = 0.05$

$C_B = C_C = C_D = 0$



semibatch reactor equations in terms of mol. no.



$$\frac{dN_A}{dt} = r_A \cdot V \quad , \quad \frac{dN_B}{dt} = r_A \cdot V + F_{B0}$$

A+B →

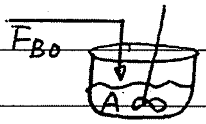
$$V = V_0 + v_0 t$$

$$\text{if } -r_A = kC_AC_B = k\frac{N_A}{V}\cdot\frac{N_B}{V} = k\frac{N_AN_B}{V^2}$$

$$\therefore \frac{dN_A}{dt} = -k\frac{N_AN_B}{V_0+v_0t}$$

$$\frac{dN_B}{dt} = -k\frac{N_AN_B}{V_0+v_0t} + F_{B0}$$

Semibatch reactor equations in terms of conversion



$$A + B \rightleftharpoons C + D$$

$$N_A = N_{A0} - N_{A0}X$$

$$N_B = N_{Bi} + \int_0^t F_{B0}\,dt - N_{A0}X = N_{Bi} + F_{B0}t - N_{A0}X$$

$\uparrow$ initially in the vat

$$N_C = \cancelto{0}{N_{Ci}} + N_{A0}X \qquad N_D = \cancelto{0}{N_{Di}} + N_{A0}X$$

mol. bal. $\quad r_AV = dN_A/dt \qquad N_{A0}\frac{dX}{dt} = -r_A\cdot V$

rate law $\quad -r_A = k\left(C_AC_B - \frac{C_CC_D}{K_C}\right)$

stoichiometry $\quad C_A = \frac{N_{A0}(1-X)}{V_0+v_0t} \qquad C_B = \frac{N_{Bi}+F_{B0}t-N_{A0}X}{V_0+v_0t}$

$$C_C = \frac{N_{A0}X}{V_0+v_0t} \qquad C_D = \frac{N_{A0}X}{V_0+v_0t}$$

Combine $\quad \frac{dX}{dt} = \frac{k[(1-X)(N_{Bi}+F_{B0}t-N_{A0}X)-(N_{A0}X^2/K_C)]}{V_0+v_0t}$

$$\left(N_{A0}\frac{dX}{dV} = k\left[\frac{N_{A0}(1-X)}{V_0+v_0t}\cdot\frac{(N_{Bi}+F_{B0}t-N_{A0}X)}{V_0+v_0t} - \frac{N_{A0}^2X^2}{(V_0+v_0t)^2}\cdot\frac{1}{K_C}\right]\cdot V\right)$$