Lecture 8

Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Lecture 8 – Tuesday

- Block 1: **Mole Balances**
- Block 2: **Rate Laws**
- Block 3: **Stoichiometry**
- Block 4: **Combine**

- **Pressure Drop**
  - Liquid Phase Reactions
  - Gas Phase Reactions

  - Engineering Analysis of Pressure Drop

Pressure Drop in PBRs

Concentration Flow System: $C_A = \frac{F_A}{\upsilon}$

Gas Phase Flow System: $\upsilon = \upsilon_0 (1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P}$

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1 - X)}{\upsilon_0 (1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P}} = \frac{C_{A0}(1 - X)}{(1 + \varepsilon X)} \frac{T_0}{T} \frac{P}{P_0}$$

$$C_B = \frac{F_B}{\upsilon} = \frac{F_{A0}\left(\Theta_B - \frac{b}{a} X\right)}{\upsilon_0 (1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P}} = \frac{C_{A0}\left(\Theta_B - \frac{b}{a} X\right)}{(1 + \varepsilon X)} \frac{T_0}{T} \frac{P}{P_0}$$

Pressure Drop in PBRs

Note: Pressure Drop does NOT affect liquid phase reactions

Sample Question:

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

A→B

Mole Balances

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

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

Rate Laws

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

Pressure Drop in PBRs

Stoichiometry

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

Isothermal, $T=T_0$

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

Combine:

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

Need to find (P/P_0) as a function of W (or V if you have a PFR)

Pressure Drop in PBRs

Ergun Equation:

$$\frac{dP}{dz} = \frac{-G}{\rho g_c D_p}\left(\frac{1-\phi}{\phi^3}\right)\left[\underbrace{\frac{150(1-\phi)\mu}{D_p}}_{LAMINAR} + \underbrace{1.75G}_{TURBULENT}\right]$$

Constant mass flow:

$$\dot{m} = \dot{m}_0$$

$$\rho\upsilon = \rho_0\upsilon_0$$

$$\rho = \rho_0\frac{\upsilon_0}{\upsilon}$$

$$\upsilon = \upsilon_0\frac{F_T}{F_{T0}}\frac{P_0}{P}\frac{T}{T_0}$$

$$\upsilon = \upsilon_0(1+\varepsilon X)\frac{P_0}{P}\frac{T}{T_0}$$

Pressure Drop in PBRs

Variable Density $$\rho = \rho_0 \frac{P}{P_0}\frac{T_0}{T}\frac{F_{T0}}{F_T}$$

$$\frac{dP}{dz} = \frac{-G}{\rho_0 g_c D_p}\left(\frac{1-\phi}{\phi^3}\right)\left[\frac{150(1-\phi)\mu}{D_p} + 1.75G\right]\frac{P_0}{P}\frac{T}{T_0}\frac{F_T}{F_{T0}}$$

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

Pressure Drop in PBRs

Catalyst Weight $$W = zA_c \rho_b = zA_c (1-\phi)\rho_c$$

Where
$$\rho_b = bulk\ \ density$$
$$\rho_c = solid\ \ catalyst\ \ density$$
$$\phi = porosity\,(a.k.a.,\ \ void\ \ fraction)$$
$$(1-\phi) = solid\ fraction$$

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

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

Pressure Drop in PBRs

$$\frac{dy}{dW} = -\frac{\alpha}{2y}\frac{T}{T_0}\frac{F_T}{F_{T0}}$$

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

We will use this form for single reactions:

$$\frac{d\left(P/P_0\right)}{dW} = -\frac{\alpha}{2}\frac{1}{\left(P/P_0\right)}\frac{T}{T_0}\left(1+\varepsilon X\right)$$

$$\boxed{\frac{dy}{dW} = -\frac{\alpha}{2y}\frac{T}{T_0}\left(1+\varepsilon X\right)}$$

$$\boxed{\frac{dy}{dW} = -\frac{\alpha}{2y}\left(1+\varepsilon X\right)}$$

Isothermal case

Pressure Drop in PBRs

$$\frac{dX}{dW}=\frac{kC_{A0}^2(1-X)^2}{F_{A0}(1+\varepsilon X)^2}y^2$$

$$\frac{dX}{dW}=f(X,P) \text{ and } \frac{dP}{dW}=f(X,P) \text{ or } \frac{dy}{dW}=f(y,X)$$

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

Polymath will combine the **Mole Balances**, **Rate Laws** and **Stoichiometry**.

Packed Bed Reactors

$$For \quad \varepsilon = 0$$

$$\frac{dy}{dW} = \frac{-\alpha}{2y}(1+\varepsilon X)$$

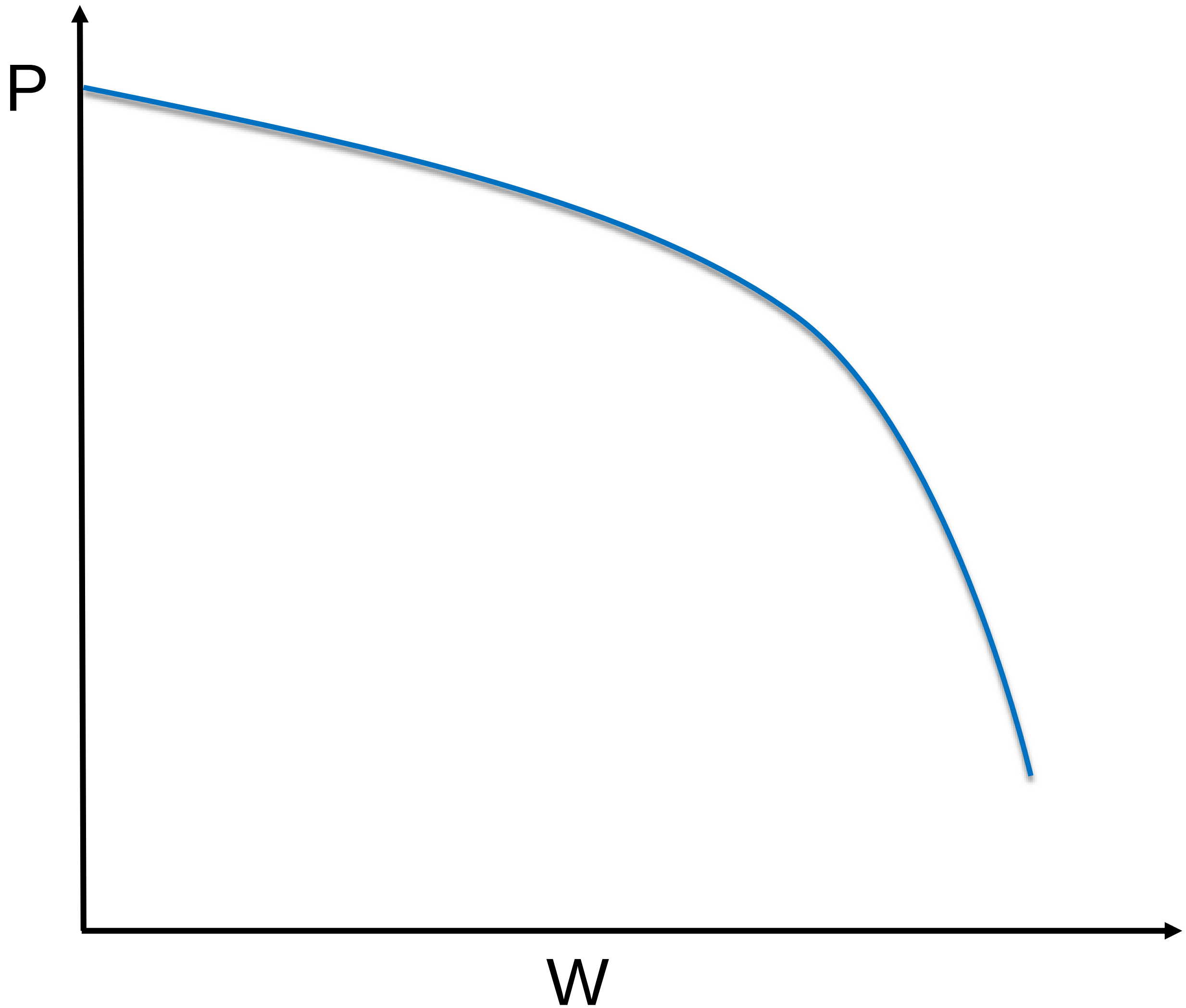
$$When \quad W = 0 \quad y = 1$$

$$dy^2 = -\alpha \, dW$$

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

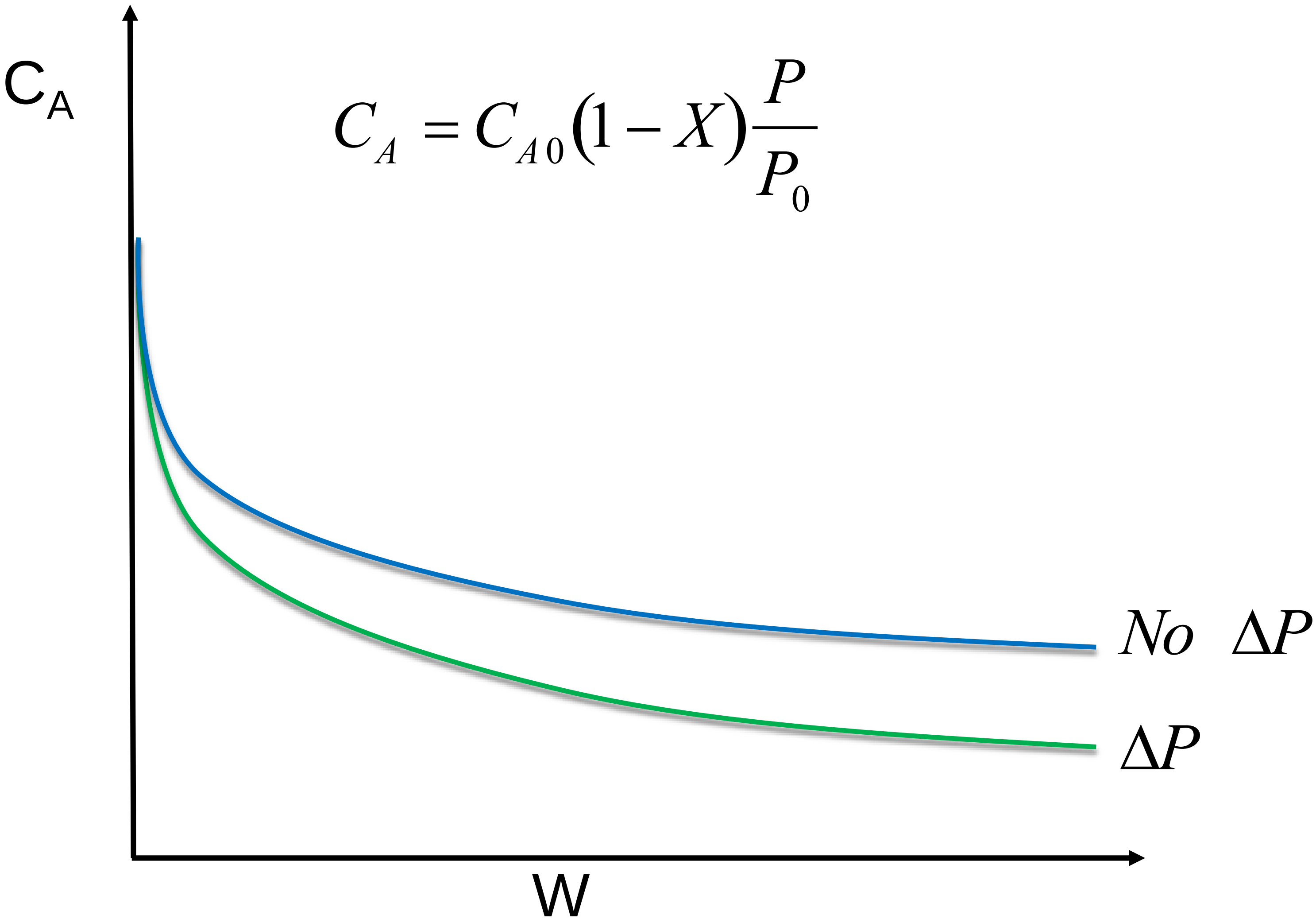
$$y = (1-\alpha W)^{1/2}$$

1 Pressure Drop in a PBR

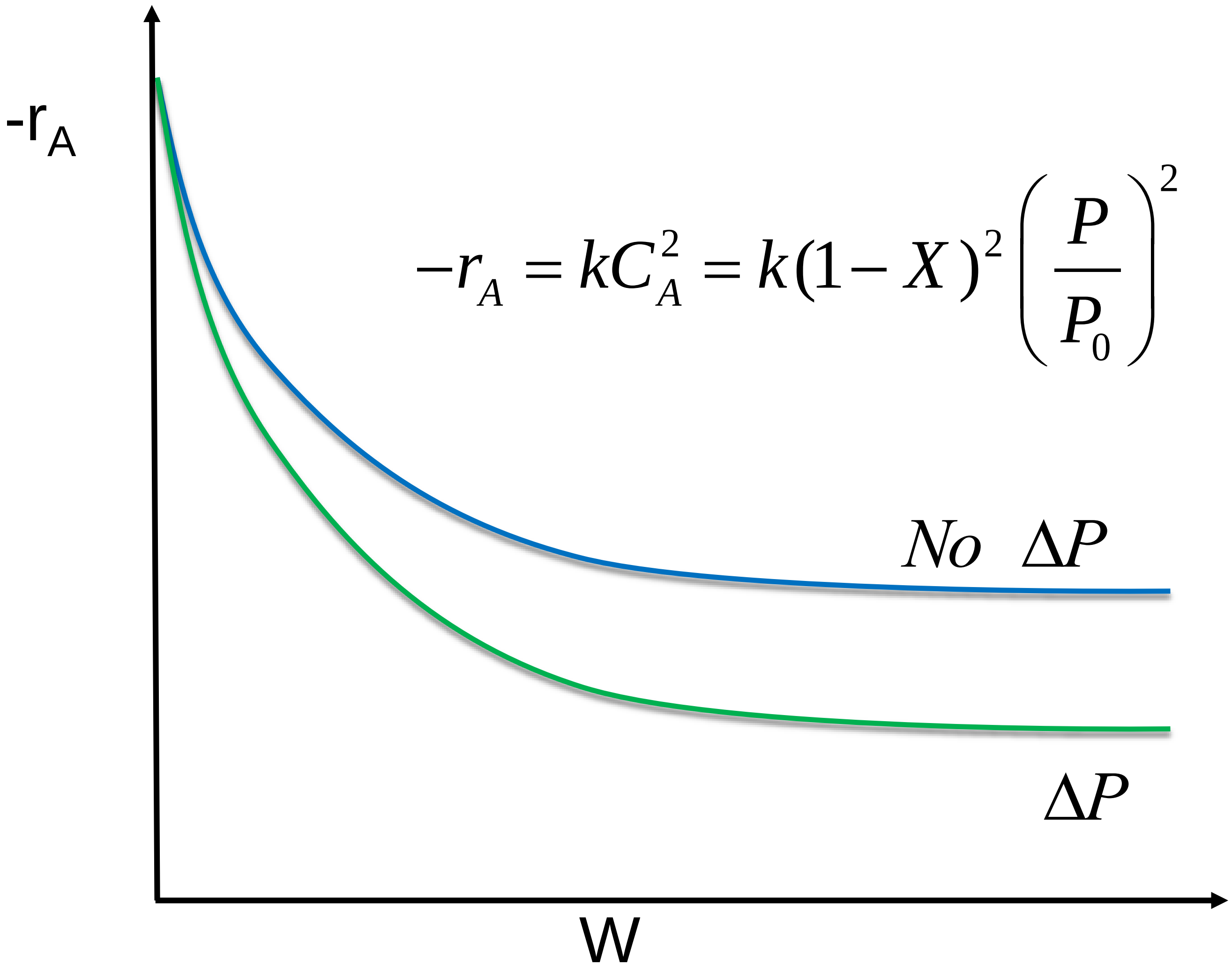


2 Concentration Profile in a PBR

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

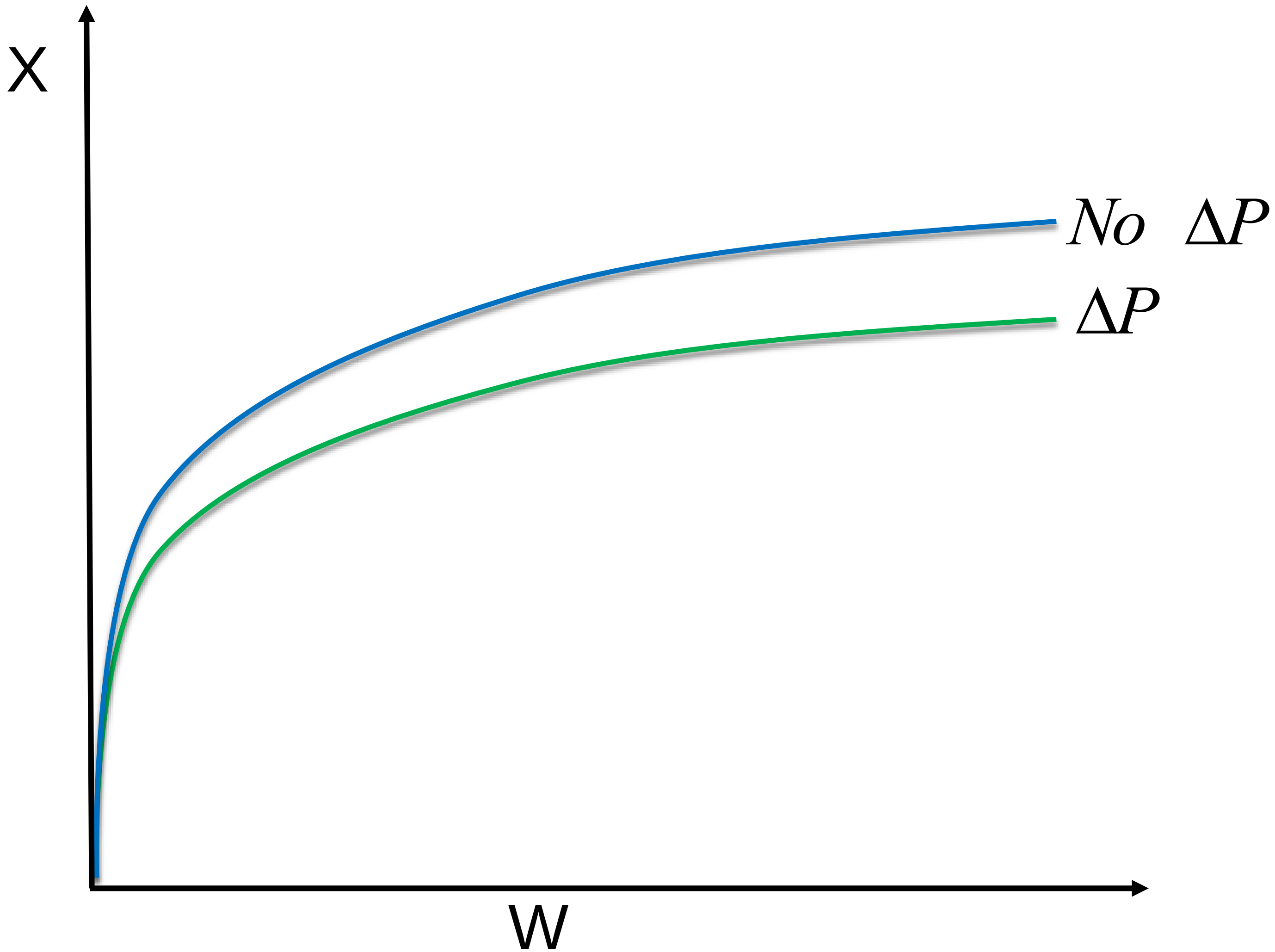


3 Reaction Rate in a PBR



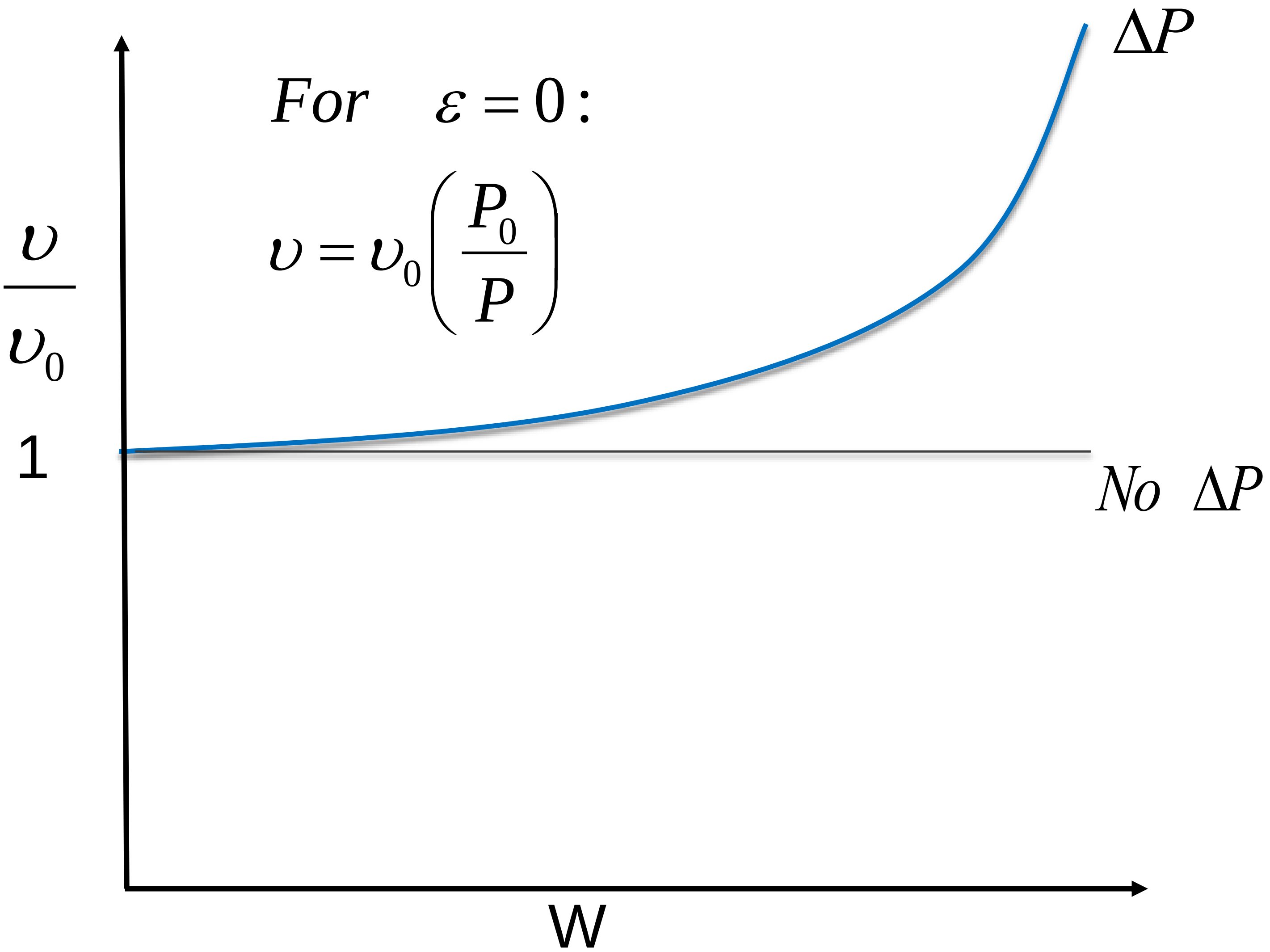
$$-r_A = kC_A^2 = k(1-X)^2\left(\frac{P}{P_0}\right)^2$$

4 Conversion in a PBR



5 Flow Rate in a PBR

$$f = \frac{\upsilon}{\upsilon_0}$$



$$For \quad \varepsilon = 0:$$

$$\upsilon = \upsilon_0 \left(\frac{P_0}{P} \right)$$

$$\upsilon = \upsilon_0 \left(1 + \varepsilon X\right) \frac{P_0}{P} \frac{T}{T_0}$$

$$T = T_0 \qquad y = \frac{P_0}{P}$$

$$f = \frac{\upsilon_0}{\upsilon} = \frac{1}{(1 + \varepsilon X)y}$$

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

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

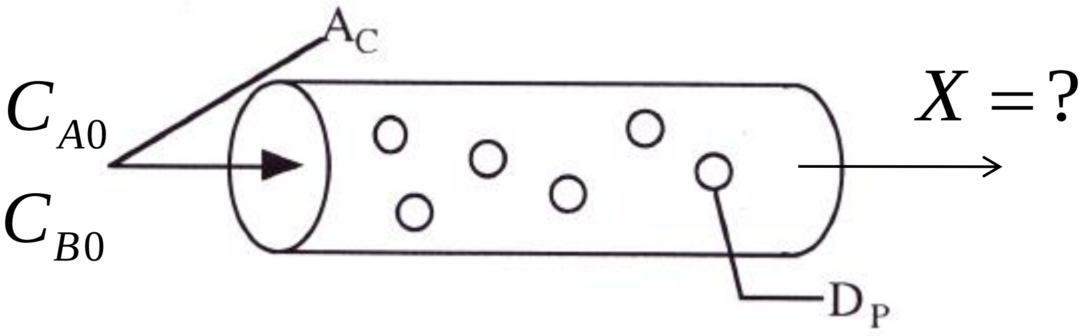
$$A + B \rightarrow 2C$$

Repeat the previous one with equimolar feed of A and B and:

k_A = 1.5dm^6/mol/kg/min $C_{A0} = C_{B0}$

α = 0.0099 kg^{-1}

Find X at 100 kg



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

1) Mole Balance

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

2) Rate Law

$$-r'_A = kC_AC_B$$

3) Stoichiometry

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

$$C_B = C_{A0}(1-X)y$$

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

$$\frac{dy}{dW} = -\frac{\alpha}{2y} \qquad 2ydy = -\alpha dW$$

$$W = 0 \quad , \quad y = 1 \qquad y^2 = 1 - \alpha W$$

$$\boxed{y = (1 - \alpha W)^{1/2}}$$

4) Combine

$$-r_A = kC_{A0}^2 (1 - X)^2 y^2 = kC_{A0}^2 (1 - X)^2 (1 - \alpha W)$$

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

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

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

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

$$W = 0,\ X = 0,\ W = W,\ X = X$$

$$X = 0.6\,(with\ pressure drop)$$

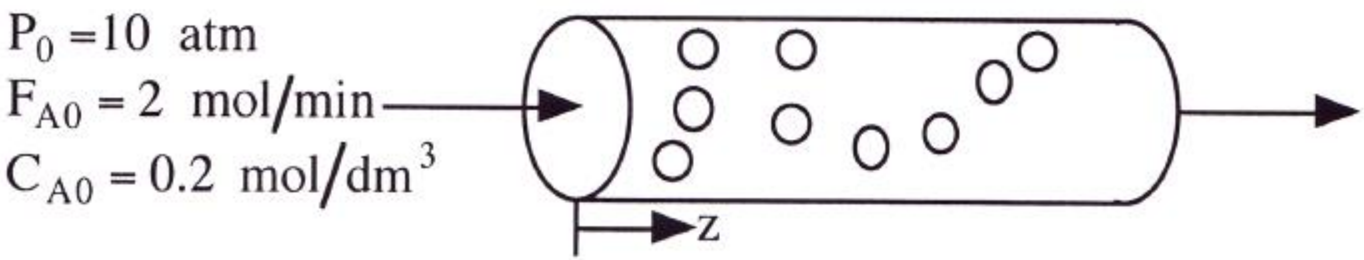
$$X = 0.75\,(without\ pressure drop, i.e.\ \alpha = 0)$$

Example 2:
Gas Phase Reaction in PBR for δ≠0

The reaction

$$A + 2B \rightarrow C$$

is carried out in a packed bed reactor in which there is pressure drop. The feed is stoichiometric in A and B.



Plot the conversion and pressure ratio $y = P/P_0$ as a function of catalyst weight up to 100 kg.

<u>Additional Information</u>

$k_A = 6$ dm^9/mol^2/kg/min

$\alpha = 0.02$ kg^{-1}

Example 2:
Gas Phase Reaction in PBR for δ≠0

A + 2B → C

1) Mole Balance

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

2) Rate Law

$$-r_A' = kC_A C_B^2$$

3) Stoichiometry: Gas, Isothermal

$$\upsilon = \upsilon_0 (1 + \varepsilon X)\frac{P_0}{P}$$

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

Example 2:
Gas Phase Reaction in PBR for δ≠0

4) $$C_B = C_{A0}\frac{\left(\Theta_B - 2X\right)}{\left(1+\varepsilon X\right)}y$$

5) $$\frac{dy}{dW} = -\frac{\alpha}{2y}\left(1+\varepsilon X\right)$$

6) $$f = \frac{\upsilon}{\upsilon_0} = \frac{\left(1+\varepsilon X\right)}{y}$$

7) $$\varepsilon = y_{A0}[1-1-2] = \frac{1}{3}[-2] = -\frac{2}{3}$$

$$C_{A0} = 2, F_{A0} = 2, k = 6, \alpha = 0.02$$

Initial values: W=0, X=0, y=1

Final values: W=100

Combine with Polymath.

If δ≠0, polymath must be used to solve.

Example 2:
Gas Phase Reaction in PBR for δ≠0

POLYMATH Results

POLYMATH Report 01-30-2006, Rev5.1.233

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
W	0	0	100	100
X	0	0	0.8587763	0.8587763
y	1	0.1148659	1	0.1148659
eps	-0.6666667	-0.6666667	-0.6666667	-0.6666667
Cao	0.2	0.2	0.2	0.2
TheataB	2	2	2	2
Cb	0.4	0.0151789	0.4	0.0151789
Fao	2	2	2	2
k	6	6	6	6
Ca	0.2	0.0075895	0.2	0.0075895
alpha	0.02	0.02	0.02	0.02
ra	-0.192	-0.192	-1.049E-05	-1.049E-05

ODE Report (RKF45)

Differential equations as entered by the user

[1] d(X)/d(W) = -ra/Fao

[2] d(y)/d(W) = -alpha*(1+eps*X)/2/y

Explicit equations as entered by the user

[1] eps = (1-2-1)/3

[2] Cao = 0.2

[3] TheataB = 2

[4] Cb = Cao*(TheataB-2*X)/(1+eps*X)*y

[5] Fao = 2

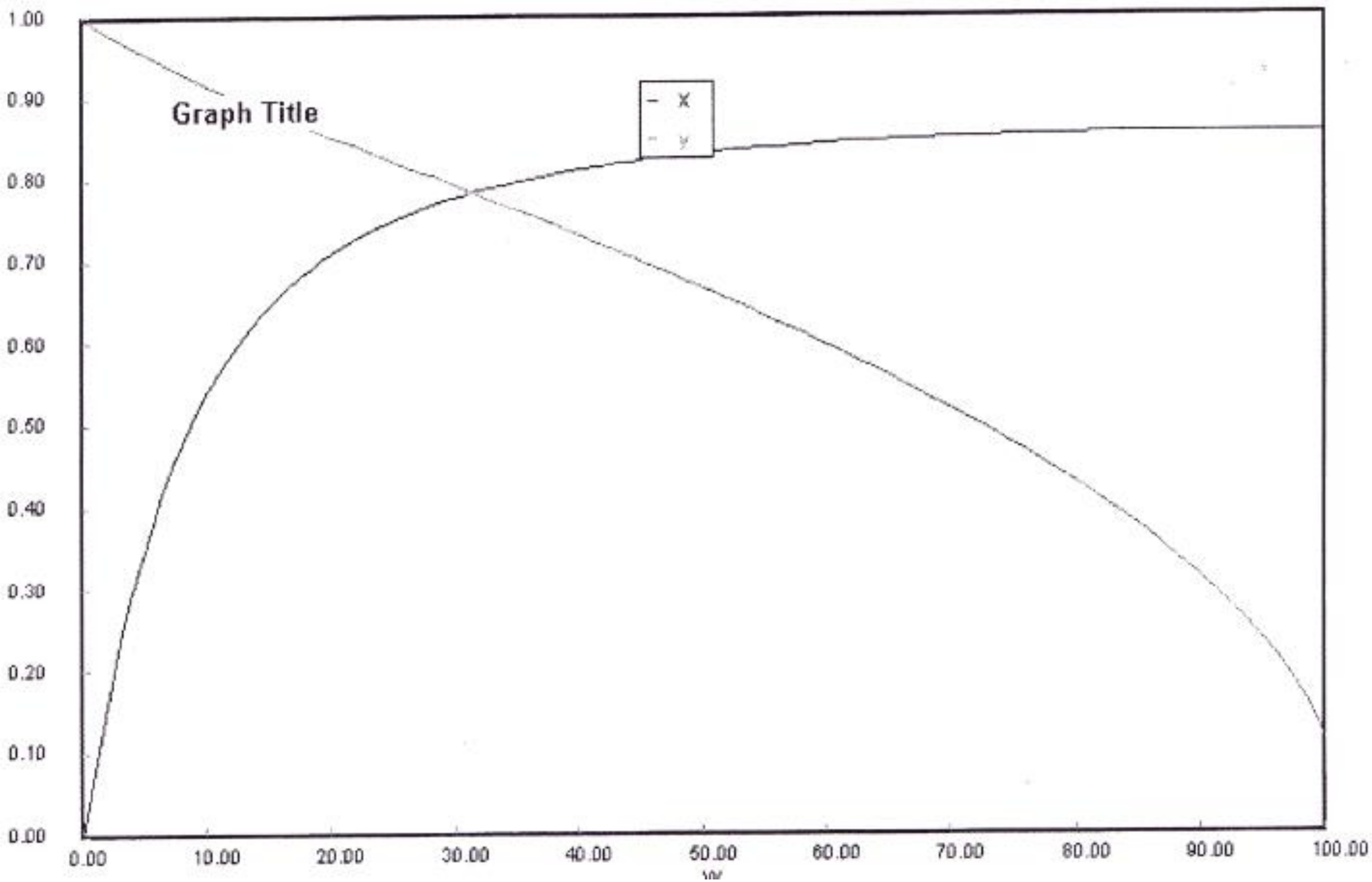
[6] k = 6

[7] Ca = Cao*(1-X)/(1+eps*X)*y

[8] alpha = 0.02

[9] ra = -k*Ca*Cb^2

Example 2:
Gas Phase Reaction in PBR for δ≠0



Gas Phase Reaction in PBR with Pressure Drop $T = T_0$

Mole Balance (1) $$\frac{dX}{dW} = -r_A'/F_{A0}$$

Rate Law (2) $$-r_A' = kC_A$$

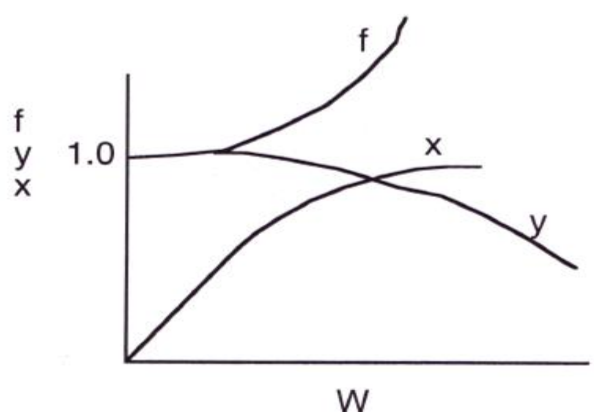
Stoichiometry Gas $T = T_0$

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

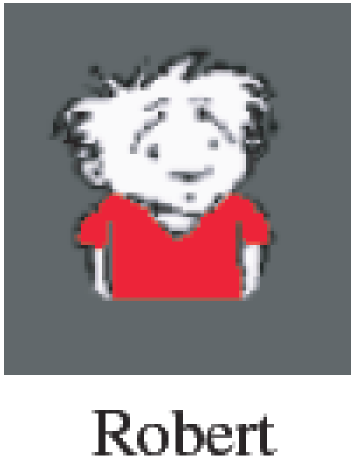
(4) $$\frac{dy}{dw} = -\frac{\alpha(1+\varepsilon X)}{2y}$$

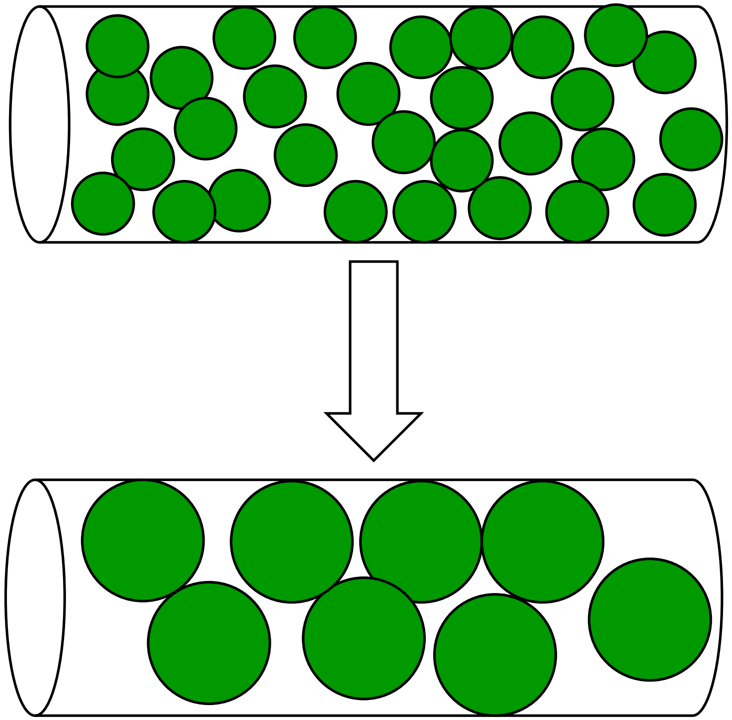
(5) – (9) Parameters, ε, α, …

Combine: Polymath with combine for you



Robert the Worrier wonders: *What if* we increase the catalyst size by a factor of 2?





Pressure Drop
Engineering Analysis

$$\alpha = \frac{2}{A_C(1-\phi)\rho_C P_0}\beta_0 = \frac{2}{A_C(1-\phi)\rho_C P_0}\left[\frac{G(1-\phi)}{\rho_0 g_C D_P \phi^3}\left[\frac{\overbrace{150(1-\phi)\mu}^{\text{Laminar}}}{D_P} + \overbrace{1.75G}^{\text{Turbulent}}\right]\right]$$

$$\rho_0 = MW * C_{T0} = \frac{MW * P_0}{RT_0}$$

$$\alpha = \frac{2RT_0}{A_C \rho_C g_C P_0^2 D_P \phi^3 MW} G\left[\frac{150(1-\phi)\mu}{D_P} + 1.75G\right]$$

$$\alpha \approx \left(\frac{1}{P_0}\right)^2$$

Pressure Drop

Engineering Analysis

A. Laminar Flow Dominant (Term 1 >> Term 2)

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

Case 1 / Case 2

$$\alpha_2 = \alpha_1 \left(\frac{G_2}{G_1}\right)\left(\frac{A_{C1}}{A_{C2}}\right)\left(\frac{D_{P1}}{D_{P2}}\right)^2\left(\frac{P_{01}}{P_{02}}\right)^2$$

Example

How will the pressure drop (e.g., α) change if you decrease the particle diameter by a factor of 4 and increase entering pressure by a factor of 3

$$D_{P2} = \frac{1}{4} D_{P1} \text{ and } P_{02} = 3P_{01}$$

$$\alpha_2 = \alpha_1 \left(\frac{D_{P1}}{\frac{1}{4} D_{P1}}\right)^2 \left(\frac{P_{01}}{3P_{01}}\right)^2 = \frac{16}{9}\alpha_1$$

Pressure Drop
Engineering Analysis

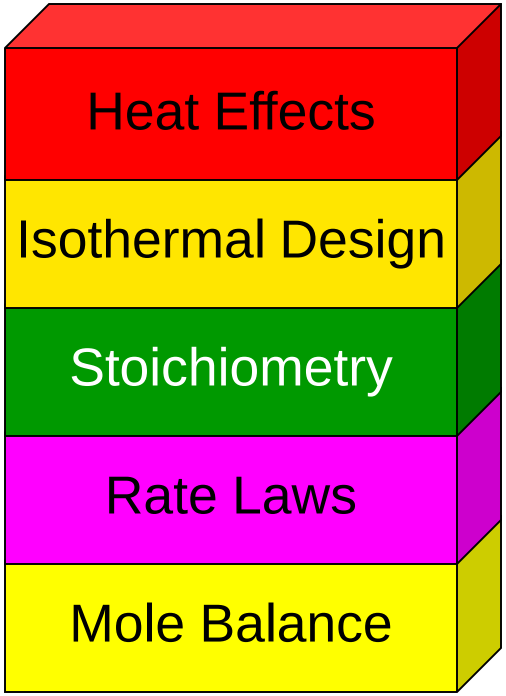
B. Turbulent Flow Dominates (Term 2 >> Term 1)

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

$$\alpha_2 = \alpha_1 \left(\frac{G_2}{G_1}\right)^2 \left(\frac{A_{C1}}{A_{C2}}\right) \left(\frac{P_{01}}{P_{02}}\right)^2 \left(\frac{D_{P1}}{D_{P2}}\right)$$

Again $D_{P2} = \frac{1}{4} D_{P1}$ and $P_{02} = 3P_{01}$

$$\alpha_2 = \alpha_1 \left(\frac{D_{P1}}{\frac{1}{4} D_{P1}}\right) \left(\frac{P_{01}}{3P_{01}}\right)^2 = \frac{4}{9}\alpha_1$$


Heat Effects
Isothermal Design
Stoichiometry
Rate Laws
Mole Balance

End of Lecture 8

Pressure Drop - Summary

- **Pressure Drop**
  - **Liquid Phase Reactions**
    - Pressure Drop does not affect concentrations in liquid phase reactions.
  - **Gas Phase Reactions**
    - Epsilon does not equal to zero

      d(P)/d(W)=…

      Polymath will combine with d(X)/d(W) =… for you
    - Epsilon = 0 and isothermal

      P=f(W)

      Combine then separate variables (X,W) and integrate
    - Engineering Analysis of Pressure Drop

Pressure Change – Molar Flow Rate

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

$$\frac{dy}{dW} = -\frac{\beta_0 \frac{F_T}{F_{T0}} \frac{T}{T_0}}{y P_0 A_c (1-\varphi)\rho_c}$$

$$\alpha = \frac{2\beta_0}{P_0 A_C (1-\varphi)\rho_C}$$

$$\frac{dy}{dW} = -\frac{\alpha}{2y} \frac{F_T}{F_{T0}} \frac{T}{T_0}$$

Use for heat effects, multiple rxns

$$\frac{F_T}{F_{T0}} = (1+\varepsilon X)$$

Isothermal: $T = T_0$

$$\frac{dX}{dW} = -\frac{\alpha}{2y}(1+\varepsilon X)$$

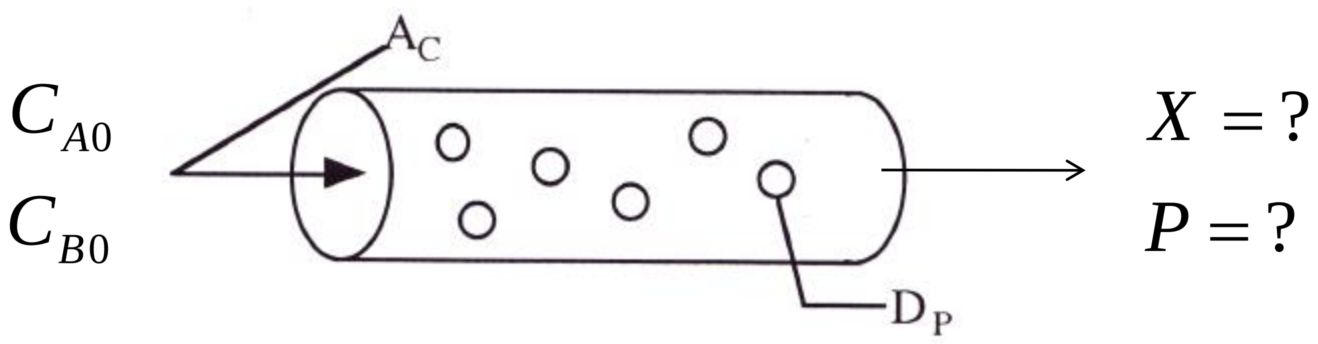
Example 1:
Gas Phase Reaction in PBR for δ=0

A + B → 2C

$$k = 1.5\frac{dm^6}{mol \cdot kg \cdot \min} \quad , \quad \alpha = 0.0099 kg^{-1} \quad , \quad C_{B0} = C_{A0}$$

Case 1: $W = 100 kg \quad , \quad X = ? \quad , \quad P = ?$

Case 2: $D_P = 2D_{P1} \quad , \quad P_{02} = \frac{1}{2}P_{01} \quad , \quad X = ? \quad , \quad P = ?$



PBR

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

$$r_A = -kC_AC_B$$

$$C_A = \frac{F_A}{F_T}y$$

$$C_A = C_B$$

$$\delta = 0 \text{ and } T = T_0 \ \therefore \ y = (1-\alpha W)^{1/2}$$