Gases in PFRs (& batch reactors)

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

Fogler defines $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

$$\Delta = (c+d) - (a+b)$$ .... stoichiometric change

① Case 1: Temp. & volume constant

$$\Delta \neq 0$$

$$P_{A_0} = n_{A_0} \frac{RT}{\dot{V}}$$ .... $\underline{\dot{V} \text{ or } v}$

$$P_A = n_A \frac{RT}{\dot{V}}$$

$$\therefore \; P_{A_0} - P_A = (n_{A_0} - n_A) \frac{RT}{\dot{V}}$$

From stoichiometry:

For every $\underline{a}$ moles of A that reacts, the change of moles is $\underline{\Delta}$

$\therefore$ For $(n_{A_0} - n_A)$, the change is $\frac{\Delta}{a}(n_{A_0} - n_A)$

For the whole system:

$$\Delta P = \Delta n \frac{RT}{v}$$

$$\& \ \Delta n = \frac{\Delta}{a}\left(n_{A0} - n_A\right)$$

$$\therefore \overset{\text{final - initial}}{\left(-\pi_0 + \pi\right)} = \frac{\Delta}{a} \underbrace{\left(n_{A0} - n_A\right)\frac{RT}{v}}_{\downarrow}$$

$$\therefore \quad \pi - \pi_0 = \frac{\Delta}{a}\left(P_{A0} - P_A\right)$$

$$\therefore \quad P_{A0} - P_A = \frac{a}{\Delta}\left(\pi - \pi_0\right)$$

$$\boxed{\therefore \quad P_A = P_{A0} + \frac{a}{\Delta}\left(\pi_0 - \pi\right)}$$

For products:

$$\boxed{P_C = P_{C0} - \frac{c}{\Delta}\left(\pi_0 - \pi\right)}$$ ..... derive using stoichiometry

What happens if $\Delta = 0$ & T & v are constant?

$\underline{P = \text{constant}}$!

② Case 2: T & P constant, V & n change

i.e. $\Delta \neq 0$

$$\boxed{\text{Definition} \equiv \quad \varepsilon = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}}}$$

For $X_A = 1$, moles of A reacted $= n_{A_0}$

$\therefore$ total change in moles $= \frac{\Delta \cdot n_{A_0}}{a}$

$$\therefore \quad \Delta V = \Delta n \left(\frac{RT}{P}\right)$$

$$\therefore \quad V - V_0 = \frac{\Delta n_{A_0}}{a}\left(\frac{RT}{P}\right) \quad \text{---- } \underline{\underline{\text{for } \varepsilon}}$$

$$\therefore \quad V = V_0 + \frac{RT}{P}\left(\frac{\Delta \cdot n_{A_0}}{a}\right)$$

all moles of A have reacted

$V_{X_A=1}$ $\quad$ $V_{X_A=0}$

$$\varepsilon = \frac{V - V_0}{V_0} = \frac{RT}{P V_0}\left(\frac{\Delta \cdot n_{A_0}}{a}\right)$$

fn. of mole fraction & stoichiometry

$$\boxed{\varepsilon = \begin{pmatrix}\text{initial}\\ \text{mole}\\ \text{frac.}\end{pmatrix} \times \frac{\Delta}{a}}$$

$$\therefore \quad \varepsilon = \frac{RT}{P\upsilon_0}\left(\frac{\Delta \cdot n_{A0}}{a}\right)$$

$$\boxed{\therefore \quad \varepsilon = \frac{n_0^{-1} n_{A0}\,\Delta}{a}}$$

basis for problem (can be any species)

$$\text{But,} \quad \underbrace{\upsilon - \upsilon_0}_{\text{general case}} = \frac{\Delta}{a}\left(n_{A0} - n_A\right)\frac{RT}{P}$$

$$\therefore \quad \upsilon - \upsilon_0 = \frac{\Delta}{a}\, n_{A0}\left(\frac{n_{A0} - n_A}{n_{A0}}\right)\frac{RT}{P}$$

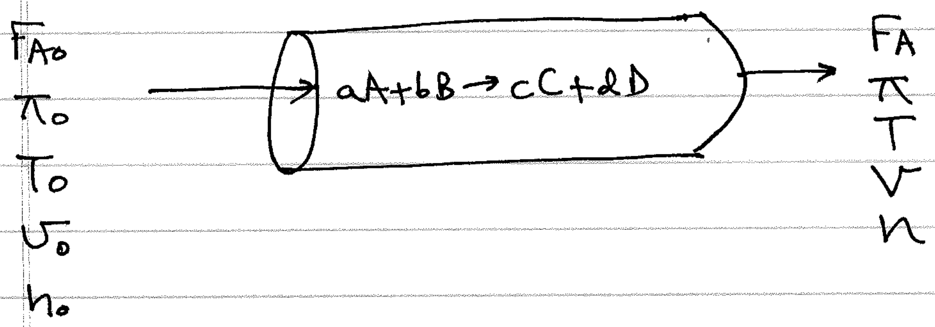
$$\therefore \quad \upsilon - \upsilon_0 = \left(\frac{\Delta n_{A0}}{a}\right) X_A \left(\frac{RT}{P\upsilon_0}\right)\upsilon_0$$

$$\therefore \quad \upsilon - \upsilon_0 = \left(\frac{n_0^{-1}\Delta n_{A0}}{a}\right) X_A\, \upsilon_0 \quad \ldots\ldots \varepsilon = \frac{n_{A0}\Delta}{n_0 a}$$

$$\therefore \quad \upsilon = \upsilon_0 + \upsilon_0\, \varepsilon X_A$$

$$\boxed{\therefore \quad \upsilon = \upsilon_0\left(1 + \varepsilon X_A\right)}$$

Case 3 : Generalized flow case
(T, P, V, n changing)



As before, $\Delta = d + c - b - a$

Fogler uses: $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

$$\boxed{\therefore \frac{\Delta}{a} = \delta}$$

Let us start from the ideal gas law,

$$\boxed{PV = nRT}$$

For our system:

$$\pi_o \upsilon_o = n_o R T_o$$

$$\& \ \pi \upsilon = n R T$$

Dividing these equations, we get:

$$\frac{\Pi_0 v_0}{\pi v} = \frac{n_0 T_0}{n T}$$

$$\therefore \frac{\pi_0 v_0 n T}{\pi n_0 T_0} = v$$

$$\therefore v = v_0 \left\{ \frac{\Pi_0}{\pi} \cdot \frac{n}{n_0} \cdot \frac{T}{T_0} \right\}$$

In case of non-ideality:

$$\boxed{PV = ZnRT}$$

compressibility factor

FYI: when does the ideal gas law start to fail?

High P, low T (HPLT!) → instead of HPLC ☺

* what happens when you pressurise a gas
↳ becomes liquid!

Recollect from thermodynamics:

$$Z = f(T, P, v)$$

Example: Virial Equations of State

The virial equation in pressure:

$$Z = 1 + B'P + C'P^2 + D'P^3 + \dots$$

$$B' = \frac{B}{RT}, \quad C' = \frac{C - B^2}{(RT)^2} \text{ \& so on}$$

mole fractions

$$B = \sum_i \sum_j y_i \, y_j \, B_{ij}$$

interaction parameter

depends on composition

$$C = \sum_i \sum_j \sum_k y_i \, y_j \, y_k \, C_{ij}$$

Nevertheless,

or π

$$P_0 v_0 = n_0 Z_0 R T_0$$

$$P v = n Z R T$$

$$\therefore \frac{P_0 v_0}{P v} = \left(\frac{n_0}{n}\right)\left(\frac{Z_0}{Z}\right)\left(\frac{T_0}{T}\right)$$

$$\therefore \quad v = v_0 \left\{ \frac{\pi_0}{\pi} \cdot \frac{n}{n_0} \cdot \frac{T}{T_0} \frac{Z}{Z_0} \right\}$$

Recollect

$$\Delta n = n - n_0$$ .... change in moles can be related to conversion

If a moles $\longrightarrow$ Δ moles (from stoich.)

$n_{A0} - n_A \longrightarrow \Delta n$

$$\therefore \quad \underline{\underline{\Delta n}} = (n_{A0} - n_A) \frac{\Delta}{a}$$

stoich coeff.

change

$$\therefore \quad \Delta n = \left(\frac{n_{A0} - n_A}{n_{A0}} \right) \frac{\Delta n_{A0}}{a}$$

$$\therefore \quad \Delta n = \frac{X_A \left(\Delta \right) n_{A0}}{\left(a \right)}$$

$$\therefore \quad \Delta n = X_A \underbrace{\left(\frac{\Delta}{a} \right) \frac{n_{A0}}{n_0}}_{\varepsilon} \cdot n_0$$

$$\therefore \quad \Delta n = X_A \varepsilon n_0$$

$$\therefore \quad n - n_0 = n_0 \varepsilon X_A$$

$$\therefore \quad n = n_0 (1 + \varepsilon X_A)$$

$$\therefore \quad \frac{n}{n_0} = 1 + \varepsilon X_A \longrightarrow$$ subst. in volume term

$$\boxed{\therefore \quad v = v_0 \left(\frac{\pi_0}{\pi}\right)\left(\frac{T}{T_0}\right)\left(\frac{z}{z_0}\right)(1 + \varepsilon X_A)}$$

Compare to case when T & P were constant.

<u>Other definitions:</u>

$$\Theta_i = \frac{F_{i0}}{F_{A0}}$$

basis species (for which we define X_A)

Also, stoichiometry is <u>key</u>

Consider $\underline{aA + bB \longrightarrow cC + dD}$

$$\underset{\text{final}}{\underset{\uparrow}{N_A}} = \underset{\text{original}}{\underset{\uparrow}{N_{A0}}} - \underset{\text{change}}{\underset{\uparrow}{N_{A0} X_A}}$$

& from stoichiometry:

$$\left.\begin{aligned} &\text{moles of A reacted} = N_{A0} X_A \\ &\therefore \text{ moles of B reacted} = \left(\frac{b}{a}\right) N_{A0} X_A \\ &\therefore \text{ moles of C produced} = \left(\frac{c}{a}\right) N_{A0} X_A \\ &\therefore \text{ moles of D produced} = \left(\frac{d}{a}\right) N_{A0} X_A \end{aligned}\right\} \text{change terms}$$

$$\therefore \quad N_B = N_{B0} - N_{A0} X_A \left(\frac{b}{a}\right)$$

$$N_C = N_{C0} + \left(\frac{c}{a}\right) N_{A0} X_A$$

$$N_D = N_{D0} + \left(\frac{d}{a}\right) N_{A0} X_A$$

Also, $N_{B0} = \Theta_B N_{A0}$

$$N_{C0} = \Theta_C N_{A0}$$

$$N_{D0} = \Theta_D N_{A0}$$

$$\boxed{\begin{aligned} \therefore\ N_A &= N_{A0}\left(1 - X_A\right) \\ N_B &= N_{A0}\left(\theta_B - \frac{b X_A}{a}\right) \\ N_C &= N_{A0}\left(\theta_C + \frac{c X_A}{a}\right) \\ N_D &= N_{A0}\left(\theta_D + \frac{d X_A}{a}\right) \end{aligned}}$$

→ all species written in terms of N_{A0}, X_A

Consider N_A & C_A:

(consider ideal gas)
(if non-ideal, correlation will be given)

$$C_A = \frac{N_A}{v} = \frac{N_{A0}\left(1 - X_A\right)}{v_0\left(\frac{\pi_0}{\pi}\frac{T}{T_0}\right)\left(1 + \varepsilon X_A\right)}$$

$$\therefore\ C_A = \left(\frac{N_{A0}}{v_0}\right)\frac{\left(1 - X_A\right)}{\left(1 + \varepsilon X_A\right)}\left(\frac{\pi T_0}{\pi_0 T}\right)$$

$$\boxed{\therefore\ C_A = C_{A0}\left(\frac{\pi T_0}{\pi_0 T}\right)\left(\frac{1 - X_A}{1 + \varepsilon X_A}\right)}$$

What is the protocol for batch & flow reactors?

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

i.e. $A + (b/a)B \longrightarrow \left(\frac{c}{a}\right)C + \left(\frac{d}{d}\right)D$

Species	Initial	Change	Final	Final Conc.
A	N_{A0}	$-N_{A0}X_A$	$N_{A0}(1-X_A)$	$N_A/\upsilon = C_A$
B	$\Theta_B N_{A0}$	$-(b/a)N_{A0}X_A$	$N_{A0}\left(\Theta_B - \frac{bX_A}{a}\right)$	$\frac{N_B}{\upsilon} = C_B$
C	$\Theta_C N_{A0}$	$+(c/a)N_{A0}X_A$	$N_{A0}(\Theta_C + c/a\, X_A)$	$\frac{N_C}{\upsilon} = C_C$
D	$\Theta_D N_{A0}$	$+(d/a)N_{A0}X_A$	$N_{A0}\left(\Theta_D + \frac{d}{a}X_A\right)$	$\frac{N_D}{\upsilon} = C_D$
I	$\Theta_I N_{A0}$	0	$\Theta_I N_{A0}$	$\frac{N_I}{\upsilon} = C_I$

inert species

$$\upsilon = \upsilon_0 \left(\frac{\pi_0 T\ Z}{\pi T_0 Z_0}\right)(1+\varepsilon X_A)$$

Eg. $\therefore$ $$C_A = \frac{N_{A0}(1-X_A)}{\upsilon_0 \left(\frac{\pi_0 T\ Z}{\pi T_0 Z_0}\right)(1+\varepsilon X_A)}$$

assume ideal when true

$$\therefore C_A = \frac{N_{A0}}{\upsilon_0}\left(\frac{\pi T_0 Z_0}{\pi_0 T Z}\right)\left(\frac{1-X_A}{1+\varepsilon X_A}\right)$$

$$\boxed{\therefore C_A = C_{A0}\left(\frac{\pi T_0 Z_0}{\pi_0 T Z}\right)\left(\frac{1-X_A}{1+\varepsilon X_A}\right)}$$

Similarly,

$$C_B = C_{A_0}\left(\frac{\pi T_0 Z_0}{\pi_0 T Z}\right)\left(\frac{\theta_B - (b/a)X_A}{1+\varepsilon X_A}\right)$$

$$C_C = C_{A_0}\left(\frac{\pi T_0 Z_0}{\pi_0 T Z}\right)\left(\frac{\theta_C - \frac{cX_A}{a}}{1+\varepsilon X_A}\right) \text{ \& so on}$$

$$\boxed{\frac{C_{B0}}{C_{C0}} = \frac{\theta_B}{\theta_C}} \quad \& \quad \boxed{\frac{C_B}{C_C} = \frac{\theta_B - b/a\, X_A}{\theta_C - \frac{c}{a} X_A}}$$

Now, $\boxed{dV = \left(\frac{F_{A0}}{-r_A}\right) dX_A}$ ...... volume of a PFR

If $-r_A = k C_A C_B$

$$\therefore -r_A = k\left[C_{A0}\left(\frac{\pi T_0 Z_0}{\pi_0 T Z}\right)\right]^2\left(\frac{1-X_A}{1+\varepsilon X_A}\right)\left(\frac{\theta_B - b/a\, X_A}{1+\varepsilon X_A}\right)$$

$$\therefore -r_A = k\left(\frac{C_{A0}\pi T_0 Z_0}{\pi_0 T Z}\right)^2 \frac{(1-X_A)\left(\theta_B - \frac{b}{a}X_A\right)}{(1+\varepsilon X_A)^2}$$

$$\therefore \frac{F_{A0}}{-r_A} = \frac{(1+\varepsilon X_A)^2}{(1-X_A)\left(\theta_B - \frac{b}{a}X_A\right)}\left(\frac{\pi_0 T Z}{C_{A0}\pi T_0 Z_0}\right)^2 \frac{1}{k} \cdot C_{A0}\upsilon_0$$

$$\therefore \frac{F_{A0}}{-r_A} = \frac{(1+\varepsilon X_A)^2}{(1-X_A)\left(\theta_B - \frac{b}{a}X_A\right)} \left(\frac{\pi_0 T Z}{\pi T_0 Z_0}\right)^2 \frac{\upsilon_0}{kC_{A0}}$$

$$\boxed{\therefore\ dV = \left(\frac{\pi_0 T Z}{\pi T_0 Z_0}\right)^2 \frac{\upsilon_0}{kC_{A0}} \frac{(1+\varepsilon X_A)^2}{(1-X_A)\left(\theta_B - \frac{b}{a}X_A\right)}\, dX_A}$$

$$\Downarrow$$

<u>Solve ODE</u>