# Chap-4
# Variable volume reaction

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# Stoichiometric table for flow reactor (i.e. CSTR and PFR)

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

Like batch reactor

$$\theta_B = \frac{F_{B0}}{F_{A0}} = \frac{y_{B0}}{y_{A0}};\ \theta_C = \frac{F_{C0}}{F_{A0}} = \frac{y_{C0}}{y_{A0}};\ \theta_D = \frac{F_{D0}}{F_{A0}} = \frac{y_{D0}}{y_{A0}}$$

| Initial Feed Rate | Effluent Rate | Effluent Concentrations |
|---|---|---|
| $F_A = F_{A0}$ | $F_A = F_{A0}(1 - X_A)$ | $C_A = \frac{F_A}{v} = \frac{F_{A0}(1 - X_A)}{v_0}$ |
| $F_B = \theta_B F_{A0}$ | $F_B = F_{A0}(\theta_B - \frac{b}{a}X_A)$ | $C_B = \frac{F_B}{v} = \frac{F_{A0}(\theta_B - \frac{b}{a}X_A)}{v_0}$ |
| $F_C = \theta_C F_{A0}$ | $F_C = F_{A0}(\theta_C + \frac{c}{a}X_A)$ | $C_C = \frac{F_C}{v} = \frac{F_{A0}(\theta_C + \frac{c}{a}X_A)}{v_0}$ |
| $F_D = \theta_D F_{A0}$ | $F_D = F_{A0}(\theta_D + \frac{d}{a}X_A)$ | $C_D = \frac{F_D}{v} = \frac{F_{A0}(\theta_D + \frac{d}{a}X_A)}{v_0}$ |

# Variable volume Reaction for volume changes

$$Total\ feed\ rate\ , F_{T0} = F_{A0}(1 + \theta_B + \theta_C + \theta_D)$$

*Total effluent rate ,* $F_T = F_{A0}(1 + \theta_B + \theta_C + \theta_D) + F_{A0}\left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)X$

$$if\ \delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\ , \qquad F_T = F_{T0} + F_{A0}\delta X$$

$$\frac{F_T}{F_{T0}} = 1 + \frac{F_{A0}}{F_{T0}}\delta X = 1 + y_{A0}\delta X$$

Similarly, for Batch Reactor

$$N_T = N_{T0} + N_{A0}\delta X, \qquad \frac{N_T}{N_{T0}} = 1 + \frac{N_{A0}}{N_{T0}}\delta X = 1 + y_{A0}\delta X$$

Assuming $PV = zN_TRT$

$$V = V_0\left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)\left(\frac{z}{z_0}\right)\frac{N_T}{N_{T0}}$$

# Variable volume Reaction for volume changes

$$v = v_0 \left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)\left(\frac{z}{z_0}\right)\frac{F_T}{F_{T0}}$$

$$for\ ideal\ behavior, \left(\frac{z}{z_0}\right) = 1$$

If there is no pressure and temperature variation inside the reactor

$V = V_0 \frac{N_T}{N_{T0}} = V_0 \left(1 + \frac{N_{A0}}{N_{T0}} \delta X\right)$and $v = v_0 \frac{F_T}{N_{T0}} = v_0 \left(1 + \frac{F_{A0}}{F_{T0}} \delta X\right)$

$$\frac{F_{A0}}{F_{T0}} \delta \ \ or, \frac{N_{A0}}{N_{T0}} \delta = y_{A0}\delta = \varepsilon_A$$

$$\boldsymbol{V = V_0(1 + \varepsilon_A X)}$$

# Variable volume Reaction for volume changes

- For j$^{th}$ species concentrations in different reactors
- $C_j = \frac{N_j}{V} = \frac{N_{j0}(\theta_j + \frac{j}{a}X_A)}{V_0\left(1 + \frac{N_{j0}}{N_{T0}}\delta X\right)}$
- $C_j = \frac{F_j}{v} = \frac{F_j}{v_0\left(1 + \frac{F_{j0}}{F_{T0}}\delta X\right)}$
- $where,\ v = v_0\left(1 + \frac{F_{j0}}{F_{T0}}\delta X\right) = v_0(1 + \varepsilon_j X)$
- $and\ also\ \ V = V_0(1 + \varepsilon_j X)$
- For reactant 'A' we can write
- $\varepsilon_A X = \frac{V}{V_0} - 1\ or,\ \ X = \frac{\Delta V}{V_0 \varepsilon_A}$

# Variable volume Reaction for volume changes

$$for\ X = 1, \qquad i.e. complete\ conversion\ , \varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}}$$

$$\boldsymbol{\varepsilon_A = fractional\ \ volume\ \ change}$$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(\theta_a - \frac{a}{a}X_A)}{V_0\left(1 + \frac{N_{A0}}{N_{T0}}\delta X\right)} \quad \text{or,} \quad C_A = \frac{N_A}{V} = \frac{N_{A0}(1 - X_A)}{V_0(1 + \varepsilon_A X)}$$

$$C_B = \frac{N_B}{V} = \frac{N_{A0}(\theta_b - \frac{b}{a}X_A)}{V_0(1 + \varepsilon_A X)} \quad \text{and} \quad C_C = \frac{N_C}{V} = \frac{N_{A0}(\theta_C + \frac{c}{a}X_A)}{V_0(1 + \varepsilon_A X)}$$

$$e.g.\ N_2 + \ 3H_2 \ \rightleftarrows 2NH_3 \quad \varepsilon_A = \frac{2-4}{4} = -\ 0.5,$$

if reactants are added in their stoichiometric proportion.

# Variable Volume Reaction in A Batch Reactor

Mole balance for first-order reaction A→ P

$$-\frac{1}{V}\frac{dN_A}{dt} = k\ C_A = k\frac{N_A}{V}$$

$$V = V_0(1 + \varepsilon_A X_A)$$

$$-\frac{N_{A0}}{V_0(1 + \varepsilon_A X_A)}\left(\frac{-dX_A}{dt}\right) = k\frac{N_{A0}(1 - X_A)}{V_0(1 + \varepsilon_A X_A)}$$

$$C_{A0}\frac{dX_A}{dt} = kC_{A0}(1 - X_A)$$

$$\frac{dX_A}{dt} = k(1 - X_A)$$

# Variable Volume Reaction in A Batch Reactor

$$-\ln(1-X_A)=\ln\left(1-\frac{\Delta V}{\varepsilon_A V_0}\right)=kt$$

So, the equation is same first-order reaction

Mole balance  for second-order reaction 2A → P

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

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

$$\frac{C_{A0}}{1+\varepsilon_A X_A}\frac{dX_A}{dt}=k\left[\frac{C_{A0}(1-X_A)}{(1+\varepsilon_A X_A)}\right]^2$$

$$\frac{dX_A}{dt}=kC_{A0}\,\frac{(1-X_A)^2}{(1+\varepsilon_A X_A)}$$

# Variable Volume Reaction in A Batch Reactor

$$\int_0^{X_A} \frac{dX_A}{(1-X_A)^2} + \int_0^{X_A} \frac{\varepsilon_A dX_A}{(1-X_A)^2} = kC_{A0} \int_0^t dt$$

$$\frac{(1+\varepsilon_A)X_A}{1-X_A} + \varepsilon_A \ln(1-X_A) = kC_{A0}t$$

$$Where, \qquad X_A = \frac{\Delta V}{\varepsilon_A V_0}$$

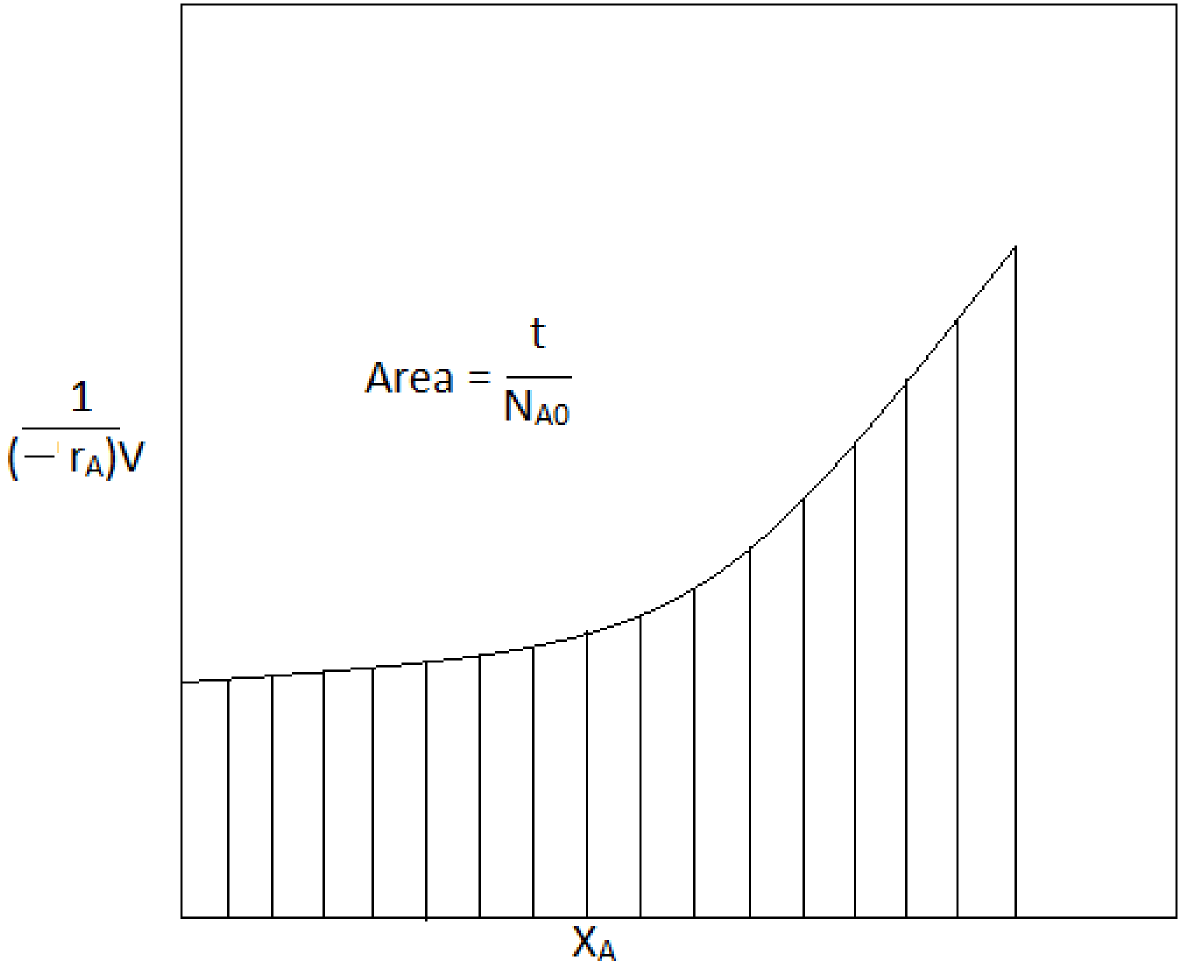
For nth order reaction,

$$\int_0^{X_A} \frac{(1+\varepsilon_A X_A)^{n-1}}{(1-X_A)^n} = dX_A C_{A0}^{n-1} kt$$

**Design Equation:** $t = N_{A0} \int_0^{X_A} \frac{dX_A}{V(-r_A)} = N_{A0} \int_0^{X_A} \frac{dX_A}{V_0(1+\varepsilon_A X_A)(-r_A)}$

- $t = C_{A0} \int_0^{X_A} \frac{dX_A}{(1+\varepsilon_A X_A)(-r_A)}$

# Graphical analysis for batch reactor



# Ideal CSTR or Mixed Flow Reactor

$$F_{A0}(1 - X_{A0}) = F_{A0}(1 - X_A) + (-r_A)V$$

$$At\ \ X_{A0} = 0, \qquad F_{A0}X_A = (-r_A)V$$

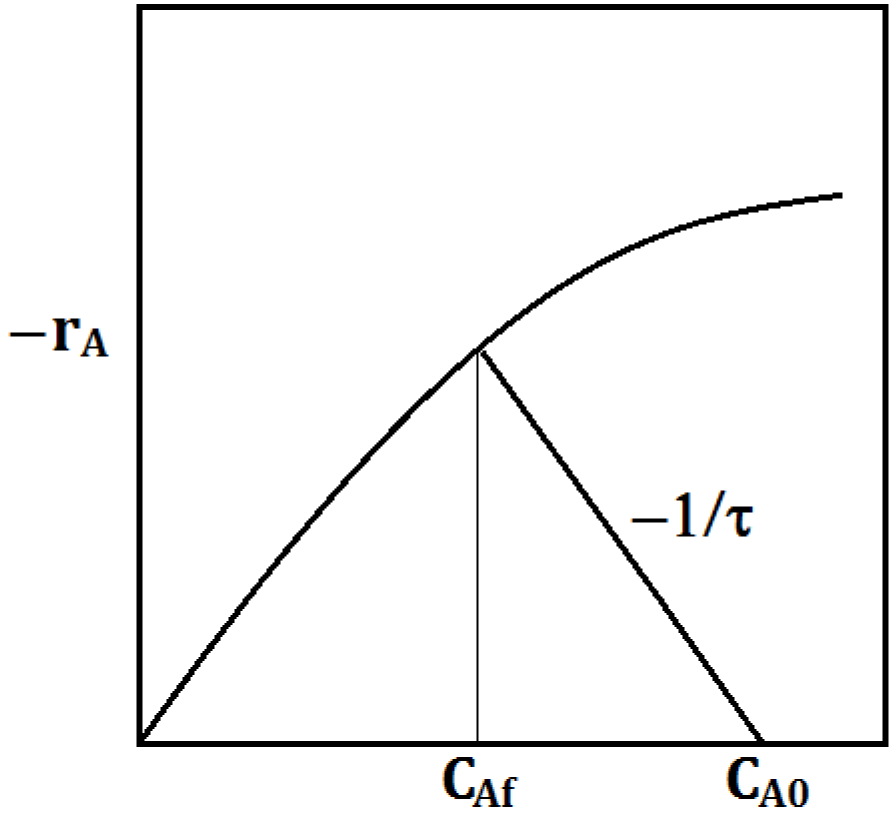
$$\frac{V}{F_{A0}} = \frac{X_A}{-r_A} = \frac{C_{A0} - C_{Af}}{C_{A0}(-r_A)}$$

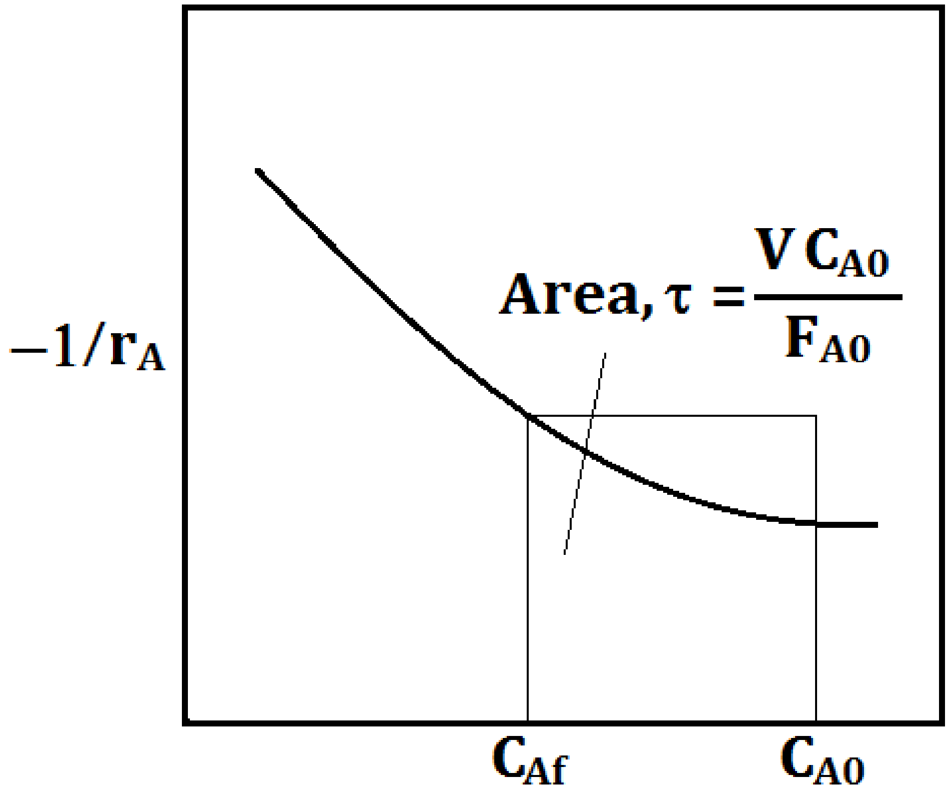
$$\tau = \frac{C_{A0} - C_{Af}}{(-r_A)} \qquad or, \qquad \tau = \frac{C_{A0}(X_{Af} - X_{A0})}{(-r_A)}$$

$$(-r_A) = (C_{Af} - C_{A0})(-1/\tau)$$

$$\boldsymbol{Area = \tau = \frac{VC_{A0}}{F_{A0}} = \left(C_{A0} - C_{Af}\right)\frac{1}{-r_A} = C_{A0}\frac{X_{Af} - X_{A0}}{-r_A}}$$

# Graphical presentation




**$C_A$ vs. $-r_A$ plot**