University Of Jordan
Faculty of Engineering and Technology
Department of Chemical Engineering

Chemical Reaction Engineering

Mole Balances

Dr.-Eng. Zayed Al-Hamamre

Content

- Introduction
- Reaction Rate
- General Mole Balance
- Balance on Batch Reactor
- Balance on CSTR
- Balance on PFR
- Packed Bed Reactor

Text Book

Fogler, The Elements of Chemical Reaction Engineering, 3rd or 4th ed.,Upper Saddle River, NJ, Prentice Hall, 2006

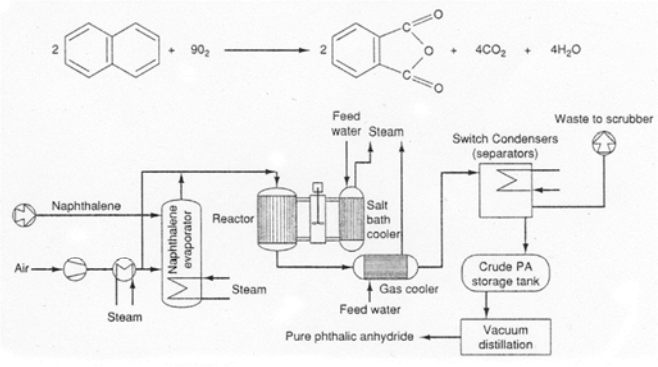
Materials on the Web and CDROM

http://www.engin.umich.edu/~cre/

Introduction

- Chemical **kinetics** is the study of chemical reaction rates and reaction mechanisms.
- The study of chemical reaction engineering (CRE) combines the **study** of chemical kinetics with the reactors in which the reactions occur.
- Chemical kinetics and reactor design are at **the** heart of producing almost all industrial chemicals.
- The Chemical Reaction Engineering **(CRE)** principles learned here can also he applied in areas such as waste treatment, microelectronics, nanoparticles and living systems in addition to the more traditional areas of the manufacture of chemicals and pharmaceuticals

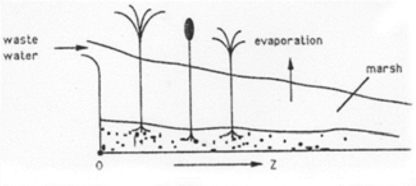
Introduction



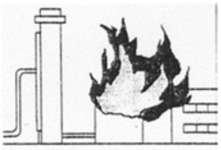
Manufacture of Phthalic Anhydride (Ch. 3)

Effective Lubricant Design
Scavenging Free Radicals

Lubricant Design
(Ch. 7)

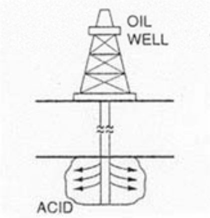


Wetlands (Ch. 4)

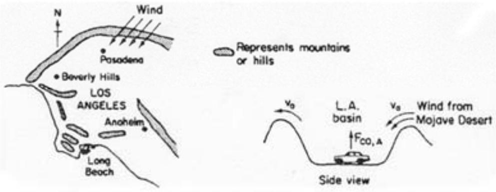


Nitroanaline Plant Explosion
Exothermic Reactions That
Runaway

Plant Safety
(Ch. 8 & 9)



Oil Recovery
(Ch. 5)

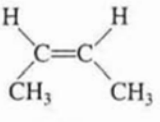


Smog (Ch. 1, Ch. 7)

Chemical Identity

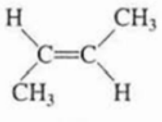
- A chemical species is said to have reacted when it has lost its chemical identity.
- The identity of a chemical species is determined by the kind, number, and configuration of that species' atoms.
- A chemical species is said to have reacted when it has lost its chemical identity.

1. **Decomposition** $CH_3CH_3 \rightarrow H_2 + H_2C = CH_2$
2. **Combination** $N_2 + O_2 \rightarrow 2NO$
3. **Isomerization** $C_2H_5CH = CH_2 \rightarrow CH_2 = C(CH_3)_2$



cis-2-butene

and



trans-2-butene

➢ Two isomers display different chemical and physical properties

Reaction Rate

- The reaction rate is the rate at which a species looses its chemical identity per unit volume.
- The rate of a reaction (mol/dm^3/s) can be expressed as either

the rate of Disappearance: **$-r_A$**

or as

the rate of Formation (Generation): **r_A**

- Consider the isomerization **$A \rightarrow B$**

r_A = the rate of formation of species A per unit volume

$-r_A$ = the rate of a disappearance of species A per unit volume

r_B = the rate of formation of species B per unit volume

Reaction Rate

- The rate of reaction tells us how fast a number of moles of one chemical species are being consumed to form another chemical species.
- It is assumed that the total mass is neither created nor destroyed when a chemical reaction occurs.

EXAMPLE: **$A \rightarrow B$**

If Species B is being formed at a rate of

0.2 moles per decimeter cubed per second, i.e.,

$r_B = 0.2$ mole/dm^3/s

Reaction Rate

- EXAMPLE: A→B

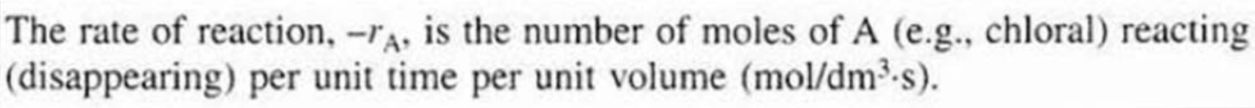
r_B = 0.2 mole/dm^3/s

Then A is disappearing at the same rate:

$-r_A$= 0.2 mole/dm^3/s

The rate of formation (generation of A) is

r_A= -0.2 mole/dm^3/s

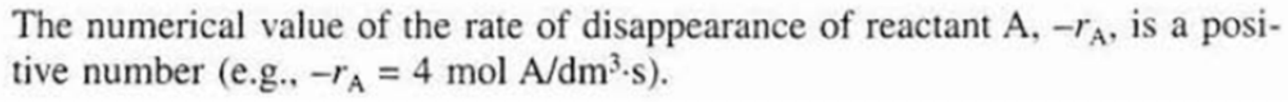


The rate of reaction, $-r_A$, is the number of moles of A (e.g., chloral) reacting (disappearing) per unit time per unit volume (mol/dm^3·s).

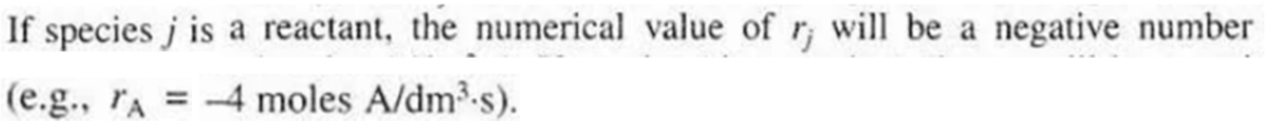
Reaction Rate

EXAMPLE:

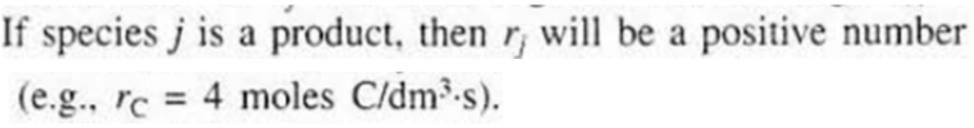
$$A + 2B \longrightarrow C + D$$



The numerical value of the rate of disappearance of reactant A, $-r_A$, is a positive number (e.g., $-r_A$ = 4 mol A/dm^3·s).



If species j is a reactant, the numerical value of r_j will be a negative number (e.g., r_A = –4 moles A/dm^3·s).



If species j is a product, then r_j will be a positive number (e.g., r_C = 4 moles C/dm^3·s).

Reaction Rate

- For a catalytic reaction, we refer to $-r_A'$,

which is the rate of disappearance of species A on a per mass of catalyst basis (mol/gcat/s)

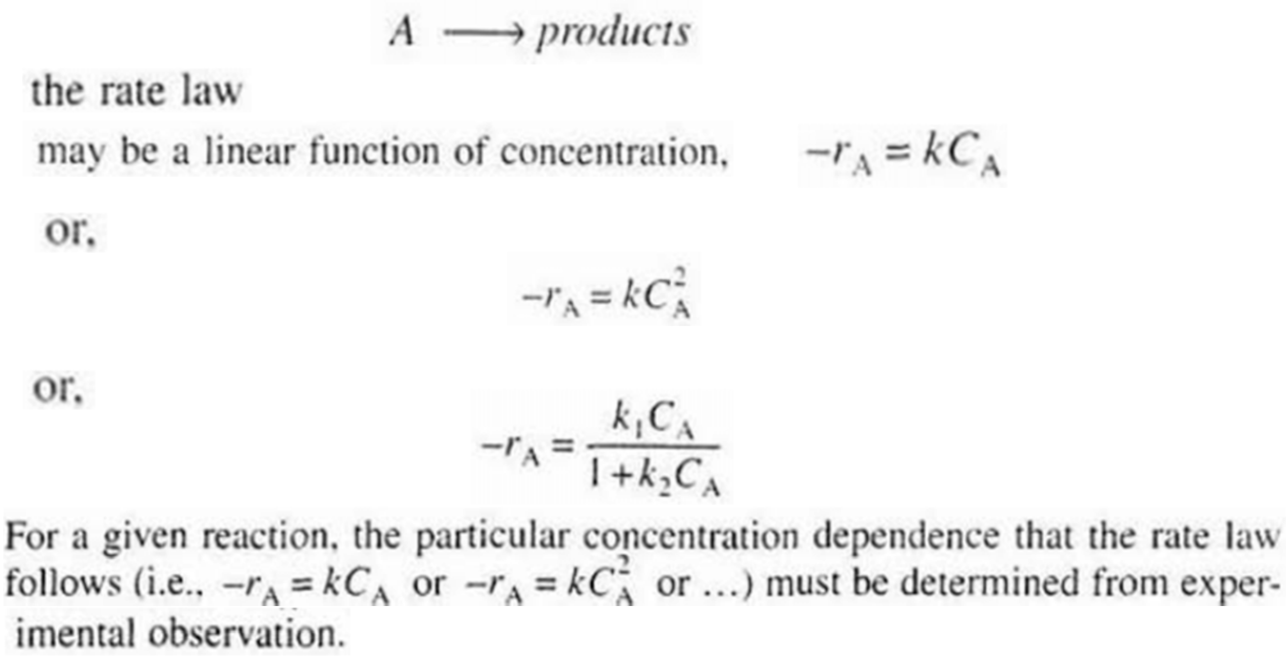
NOTE: dC_A/dt is not the rate of reaction

- **It is** simply a mole balance that **is** only valid for a constant volume batch system

Consider species j:

- r_j is the rate of formation of species j per unit volume [e.g. mol/dm^3/s]
- r_j is a function of concentration, temperature, pressure, and the type of catalyst (if any)
- r_j is independent of the type of reaction system (batch, plug flow, etc.)
- **r_j is an algebraic equation, not a differential equation**

Reaction Rate



$$A \longrightarrow products$$

the rate law

may be a linear function of concentration, $-r_A = kC_A$

or,

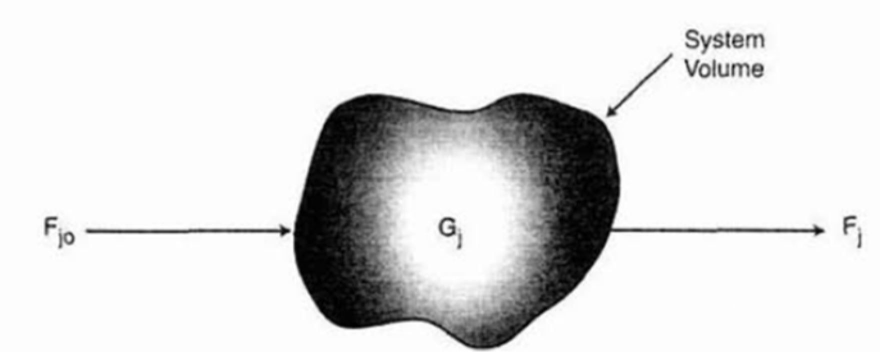
$$-r_A = kC_A^2$$

or,

$$-r_A = \frac{k_1 C_A}{1 + k_2 C_A}$$

For a given reaction, the particular concentration dependence that the rate law follows (i.e., $-r_A = kC_A$ or $-r_A = kC_A^2$ or …) must be determined from experimental observation.

General Mole Balance



mole balance on species *j* at any instant in time, *t*,

$$\left[\begin{array}{c}\text{Rate of flow}\\ \text{of } j \text{ into}\\ \text{the system}\\ \text{(moles/time)}\end{array}\right] - \left[\begin{array}{c}\text{Rate of flow}\\ \text{of } j \text{ out of}\\ \text{the system}\\ \text{(moles/time)}\end{array}\right] + \left[\begin{array}{c}\text{Rate of generation}\\ \text{of } j \text{ by chemical}\\ \text{reaction within}\\ \text{the system}\\ \text{(moles/time)}\end{array}\right] = \left[\begin{array}{c}\text{Rate of}\\ \text{accumulation}\\ \text{of } j \text{ within}\\ \text{the system}\\ \text{(moles/time)}\end{array}\right]$$

General Mole Balance

$$\begin{array}{ccccccccc}\textbf{In} & - & \textbf{Out} & + & \textbf{Generation} & = & \textbf{Accumulation}\\ F_{j0} & - & F_j & + & G_j & = & \dfrac{dN_j}{dt}\end{array}$$

where N_j represents the number of moles of species *j* in the system at time *t*.

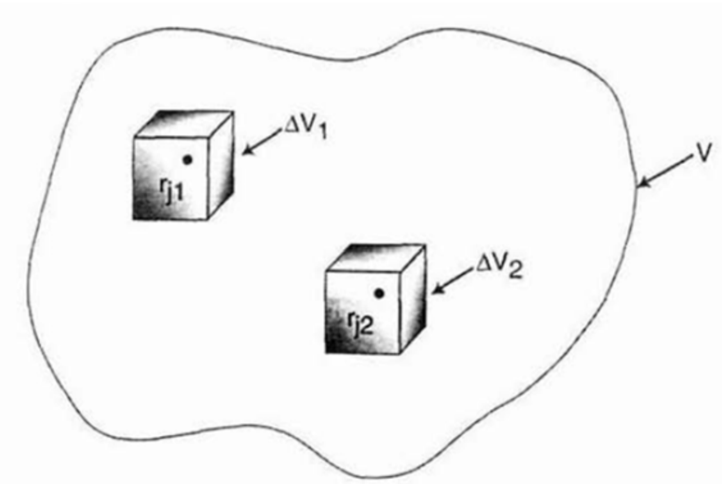
If all the system variables (e.g., temperature, catalytic activity, concentration of the chemical species) are spatially uniform throughout the system volume,

$$G_j = r_j \cdot V$$

$$\frac{moles}{time} = \frac{moles}{time \cdot volume} \cdot volume$$

General Mole Balance

- If the rate of formation **of** *species* j for the reaction varies with the position *in* the system volume



The rate of generation, ΔG_{j1}, in terms of r_{j1} and subvolume ΔV_1, is

$$\Delta G_{j1} = r_{j1}\, \Delta V_1$$

General Mole Balance

- If the total system volume *is* divided into M subvolumes, the *total* rate of generation is

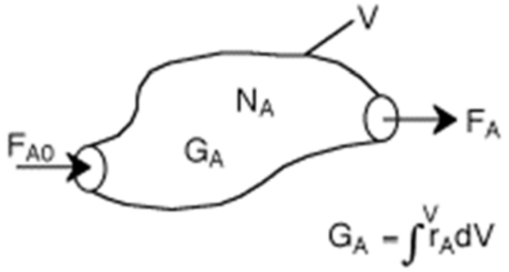
$$G_j = \sum_{i=1}^{M} \Delta G_{ji} = \sum_{i=1}^{M} r_{ji}\, \Delta V_i$$

let $M \to \infty$ and $\Delta V \to 0$)

$$G_j = \int^{V} r_j\, dV$$

$$F_{j0} - F_j + \int^{V} r_j\, dV = \frac{dN_j}{dt}$$

General Mole Balance

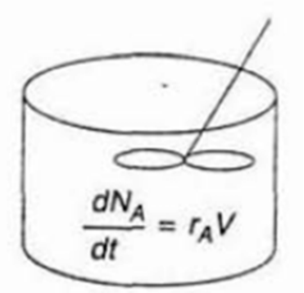


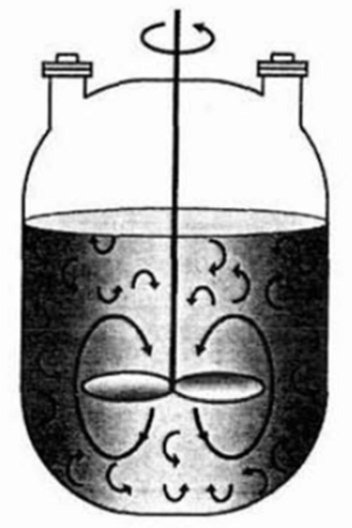
General Mole Balance on System Volume V

$$\text{In} - \text{Out} + \text{Generation} = \text{Accumulation}$$

$$F_{A0} - F_A + \int r_A dV = \frac{dN_A}{dt}$$

Batch Reactor Mole Balance





$$A \longrightarrow B$$

Batch

$$F_{A0} - F_A + \int r_A dV = \frac{dN_A}{dt}$$

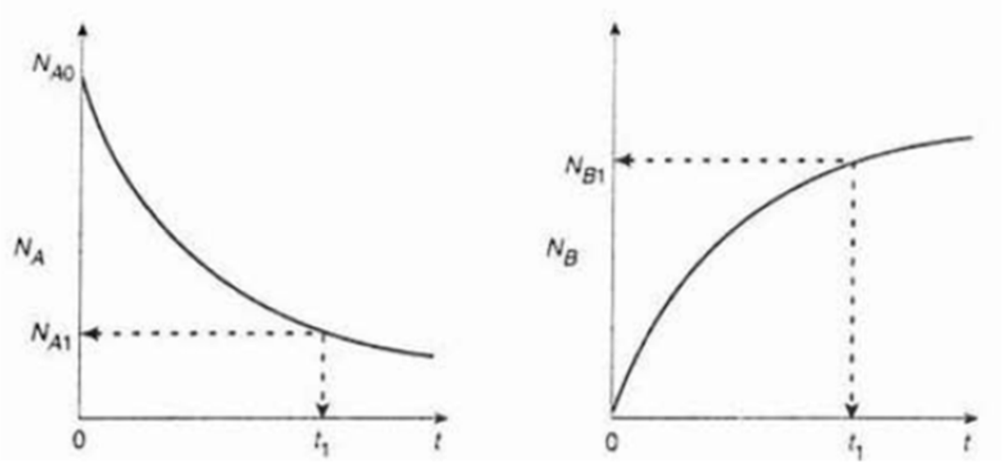
$$F_{A0} = F_A = 0$$

Well mixed

$$\int r_A dV = r_A V$$

$$\frac{dN_A}{dt} = r_A V$$

Batch Reactor Mole Balance



Mole-time trajectories.

Batch Reactor Mole Balance

rearranging,

$$dt = \frac{dN_A}{r_A V}$$

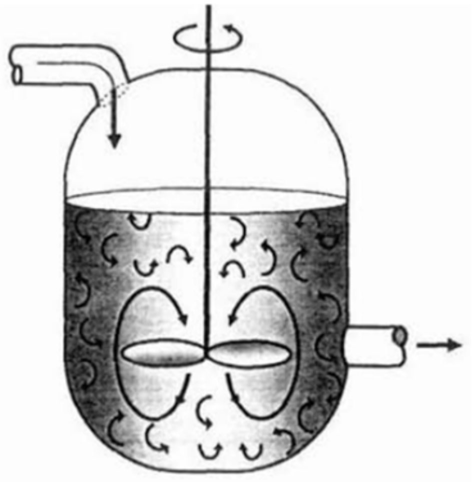
integrating with limits that at $t = 0$, then $N_A = N_{A0}$, and at $t = t_1$, then $N_A = N_{A1}$.

$$t_1 = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{r_A V}$$

This equation is the integral form of the mole balance on a batch reactor. It gives the time, t_1, necessary to reduce the number of moles from N_{A0} to N_{A1} and also to form N_{B1} moles of B.

CSTR Mole Balance

$$F_{j0} - F_j + \int^V r_j \, dV = \frac{dN_j}{dt}$$



- At steady state

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

- also

$$\int^V r_j \, dV = V r_j$$

Why?

$$\Rightarrow \quad V = \frac{F_{j0} - F_j}{-r_j}$$

CSTR Mole Balance

The CSTR design equation gives the reactor volume V necessary to reduce the entering flow rate of species j, from F_{j0} to the exit flow rate F_j, when species j is disappearing at a rate of $-r_j$.

The molar flow rate F_j is just the product of the concentration of species j and the volumetric flow rate v :

$$F_j = C_j \cdot v$$

$$\frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{\text{volume}} \cdot \frac{\text{volume}}{\text{time}}$$

$$\Rightarrow \quad V = \frac{v_0 C_{A0} - v C_A}{-r_A}$$

Plug Flow Reactor

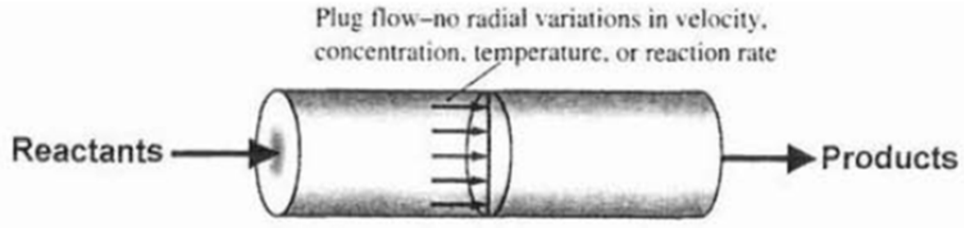
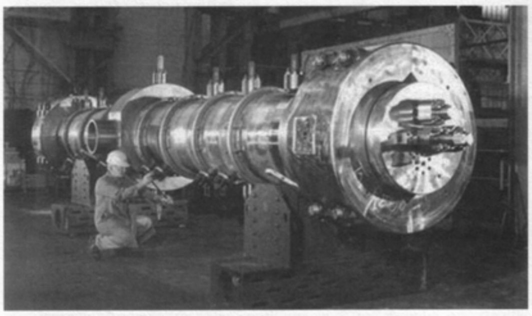


Figure 1-9 Plug-flow tubular reactor.

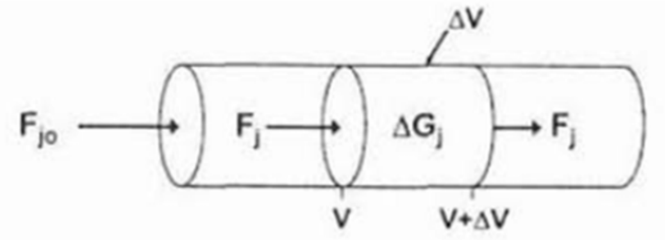
The general mole balance equation

$$F_{j0}-F_j+\int^{V} r_j\,dV=\frac{dN_j}{dt}$$



Polyethylene reactor; this 16-in inner-diameter reactor is designed to operate at 35,000 psi and 600°F; in operation, this reactor is in a vertical configuration. Courtesy of Autoclave Engineers, Division of Snap-tite, Inc.

Plug Flow Reactor



$$\Delta G_j=\int^{\Delta V} r_j\,dV=r_j\,\Delta V$$

$$\begin{bmatrix}\text{Molar flow}\\ \text{rate of species } j\\ \mathit{In}\text{ at V}\end{bmatrix}-\begin{bmatrix}\text{Molar flow}\\ \text{rate of species } j\\ \mathit{Out}\text{ at }(V+\Delta V)\end{bmatrix}+\begin{bmatrix}\text{Molar rate of}\\ \mathit{Generation}\\ \text{of species } j\\ \text{within } \Delta V\end{bmatrix}=\begin{bmatrix}\text{Molar rate of}\\ \mathit{Accumulation}\\ \text{of species } j\\ \text{within } \Delta V\end{bmatrix}$$

In – Out + Generation = Accumulation

Plug Flow Reactor

$$F_j\big|_V - F_j\big|_{V+\Delta V} + r_j \Delta V = 0$$

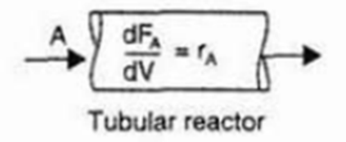
Dividing by ΔV and rearranging

$$\left[\frac{F_j\big|_{V+\Delta V} - F_j\big|_V}{\Delta V}\right] = r_j$$

Taking the limit as ΔV approaches zero,

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

Plug Flow Reactor



Tubular reactor

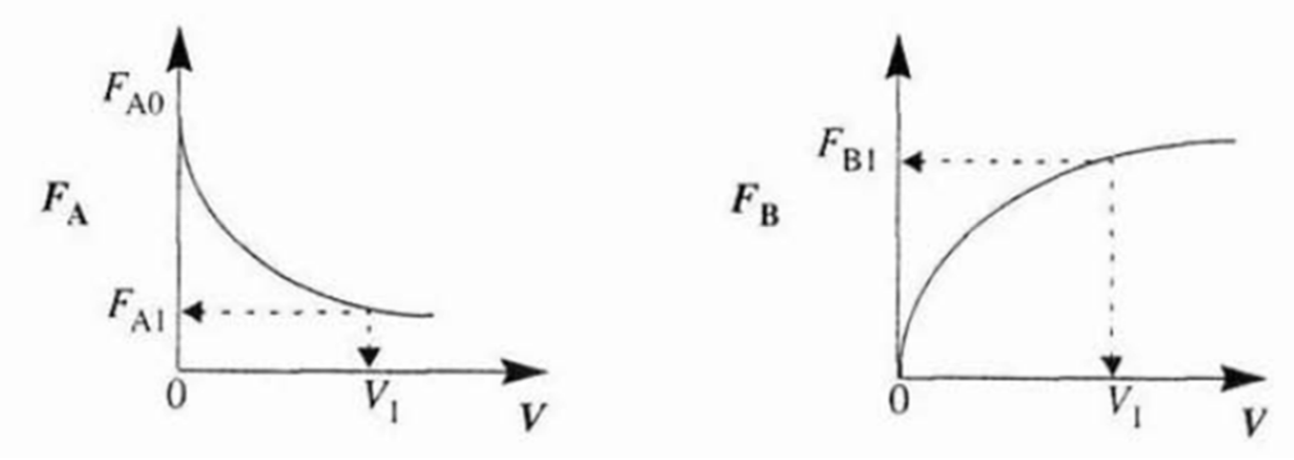
$$dV = \frac{dF_A}{r_A}$$

and integrating with limits at $V = 0$, then $F_A = F_{A0}$, and at $V = V_1$, then $F_A = F_{A1}$.

$$V_1 = \int_{F_{A0}}^{F_{A1}} \frac{dF_A}{r_A} = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A}$$

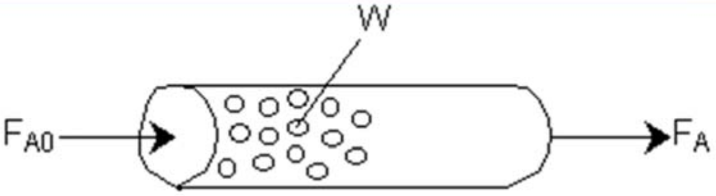
- This is the volume necessary to reduce the entering molar flow rate (mol/s) from F_{A0} to the exit molar flow rate of F_A.

Plug Flow Reactor



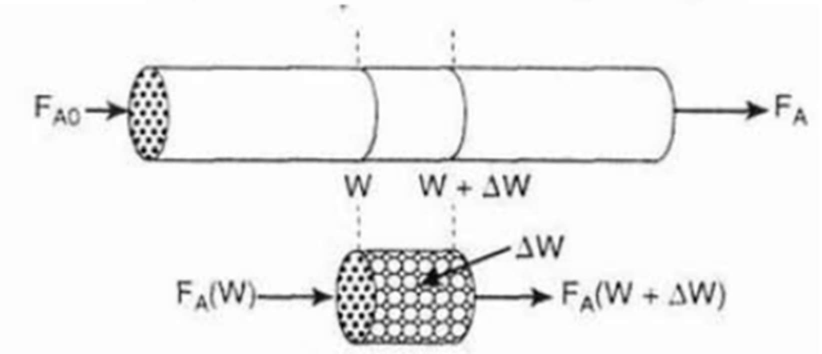
Profiles of molar flow rates in a PFR.

Packed Bed Reactor Mole Balance



For a fluid–solid heterogeneous system,

$$-r'_A = \text{mol A reacted/s} \cdot \text{g catalyst}$$



Packed Bed Reactor Mole Balance

$$\text{In} \quad - \quad \text{Out} \quad + \quad \text{Generation} \quad = \quad \text{Accumulation}$$

$$F_{A|W} \quad - \quad F_{A|(W+\Delta W)} \quad + \quad r'_A \, \Delta W \quad = \quad 0$$

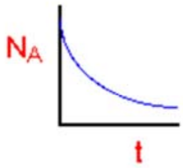
$$(r'_A)\,\Delta W \equiv \frac{\text{moles } A}{(\text{time})(\text{mass of catalyst})} \cdot (\text{mass of catalyst}) \equiv \frac{\text{moles } A}{\text{time}}$$

$$\boxed{\frac{dF_A}{dW} = r'_A}$$

$$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A} = \int_{F_A}^{F_{A0}} \frac{dF_A}{-r'_A}$$

W is the catalyst weight necessary to reduce the entering molar flow rate of species A, F_{A0}, to a flow rate F_A.

Reactor Mole Balance Summary

Reactor	Differential	Algebraic	Integral	
Batch	$\frac{dN_A}{dt} = r_A V$		$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A V}$	
CSTR		$V = \frac{F_{A0} - F_A}{-r_A}$		
PFR	$\frac{dF_A}{dV} = r_A$		$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$