Chapter 1

Mole Balances

Notes on
Elements of chemical reaction engineering,
H. Scott Fogler
- Ranjeet Utikar

Why study chemical reaction engineering?

- Knowledge of chemical kinetics and reactor design distinguishes chemical engineers from other engineers.

- Selection of reactor system is key to economic success or failure of a chemical plant.

- Principles of reaction engineering can be applied to other areas like
  - Living systems
  - waste treatment
  - air / water pollution.

- Analysis of a reactor begins with accounting for the various chemical species entering and leaving a reaction system.
  - ⇒ Overall mole balance on individual species
  - ⇒ requires definition of reaction rate $(-r_A)$
  - ⇒ $\boxed{\text{General mole balance equation.}}$

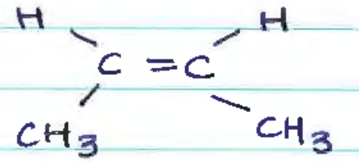
Chemical ~~reactor~~ reaction engineering concerns with the mechanism, and rate at which chemical reactions take place. It also deals with the design of reactors in which the reactions take place.

what is chemical species ?

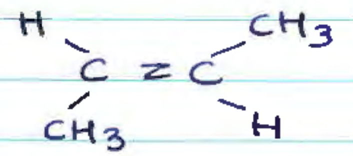
- <u>Chemical species</u> : A chemical compound with a given identity

  <u>Identity</u> : → kind
  → number
  → configuration

  } species atoms



cis - 2 butane



trans - 2 butane

[same no. atoms] but different species (different arrangement)

Chemical reaction

- <u>Chemical reaction</u> : An event in which a detectable number of molecules of one or more species loose their identity and assume a new form by a change in the kind or number of atoms in the compound and/or by a change in structure or configuration of these atoms.

  ➡ The <u>total mass</u> is neither created nor destroyed when a chemical reaction occurs.

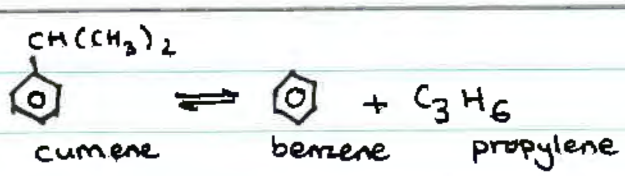
- A particular species may be created or ~~destroyed~~ destroyed during a chemical reaction

Rate of disappearance	The rate of disappearance of any species A is the number of A molecules that lose their chemical identity per unit time per unit volume through the breaking and subsequent re-forming of chemical bonds during the course of ~~ac~~ the reaction.

Ways in which species may ~~too~~ lose its identity

- <u>decomposition</u> : Breaking down of ~~molecule~~ molecule into smaller molecules, atoms, atom fragments
- <u>Combination</u> : with other molecule or atom
- <u>Isomerization</u> : change in configuration

$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_2CH_3 \longrightarrow CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_3$$



definition of reaction rate.

- Rate of disappearance of reactant

$$-r_A$$

- Rate of formation of product

$$r_A$$

rate of reaction unit
moles / time / volume
e.g : mol/m^3s

For constant volume batch reactor

$$\boxed{r_A = \frac{dC_A}{dt}}$$

This is not a generic definition and not applicable to continuous systems / systems with volume change.

r_j : rate of formation of species j per unit volume ⇒ No. of moles generated per unit volume per unit time

What does rate depend on?

Reaction rate

- species concentration
- pressure
- temperature
- Type of catalyst

$$\boxed{\text{Reaction rate is an intensive quantity and depends on temperature \& conc.}}$$

$$A \longrightarrow \text{products}$$

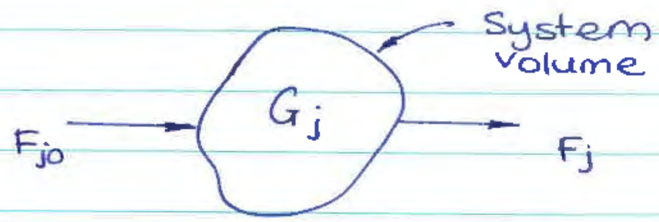
$$-r_A = f(C_A, T)$$

e.g. $-r_A = k C_A$ — First order rate law

$k = f(T)$ concentration

- rate law is an algebraic equation
- The concentration and temperature dependence of rate law must be determined experimentally.

General mole balance equation



- System boundaries must be specified
- volume enclosed by the boundaries is called system volume

mole balance on species j at any instant t :

$$\begin{bmatrix}\text{rate of} \\ \text{flow of} \\ \text{j into the} \\ \text{system}\end{bmatrix} - \begin{bmatrix}\text{rate of} \\ \text{flow of} \\ \text{j out of} \\ \text{the system}\end{bmatrix} + \begin{bmatrix}\text{rate of generation} \\ \text{of j by chemical} \\ \text{reaction within} \\ \text{the system}\end{bmatrix} = \begin{bmatrix}\text{rate of} \\ \text{accumulation of j} \\ \text{within} \\ \text{the system}\end{bmatrix}$$

mol/time   mol/time   mol/time   mol/time

in − out + generation = accumulation

$$\boxed{F_{jo} - F_j + G_j = \frac{dN_j}{dt}}$$

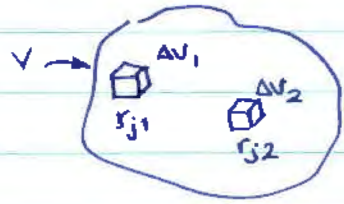
N_j : No. of moles of species j in the system at time t.

- If all variables are uniform throughout the system volume

$$G_j = r_j V$$

$$\frac{\text{mol}}{\text{time}} \qquad \frac{\text{mol}}{\text{time}\cdot\text{volume}} \cdot \text{volume}$$

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



$$\Delta G_{j1} = r_{j1}\,\Delta V_1 \quad ; \quad \Delta G_{j2} = r_{j2}\,\Delta V_2$$

subvolumes

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

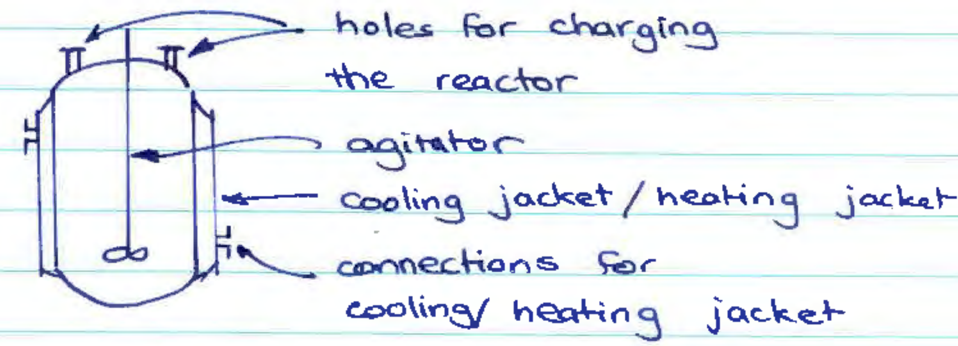
taking limit as $M \to \infty$ and $\Delta V \to 0$

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

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

Batch reactors :

- Used for small scale operations
  - test new processes that have not been fully developed
  - manufacture of expensive products
  - processes that are difficult to convert to continuous operations



Advantages :

- simple operations
- high conversion can be obtained by leaving the reactant for long periods of time

Disadvantages :

- High labour cost per batch
- variability of products from batch to batch
- Difficulty in large scale production.

Mole balance

$$\cancel{F_{j0}}^{\,0} - \cancel{F_j}^{\,0} + \int^{V} r_j \, dV = \frac{dN_j}{dt}$$

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

$$\boxed{\frac{dN_j}{dt} = r_j V}$$

assumptions :

1. No inflow/outflow
2. Reaction mixture is perfectly mixed

Consider isomerization of species A in a batch reactor

$$A \longrightarrow B$$

mole balance : $\dfrac{dN_A}{dt} = r_A V$

rearranging : $dt = \dfrac{dN_A}{r_A V}$

Integrating with limits at $t = 0$; $N_A = N_{A0}$

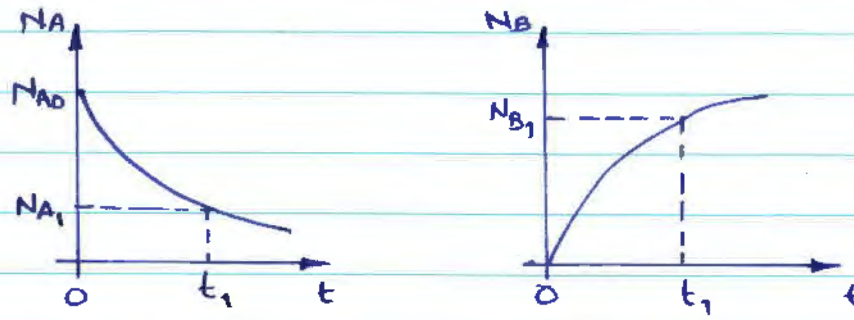
$t = t_1$; $N_A = N_{A1}$

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

← Time required to reduce the number of moles of A from N_{A0} to N_{A1}.

↓

to form N_{B1} moles of B.



mole - time trajectories for batch reactor.

Continuous flow reactors

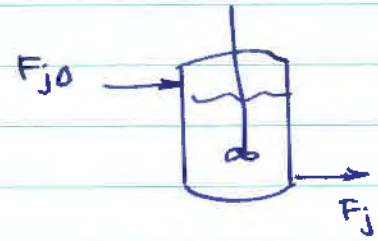
- Most common in large scale production
- Almost always operated at steady state

Three types
- Continuous stirred tank reactor (CSTR)
- plug flow reactor (PFR)
- packed bed reactor (PBR)

Continuous stirred tank reactor (CSTR)

- vat / backmix reactor
- used primarily for liquid phase reactions
- operated at steady state
- assumed to be completely mixed.
  (No time / position dependence of temperature, concentration, reaction rate
- Concentration are identical everywhere within the reactor → same as exit point

General mole balance



$$F_{j0} - F_j + G_j = \frac{dN_j}{dt}$$

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

$\frac{dN_j}{dt} = 0 \Rightarrow$ steady state

$\int^{V} r_j dV = V r_j \Rightarrow$ uniform conc throughout the reactor

$$F_{j0} - F_j + V r_j = 0$$

$$\boxed{V = \frac{F_{j0} - F_j}{r_j}}$$ CSTR design equation.

$F_j = C_j v$ $\quad$ v : volumetric flow rate (vol/time)

$F_{j0} = C_{j0} v_0$ $\quad$ C : conc (mol/vol)

$$V = \frac{C_{j0} v_0 - C_j v}{r_j}$$

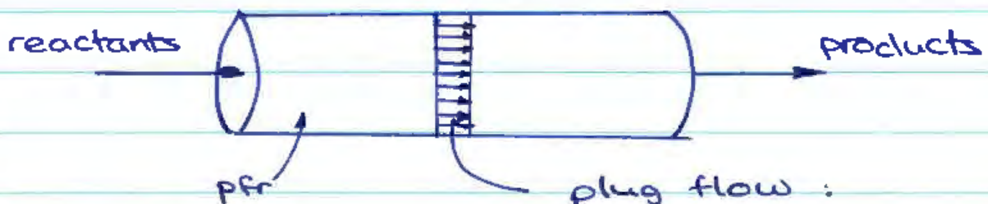
- The ideal CSTR mole balance equation is an algebraic equation, not a differential equation.

Tubular reactor

- most often used for gas phase reactions
- reactants are continuously consumed as they flow down the length of the reactor.
- concentration varies continuously in axial direction
  - ↳ reaction rate will vary axially (except for 0^{th} order reactions)

plug flow reactor

- Flow field modelled by plug flow profile
  - uniform velocity as in turbulent flow

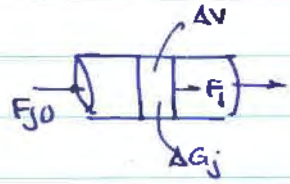


plug flow :
- no radial variation in velocity, conc. or reaction rate

mole balance

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

- consider a small differential segment of the reactor



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

spatial variation in reaction rate within ΔV is 0.

Mole balance

steady state.

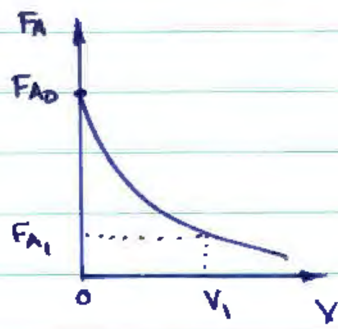
$$F_j\Big|_V - F_j\Big|_{V+\Delta V} + r_j \Delta V = 0$$

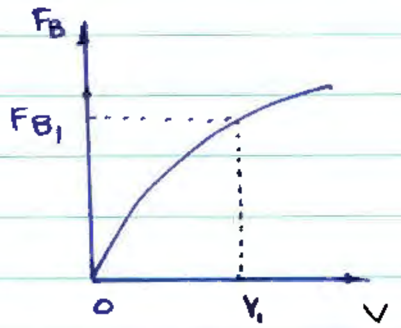
$$\frac{F_j\Big|_{V+\Delta V} - F_j\Big|_V}{\Delta V} = r_j$$

take limit as $\Delta V \to 0$

$$\lim_{\Delta V \to 0} \left(\frac{F_j|_{V+\Delta V} - F_j|_V}{\Delta V} \right) = \frac{dF_j}{dV}$$

$$\therefore \boxed{\frac{dF_j}{dV} = r_j} \Rightarrow V = \int_{F_A}^{F_{A0}} \frac{dF_A}{-r_A}$$





consider isomerization reaction

$$A \longrightarrow B$$

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

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

at $V = 0$ $\quad F_A = F_{A0}$

$V = V_1$ $\quad F_A = F_{A1}$

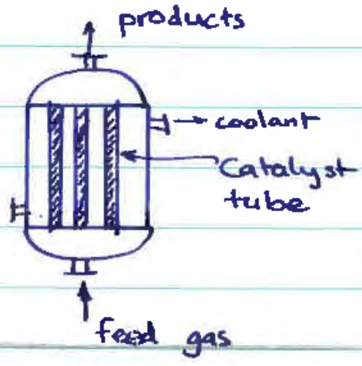
$$V_1 = \int_{F_{A0}}^{F_{A1}} \frac{dF_A}{r_A} = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A}$$

V_1 : Volume necessary to reduce the entering molar flow rate F_{A0} to F_{A1}

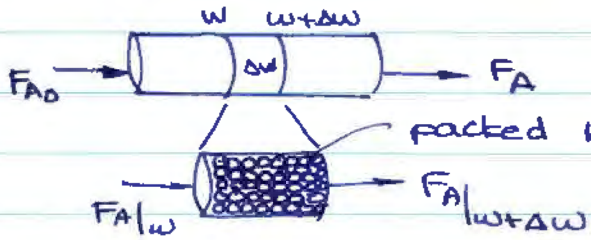
Packed bed reactor

- reaction takes place on the surface of the catalyst
- rate is based on mass of solid catalyst

$$r'_A = \frac{\text{mol A reacted}}{\text{time} \times \text{mass of catalyst}}$$



→ derivation of balance equation similar to PFR



balance equation

in − out + generation = accumulation

$$F_A|_W - F_A|_{W+\Delta W} + r_A' \Delta W = 0$$ ← steady state

$$\Rightarrow \boxed{\frac{dF_A}{dW} = r_A'}$$

$$\boxed{W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A'} = \int_{F_A}^{F_{A0}} \frac{dF_A}{-r_A'}}$$

W is the catalyst weight required to reduce the entering flow rate of A from F_{A0} to F_A

Industrial reactors

- Many variations of the basic types of reactors