

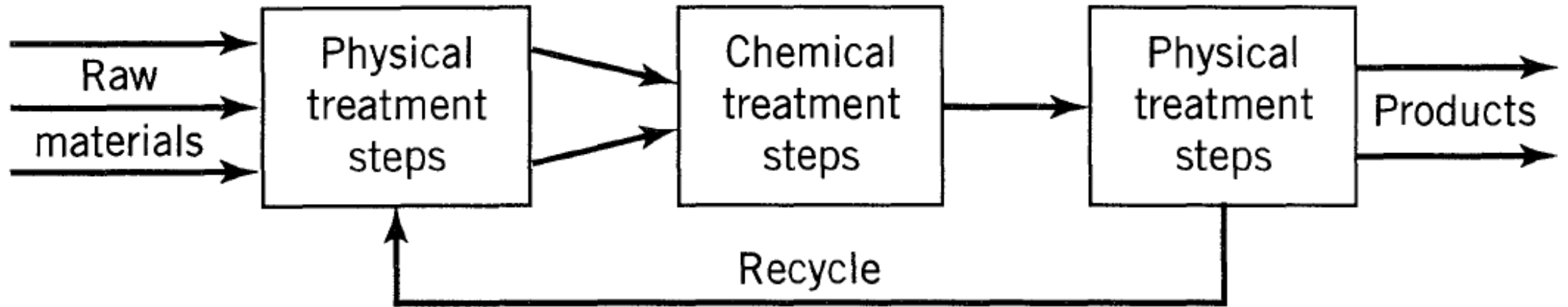
# Chemical Reaction Kinetics

# Basics:



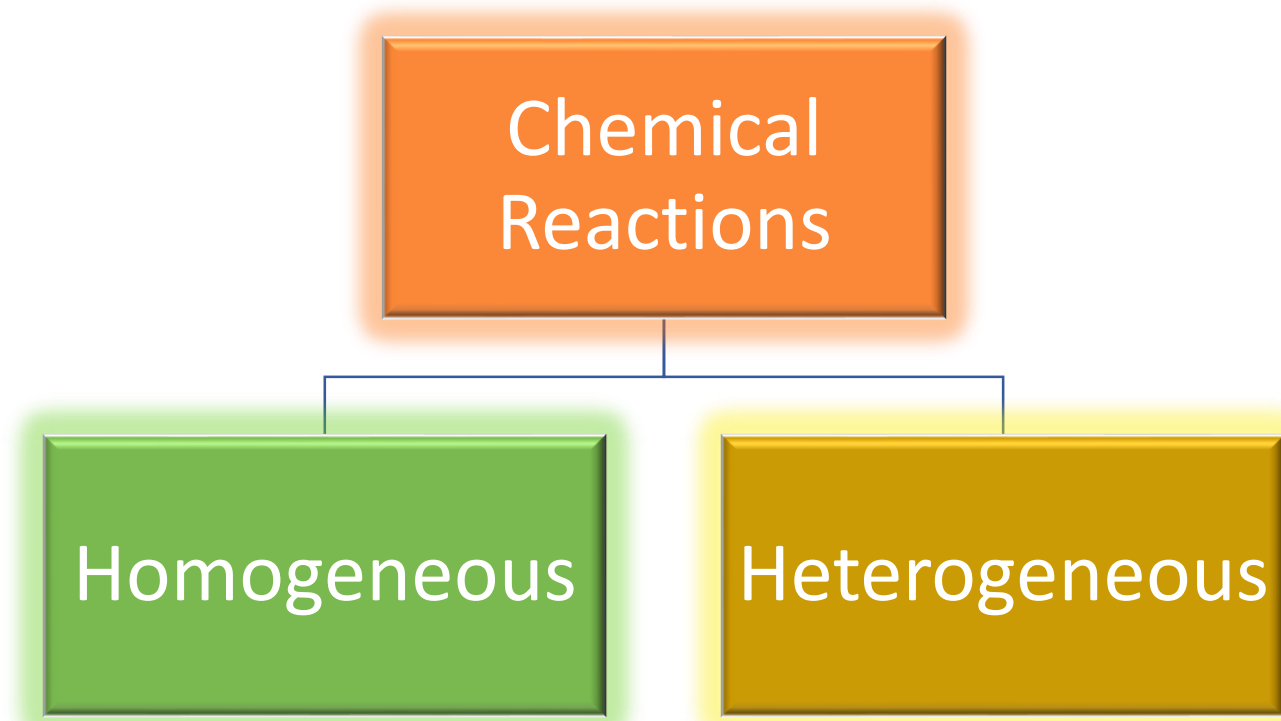
- Chemical engineering is the **basis** of biochemical engineering
- How can chemical reactions be expressed?
- How can different kinetic constants be expressed?
- Irreversible reaction?
- Reversible reaction?
- Chain reaction?
- Biological reactions are reversible and chain reactions

# Overview of Chemical Process:



The chemical treatment step is the heart of the process, the thing that makes or breaks the process economically

# Classification of Chemical Reactions:



# Classification of Chemical Reactions:

- **Homogeneous Reactions:**

- The reaction which takes place in one single phase



- **Heterogeneous Reactions:**

- For the reaction to take place minimum of two phases are required.



- Reaction and mass transfer occur simultaneously
- If the **Diffusion rate** > **reaction rate**, then the reaction will be the controlling factor
- If the **Diffusion rate** < **reaction rate**, then diffusion will be the controlling factor

# Classification of Chemical Reactions :

	Noncatalytic	Catalytic
Homogeneous	Most gas-phase reactions Fast reactions such as burning of a flame	Most liquid-phase reactions Reactions in colloidal systems Enzyme and microbial reactions
Heterogeneous	Burning of coal Roasting of ores Attack of solids by acids Gas-liquid absorption with reaction Reduction of iron ore to iron and steel	Ammonia synthesis Oxidation of ammonia to pro- duce nitric acid Cracking of crude oil Oxidation of $\text{SO}_2$ to $\text{SO}_3$

# Rate of Reaction:

- To define the rate of reaction,
- Assume a homogeneous reaction occurs in a closed system at uniform pressure, temperature, and composition



- The rate at which product B is formed is equal to the rate at which reactant A disappears.
- The rate of reaction for reactant A is,

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

- Negative sign denotes the disappearance of reactant A.
- The right hand side is the depletion of concentration of reactant A with respect to time.

# Rate of Reaction:

- The rate of production of product B is,

$$r_B = \frac{dC_B}{dt}$$

- The negative sign disappears from the right-hand side of the equation.
- Because product B is being produced from reactant A.
- Concentration is the ratio of the number of moles per unit volume (V).

$$r_A = -\frac{d(N_A/V)}{dt} \qquad r_B = \frac{d(N_B/V)}{dt}$$

- $N_A$  and  $N_B$  represent the number of moles of A and B taking part in the reaction, respectively.
- **The rate of reaction is the rate of change in the number of moles of the components taking part in the reaction per unit volume**
- **Alternatively, the rate of change in concentration of the species participating in the chemical reaction.**



# Rate of Reaction:

- Reaction rate  $r_A$  refers to the rate at which component A gets depleted in a system.
- The variation in concentration for the participating species in a chemical reaction mostly results in the variation in the rate of the reaction.
- An equation describing the rate of the reaction is termed as the **rate equation**.

- For the given reaction,  $-r_A \propto C_A^n$

- After removing the proportionality sign, the rate equation describing the depletion of reactant A may be written as follows:

$$-r_A = -\frac{dC_A}{dt} = k C_A^n$$

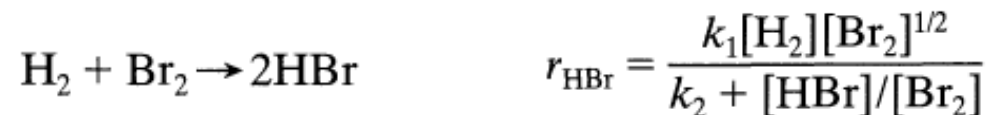
- k is the rate constant of the reaction,
- $C_A$  is the concentration of components,
- n is the order of reaction: power to which concentration terms are raised

# Rate of Reaction:

- The unit of the rate equation is mol/m<sup>3</sup>s,
- k has dimensions of (concentration)<sup>1-n</sup>/time.
- k is a function of temperature T in many cases.
- **Molecularity:** Number of molecules involved in a chemical reaction  
Molecularity is always a whole number, one, two, three, **not zero**.
- **Elementary reaction:** The reaction in which molecularity and order of reaction are the same. The rate equation corresponds to the stoichiometric equation.



- **Non-elementary reaction:** There is no relation between molecularity and order of reaction. No direct relation between stoichiometry and rate



# Problem statement:

- For the reaction and data given below, evaluate the rate law and rate constant at 298 K:



Trial	$C_A$ (mol/m <sup>3</sup> )	$C_B$ (mol/m <sup>3</sup> )	$r_{\text{initial}}$ (mol/m <sup>3</sup> s)
1	1	1	2
2	1	2	8.1
3	2	2	15.9

- Solution:**
- Let us first take into account trials 1 and 2:
- Trial 1:  $r_1 = kC_A^x C_B^y = k(1.00)^x(1.00)^y$
- Trial 2:  $r_2 = kC_A^x C_B^y = k(1.00)^x(2.00)^y$

# Solution:

- Dividing the second equation by the first equation, we get

$$\frac{8.1}{2} \approx 4 = (2.00)^y \qquad 2^2 = 2^y \qquad y = 2$$

- Let us first take into account trials 2 and 3:
- Trial 2:  $r_2 = kC_A^x C_B^y = k (1.00)^x (2.00)^y$
- Trial 3:  $r_3 = kC_A^x C_B^y = k (2.00)^x (1.00)^y$
- Dividing the second equation by the first gives us

$$2 = (2.00)^x \qquad x = 1$$

- Since we got the orders corresponding to the components A and B, we can now write the rate law as

$$r = 2.0C_A C_B^2$$

# Solution:

- The overall order of the reaction is  $1 + 2 = 3$ .
- Once we got the overall order of the reaction, it is easy to calculate the rate constant  $k$ .
- Replace the values in any of the rate equations corresponding to trials 1–3.

$$2.0 \text{ mol/m}^3\text{s} = k (1.00 \text{ mol/m}^3) (1.00 \text{ mol/m}^3)^2$$

$$k = 2.0 \text{ mol}^{-2}/\text{m}^6 \text{ s}$$

# The Rate Equation:

- Suppose a single-phase reaction  $aA + bB \rightarrow rR + sS$ . The most useful measure of reaction rate for reactant A is then

The diagram shows the equation  $-r_A = \frac{1}{V} \frac{dN_A}{dt} = \frac{(\text{amount of A disappearing})}{(\text{volume})(\text{time})}$  with units  $\left[ \frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right]$ . Annotations include: an arrow from 'rate of disappearance of A' to  $-r_A$ ; an arrow from 'note that this is an intensive measure' to  $-r_A$ ; and an arrow from 'the minus sign means disappearance' to the minus sign in  $-r_A$ .

$$-r_A = \frac{1}{V} \frac{dN_A}{dt} = \frac{(\text{amount of A disappearing})}{(\text{volume})(\text{time})}, \left[ \frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right]$$

rate of disappearance of A

note that this is an intensive measure

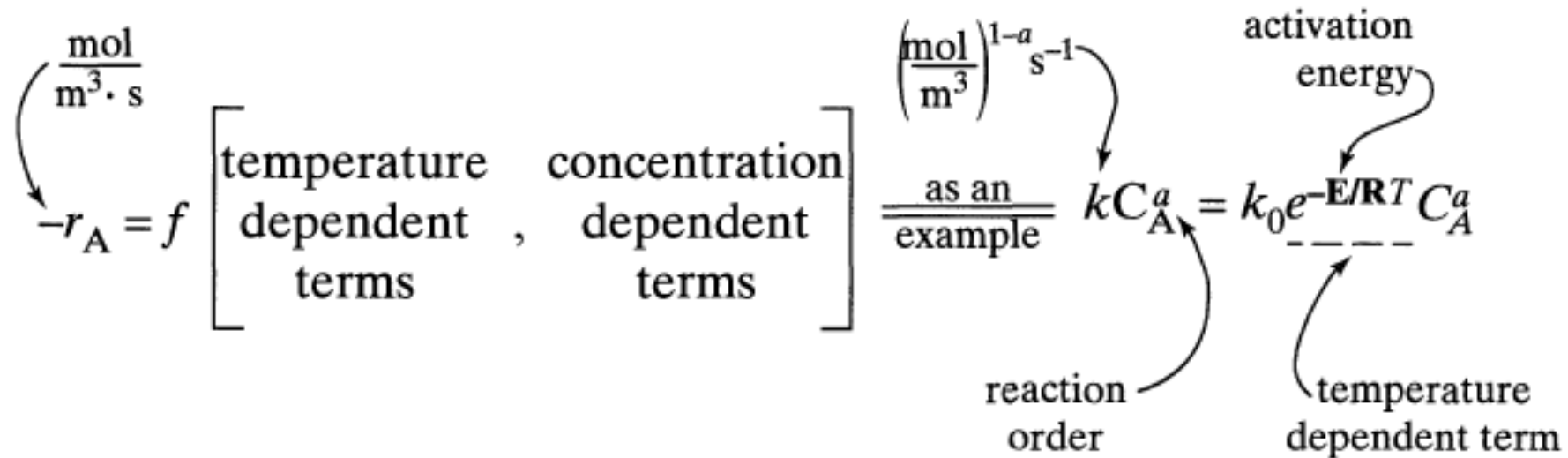
the minus sign means disappearance

- In addition, the rates of reaction of all materials are related by

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s}$$

# The Rate Equation:

- The rate of reaction is influenced by the composition and the energy of the material.
- By energy we mean the temperature (random kinetic energy of the molecules), the light intensity within the system (this may affect the bond energy between atoms), the magnetic field intensity, etc.
- Ordinarily we only need to consider the temperature



# Definition of Conversion

- Consider the general reaction  $aA + bB \longrightarrow cC + dD$
- Where,     A, B, C, D - Chemical Species  
              a, b, c, d - Stoichiometric Coefficients
- Choose limiting reactant A as basis of calculations  $A + \frac{b}{a} B \longrightarrow \frac{c}{a} C + \frac{d}{a} D$
- The limiting reactant is the reactant that will be completely consumed first after the reactants have been mixed
- How can we quantify ?????? how far a reaction proceeds to the right?
- How many moles of C are formed for every mole of A consumed?
- **Conversion**



# Definition of Conversion:

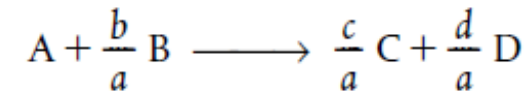
- Let us suppose that the initial concentration of A is  $C_{A0}$  at time  $t = 0$ ,
- $C_A$  is the amount present at time  $t$ .
- Then the conversion of A in the constant-volume system is given by the ratio of the concentration of A converted to the concentration of A fed,

$$X_A = \frac{C_{A0} - C_A}{C_{A0}} = 1 - \frac{C_A}{C_{A0}}$$

$$C_A = C_{A0}(1 - X_A)$$

# Stoichiometric Table for A Batch System:

In formulating our stoichiometric table, we shall take **species A as our basis of calculation** (i.e., the limiting reactant) and then divide through by the stoichiometric coefficient of A



Species	Initially (mol)	Change (mol)	Remaining (mol)
A	$N_{A0}$	$-(N_{A0}X)$	$N_A = N_{A0} - N_{A0}X$
B	$N_{B0}$	$-\frac{b}{a} (N_{A0}X)$	$N_B = N_{B0} - \frac{b}{a} N_{A0}X$
C	$N_{C0}$	$\frac{c}{a} (N_{A0}X)$	$N_C = N_{C0} + \frac{c}{a} N_{A0}X$
D	$N_{D0}$	$\frac{d}{a} (N_{A0}X)$	$N_D = N_{D0} + \frac{d}{a} N_{A0}X$
I (inerts)	$N_{I0}$	—	$N_I = N_{I0}$
Totals	$N_{T0}$		$N_T = N_{T0} + \underbrace{\left( \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right)}_{\delta} N_{A0}X$

$$\delta = \frac{\text{Change in the total number of moles}}{\text{Mole of A reacted}}$$

# Problem statement :

- In an irreversible reaction  $A \rightarrow \text{products}$ , 50% of A is converted into products. If the initial concentration of A is  $10 \text{ mol/m}^3$ , then find the final or residual concentration of A.
- **Solution:**
- The final concentration of A can be calculated as follows:

$$C_A = 10(1 - 0.5) = 5 \text{ mol/m}^3$$

# Irreversible first-order reaction:

- Now let us consider the reaction,  $A \rightarrow \text{products}$
- Assuming this is a first-order reaction, Eq. can be written as

$$-r_A = -\frac{dC_A}{dt} = kC_A$$

$$-\ln \frac{C_A}{C_{A0}} = k.t$$

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k \cdot \int_0^t dt$$

$$C_A = C_{A0}e^{-kt}$$

- Hence, Eq. clearly demonstrates that the concentration of A decays exponentially with time t. In terms of conversion, the rate equation becomes

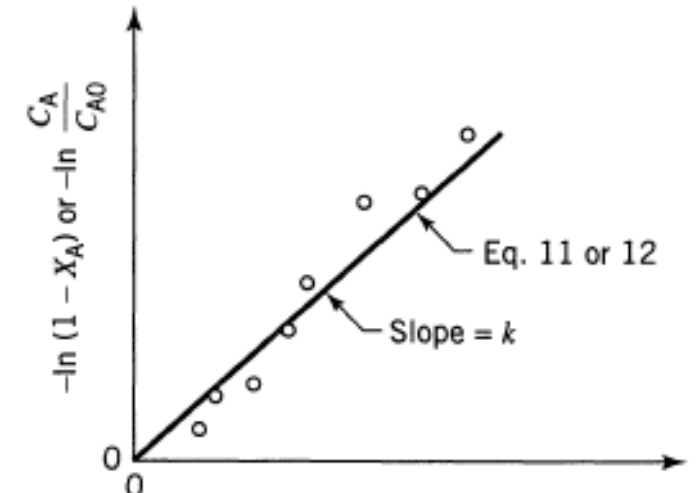
$$-\frac{d}{dt}C_{A0}(1 - X_A) = kC_{A0}(1 - X_A)$$

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

$$\int_0^{X_A} \frac{dX_A}{1 - X_A} = k \int_0^t dt$$

Integrating Eq., we get

$$-\ln(1 - X_A) = kt$$



# Irreversible first-order reaction:

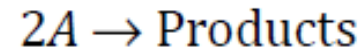
- For an irreversible first-order reaction, 50% of A is converted to the product after 3 min. What is the rate constant  $k$ ?

$$-\ln(1 - X_A) = kt$$

$$k = \frac{-\ln(1 - 0.5)}{3} = 0.231 \text{ min}^{-1}$$

# Irreversible Second-Order Reaction:

- In the case of a single reactant resulting in product formation and the reaction is of second order. A typical example of such a reaction is as follows:



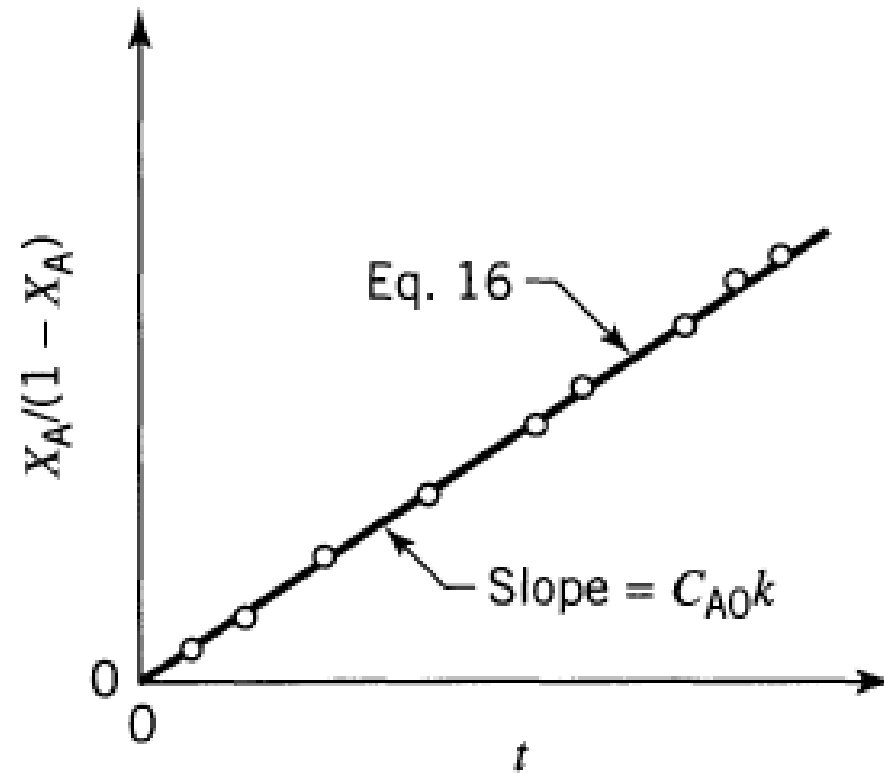
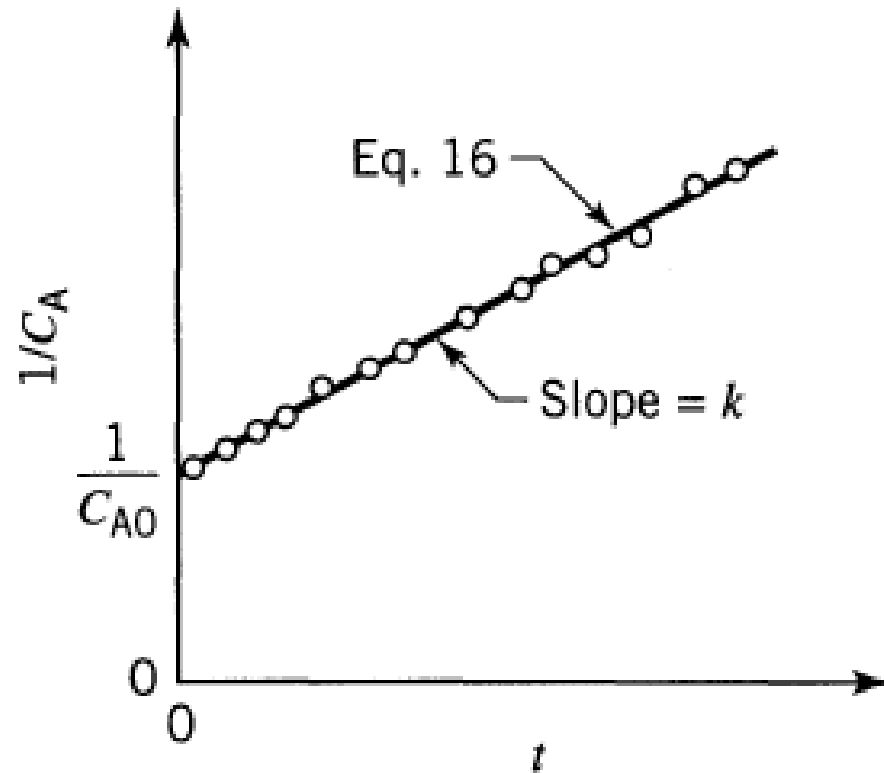
- Let us assume that the stoichiometric coefficient of the reactant and the order of the reaction is identical. We can write the rate equation as follows:

$$-r_A = -\frac{dC_A}{dt} = kC_A^2 = kC_{A0}^2 (1 - X_A)^2$$

- Integrating,

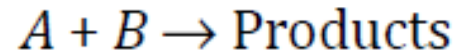
$$\frac{1}{C_{A0}} - \frac{1}{C_A} = kt = \frac{1}{C_{A0}} \frac{X_A}{1 - X_A}$$

# Irreversible Second-Order Reaction:



# Irreversible Second-Order Reaction:

- Let us consider the following second-order reaction:



- The two reactants A and B react together and form products. The rate equation for the reactants can be written as follows:

$$-r_A = -r_B = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = k C_A C_B$$

- Since  $r_A$  and  $r_B$  have similar expressions, we express the later part of the rate equation with respect to reactant A. Hence, Eq. can be simplified as,

$$-\frac{dC_A}{dt} = k C_A C_B$$

- If  $C_{A0} X_A$  is the amount of A reacted after any time t, one can express the final concentration of A and B after time t as follows:

$$C_A = C_{A0} - C_{A0} X_A$$

$$C_B = C_{B0} - C_{A0} X_A$$



# Irreversible Second-Order Reaction:

- $C_{B0}$  refers to the initial concentration of B.
- Now the rate equation can be modified as,

$$-\frac{d}{dt}C_{A0}(1 - X_A) = kC_{A0}(1 - X_A)C_{A0}\left(\frac{C_{B0}}{C_{A0}} - X_A\right)$$

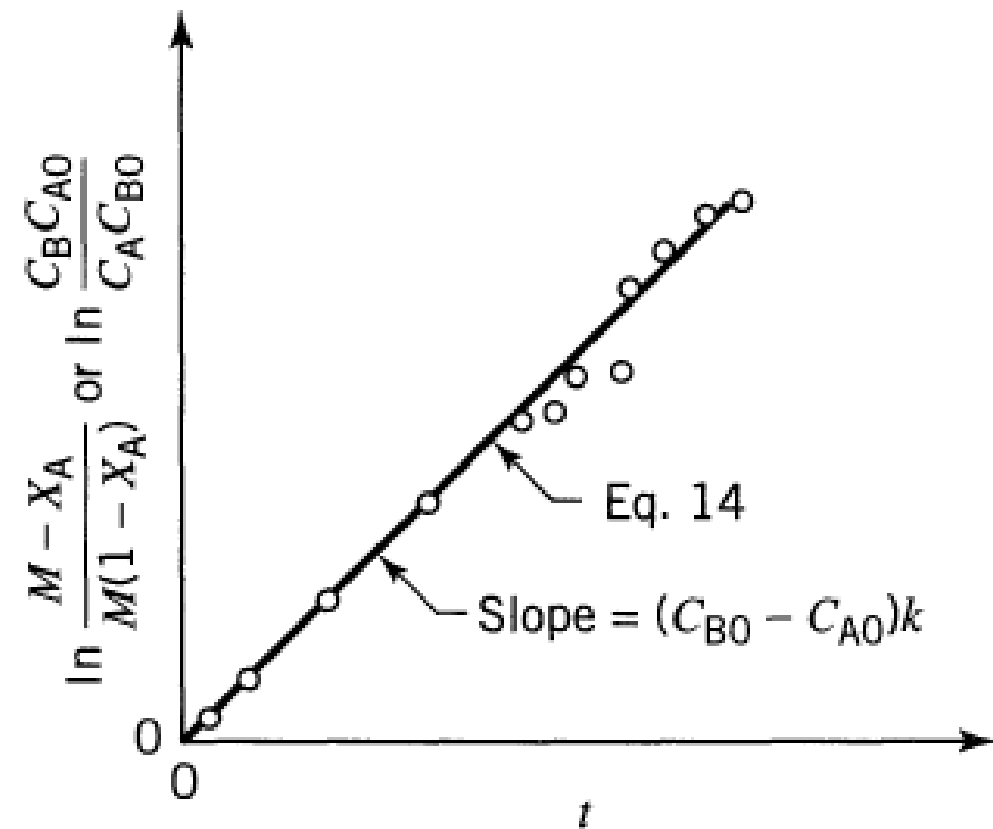
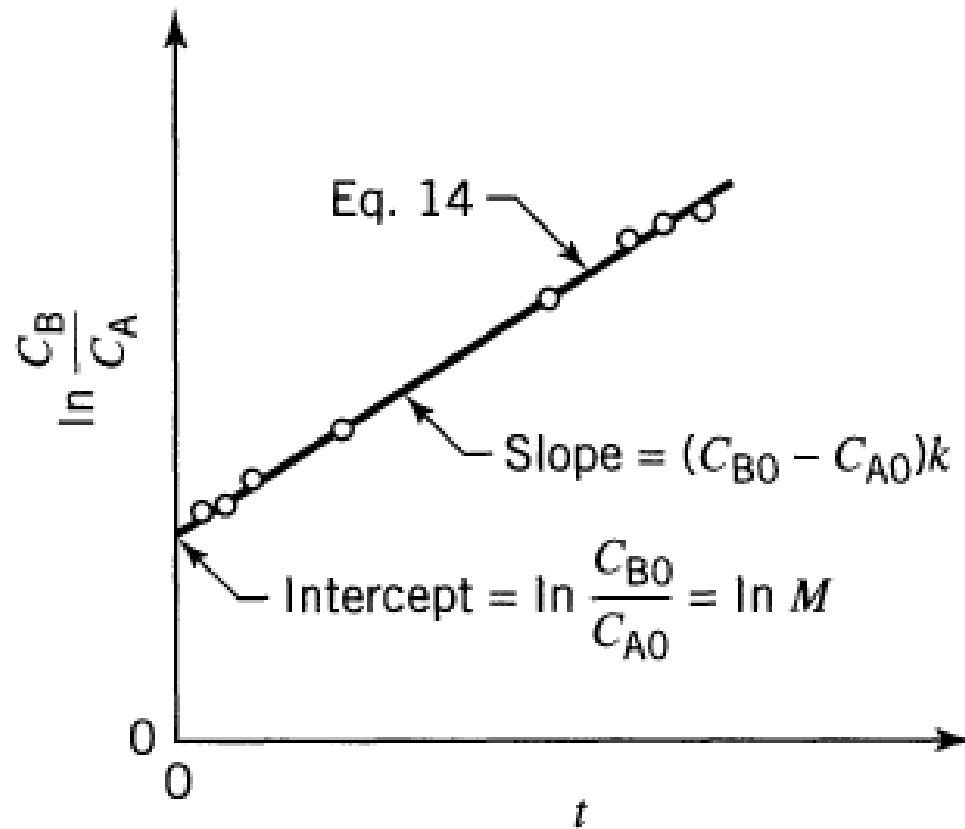
- the ratio  $C_{B0}/C_{A0}$  may be denoted by M. Differentiating and simplifying Eq., we get

$$-r_A = C_{A0} \frac{dX_A}{dt} = kC_{A0}^2(1 - X_A)(M - X_A) \qquad \int_0^{X_A} \frac{dX_A}{(1 - X_A)(M - X_A)} = C_{A0}k \int_0^t dt$$

- Integrating, we get,

$$\begin{aligned} \ln \frac{1 - X_B}{1 - X_A} &= \ln \frac{M - X_A}{M(1 - X_A)} = \ln \frac{C_B C_{A0}}{C_{B0} C_A} = \ln \frac{C_B}{M C_A} \\ &= C_{A0}(M - 1)kt = (C_{B0} - C_{A0})kt \end{aligned}$$

# Irreversible Second-Order Reaction:



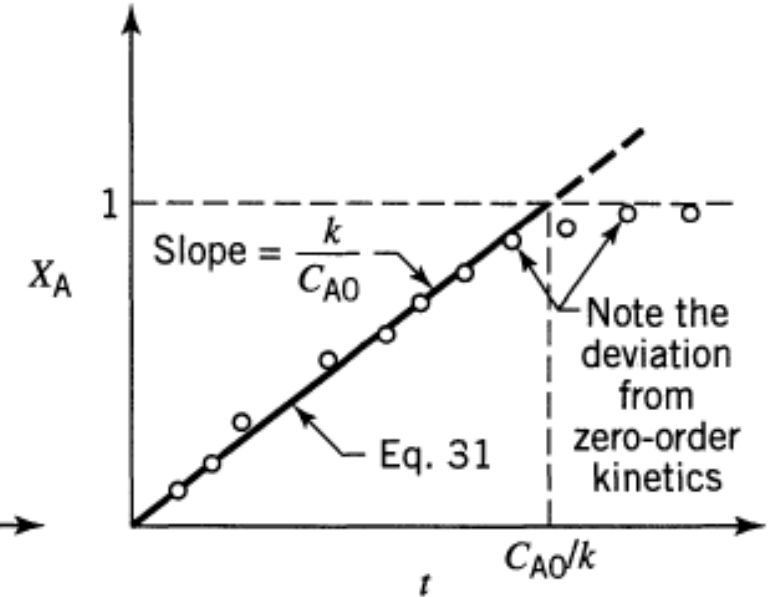
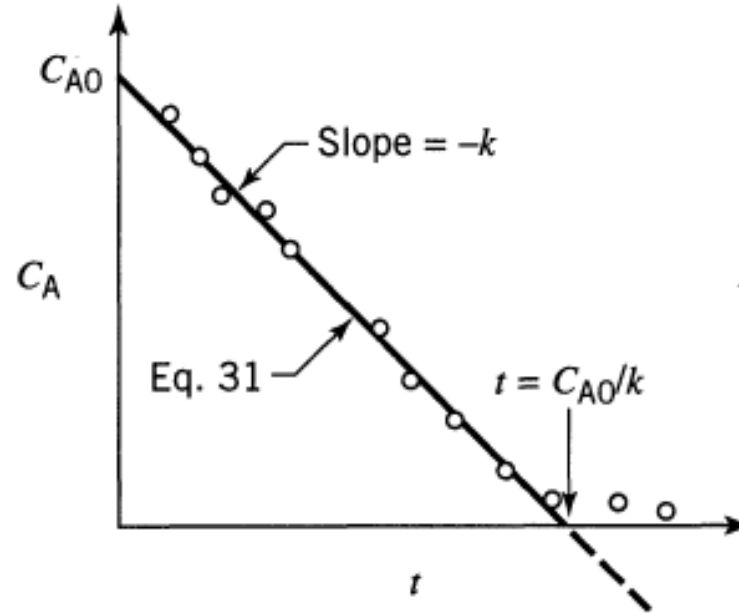
# Irreversible Second-Order Reaction:

- for  $n = 0$  (**a zero-order reaction**), the rate equation becomes independent of the concentration of the reactant. Hence,

$$-r_A = -\frac{dC_A}{dt} = k$$

$$C_{A0} - C_A = C_{A0}X_A = kt \quad \text{for } t < \frac{C_{A0}}{k}$$

$$C_A = 0 \quad \text{for } t \geq \frac{C_{A0}}{k}$$



- Expression for the nth-order reaction,

$$-r_A = -\frac{dC_A}{dt} = k C_A^n$$

$$C_A^{1-n} - C_{A0}^{1-n} = (n-1)kt$$

# Irreversible Reaction:

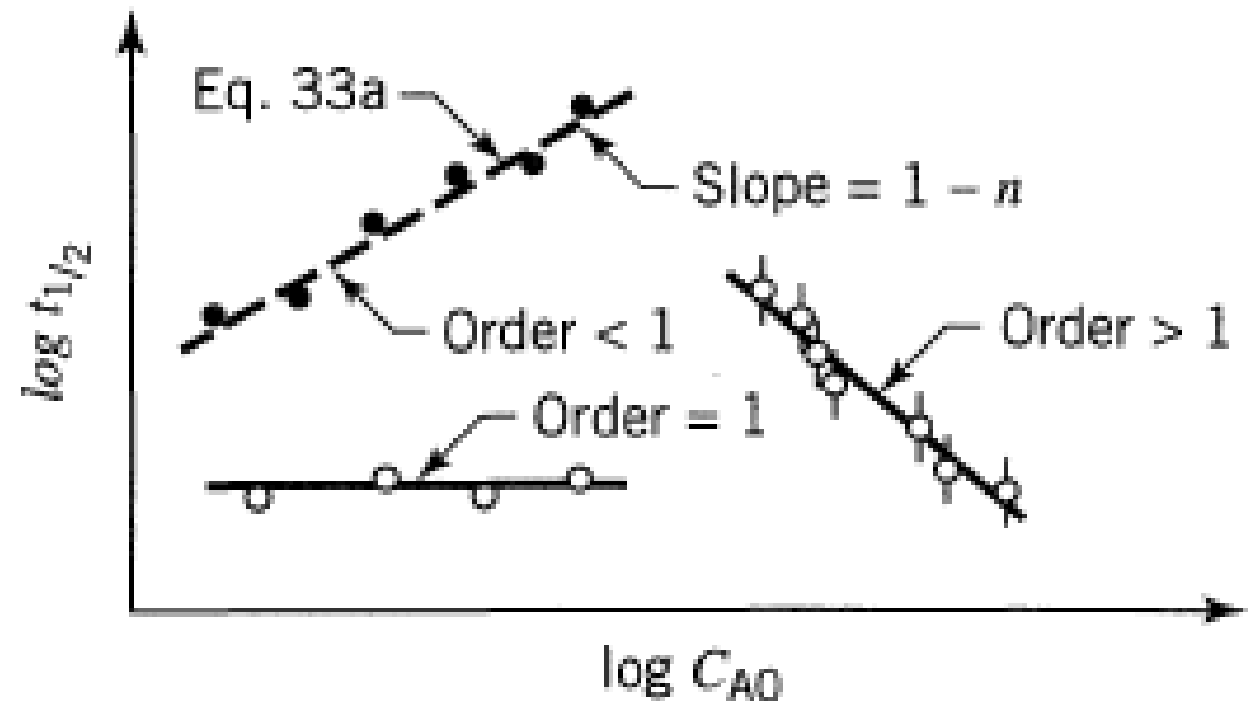
- **The reaction half-life ( $t_{1/2}$ ):** a situation where the reactant concentration is reduced to one-half or 50 % of the original reactant concentration participating in the reaction.
- In other words, we can mathematically express such situations as follows:

$$C_A^{1-n} - C_{A0}^{1-n} = (n-1)kt$$

$$C_A = \frac{C_{A0}}{2}$$

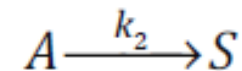
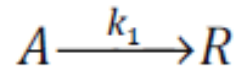
$$t_{1/2} = \frac{0.5^{1-n} - 1}{k(n-1)} C_{A0}^{1-n}$$

- We get,



# Irreversible Reactions in parallel:

- Irreversible reactions in parallel are very common in biochemical reaction pathways where a single reactant gives two or more parallel products.
- Let us consider the following simple example in order to illustrate the phenomenon of parallel reaction.

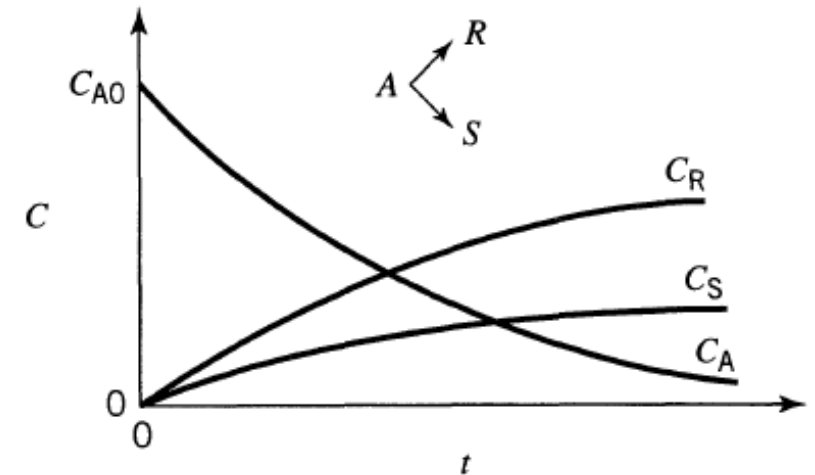


- Reactant  $A$  gives two parallel products  $R$  and  $S$ , separately.
- The rate equations for reactant  $A$  and products  $R$  and  $S$  can be expressed as follows:

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A + k_2 C_A \quad \text{--- (a)}$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A \quad \text{--- (b)}$$

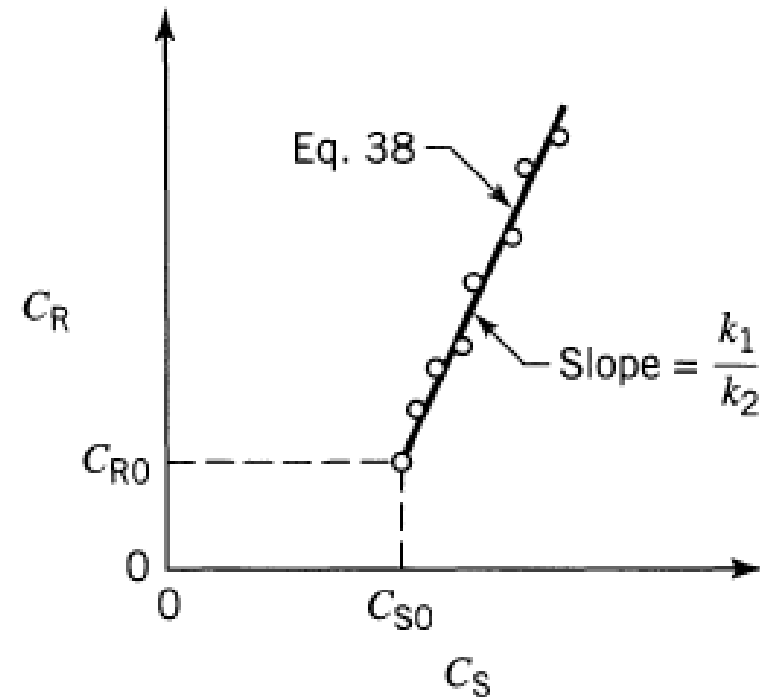
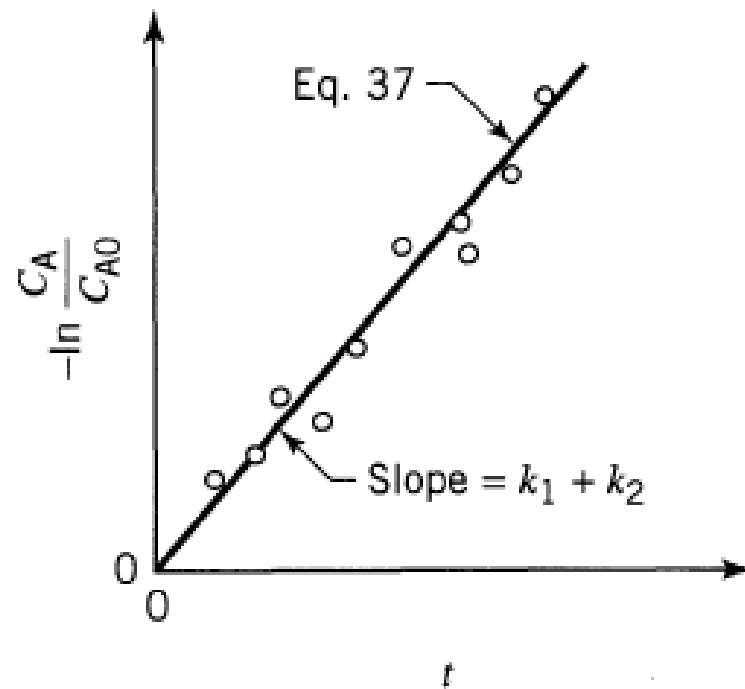
$$r_S = \frac{dC_S}{dt} = k_2 C_A \quad \text{--- (c)}$$



# Irreversible Reactions in parallel:

- Integrating eq (a), 
$$-\ln \frac{C_A}{C_{A0}} = (k_1 + k_2)t$$
- Dividing eq (b) and eq (c), 
$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2}$$
- taking the limits from the initial concentration of R ( $C_{R0}$ ) and S ( $C_{S0}$ ) to the final concentration of R ( $C_R$ ) and S ( $C_S$ ), we get 
$$\frac{C_R - C_{R0}}{C_S - C_{S0}} = \frac{k_1}{k_2}$$
- The slope of plots  $C_R$  versus  $C_S$  will give the ratio  $k_1/k_2$ .
- Also if we plot  $C_A$  and  $t$ , we will get the slope as  $(k_1 + k_2)$ .
- Hence, by knowing  $k_1/k_2$  and  $(k_1 + k_2)$ , the  $k_1$  and  $k_2$  can easily be calculated.

# Irreversible Reactions in parallel:



# Autocatalytic Reactions:

- In an autocatalytic reaction, the product of the reaction acts as the catalyst.



- The rate equation is given as follows:

$$-r_A = -\frac{dC_A}{dt} = kC_A C_R$$

- The total concentration equals the sum of the reactant and catalyst concentrations

$$C_0 = C_A + C_R = C_{A0} + C_{R0} = \text{constant}$$

$$-r_A = -\frac{dC_A}{dt} = kC_A(C_0 - C_A)$$

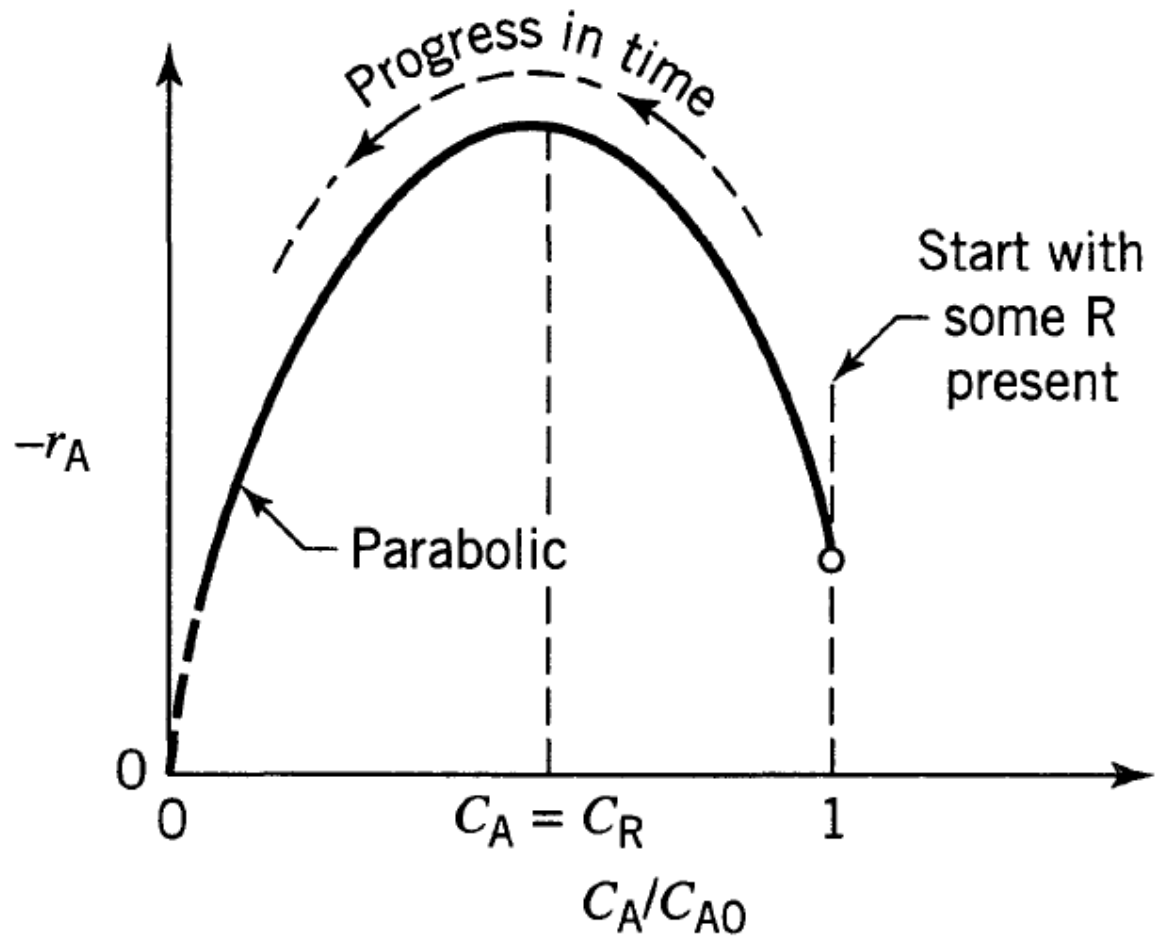
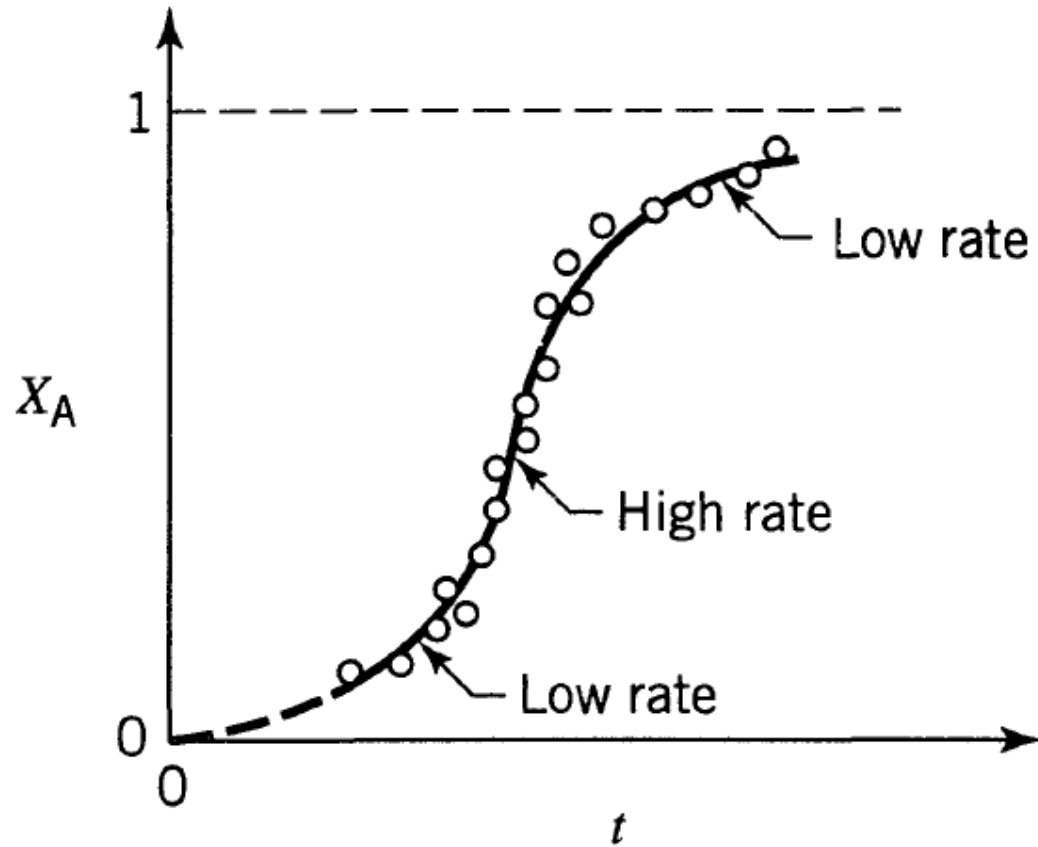
- On integrating. We get

$$\ln \frac{C_{A0}(C_0 - C_A)}{C_A(C_0 - C_{A0})} = \ln \frac{C_R/C_{R0}}{C_A/C_{A0}} = (C_{A0} + C_{R0})kt$$

- Microbial fermentation process is an example of autocatalytic reaction.

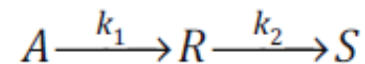


# Autocatalytic Reactions:



# Irreversible Reactions in series:

- A series reaction is defined as one where the product formed from the reactants reacts and forms further products.
- These types of reactions are very common in enzymatic systems where the enzyme combines with a substrate to form an enzyme-substrate complex, which further results in the formation of a product.
- Let us consider the following first-order reaction in series where reactant A forms an intermediate product R, which further reacts and forms the final product S.



- The rate equations for A, R, and S can be written as follows:

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A$$

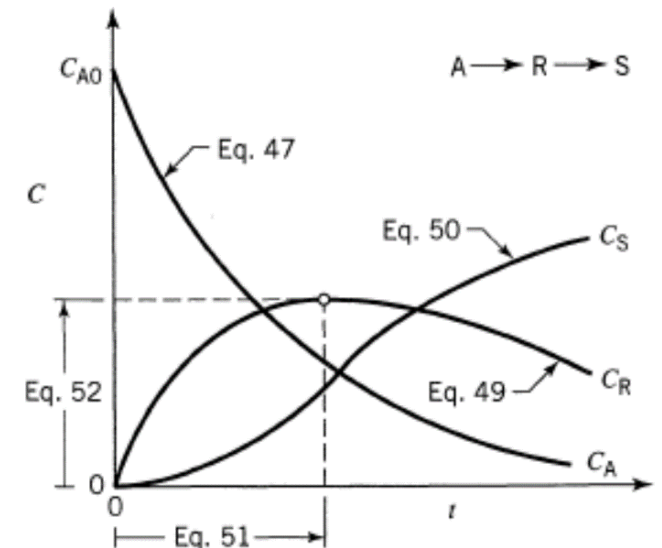
--- (a)

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2 C_R$$

--- (b)

$$r_S = \frac{dC_S}{dt} = k_2 C_R$$

--- (c)



# Irreversible Reactions in series:

- Integrating eq. (a)
- the rate of change of R

$$C_A = C_{A0}e^{-k_1t}$$

$$\frac{dC_R}{dt} + k_2C_R = k_1C_{A0}e^{-k_1t}$$

- Using first-order linear differential equation of the form

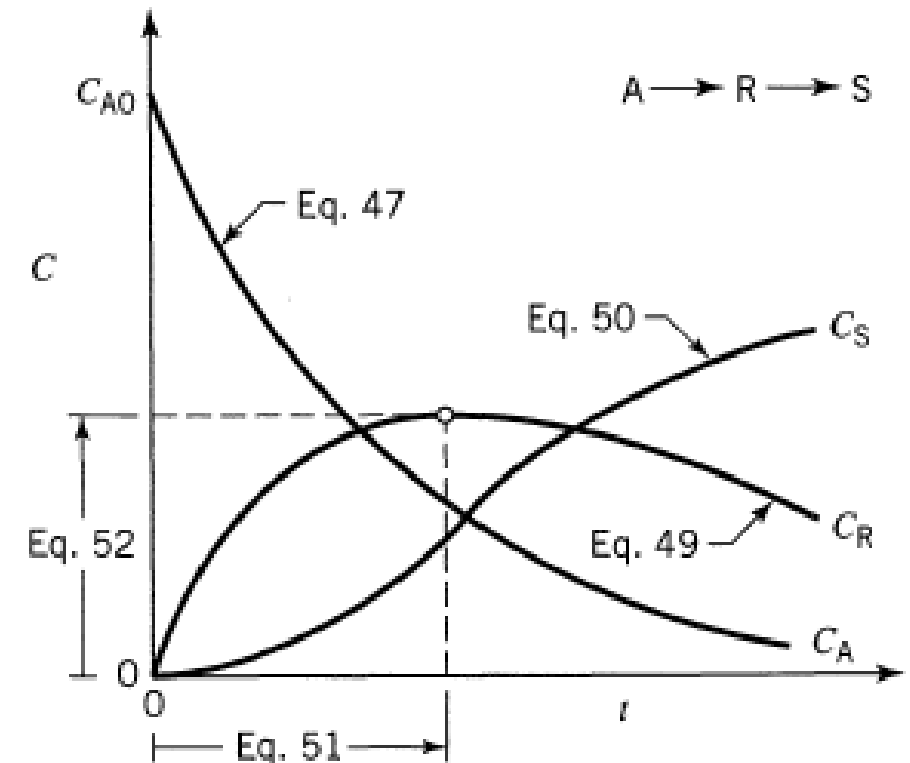
$$\frac{dy}{dx} + Py = Q$$

- The solution is,

$$ye^{\int P dx} = \int Qe^{\int P dx} dx + \text{constant}$$

- Further integrating eq. (b),

$$C_R = C_{A0}k_1 \left( \frac{e^{-k_1t}}{k_2 - k_1} + \frac{e^{-k_2t}}{k_1 - k_2} \right)$$



# Irreversible Reactions in series:

- Based on the stoichiometry and assuming that there is no loss in the number of moles, one can simply write,

$$C_{A0} = C_A + C_R + C_S$$

- Further integrating the modified differential equation, we get

$$C_S = C_{A0} \left( 1 + \frac{k_2 e^{-k_1 t}}{k_1 - k_2} + \frac{k_1 e^{-k_2 t}}{k_2 - k_1} \right)$$

- The values of  $k_1$  and  $k_2$  also govern the location and maximum concentration of R. This may be found by differentiating and setting  $dC_R/dt = 0$ . The time at which the maximum concentration of R occurs is thus

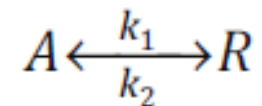
$$t_{\max} = \frac{1}{k_{\log \text{ mean}}} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$

- The maximum concentration of R, using  $t_{\max}$  and  $C_R$

$$\frac{C_{R,\max}}{C_{A0}} = \left( \frac{k_1}{k_2} \right)^{k_2/(k_2 - k_1)}$$

# Reversible Reactions:

- Many enzymatic reactions are reversible; hence, it is important to learn the kinetics of reversible reactions.
- For example, enzyme-substrate complex formation by the combination of enzyme and substrate is a typical example of a reversible first-order reaction.
- A typical reversible reaction can be expressed as follows:



- Let the symbol M denote the ratio of  $C_{R0}/C_{A0}$ ;
- the rate equation can be written as

$$-r_A = r_R = -\frac{dC_A}{dt} = \frac{dC_R}{dt} = k_1 C_A - k_2 C_R = k_1 (C_{A0} - C_{A0} X_A) - k_2 (M C_{A0} + C_{A0} X_A)$$

--- (a)

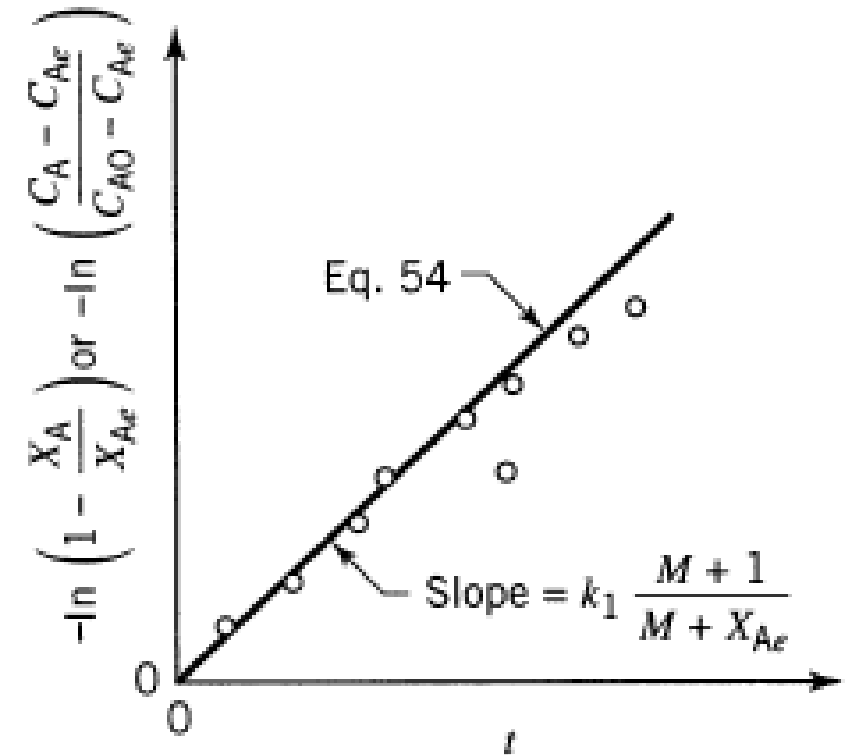
# Reversible Reactions:

- The value of  $dC_A/dt$  corresponds to 0 at the equilibrium. One will get the following expression:

$$K_C = \frac{C_{Re}}{C_{Ae}} = \frac{M + X_{Ae}}{1 - X_{Ae}}$$

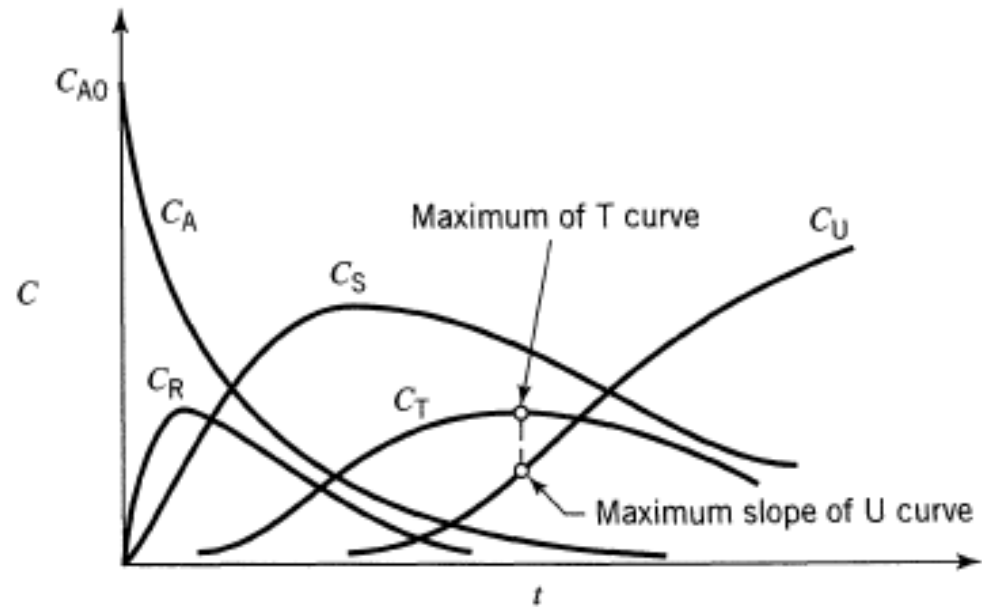
- $K_C$  may be defined as the ratio of  $k_1/k_2$ .
- Also,  $X_{Ae}$  is the percentage conversion at equilibrium.
- Using these values in eq (a) and integrating, we get

$$-\ln \left( 1 - \frac{X_A}{X_{Ae}} \right) = -\ln \frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}} = \frac{M + 1}{M + X_{Ae}} k_1 t$$



- The above equation demonstrates that if  $\ln(1 - X_A/X_{Ae})$  is plotted for various  $t$ , then a straight line will be obtained with a slope of  $(M + 1)k_1/(M + X_{Ae})$ .

# Chain Reactions:



# Dependency of Reaction Rate on Temperature:

- Till now, it has been assumed that the concentration of reactant and product has a significant effect on the reaction rate at a specified temperature.
- However, in order to achieve the rate expression, the role of temperature dependency cannot be neglected, which plays a pivotal role in the reaction rate.

- A typical rate equation mostly looks like

$$-r = k f(C)$$

- An Arrhenius relationship yields the following:

$$k = Ae^{-E/RT}$$



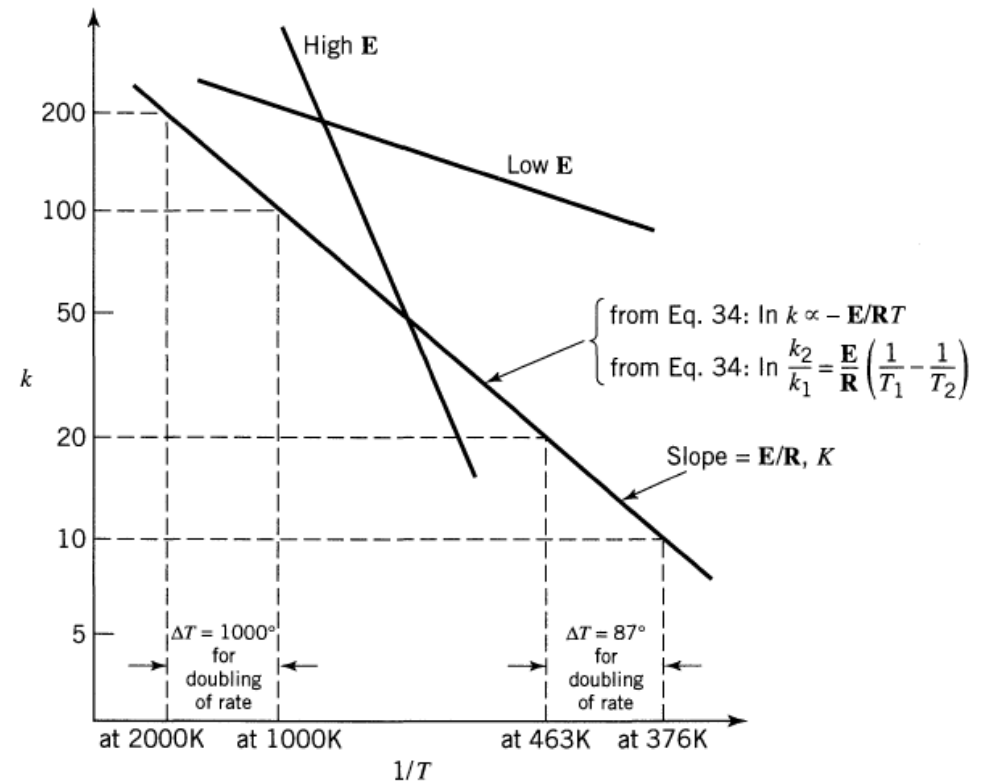
# Dependency of Reaction Rate on Temperature:

- where  $k$  is the reaction rate constant,
- $A$  is the pre-exponential factor or the steric factor,
- $E$  is the activation energy,
- $R$  is the gas constant, and
- $T$  is the temperature in K.

$$k = Ae^{-E/RT}$$

- Taking log on both sides, we get

$$\ln k = \ln A - \frac{E}{RT}$$



- If we plot  $\ln k$  versus  $1/T$ , we get a straight line with the intercept  $\ln A$  and the slope  $-E/R$ .
- For two rate constants  $k_1$  and  $k_2$  at temperatures  $T_1$  and  $T_2$ , one can easily get

$$\ln \frac{k_2}{k_1} = \frac{E}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

# Dependency of Reaction Rate on Temperature:

- **Important points to note:**
- Reactions associated with higher activation energy are largely dependent on temperature and vice versa.
- Any given reaction is much more temperature sensitive at a low temperature than at a high temperature.
- According to the Arrhenius law, the value of  $A$  (frequency factor) does not affect temperature sensitivity.

# Problem statement:

- Milk is pasteurized if heated to 63°C for 30 min, but if heated to 74°C, it only needs 15 s for the same result. Find the activation energy of this sterilization process.

- **Solution:**

**Given**                       $t_1 = 30 \text{ min at a } T_1 = 336 \text{ K}$

$t_2 = 15 \text{ sec at a } T_2 = 347 \text{ K}$

Now the rate is inversely proportional to the reaction time

$$\ln \frac{r_2}{r_1} = \ln \frac{t_1}{t_2} = \frac{\mathbf{E}}{\mathbf{R}} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{30}{0.25} = \frac{\mathbf{E}}{8.314} \left( \frac{1}{336} - \frac{1}{347} \right)$$

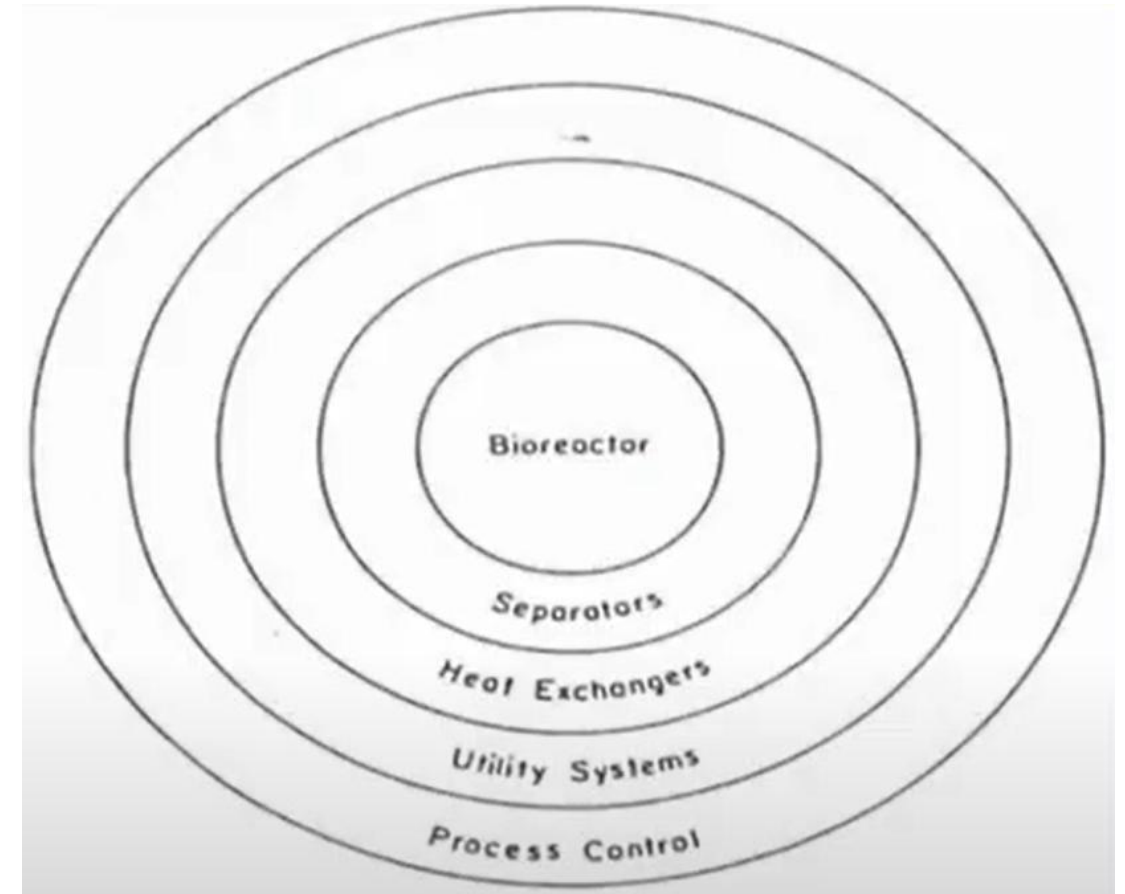
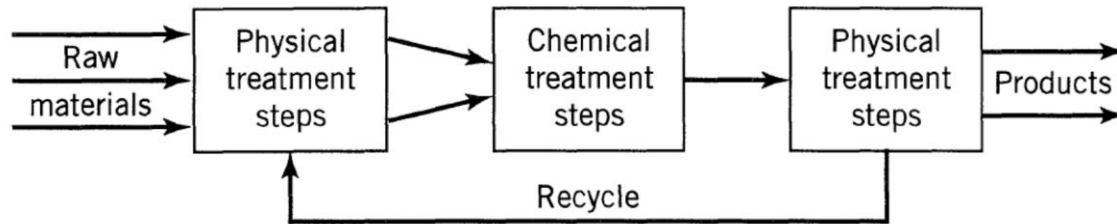
$$\underline{\underline{\mathbf{E} = 422\,000 \text{ J/mol}}}$$

# Different Types of Reactors

# Reactor:

- Reactor is the heart of any chemical process.
- A reactor is a vessel in a process plant where different reactions occur to generate a desirable product.
- **Bioreactor** deals with organisms or biochemically active substances derived from such organisms.
- How to pick the best options for our application is a crucial task.

# Bioreactor and unit operation: (Bioprocess design hierarchy)

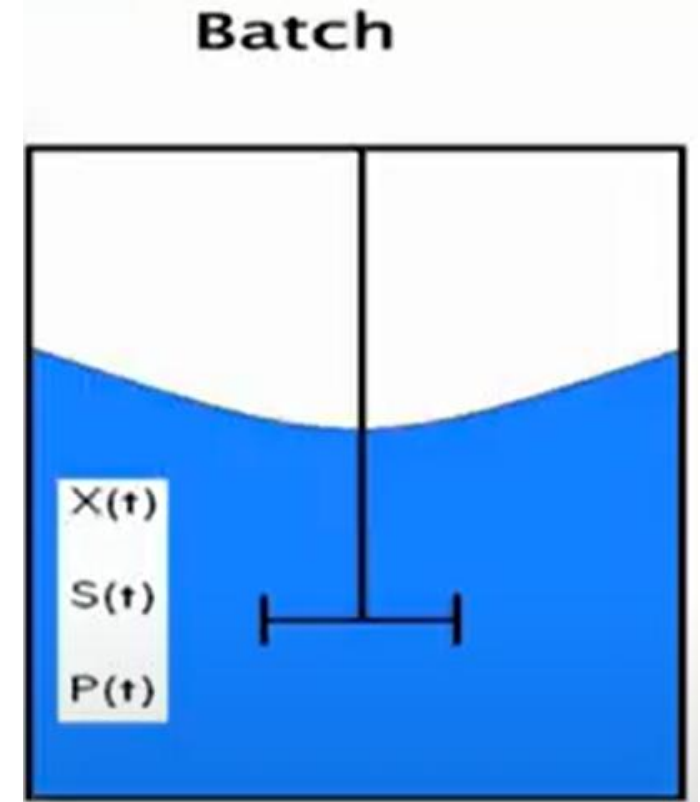


# Classification of the reactors:

- Reactors are classified depending on three main characteristics:
- **Mode of operation**
  - Batch, Fed-batch, Continuous
- **Geometric configuration**
  - Tubular, Agitated tank reactor
- **Contacting pattern between phases**
  - Packed bed, fluidized bed, trickle bed, bubble column, airlift reactor

# Batch reactors:

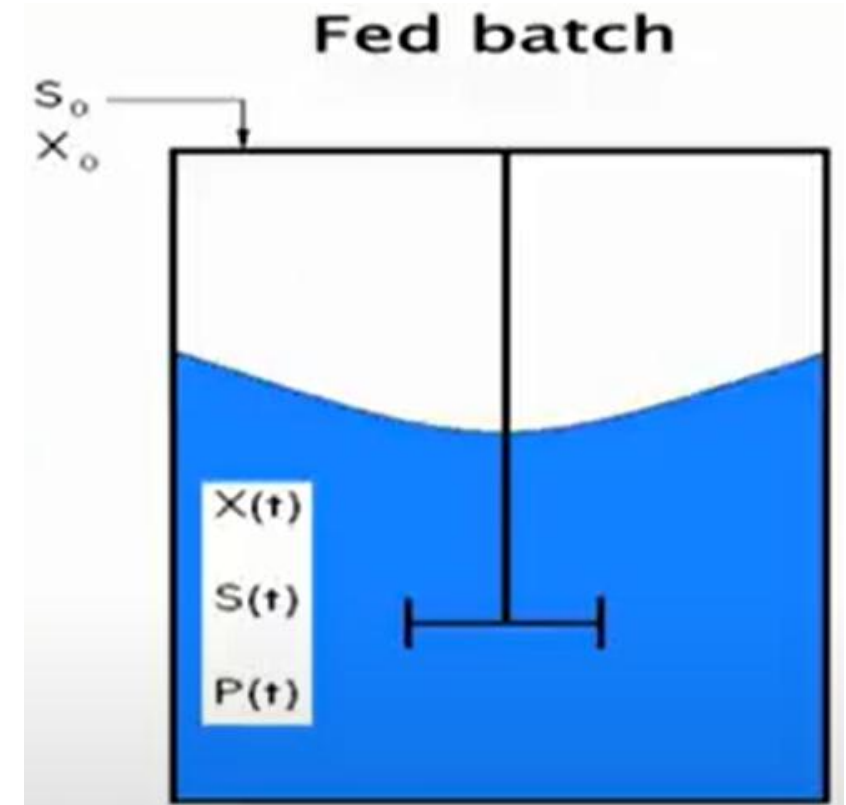
- Reactants are fed into the vessel at the start of the operation and products are removed at the end of the operation.
- Therefore, during the process there is no feed addition and product removal.
- The chemical reaction takes place with respect to time.
- **Applications:** fermentation of beverage products, chemical industries (dyes, inks), wastewater treatment





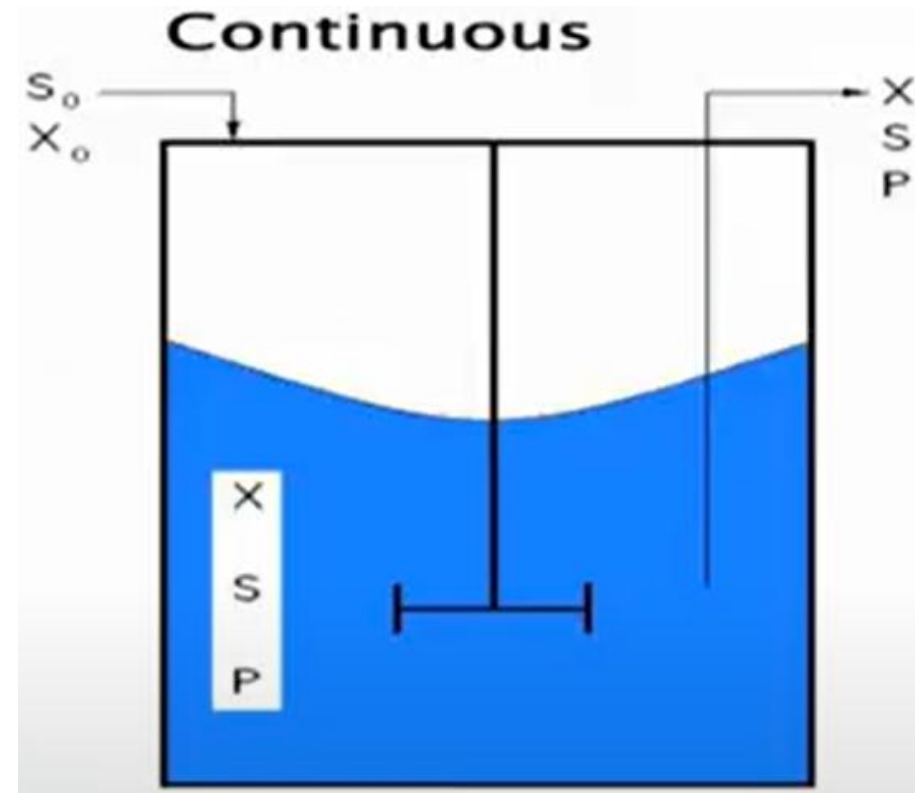
# Fed-batch reactors:

- A vessel in which reactants are charged initially and limiting reactant is added continuously during the operation
- There is no product removal during the process
- **Applications:** Chlorination of liquid, pharmaceutical industries



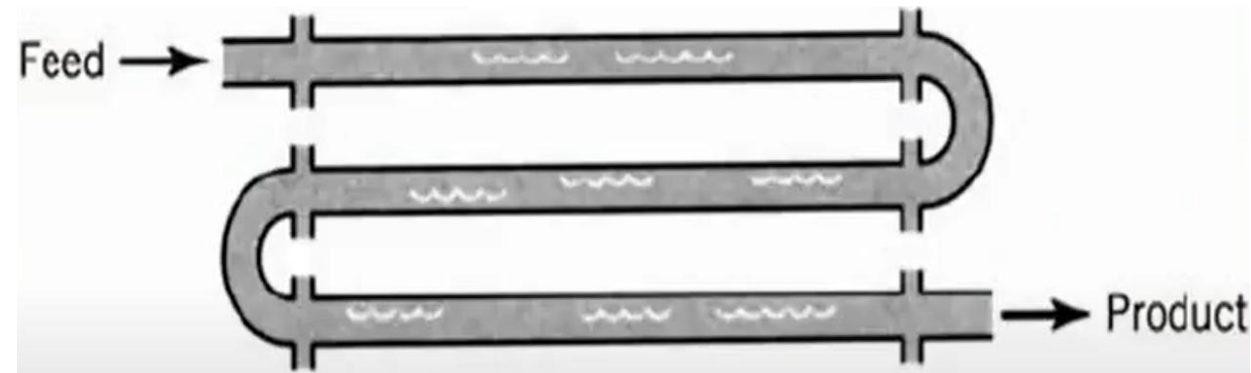
# Continuous stirred tank reactor (CSTR): (Flow reactors)

- Reactants and products are continuously added and withdrawn while the contents within the vessel are vigorously stirred using internal agitation.
- Cascade of CSTR can be used for higher conversion of reactant
- **Applications:** Chemical industries, biological industries, waste treatment



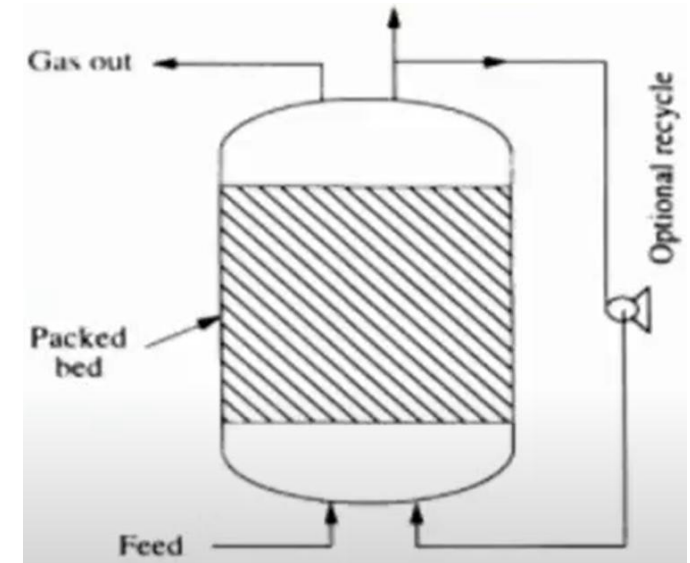
# Tubular reactors: (Flow reactors)

- A reactor consists of a hollow pipe or tube through which reactants flow. Where reactants move as a plug along the length of the reactor.
- Concentration of reactant varies along the length of the pipe.
- No axial mixing only radial mixing occurs
- **Applications:** Homogeneous or heterogeneous reactions, continuous production, high-temperature reaction



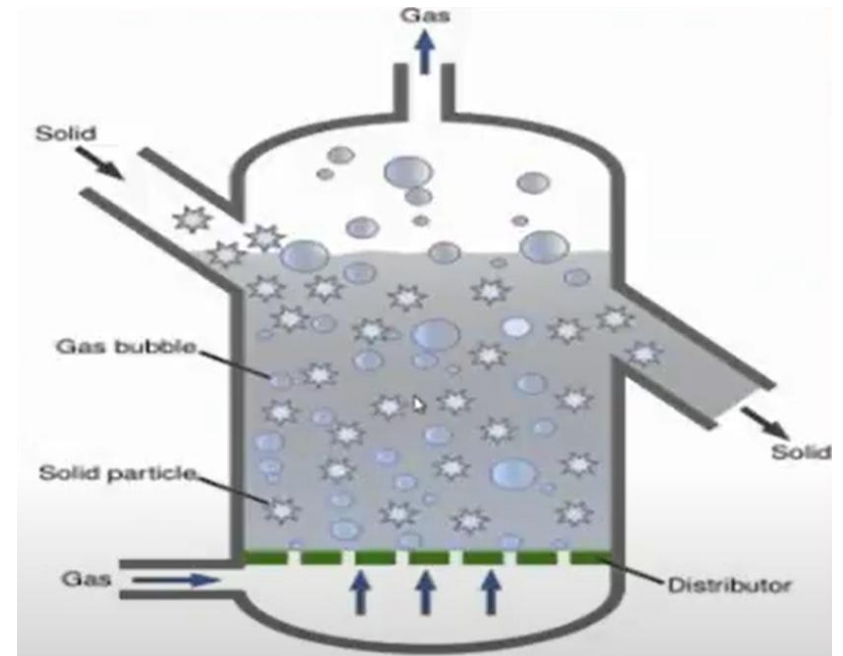
# Packed bed reactor:

- A vessel filled with catalytic pellets (larger than 1 cm to avoid excessive pressure drop) and the reacting fluid passing through the void space available between them.
- A pump may be required for fluid to move through the bed.
- **Applications:** Wastewater treatment, immobilized cell system, multiphase reactions, pharmaceutical industries



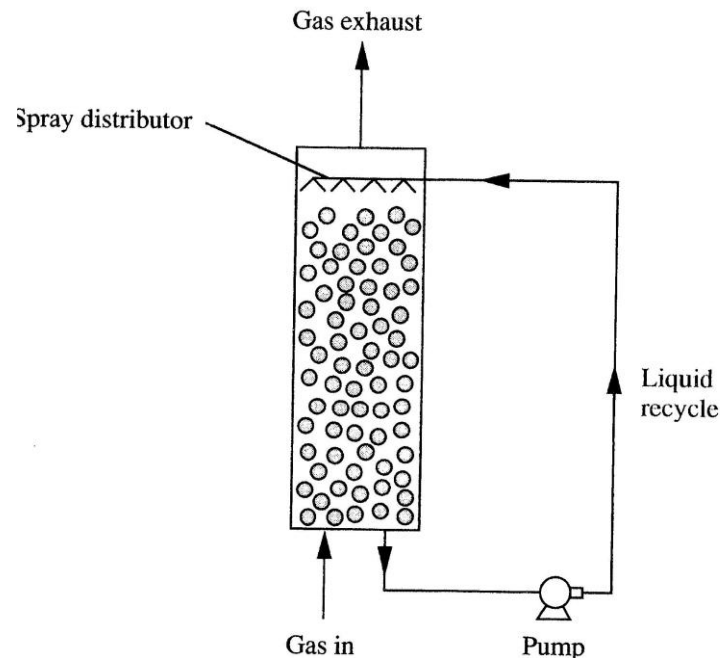
# Fluidized bed reactor:

- A vessel filled with fine particles (smaller than 500  $\mu\text{m}$ ) that are suspended by the upward-flowing fluid at high enough velocities to suspend the solids.
- Fluidized bed reactor provides good mixing of particles and uniform temperature.
- Typical velocity is 6-20 m/hr, Recycle ratio 5-500, bed expansion 30-100%.
- **Applications:** Multiphase systems with biocatalysts, food processing industries, chlorination of olefins to alkyl.



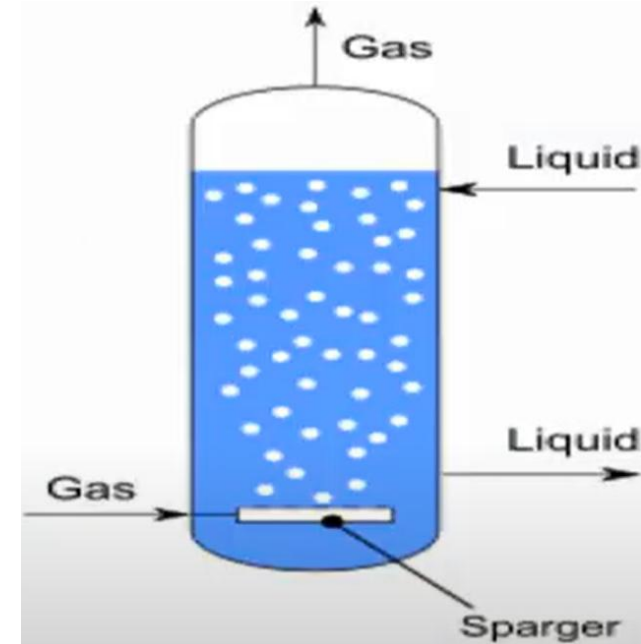
# Trickle bed reactor:

- The trickle-bed reactor is another variation of the packed bed reactors.
- Liquid is sprayed onto the top of the packing and trickles down through the bed in small rivulets.



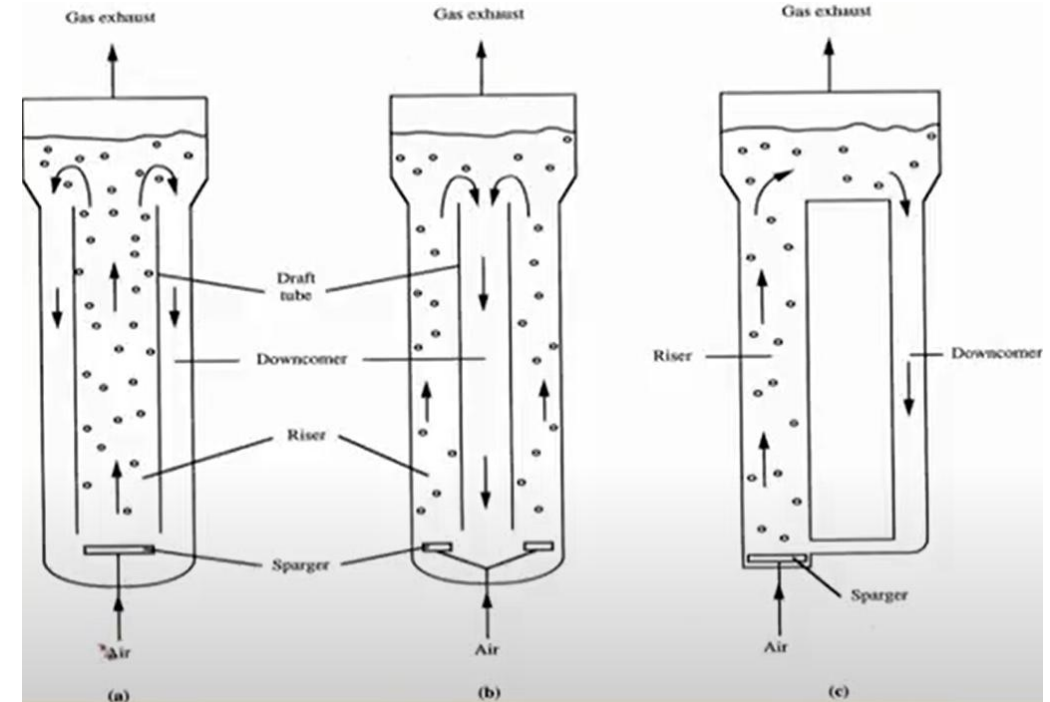
# Bubble column reactor:

- A vessel filled with liquid reactant and gas reactant is fed from the bottom and moves upward in the form of bubbles.
- A liquid reactant is fed from the top and removed from the bottom.
- A gaseous reactant is absorbed in the liquid reactant and the reaction takes place in the liquid phase.
- The flow rate of the air/gas influences the performance factor ( $O_2$  transfer and mixing).
- **Applications:** Production of single-cell protein from cheese whey, algae cultivation



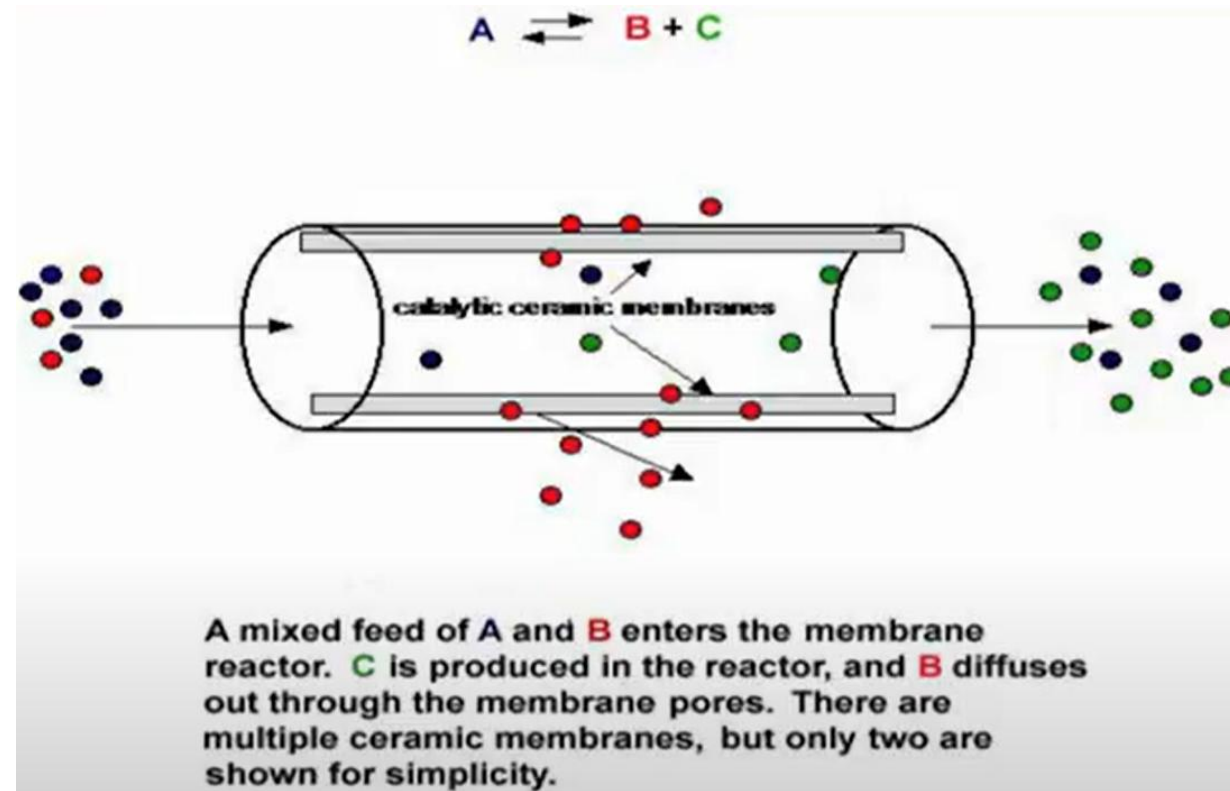
# Airlift reactor:

- Airlift bioreactors are similar to bubble column reactors but differ in the fact that they contain a draft tube.
- A draft tube is an inner tube or an external tube that improves circulation and oxygen transfer and equalizes shear forces in the reactor.
- **Applications:** Photobioreactor for algae cultivation, aerobic bioprocessing technology, single-cell protein production





# Membrane reactor:



- **Applications:** Dehydrogenation of ethane, Production of antibodies, wastewater treatment

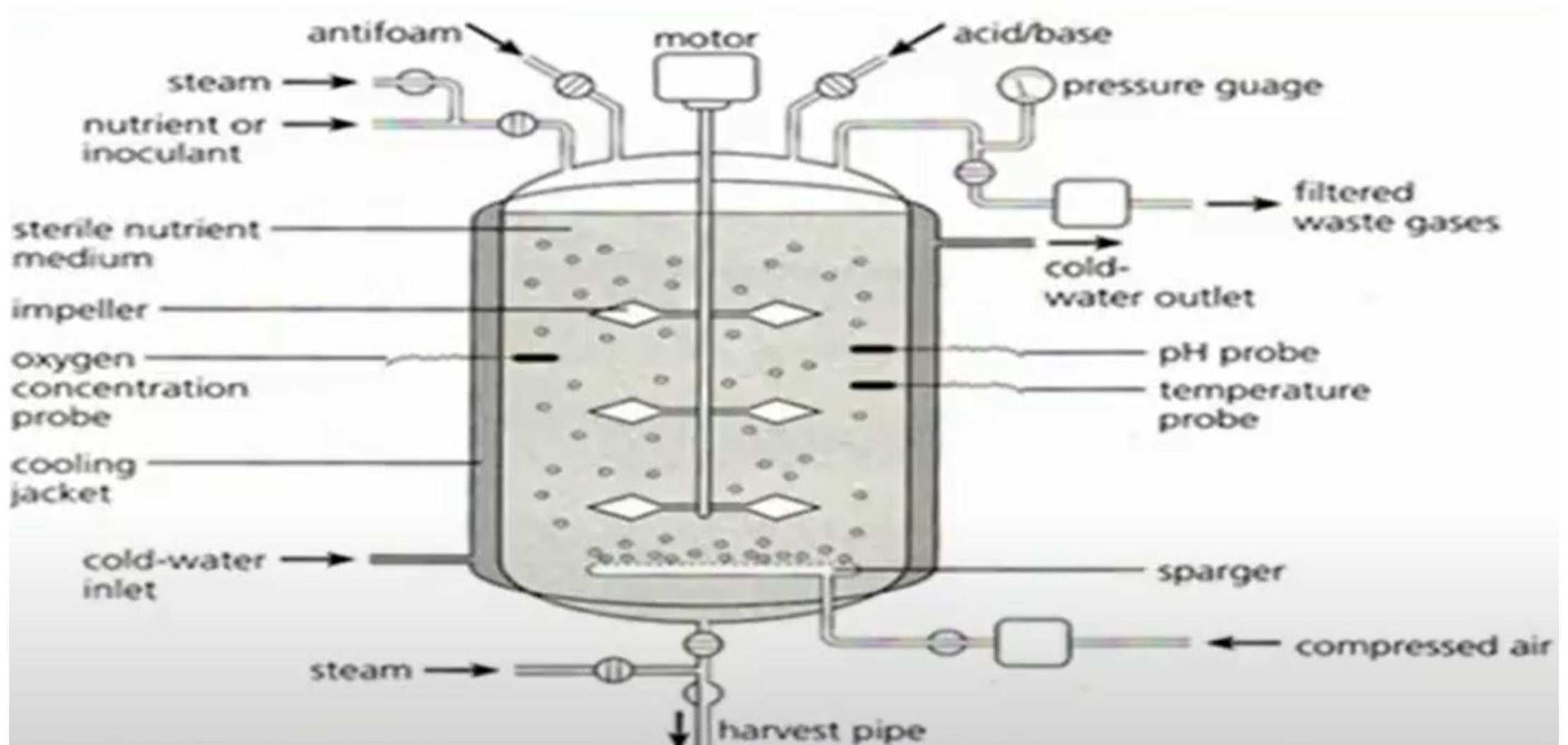
# Material of construction of the reactor:

- Construction materials differ with the scale of the reactor (bench scale, pilot scale, and large scale).
- Glass (borosilicate glass) or stainless steel (SS304, SS304L, SS316, SS316L) for **small scale processes**.
- Stainless steel (>4 % chromium, SS304, SS304L, SS316, SS316L), mild steel (coated with glass or epoxy material), wood, plastic, or concrete for **pilot and large-scale processes**.

# Lab scale and commercial scale bioreactors:



# Ideal batch reactor (fermenter) configuration:



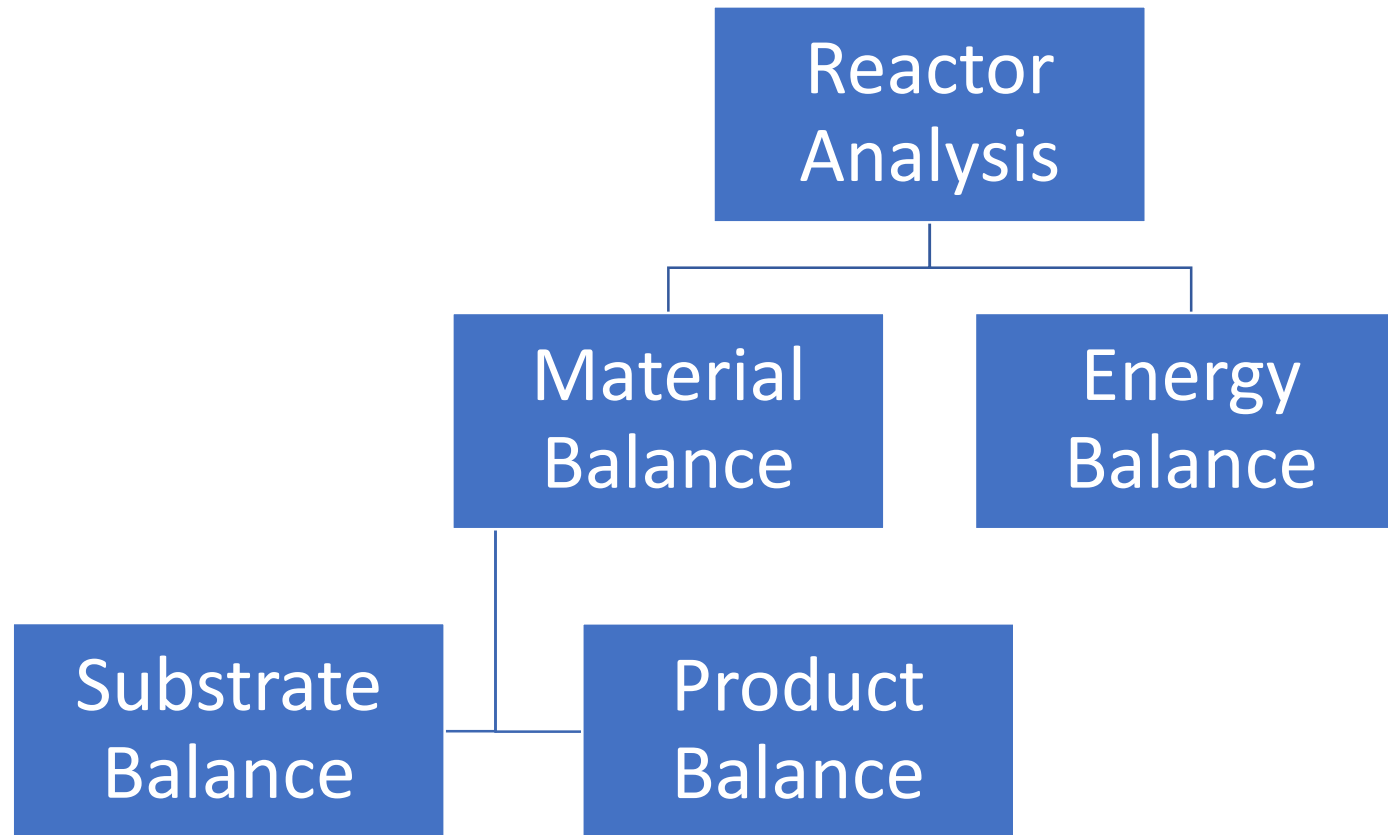


# Ideal batch reactor (fermenter) configuration:

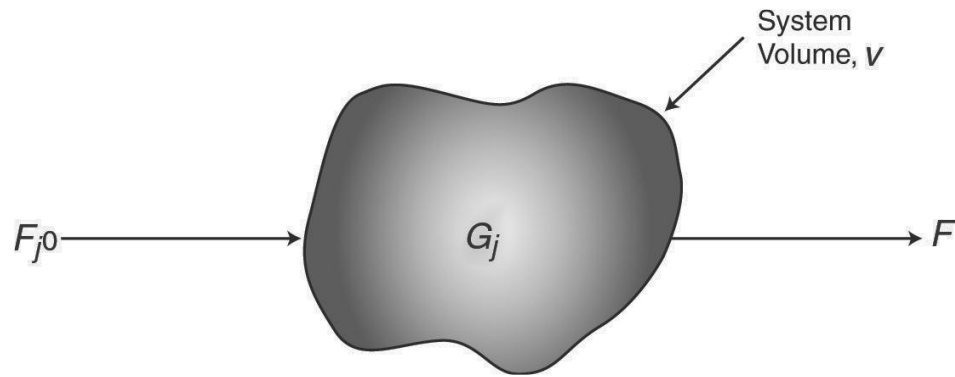
Sr.	Parts of fermenter	Function
1	Impellor (agitator)	To stir the media continuously and hence prevent cells from settling down, and distribute oxygen throughout the medium
2	Sparger (Aerator)	Introduce sterile oxygen to the media in case of aerobic fermentation process
3	Baffles (vortex breaker)	Disrupt vortex and provide better mixing
4	Inlet Air filter	Filter air before it enter the fermenter
5	Exhaust Air filter	Trap and prevent contaminants from escaping
6	Rotameter	Measure flow rate of Air or liquid
7	Pressure gauge	Measure pressure inside the fermenter
8	Temperature probe	Measure and monitor change in temperature of the medium during the process
9	Cooling Jacket	To maintain the temperature of the medium throughout the process
10	pH probe	Measure and monitor pH of the medium
11	Dissolve Oxygen Probe	Measure dissolve oxygen in the fermenter
12	Level probe	Measure the level of medium
13	Foam probe	Detect the presence of the foam
14	Acid	Maintain the required pH of the medium by neutralizing the basic environment
15	Base	Maintain the required pH of the medium by neutralizing the acidic environment
16	Antifoam	Breakdown and prevent foams
17	Sampling pint	To obtain samples during the process
18	Valves	Regulation and control the flow liquids and gases
19	Control panel	Monitor over all parameters

# Reactor Analysis

# Reactor Analysis



# General Mole Balance



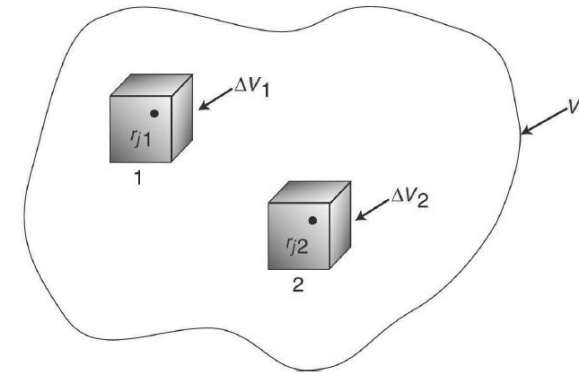
$$\begin{array}{c}
 \left[ \begin{array}{c} \text{Rate of flow} \\ \text{of } j \text{ into} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] - \left[ \begin{array}{c} \text{Rate of flow} \\ \text{of } j \text{ out of} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] + \left[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

$$\begin{array}{ccccccccc}
 \text{In} & - & \text{Out} & + & \text{Generation} & = & \text{Accumulation} & & \\
 F_{j0} & - & F_j & + & G_j & = & \frac{dN_j}{dt} & \dots \text{eq. 1} & 
 \end{array}$$

## ➤ Rate of generation of species $j$

➤ If spatially uniform  $G_j = r_j \cdot V$   $\frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{\text{time} \cdot \text{volume}} \cdot \text{volume}$

➤ If spatially not uniform  $\Delta G_{j1} = r_{j1} \Delta V_1$



➤ Total rate of generation for  $M$  sub volume

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

➤ Using  $M \rightarrow \infty$  and  $\Delta V \rightarrow 0$

$$G_j = \int_V r_j dV$$

➤ Using eq. 1

$$F_{j0} - F_j + \int_V r_j dV = \frac{dN_j}{dt}$$

**Basic Mole Balance equation for chemical reaction engineering**



# Batch Reactor

## ➤ Batch Reactor Characteristics

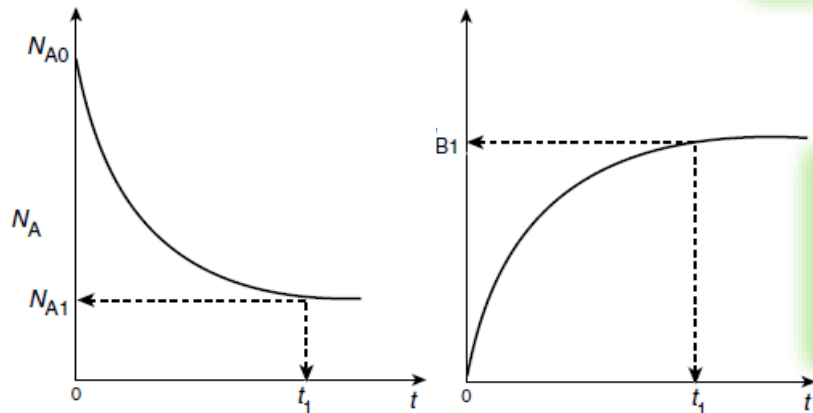
- No fluid enters or leaves the reactor during reaction
- Unsteady state operation where composition changes with time

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

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

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

➤ Consider,  $A \longrightarrow B$



$N_A$  decreases and  $N_B$  increases

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



## ➤ Advantages of using Batch Reactor

- Small instrumentation cost
- Flexibility of operation (may shut down easily and quickly)
- High conversion when reactants are in reactor for long period of time

## ➤ Disadvantages of using Batch Reactor

- High labor and handling cost
- Considerable time for empty clean out and refill the reactor
- Difficulty in handling large scale production

# Continuous Flow Reactors

## ➤ Stirred Tank Reactor (CSTR) Characteristics

- Steady state operation where composition do not change with time
- Composition is uniform throughout
- Exit stream has same composition as fluid in the reactor

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

- Steady state  $\frac{dN_j}{dt} = 0$

- Spatially uniform  $\int r_j dV = V r_j \implies V = \frac{F_{j0} - F_j}{-r_j}$

$$F_j = C_j \cdot v$$

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

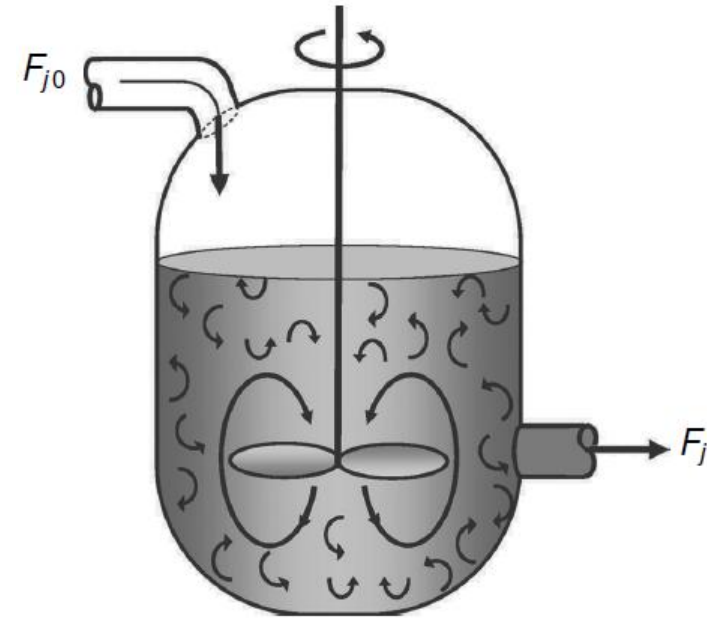
- Where,

- $F_j$  - Molar flow rate of species  $j$
- $C_j$  - Concentration of species  $j$
- $v$  - volumetric flow rate

- At the entrance to the reactor

$$F_{j0} = C_{j0} \cdot v_0$$

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



## ➤ Advantages of using CSTR

- Intense agitation
- Easy to maintain
- Good temperature control

## ➤ Disadvantages of using CSTR

- Low conversion per volume of reactor

# Continuous Flow Reactors

## ➤ Plug Flow Reactor (PFR) Characteristics

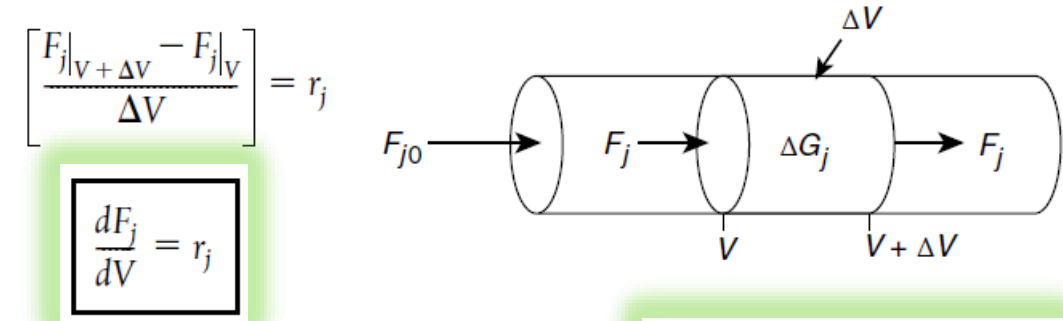
- Steady state operation where composition does not change with time
- Concentration of fluid varies from point to point along flow path
- No radial variation in reaction rate
- Residence time in reactor is same for all the elements of fluid
- Flow of fluid is orderly with no element of fluid is overtaking or mixing with other element of fluid ahead or behind
- No mixing or diffusion along the flow path, only lateral mixing occurs

➤ Steady state  $\frac{dN_j}{dt} = 0$

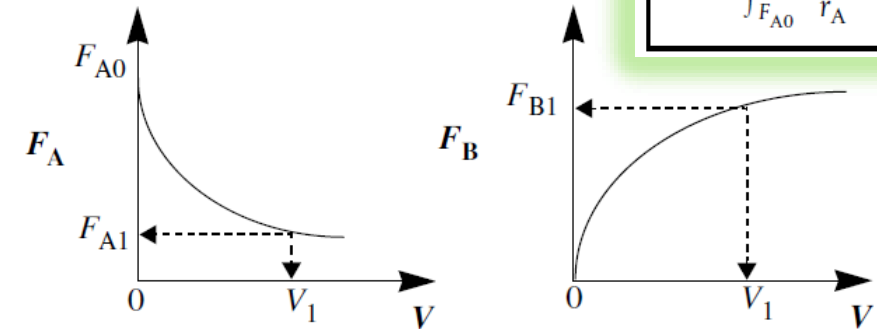
➤ Spatially uniform  $\Delta G_j = \int_V^{V+\Delta V} r_j dV = r_j \Delta V$

$$\left[ \begin{array}{c} \text{Molar flow} \\ \text{rate of species } j \\ \text{In at } V \\ \text{moles/time} \end{array} \right] - \left[ \begin{array}{c} \text{Molar flow} \\ \text{rate of species } j \\ \text{Out at } (V + \Delta V) \\ \text{moles/time} \end{array} \right] + \left[ \begin{array}{c} \text{Molar rate of} \\ \text{Generation} \\ \text{of species } j \\ \text{within } \Delta V \\ \text{moles/time} \end{array} \right] = \left[ \begin{array}{c} \text{Molar rate of} \\ \text{Accumulation} \\ \text{of species } j \\ \text{within } \Delta V \\ \text{moles/time} \end{array} \right]$$

$$\begin{array}{ccccc} \text{In} & - & \text{Out} & + & \text{Generation} & = & \text{Accumulation} \\ F_j|_V & - & F_j|_{V+\Delta V} & + & r_j \Delta V & = & 0 \end{array}$$



➤ Consider,  $A \longrightarrow B$



## ➤ Advantages of using PFR

- Highest conversion for any flow reactor

## ➤ Disadvantages of using PFR

- Difficulty in maintaining temperature within the reactor
- Hot spots can occur when reaction is exothermic

# Continuous Flow Reactors

## ➤ Packed Bed Reactor (PBR) Characteristics

- Reactor design carried out analogous PFR
- Reaction rate depends on mass of the catalyst nor on reactor volume
- Reactor volume is replaced by mass of the catalyst
- Reaction takes place on the surface of the catalyst
- Greater the mass of a catalyst greater the reactive surface area

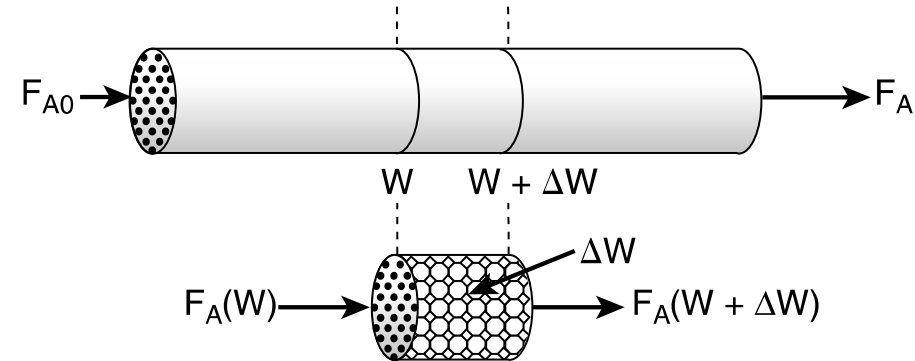
$$\text{In} - \text{Out} + \text{Generation} = \text{Accumulation}$$

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

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

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

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



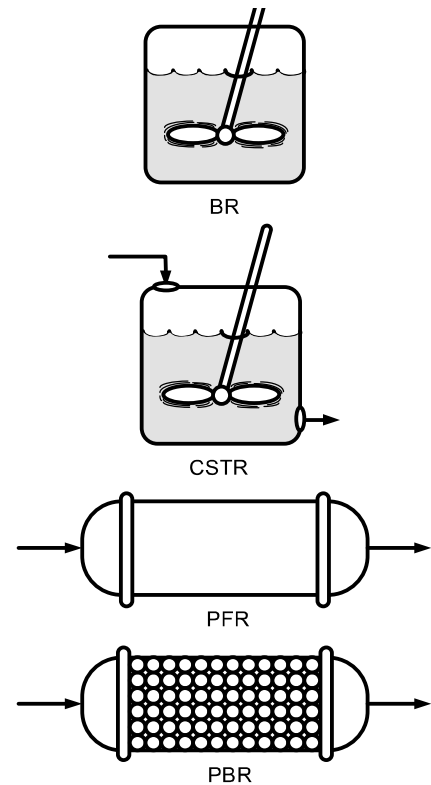
## ➤ Advantages of using PBR

- Highest conversion for any flow reactor

## ➤ Disadvantages of using PBR

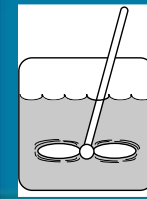
- Difficulty in maintaining temperature within the reactor
- Hot spots can occur when reaction is exothermic

# Summary of Reactor Mole Balances



<i>Reactor</i>	<i>Comment</i>	<i>Mole Balance Differential Form</i>	<i>Algebraic Form</i>	<i>Integral Form</i>
BR	No spatial variations	$\frac{dN_A}{dt} = r_A V$		$t_1 = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{-r_A V}$
CSTR	No spatial variations, steady state	—	$V = \frac{F_{A0} - F_A}{-r_A}$	—
PFR	Steady state	$\frac{dF_A}{dV} = r_A$		$V_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A}$
PBR	Steady state	$\frac{dF_A}{dW} = r'_A$		$W_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r'_A}$

# Batch Reactor



- Longer a reactant stays in the reactor, the more the reactant is converted to product
- Conversion  $X$  is a function of the time the reactants spend in the reactor
- If  $N_{A0}$  is the number of moles of A initially present in the reactor (i.e.,  $t = 0$ )
- Total number of moles of A that have reacted (i.e., have been consumed) after a time  $t$  is  $[N_{A0}X]$

$$[\text{Moles of A reacted (consumed)}] = [\text{Moles of A fed}] \cdot \left[ \frac{\text{Moles of A reacted}}{\text{Moles of A fed}} \right]$$

$$\left[ \begin{array}{c} \text{Moles of A} \\ \text{reacted} \\ \text{(consumed)} \end{array} \right] = [N_{A0}] \cdot [X]$$

- Number of moles of A that remain in the reactor after a time  $t$ ,  $N_A$

$$\left[ \begin{array}{c} \text{Moles of A} \\ \text{in reactor} \\ \text{at time } t \end{array} \right] = \left[ \begin{array}{c} \text{Moles of A} \\ \text{initially fed} \\ \text{to reactor at} \\ t = 0 \end{array} \right] - \left[ \begin{array}{c} \text{Moles of A that} \\ \text{have been} \\ \text{consumed by} \\ \text{chemical reaction} \end{array} \right]$$

$$[N_A] = [N_{A0}] - [N_{A0}X]$$

- Moles of A in the reactor at a time  $t$

$$N_A = N_{A0} - N_{A0}X = N_{A0}(1 - X)$$

- Differentiating w.r.t. time  $\frac{dN_A}{dt} = 0 - N_{A0} \frac{dX}{dt}$

- Mole balance for the batch reactor

$$-\frac{dN_A}{dt} = (-r_A)V \quad -N_{A0} \frac{dX}{dt} = r_A V \quad N_{A0} \frac{dX}{dt} = -r_A V$$

- Separating the variables in Equation

$$dt = N_{A0} \frac{dX}{-r_A V}$$

- Integrating and Using,

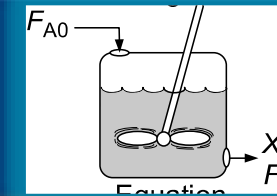
- when  $t = 0$ ,  $X = 0$  when  $t = t$ , then  $X = X$

- Batch time  $t$  to achieve a conversion  $X$

$$t = N_{A0} \int_0^X \frac{dX}{-r_A V}$$

**Batch Reactor Design Equation**

# Flow Reactors (CSTR)



- More the time the reactants take to flow completely through the reactor, the more time to react
- Conversion  $X$  is a function of reactor volume  $V$
- If  $F_{A0}$  is the molar flow rate of species A fed to a system operated at steady state (i.e.,  $t = 0$ )
- Total molar rate at which species A is reacting *within* the entire system will be  $F_{A0}X$

$$[F_{A0}] \cdot [X] = \frac{\text{Moles of A fed}}{\text{time}} \cdot \frac{\text{Moles of A reacted}}{\text{Moles of A fed}}$$

$$[F_{A0} \cdot X] = \frac{\text{Moles of A reacted}}{\text{time}}$$

- Molar flow rate of A that remain in the reactor after a time  $t$ ,  $F_A$

$$\begin{aligned} \left[ \begin{array}{c} \text{Molar flow rate} \\ \text{at which A leaves} \\ \text{the system} \end{array} \right] &= \left[ \begin{array}{c} \text{Molar flow rate} \\ \text{at which A is} \\ \text{fed to the system} \end{array} \right] - \left[ \begin{array}{c} \text{Molar rate at} \\ \text{which A is} \\ \text{consumed within} \\ \text{the system} \end{array} \right] \\ [F_A] &= [F_{A0}] - [F_{A0}X] \end{aligned}$$

- Molar flow rate of A in the reactor at a time  $t$

$$F_A = F_{A0}(1 - X)$$

- Here,

$$F_{A0} = C_{A0} v_0$$

- Where,

- $C_{A0}$  - Concentration (mol/m<sup>3</sup>)
- $v_0$  - volumetric flow rate (m<sup>3</sup>/s)

- CSTR mole balance Equation

$$V = \frac{F_{A0} - F_A}{-r_A} \quad V = \frac{F_{A0} - (F_{A0} - F_{A0}X)}{-r_A}$$

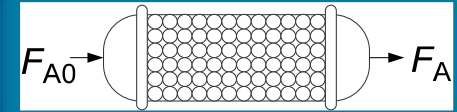
- Volume required to achieve a conversion  $X$

$$V = \frac{F_{A0}X}{(-r_A)_{\text{exit}}}$$

**CSTR Design Equation**



# Flow Reactors



- PFR design equation 
$$\frac{-dF_A}{dV} = -r_A$$

- Molar flow rate of A in the reactor at a time  $t$

$$F_A = F_{A0}(1 - X)$$

- Differentiating

$$dF_A = -F_{A0}dX$$

- Differential form of the design equation for a PFR

$$F_{A0} \frac{dX}{dV} = -r_A$$

- Integrate with the limits  $V = 0$  when  $X = 0$

- PFR volume necessary to achieve a specified conversion  $X$

$$V = F_{A0} \int_0^X \frac{dX}{-r_A}$$

**PFR Design Equation**

- PBR design equation 
$$\frac{dF_A}{dW} = r'_A$$

- Molar flow rate of A in the reactor at a time  $t$

$$F_A = F_{A0}(1 - X)$$

- Differentiating

$$dF_A = -F_{A0}dX$$

- Differential form of the design equation for a PBR

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

- Integrating

- with the limits  $X = 0$  at  $W = 0$

- when  $W = W$  then  $X = X$

- Catalyst weight  $W$  necessary to achieve a specified conversion  $X$

$$W = F_{A0} \int_0^X \frac{dX}{-r'_A}$$

**PBR Design Equation**



# Summary of Reactor Mole Balances in terms of Conversion

	Differential Form	Algebraic Form	Integral Form
Batch	$N_{A0} \frac{dX}{dt} = -r_A V$		$t = N_{A0} \int_0^X \frac{dX}{-r_A V}$
CSTR		$V = \frac{F_{A0}(X_{\text{out}} - X_{\text{in}})}{(-r_A)_{\text{out}}}$	$t = N_{A0} \int_0^X \frac{dX}{-r_A V}$
“Fluidized” CSTR		$W = \frac{F_{A0}(X_{\text{out}} - X_{\text{in}})}{(-r'_A)_{\text{out}}}$	
PFR	$F_{A0} \frac{dX}{dV} = -r_A$		$V = F_{A0} \int_{X_{\text{in}}}^{X_{\text{out}}} \frac{dX}{-r_A}$
PBR	$F_{A0} \frac{dX}{dW} = -r'_A$		$W = F_{A0} \int_{X_{\text{in}}}^{X_{\text{out}}} \frac{dX}{-r'_A}$

# Some Further Definitions

- **Space time ( $\tau$ ) / holding time / mean residence time**
- Time required to process one reactor volume of feed

$$\tau \equiv \frac{V}{v_0}$$

For a PFR  $\tau_P = \left( \frac{V_P}{v_0} \right) = C_{A0} \int_0^X \frac{dX}{-r_A}$

For a CSTR  $\tau_{CSTR} = \left( \frac{V_{CSTR}}{v_0} \right) = \frac{C_{A0}}{-r_A} X$

- **Space velocity ( $\tau$ )**
- How many reactor volume of fluid is getting treated in unit time

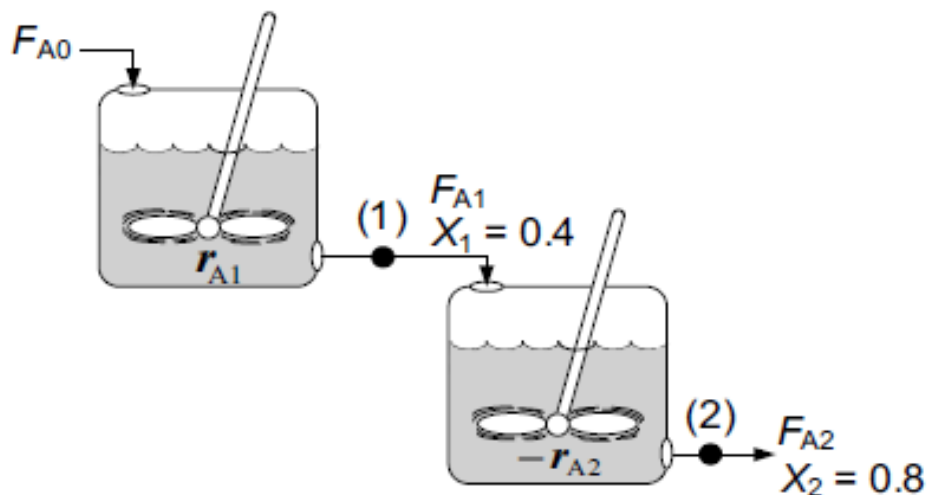
$$SV \equiv \frac{v_0}{V}$$

$$SV = \frac{1}{\tau}$$

# Reactors in series

- Many times, reactors are connected in series so that the exit stream of one reactor is the feed stream for another reactor.
- It is often possible to speed calculations by defining conversion in terms of location at a point downstream rather than with respect to any single reactor.

## ➤ CSTRs in Series



A mole balance on reactor 1 gives

Reactor 1: **In – Out + Generation = 0**

$$F_{A0} - F_{A1} + r_{A1}V_1 = 0$$

The molar flow rate of A at point 1 is

$$F_{A1} = F_{A0} - F_{A0}X_1$$

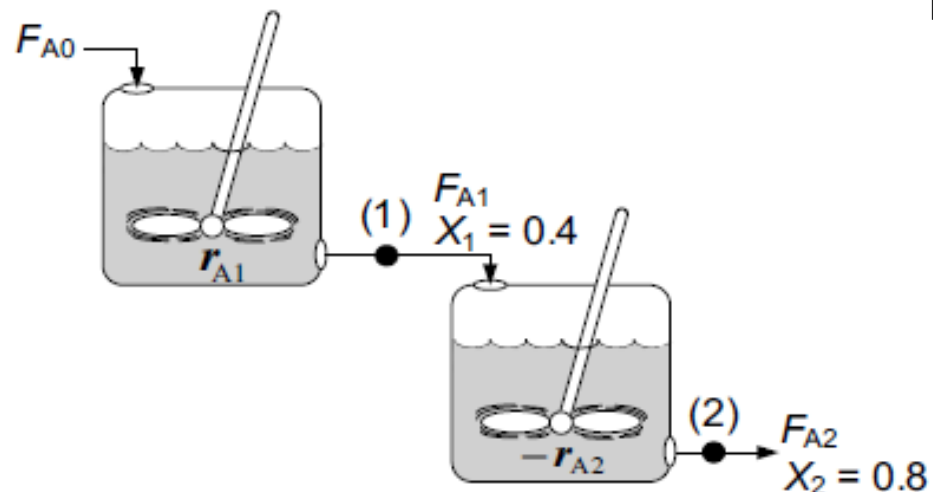
Combining Equations, and rearranging

$$V_1 = \frac{F_{A0}X_1}{-r_{A1}}$$

For the first reactor, the rate of disappearance of A is  $-r_{A1}$  at conversion  $X_1$ .

# Reactors in series

## ➤ CSTRs in Series



A mole balance on reactor 1 gives

Reactor 2: **In – Out + Generation = 0**

$$F_{A1} - F_{A2} + r_{A2}V_2 = 0$$

The molar flow rate of A at point 2 is

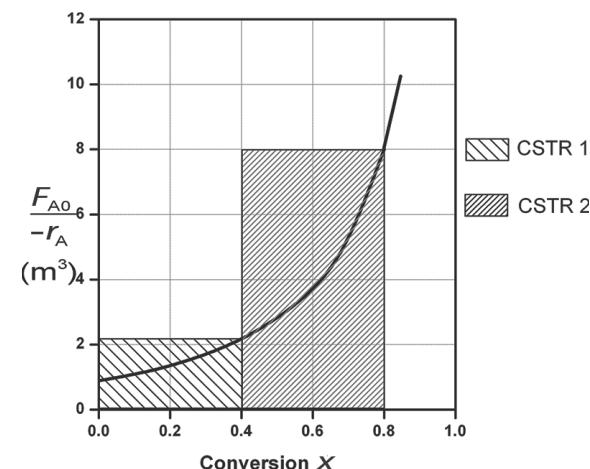
$$F_{A2} = F_{A0} - F_{A0}X_2$$

Combining Equations, and rearranging

$$V_2 = \frac{F_{A1} - F_{A2}}{-r_{A2}} = \frac{(F_{A0} - F_{A0}X_1) - (F_{A0} - F_{A0}X_2)}{-r_{A2}}$$

$$V_2 = \frac{F_{A0}}{-r_{A2}}(X_2 - X_1)$$

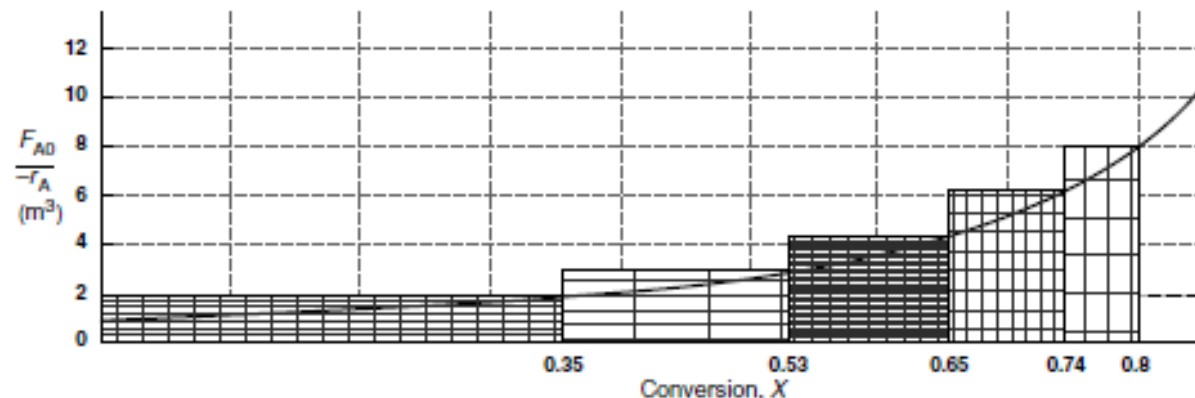
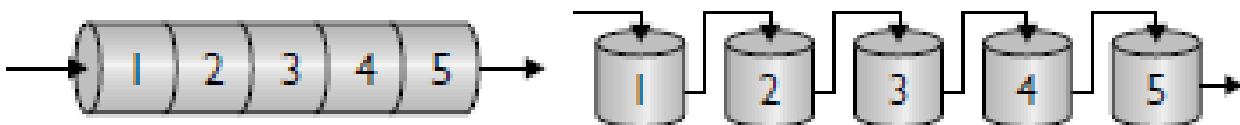
In the second reactor, the rate of disappearance of A,  $-r_{A2}$ , is evaluated at the conversion of the exit stream of reactor 2,  $X_2$ .



# Reactors in series

## ➤ Approximating a PFR by a Large Number of CSTRs in Series

- Consider approximating a PFR with a number of small, equal-volume CSTRs of  $V_i$  in series. We want to compare the total volume of all these CSTRs in series with the volume of one plug-flow reactor for the same conversion, say 80%.

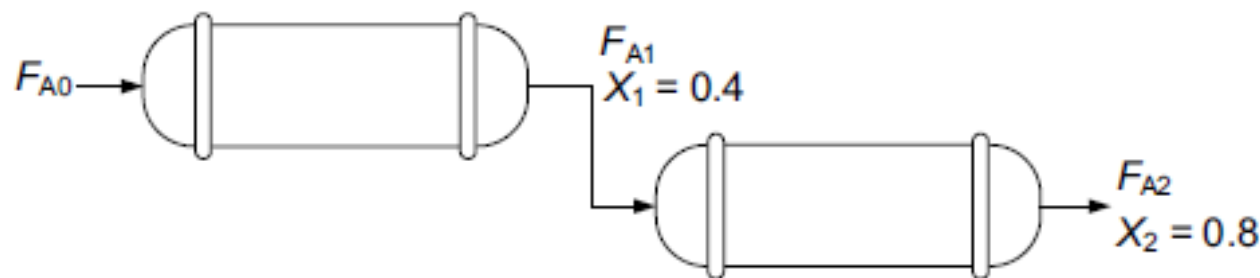


- The total volume to achieve 80% conversion for five CSTRs of equal volume in series is “roughly” the same as the volume of a PFR.
- The total volume of the CSTRs in series and the volume of the PFR will become identical. That is, we can model a PFR with a large number of CSTRs in series.

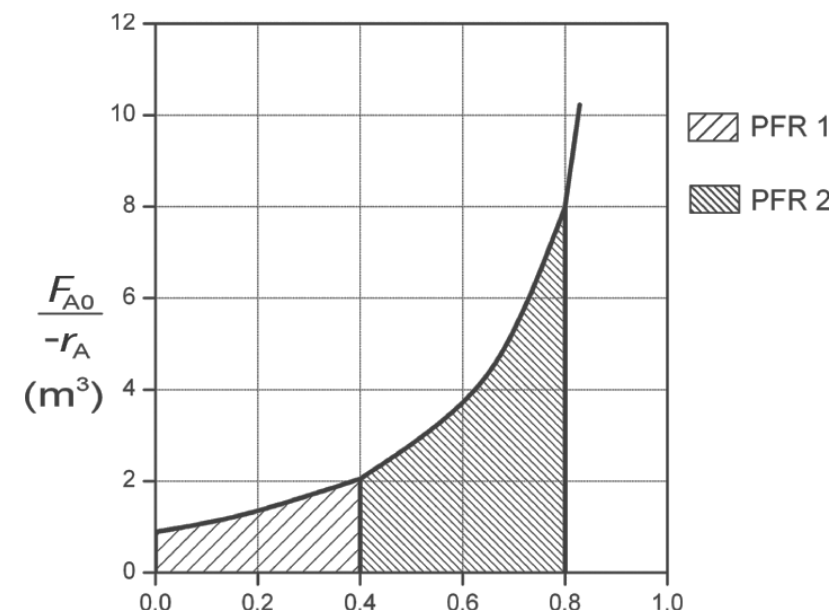
# Reactors in series

## ➤ PFRs in Series

- We saw that two CSTRs in series gave a smaller total volume than a single CSTR to achieve the same conversion. This case does not hold true for the two plug-flow reactors connected in series



$$\int_0^{X_2} F_{A0} \frac{dX}{-r_A} \equiv \int_0^{X_1} F_{A0} \frac{dX}{-r_A} + \int_{X_1}^{X_2} F_{A0} \frac{dX}{-r_A}$$

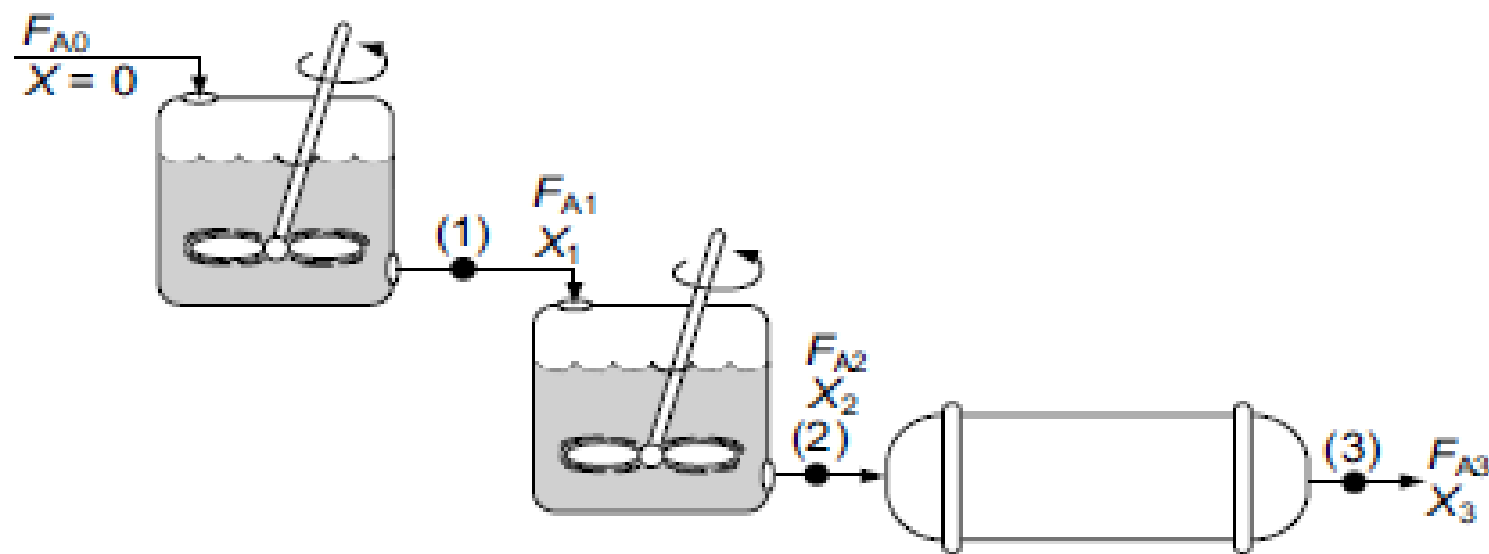


- That it is immaterial whether you place two plug-flow reactors in series or have one continuous plug-flow reactor; the total reactor volume required to achieve the same conversion is identical!

# Reactors in series

## ➤ Combinations of CSTRs and PFRs in Series

- We saw that two CSTRs in series gave a smaller total volume than a single CSTR to achieve the same conversion. This case does not hold true for the two plug-flow reactors connected in series



Reactor 1:

$$V_1 = \frac{F_{A0}X_1}{-r_{A1}}$$

Reactor 2:

$$V_2 = \frac{F_{A0}(X_2 - X_1)}{-r_{A2}}$$

Reactor 3:

$$V_3 = \int_{X_2}^{X_3} \frac{F_{A0}}{-r_A} dX$$

