

# ENVE 301

## Environmental Engineering Unit Operations

### Lecture 2

#### Reaction Kinetics, Mass Balances, and Reactor Types

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## ■ Course material is prepared using following references

- 1) Reynolds, T. D., and P. A. Richards. Unit Operations and Processes in Environmental Engineering. 2nd ed. Boston, MA: PWS Publishing Company, 1996. (Textbook)
- 2) Clark M.M. Transport Modelling for Environmental Engineers and Scientists. John Wiley&Sons, 1996 ISBN: 0-47112348X
- 3) Other sources

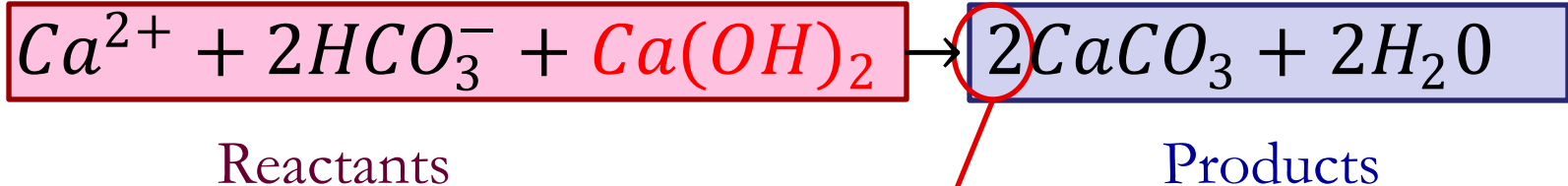
# Reaction Kinetics - Stoichiometry

- Reactions usually result in the loss of a reactant and the formation of a product.

REACTANTS  $\longrightarrow$  PRODUCTS

- In reactions we are interested in;
  - **the amount** of product formed from reactants (*stoichiometry*)
  - **the rate** at which the process occurred (*kinetics*)

# Stoichiometry



Moles or Stoichiometric coefficients

- Irreversible reactions;  
Reactants (-), products (+)
- Reversible reactions;  
Reactants and products (+)

# Reaction Types

- 1) Homogenous reactions: Reactants are in the **same phase**
  - Liquid-liquid, gas-gas
  - Components are evenly mixed
- 2) Heterogenous reactions: Reactants are in **two or more phases**
  - Reactions between gas – liquid, solid – liquid, solid – gas
  - *Surface area affects the rate* of heterogenous reactions

# Reaction rate

- Select a component in the reaction



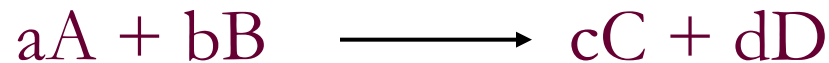
Rate of reaction  $\rightarrow$  The rate of change in the concentration of reactant or product  
(uncompressible fluids – volume is constant)

$$r_A = \frac{d[A]}{dt} = -k[A]^n \quad \frac{\text{mol}}{\text{L} \cdot \text{t}} \quad \text{Homogenous rxn}$$

$$\frac{\text{mol}}{\text{m}^2 \cdot \text{t}} \quad \text{Heterogenous rxn}$$

- If A is reactant  $r_A < 0$
- If A is product  $r_A > 0$

# Reaction Rates and Stoichiometry



$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

# Reaction rate/order

Case	Initial A Concentration (M)	Initial B Concentration (M)	Observed Initial Rate (M/s)
1	0.03	0.01	$1.2 \times 10^{-5}$
2	0.03	0.02	$2.4 \times 10^{-5}$
3	0.03	0.04	$4.8 \times 10^{-5}$
4	0.01	0.03	$2.1 \times 10^{-5}$
5	0.02	0.03	$4.2 \times 10^{-5}$
6	0.04	0.03	$8.4 \times 10^{-5}$

→ As B doubles, rate doubles

→ As A doubles, rate doubles



- Rate proportional to A
- Rate proportional to B
- Rate =  $k [A][B]$  equation is the rate law, k is the rate constant



# Reaction rate/order

$$r_A = \frac{d[A]}{dt} = -k[A]^n \quad n \text{ is the order of the reaction}$$

$$r_A = -k[A]^n [B]^m$$

$n$  is the order of the reaction wrt reactant A

$m$  is the order of the reaction wrt reactant B

**$n+m$**  is the overall order of the reaction

$$r_A = -k[A]^0$$

$$r_A = -k[A]^1$$

$$r_A = -k[A]^2$$

# Variables affecting the rate of reaction

## 1) Physical state of the reactants

- In order to react, molecules must come in contact with each other.
- The more homogeneous the mixture of reactants, the faster the molecules can react.

## 2) Concentration of reactants.

- As the concentration of **reactants increases**, so does the likelihood that **reactant molecules will collide**.
- Higher concentration of reactants causes more effective collision per unit time, which causes increasing reaction rate (except for zero order reactions)

# Variables affecting the rate of reaction

## 3) Temperature

- The rates of most chemical reactions increase with temperature.
- Temperature is defined as the measure of average kinetic energy of the molecules
- Isothermal systems → Constant temperature

## 4) Presence of catalyst

- **Catalysts speed up reactions** by changing the mechanism of the reaction.
- **Catalysts are not consumed** during the course of the reaction.

# Single or Multiple Reactions

- Single Reaction

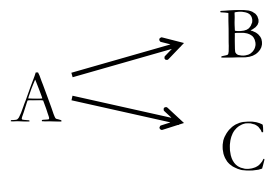
- Reaction going from reactant to products

- Multiple Reactions

- Series reactions

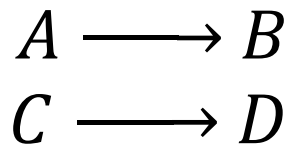


- Parallel reactions



Reactions happen at the same time,  
B and C are competitive products

- Side by side reactions



# Elementary and Nonelementary Rxns

- Elementary reactions
  - These types of reactions occur exactly as written on a molecular scale. In other words, stoichiometry dictates the kinetics.



$$r_A = -k[A][B]^2$$

# Elementary and Nonelementary Rxns

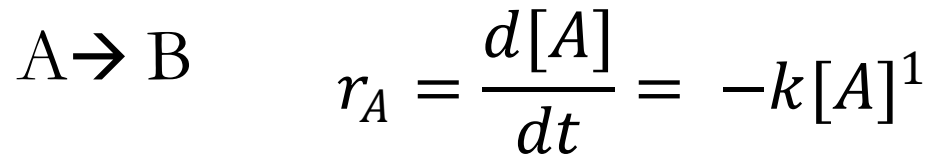
- Nonelementary reactions
  - Kinetic law is not dictated by stoichiometry



$$r_A = -k[A]^{0.5}[B]$$

# First-order reactions

1 mol A is converted to 1 mol B than the stoichiometry of an irreversible elemental reaction is:



Using calculus to integrate the rate law for a first-order process gives us

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln [A]_t - \ln [A]_0 = -kt$$

$$\ln [A]_t = -kt + \ln [A]_0$$

$$y = mx + b$$

# First-order reactions

$$\ln [A]_t = -kt + \ln [A]_0 \quad \longrightarrow \quad \text{Linear reaction}$$

Plot of  $\ln[A]$  versus  $t$  will yield a straight line. Slope of the line will be  $-k$

$$y = mx + b$$

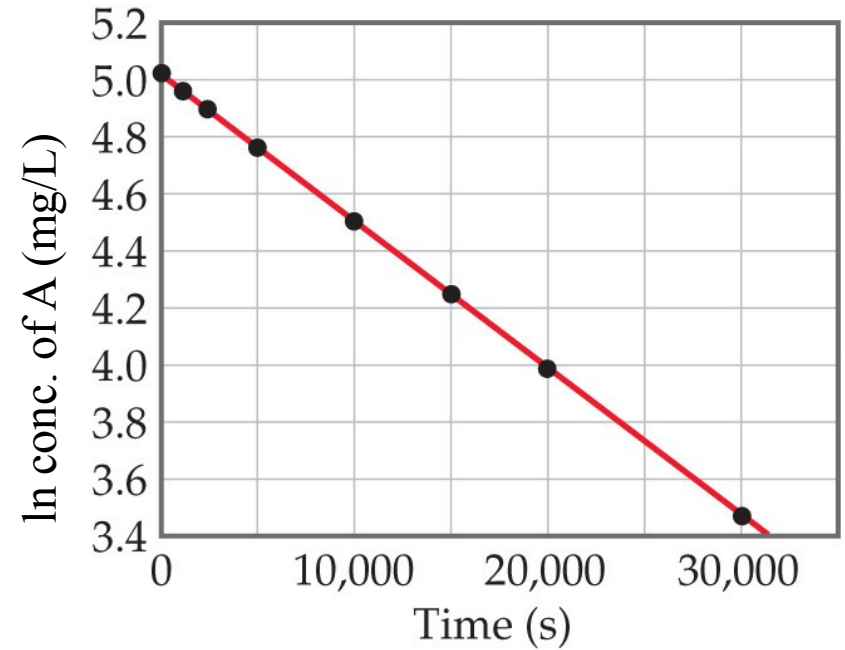
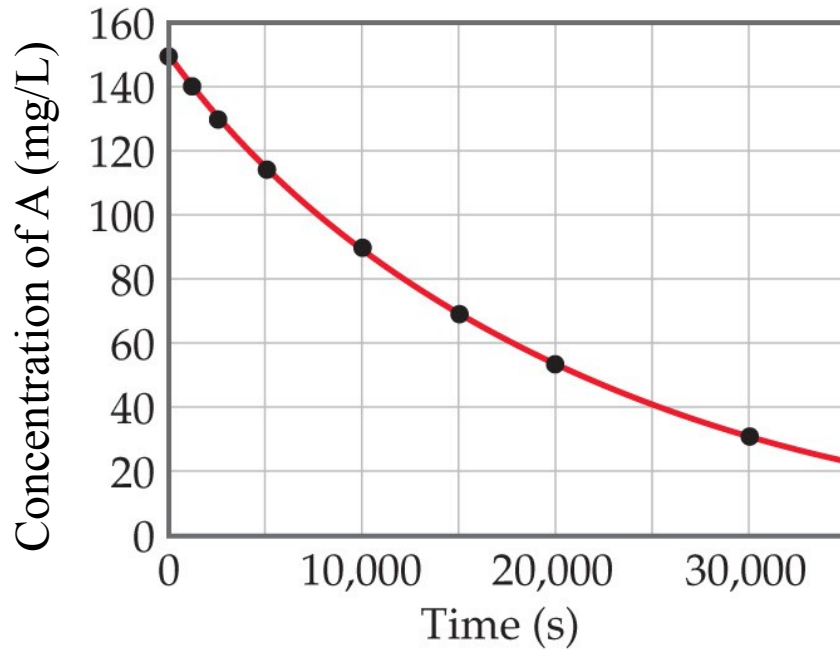
$$[A] = [A]_0 \exp(-kt)$$

$$[B] = [A]_0 [1 - \exp(-kt)]$$

Unit of  $k \rightarrow 1/\text{time}$



# First order Reactions



## Second order reactions



$$r_A = \frac{d[A]}{dt} = -k[A]^2$$

Integrating the rate law for a process that is second-order in reactant A, we get;

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

Which is also in the form of;

$$y = mx + b$$

## Second-order reactions

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \longrightarrow \text{Linear reaction}$$

Plot of  $1/[A]$  versus  $t$  will yield a straight line. Slope of the line will be  $-k$

$$y = mx + b$$

Unit of  $k \rightarrow \text{L/mol.time}$

# Pseudo-first order reactions



If concentration of B is much greater than the concentration of A then the concentration of A becomes as negligible and the reaction behaves as the first order reaction

# Zero-order reactions

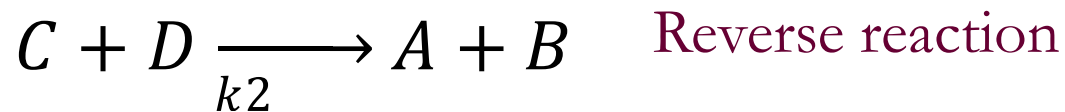
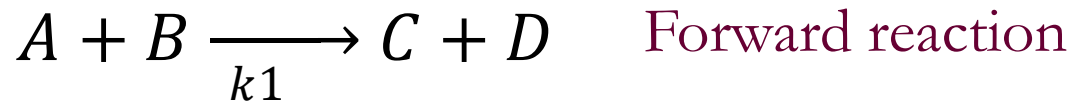


Sometimes the rate of consumption of A is not governed by first order kinetics, rate of consumption of A is independent of the concentration of A

$$r_A = \frac{d[A]}{dt} = -k$$

Unit of  $k \rightarrow \text{M/time} = \text{mol/L.time}$

# Equilibrium for Elementary reversible reactions



- At equilibrium, concentration of reactants and products are equal.
- Therefore, the forward and reverse reaction rates must balance each other

At equilibrium,  $r_f = r_b$

# Equilibrium for Elementary reversible reactions

- $r_f = k_f[A][B]$
- $r_b = -k_r[C][D]$
- Reaction rate
- $r = r_f + r_b$  at equilibrium  $r = 0$  therefore,
- $r_f + r_b = 0$
- $k_f[A][B] - k_b[C][D] = 0$

$$K = \frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

# Molecularity

- The **molecularity** of a process tells how many molecules are involved in the process.
- Molecularity has values of 1, 2 and 3

Molecularity	Elementary Reaction	Rate Law
<i>Unimolecular</i>	$A \longrightarrow \text{products}$	Rate = $k[A]$
<i>Bimolecular</i>	$A + A \longrightarrow \text{products}$	Rate = $k[A]^2$
<i>Bimolecular</i>	$A + B \longrightarrow \text{products}$	Rate = $k[A][B]$
<i>Termolecular</i>	$A + A + A \longrightarrow \text{products}$	Rate = $k[A]^3$
<i>Termolecular</i>	$A + A + B \longrightarrow \text{products}$	Rate = $k[A]^2[B]$
<i>Termolecular</i>	$A + B + C \longrightarrow \text{products}$	Rate = $k[A][B][C]$

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# Multistep Mechanisms and Rate Limiting Step

- In a multistep process, one of the steps will be slower than all others.
- The overall reaction cannot occur faster than this slowest, **rate-determining step**.



# Multistep Mechanisms and Rate Limiting Step



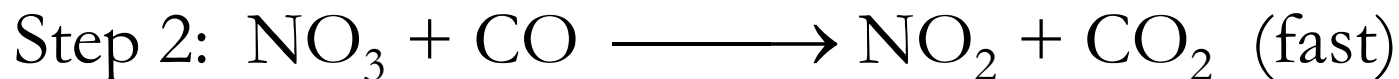
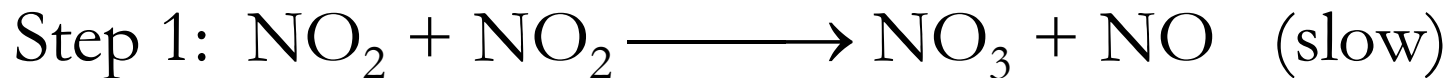
- The rate law for this reaction is found experimentally to be

$$\text{Rate} = k[\text{NO}_2]^2$$

- CO is necessary for this reaction to occur, but the *rate* of the reaction does not depend on its concentration.
- This suggests that the reaction occurs in two steps.

# Multistep Mechanisms and Rate Limiting Step

- A proposed mechanism for this reaction is



- The  $\text{NO}_3$  intermediate is consumed in the second step.
- As  $\text{CO}$  is not involved in the slow, rate-determining step, it does not appear in the rate law.

# Multistep Mechanisms and Rate Limiting Step



- The rate law for this reaction is found to be

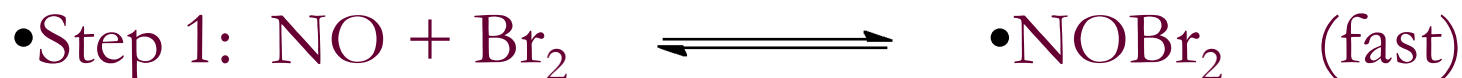
$$\text{Rate} = k[\text{NO}]^2 [\text{Br}_2]$$

- Because termolecular processes are rare, this rate law suggests a two-step mechanism.

# Multistep Mechanisms and Rate Limiting Step



■ A proposed mechanism is



• Step 1 includes the forward *and* reverse reactions.

# Multistep Mechanisms and Rate Limiting Step

- The rate of the overall reaction depends upon the rate of the slow step.
- The rate law for that step would be

$$\text{Rate} = k_2[\text{NOBr}_2] [\text{NO}]$$

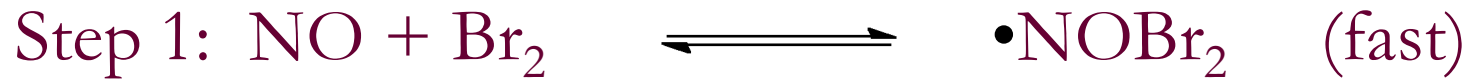
- But how can we find  $[\text{NOBr}_2]$ ?

# Multistep Mechanisms and Rate Limiting Step

- $\text{NOBr}_2$  can react two ways:
  - With  $\text{NO}$  to form  $\text{NOBr}$ .
  - By decomposition to reform  $\text{NO}$  and  $\text{Br}_2$ .
- The reactants and products of the first step are in equilibrium with each other.
- Therefore,

$$\text{Rate}_f = \text{Rate}_r$$

# Multistep Mechanisms and Rate Limiting Step



- Because  $\text{Rate}_f = \text{Rate}_r$

$$k_1[\text{NO}] [\text{Br}_2] = k_{-1}[\text{NOBr}_2]$$

- Solving for  $[\text{NOBr}_2]$ , gives us

$$\frac{k_1}{k_{-1}} \bullet [\text{NO}] [\text{Br}_2] = [\text{NOBr}_2]$$

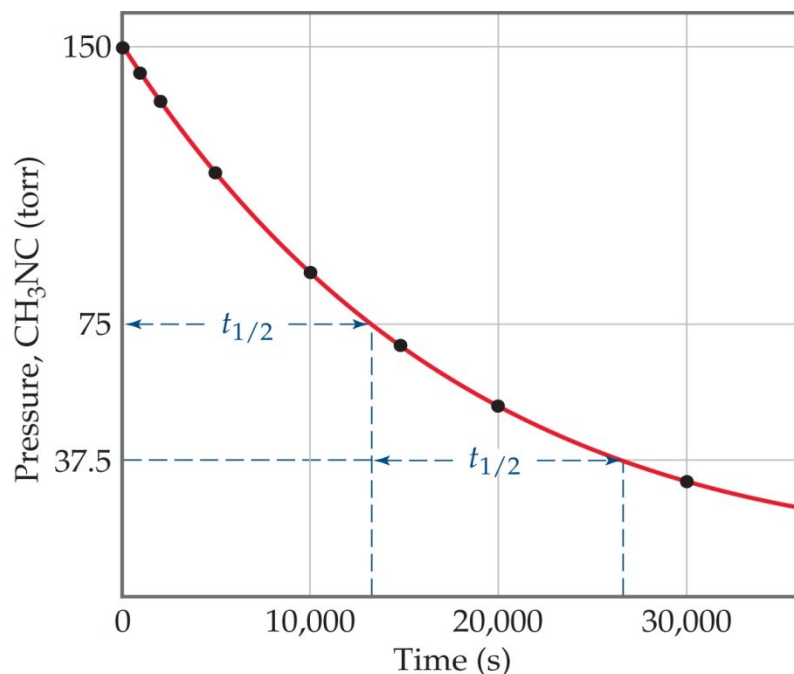


# Multistep Mechanisms and Rate Limiting Step

Substituting this expression for  $[\text{NOBr}_2]$  in the rate law for the rate-determining step, gives

$$\begin{aligned}\text{Rate} &= \frac{k_2 k_1}{k_{-1}} [\text{NO}] [\text{Br}_2] [\text{NO}] \\ &= k [\text{NO}]^2 [\text{Br}_2]\end{aligned}$$

# Half-Life



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- Half-life is defined as the time required for one-half of a reactant to react.
- Because  $[A]$  at  $t_{1/2}$  is one-half of the original  $[A]$ ,

$$[A]_t = 0.5 [A]_0.$$

# Half-Life

For a first-order process, this becomes

$$\ln \frac{0.5 [A]_0}{[A]_0} = -kt_{1/2}$$

$$\ln 0.5 = -kt_{1/2}$$

$$-0.693 = -kt_{1/2}$$

$$\frac{0.693}{k} = t_{1/2}$$

- *Note:* For a first-order process, then, the half-life *does not* depend



# Half-Life

For a second-order process,

$$\frac{1}{0.5 [A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

$$\frac{2-1}{[A]_0} = \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{1}{k[A]_0} = t_{1/2}$$

# Arrhenius Equation

**Svante Arrhenius** developed a mathematical relationship between  $k$  and  $E_a$ :

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

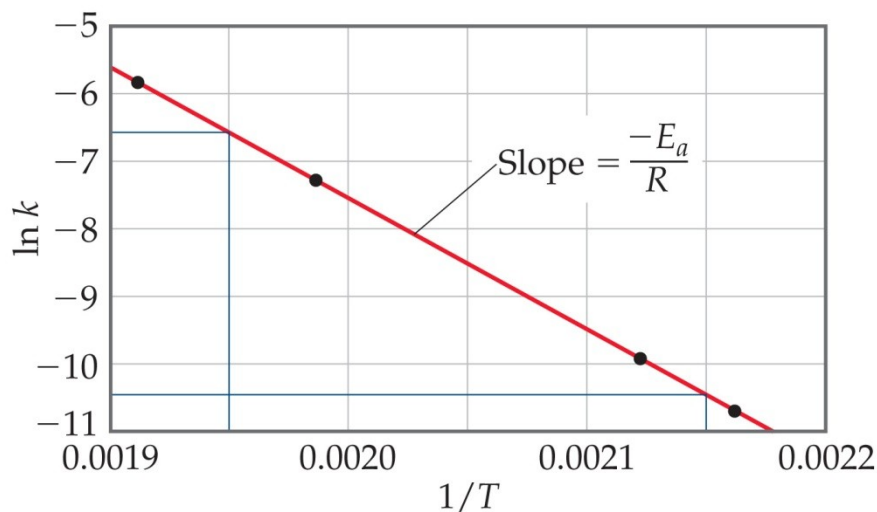
Where  $A$  is the **frequency factor**, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

Modified and simplified equation

$$k_2 = k_1\theta^{T_2-T_1}$$

$\theta$ : Dimensionless temperature coefficient

# Arrhenius Equation



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Taking the natural logarithm of both sides, the equation becomes

$$\ln k = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln A$$

$$y = mx + b$$

- Therefore, if  $k$  is determined experimentally at several temperatures,  $E_a$  can be calculated from the slope of a plot of  $\ln k$  vs.  $\frac{1}{T}$ .

# MASS BALANCE

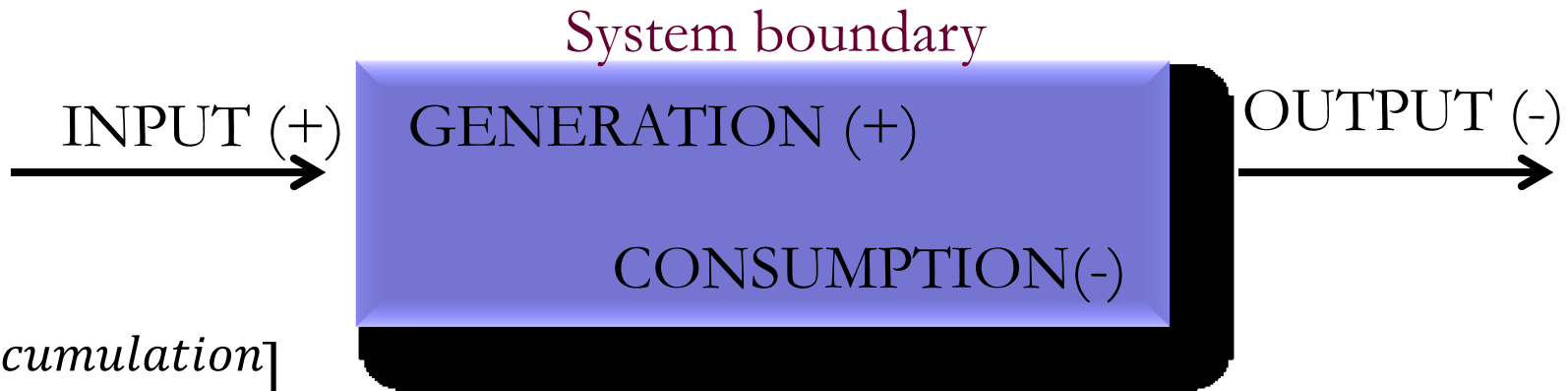


# Mass Balance

- Mass is conserved
  - Mass is neither created nor destroyed
- Conservation Law is used
- System boundaries needs to be identified



# Mass Balance



[*Accumulation  
within the  
system*]

$$= \begin{bmatrix} \text{Input} \\ \text{through the} \\ \text{system} \\ \text{boundaries} \end{bmatrix} - \begin{bmatrix} \text{Output} \\ \text{through} \\ \text{the system} \\ \text{boundaries} \end{bmatrix} + \begin{bmatrix} \text{Generation} \\ \text{within the} \\ \text{system} \end{bmatrix} - \begin{bmatrix} \text{Consumption} \\ \text{within} \\ \text{the} \\ \text{system} \end{bmatrix}$$

- Mass balance equation refers to a time interval, differential time, year, etc.

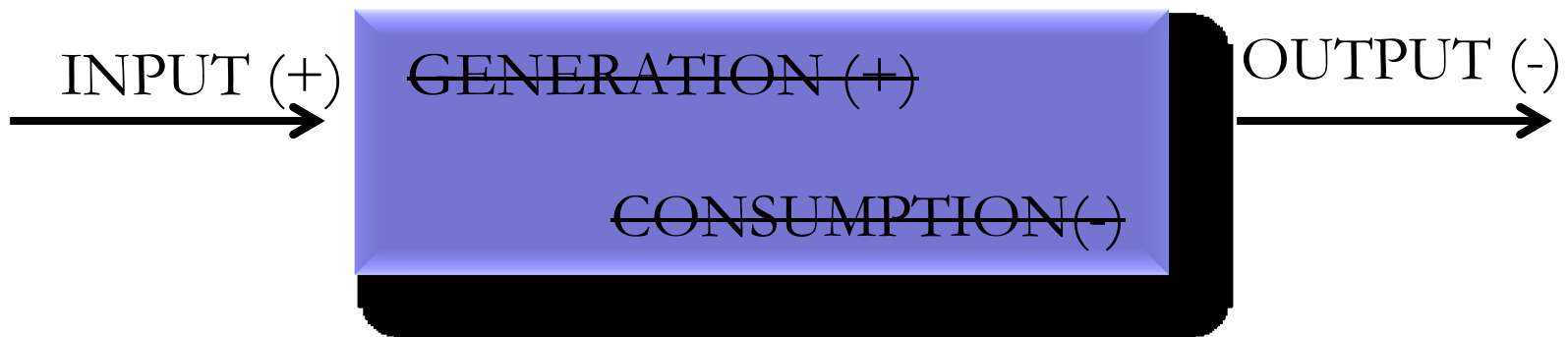
$\left[ \begin{array}{c} \textit{Accumulation} \\ \textit{within the} \\ \textit{system} \end{array} \right]$

$$= \left[ \begin{array}{c} \textit{Input} \\ \textit{through the} \\ \textit{system} \\ \textit{boundaries} \end{array} \right] - \left[ \begin{array}{c} \textit{Output} \\ \textit{through} \\ \textit{the system} \\ \textit{boundaries} \end{array} \right] + \left[ \begin{array}{c} \textit{Generation} \\ \textit{within the} \\ \textit{system} \end{array} \right] - \left[ \begin{array}{c} \textit{Consumption} \\ \textit{within} \\ \textit{the} \\ \textit{system} \end{array} \right]$$

$$[\textit{Accumulation}] = [\textit{Input}] - [\textit{Output}] + [\textit{Generation/Consumption}]$$

# Mass Balance – Conservative System

- Conservative systems are non-reactive
- There is no generation nor consumption in a conservative system



$$\left[ \begin{array}{c} \textit{Accumulation} \\ \textit{within the} \\ \textit{system} \end{array} \right] = \left[ \begin{array}{c} \textit{Input} \\ \textit{through the} \\ \textit{system} \\ \textit{boundaries} \end{array} \right] - \left[ \begin{array}{c} \textit{Output} \\ \textit{through} \\ \textit{the system} \\ \textit{boundaries} \end{array} \right]$$

# Conservative System

$$\begin{bmatrix} \textit{Accumulation} \\ \textit{within the} \\ \textit{system} \end{bmatrix} = \begin{bmatrix} \textit{Input} \\ \textit{through the} \\ \textit{system} \\ \textit{boundaries} \end{bmatrix} - \begin{bmatrix} \textit{Output} \\ \textit{through} \\ \textit{the system} \\ \textit{boundaries} \end{bmatrix}$$

$$[\textit{Accumulation}] = [\textit{Input}] - [\textit{Output}]$$

# Conservative System at Steady State Conditions

- At steady state conditions, time is not the factor.
- In mass balance time is related to accumulation
- At steady state, accumulation = 0

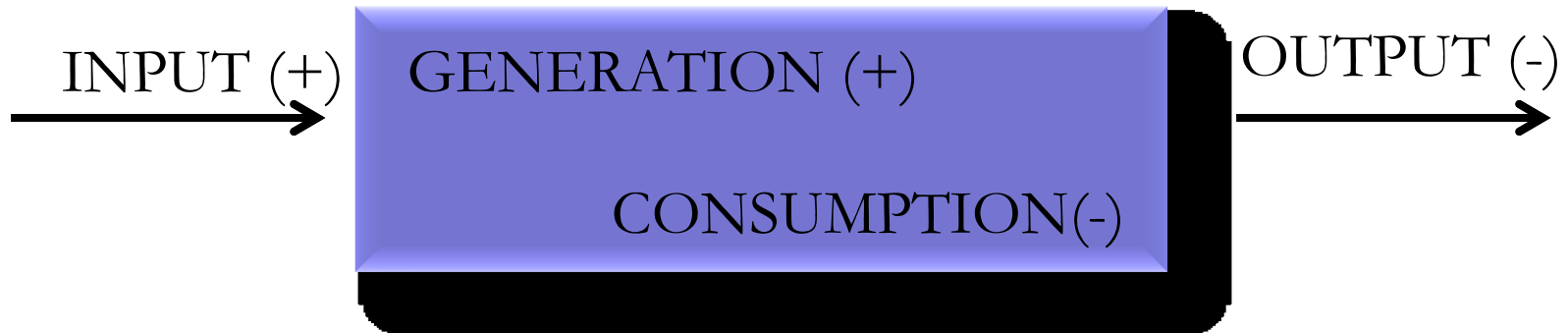
$$[Accumulation] = [Input] - [Output]$$

0

$$[Input] = [Output]$$

# Conservative System at Steady State Conditions

- To write a mass balance, you need to define your system



- Concentration: Mass/Time
- Volume:  $L^3$
- Time interval :  $\Delta t$

# Mass Balance – Conservative System

- Accumulation

Time  $\rightarrow t + \Delta t$

Input/Output: Net flow across the system boundaries

$$dC_1 V = Q C_o dt - Q C_1 dt$$

$dC_1$ : Change of component A in vessel, mass/volume

V: Vessel volume

Q: Flow rate, Volume/Time

$C_o$ : Initial concentration, Mass/Volume

$C_1$ : Final concentration, Mass/Volume

$dt$ : Time increment, time

# Mass Balance – Non-Conservative System

- Accumulation

Time  $\rightarrow t + \Delta t$

Input/Output: Net flow across the system boundaries

$$dC_1 V = QC_0 dt - QC_1 dt - Vr dt$$

$dC_1$ : Change of component A in vessel, mass/volume

V: Vessel volume

Q: Flow rate, Volume/Time

$C_0$ : Initial concentration, Mass/Volume

$C_1$ : Final concentration, Mass/Volume

$dt$ : Time increment, time

R: rate at which component A reacts, mass/volume-time



# Mass Balance – Non-Conservative System

- Check the units first

$$dC_1V = QC_o dt - QC_1 dt - Vr dt$$

Divide it by dt

$$dC_1V = QC_o dt - QC_1 dt - Vr dt$$

$$\frac{dC_1}{dt}V = QC_o - QC_1 - Vr$$

# Mass Balance – Non-Conservative System

$$\frac{dC_1}{dt} V = QC_o - QC_1 - Vr$$

If the reaction is first order:

$$\frac{dC_1}{dt} V = QC_o - QC_1 - VkC_1$$

Accumulation

# Mass Balance – First Order Non-Conservative System

$$\frac{dC_1}{dt}V = QC_o - QC_1 - VkC_1$$

Divide by V:

$$\frac{dC_1}{dt} = \frac{Q}{V}C_o - \frac{Q}{V}C_1 - kC_1$$

at steady state:

$$0 = \frac{Q}{V}C_o - \frac{Q}{V}C_1 - kC_1$$

# Mass Balance – First Order Non-Conservative System at Steady State

$$0 = \frac{Q}{V} C_o - \frac{Q}{V} C_1 - kC_1$$

- $V/Q = \theta$

$$0 = \frac{C_o}{\theta} - \frac{C_1}{\theta} - kC_1$$

$$C_1 = \frac{C_o}{1 + k\theta}$$

# Steps to be Followed for Solving Mass Balance Problems

- Find what the problem is
- Determine if you need additional data and if so find them or make assumptions if needed
- Draw a simplified picture of your system
  - Indicate important variables and provide symbols for them
  - Decide on dependent and independent variables
- If a reaction is involved, write it down and make sure its balances

# Steps to be Followed for Solving Mass Balance Problems

- Draw system boundaries on which material balance will be applied
- Select a convenient one on which numerical calculations will be based
- Set up governing equations of the problem. Write as many equations as the number of dependent variables
- CHECK your UNITS
- Write down equations in symbol not the actual numbers

# Steps to be Followed for Solving Mass Balance Problems

- Solve the equations once they are established
- Determine whether the answer seems reasonable

# REACTOR TYPES & KINETICS





# Flow Models

Processes and reactions occur in;

- Static environments (no flow)
- Environments with some type of flow
  - Sedimentation (ideal plug flow-piston flow) and
  - Coagulation (ideal completely mixed reactors) often occur in flowing systems

Flow models are useful in studies involving unit operations and unit processes

# Flow Models

- Ideal Plug Flow
  - The elements of fluid move as a plug , enters and leave the system with flow
- Ideal Completely Mixed Flow
  - The elements of the fluid that enter the system are immediately dispersed uniformly throughout the system.
  - Properties of fluid within the system are identical.

# Flow Models

Flow regimes that are classified in between the ideal models

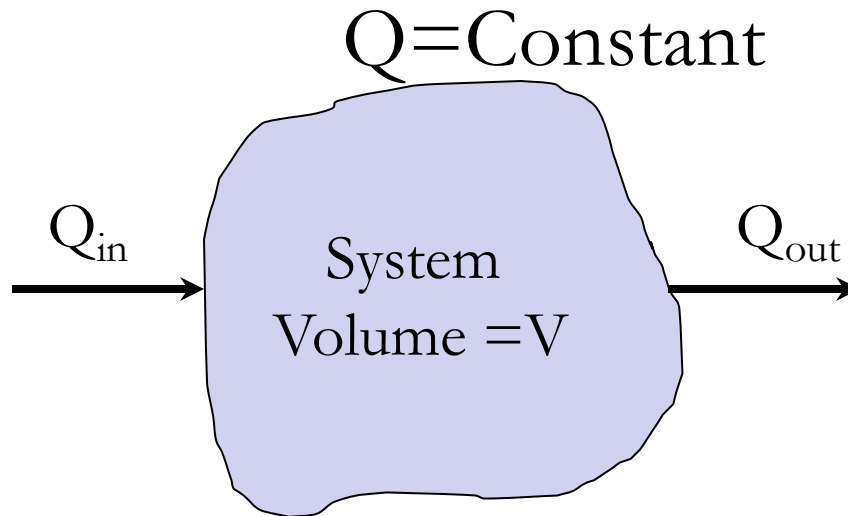
- Plug flow with dispersion
- Dispersed plug flow
- Plug flow with longitudinal mixing
- Intermediate-mixed flow
- Arbitrary flow

# Ideal Plug Flow Regime

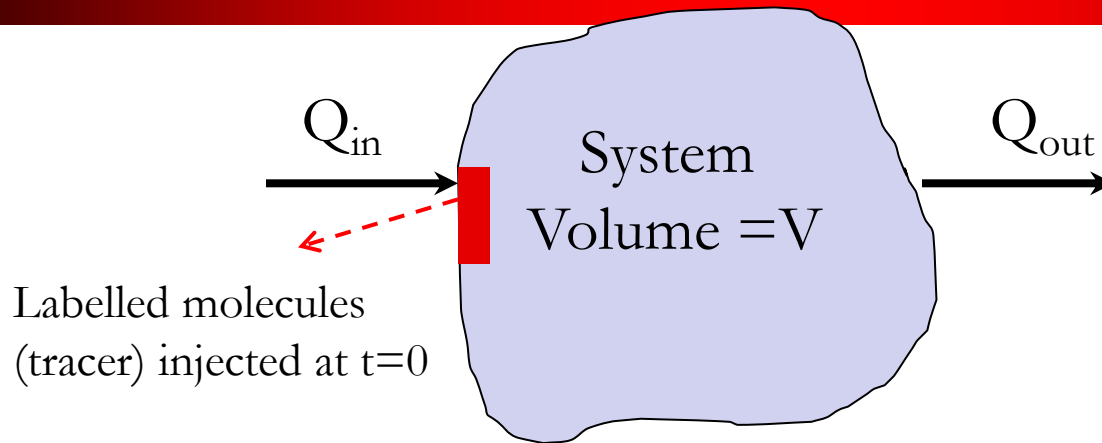
- Critical assumptions of ideal plug flow are that;
  - Velocity throughout the plug-flow system is
    - steady,
    - uniform,
    - no longitudinal mixing
    - laminar ( $Re=dV/\nu \leq 2000$ ), and
    - there is no molecular diffusion of the transported material.
- Plug flow is achieved in systems that have large length to width ratios ( $L:W, 50:1$ ).

# Simple Closed-Reactor and Residence Time Distributions

- Simple system/reactor: Single inlet and outlet
- Closed system: Enter the system once and leave the system once
- Flow is steady

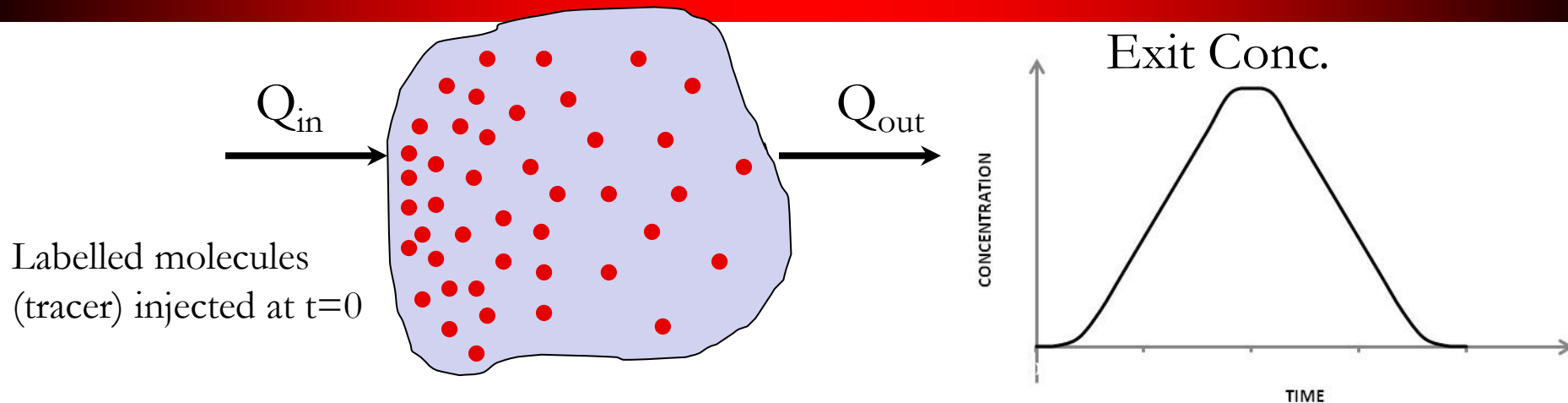


# Simple Closed-Reactor and Residence Time Distributions



- Tracer molecules: Non-reacting, non-degradable, identical molecules. Tracer molecules are different in terms of;
  - Color
  - Light absorbency
  - Conductivity
  - or has a radioactive marker

# Simple Closed-Reactor and Residence Time Distributions



- Residence time distribution (RTD) plot is  $C_1/C_0$  vs  $t/\bar{t}$  plot

$t$  = time after tracer release

$\bar{t}$  = mean residence time,  $V/Q$

$C_1$  = Concentration of tracer at the outlet

$C_0$  = Concentration of tracer released

$$\bar{t} = \frac{V}{Q}$$

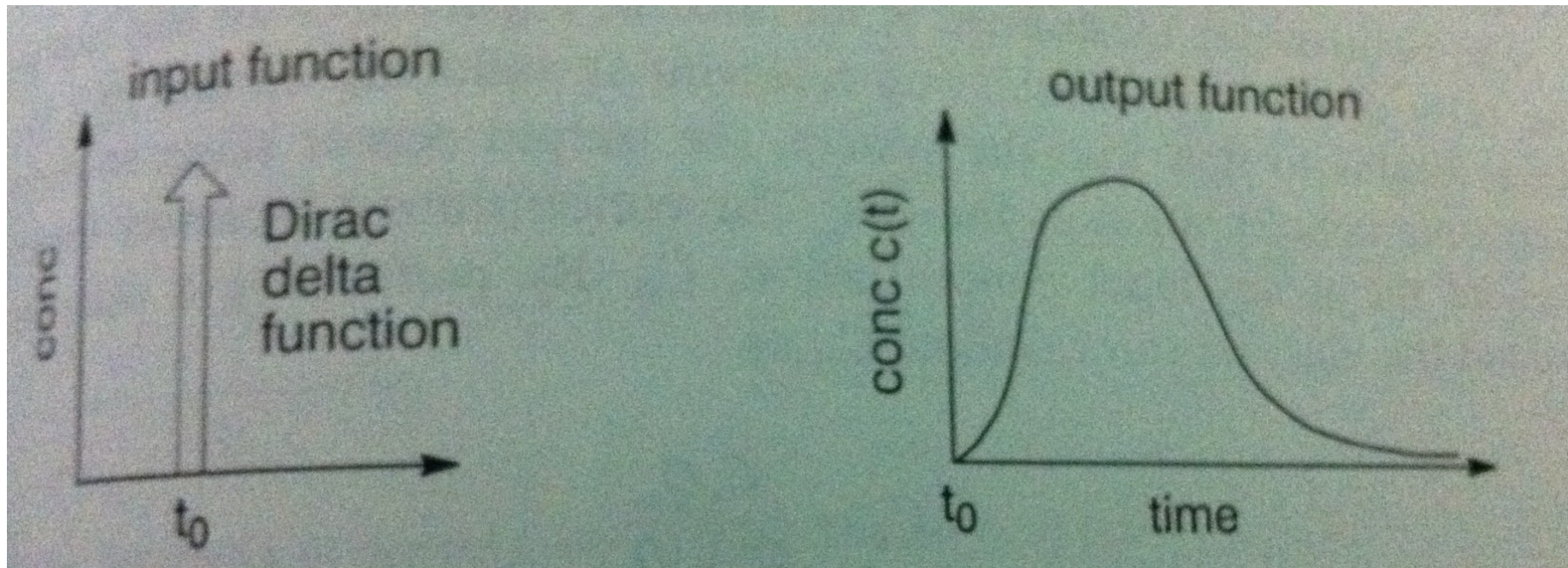
# Measurement of RTD

- If you are interested in measuring RTD in a chemical reactor, unit operation or natural systems, there are three main methods which can be used in closed systems;
  - 1) Impulse method
  - 2) Negative-step method
  - 3) Positive-step method



# Measurement of RTD

## Impulse method



## Quick injection

Figure Ref: Clark M.M. Transport Modelling for Environmental Engineers and Scientists. John Wiley&Sons, 1996, page 479 (Figure 10.4)

# Measurement of RTD

## Positive-step method

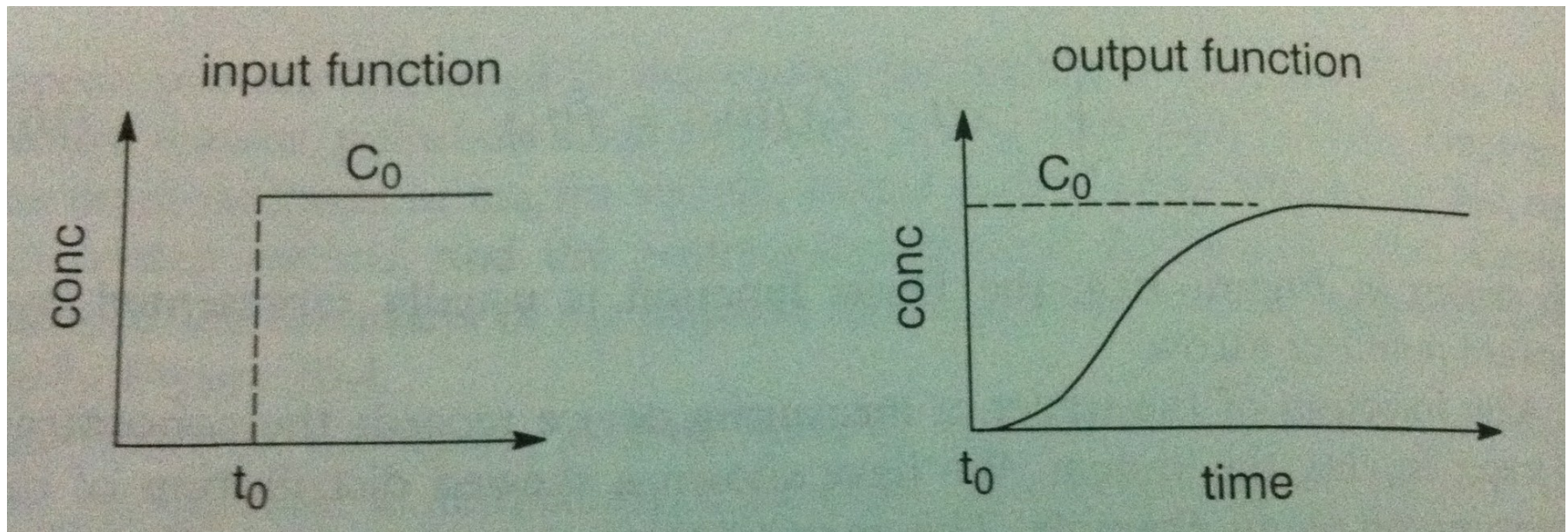


Figure Ref: Clark M.M. Transport Modelling for Environmental Engineers and Scientists. John Wiley&Sons, 1996, page 480 (Figure 10.5)

# Measurement of RTD

## Negative-step method

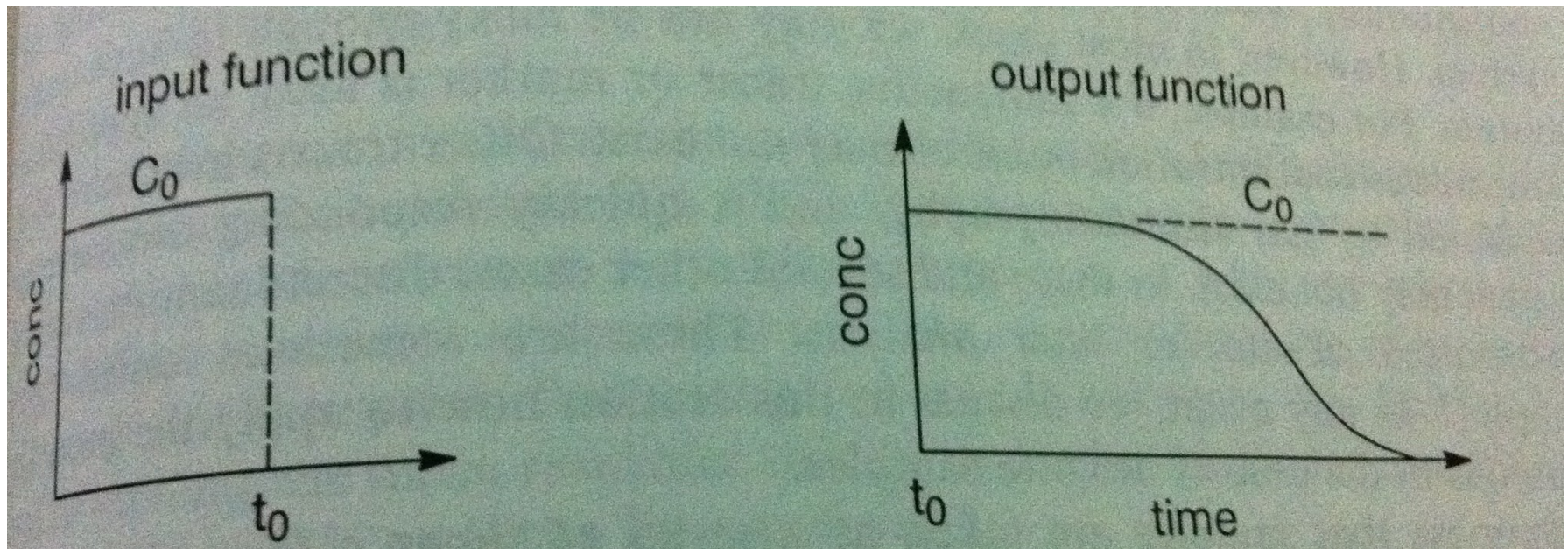
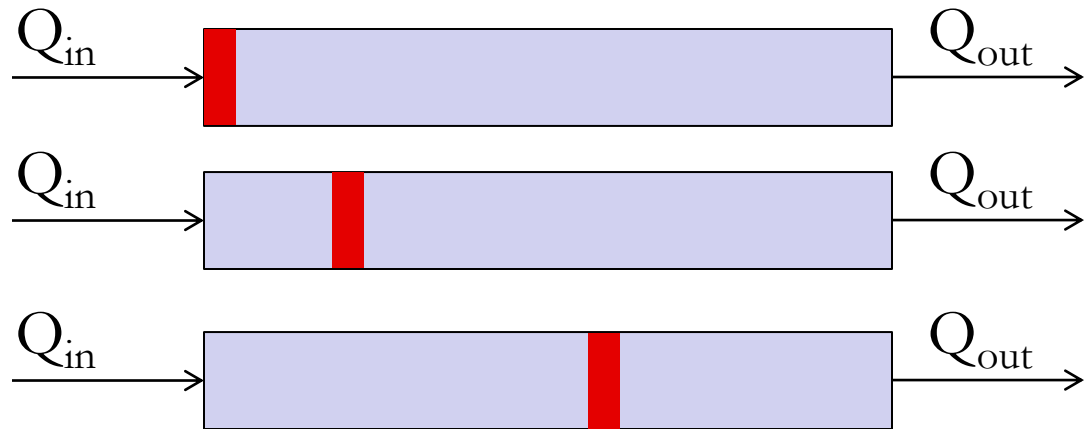


Figure Ref: Clark M.M. Transport Modelling for Environmental Engineers and Scientists. John Wiley&Sons, 1996, page 481(Figure 10.6)

# Plug-Flow



$$t/\bar{t} = 1$$

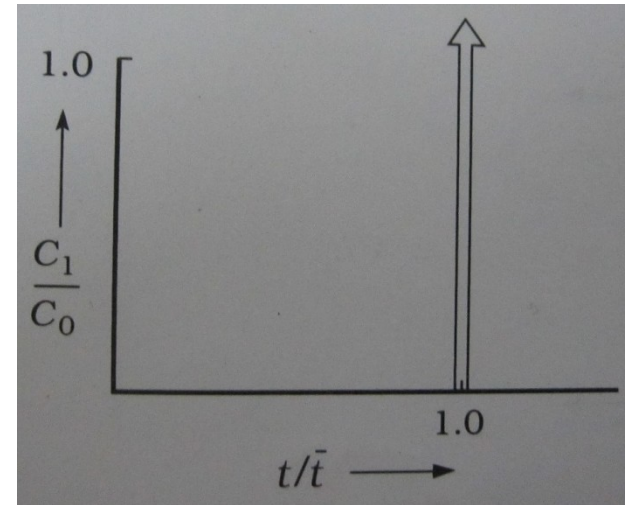
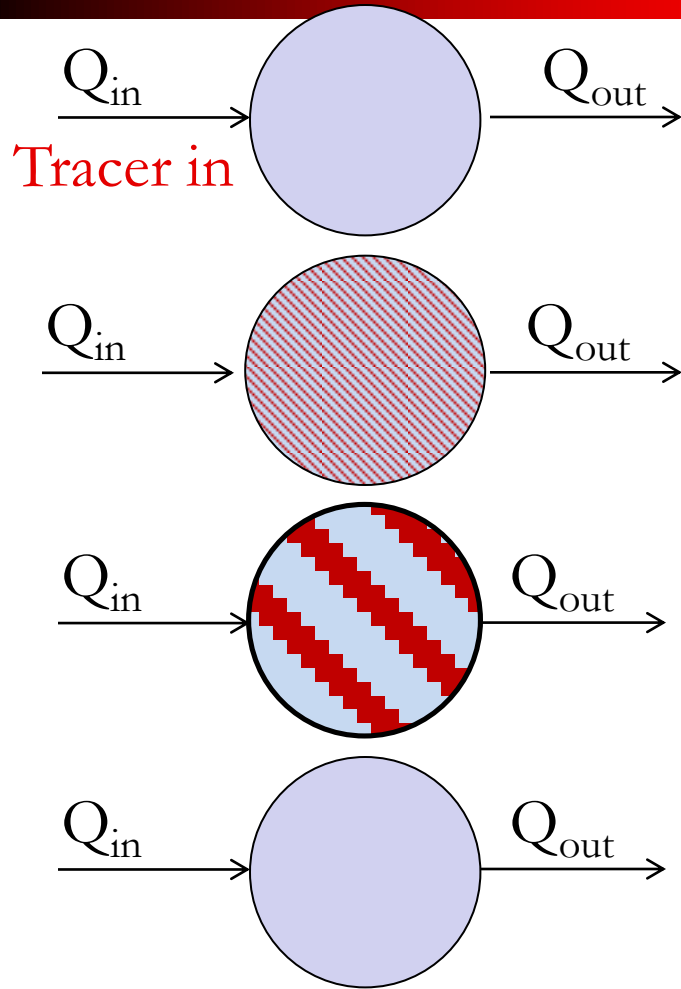


Fig Ref: Reynolds, T. D., and P. A. Richards. Unit Operations and Processes in Environmental Engineering. 2nd ed. Boston, MA: PWS Publishing Company, 1996. page, 43 Figure 3.4

# Continuous Flow



$$[Accumulation] = [Input] - [Output] - [Reaction]$$

at time=0;

$$dC_1 V = 0 - C_1 Q dt - 0$$

$$\int_{C_0}^{C_1} \frac{dC_1}{C_1} = -\frac{Q}{V} \int_0^t dt$$

$$\frac{C_1}{C_0} = e^{-\left(\frac{Q}{V}\right)t}$$

Tracer curve

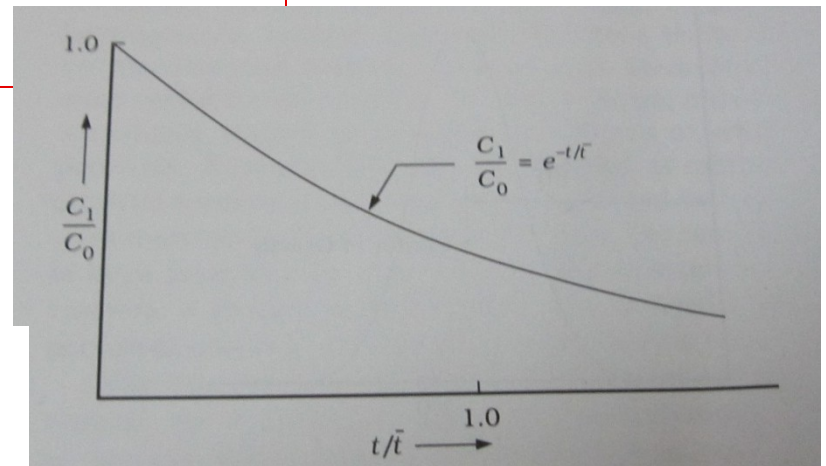
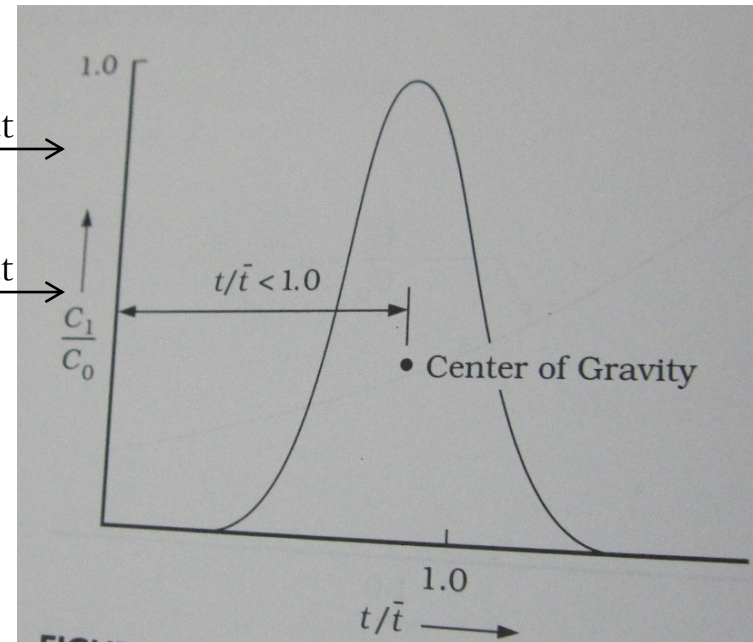
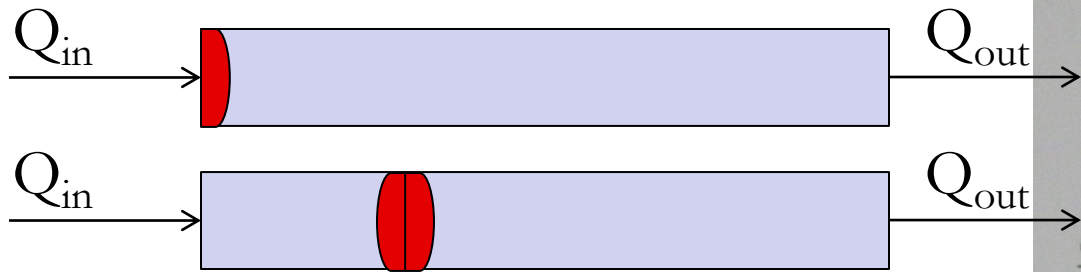


Fig Ref: Reynolds, T. D., and P. A. Richards. Unit Operations and Processes in Environmental Engineering. 2nd ed. Boston, MA: PWS Publishing Company, 1996. page, 45 Figure 3.6

# Plug Flow with Dispersion

- Plug flow with longitudinal mixing
- It is an intermediate between plug flow and completely mixed flow



# Reaction Types

- Homogenous / Heterogenous
  - not a clear-cut classification-borderline regions in enzyme-susbstrate rxns
- Exothermic / Endothermic
- Catalytic / Noncatalytic

# Reactor Types

- Homogenous & Heterogenous reactors
- Batch & Continuous reactors
- Perfectly mixed flow & Plug flow reactors & Dispersed plug flow reactor
- Isothermal and non-isothermal reactors



# Reactor Types

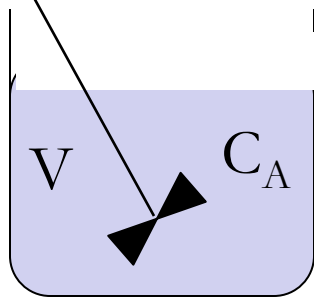
- Homogenous and Heterogenous reactors
- Homogenous reactors have one phase alone, heterogenous reactors have at least two phases
- Heterogenous reactors:
  - Fixed-bed reactor
  - Packed-bed reactor
  - Moving-bed reactor (upward fluid movement)
  - Fluidized-bed reactor

In homogenous reactions,

$$-r_A = -\frac{dC_A}{dt} = kC_A^n \quad [Accumulation] = [Input] - [Output] - [Reaction]$$

In water and wastewater treatment, solutions are dilute and heat effects from the reaction are negligible. Volume is constant and the reactors are generally under constant pressure, therefore the density of the influent is considered same as the effluent

# Batch Reactors



First order rxn

$$[Accumulation] = \cancel{[Input]} - \cancel{[Output]} - [Reaction]$$

$$[Accumulation] = -[Reaction]$$

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

$$\int_{C_{A0}}^{C_{A1}} \frac{dC_A}{C_A} = -k \int_0^\theta dt$$

$$\frac{C_{A1}}{C_{A0}} = e^{-k\theta}$$

# Plug Flow Reactor at Steady State



$$[\textit{Accumulation}] = [\textit{Input}] - [\textit{Output}] - [\textit{Reaction}]$$

$$[\textit{Input}] = [\textit{Output}] + [\textit{Reaction}]$$

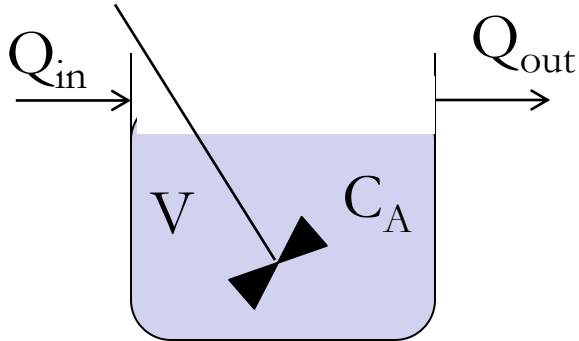
$$QC_A = Q(C_A - dC_A) + r_A dV$$

$$QdC_A = r_A dV$$

$$\int_{C_{A0}}^{C_{A1}} \frac{dC_A}{C_A} = -\frac{k}{Q} \int_0^V dt \quad \ln\left(\frac{C_{A1}}{C_{A0}}\right) = -k\theta$$

$$\frac{C_{A1}}{C_{A0}} = e^{-k\theta}$$

# Perfectly Mixed Reactors (CFSTR)



First order rxn, @ steady state,

$$[Accumulation] = [Input] - [Output] - [Reaction]$$

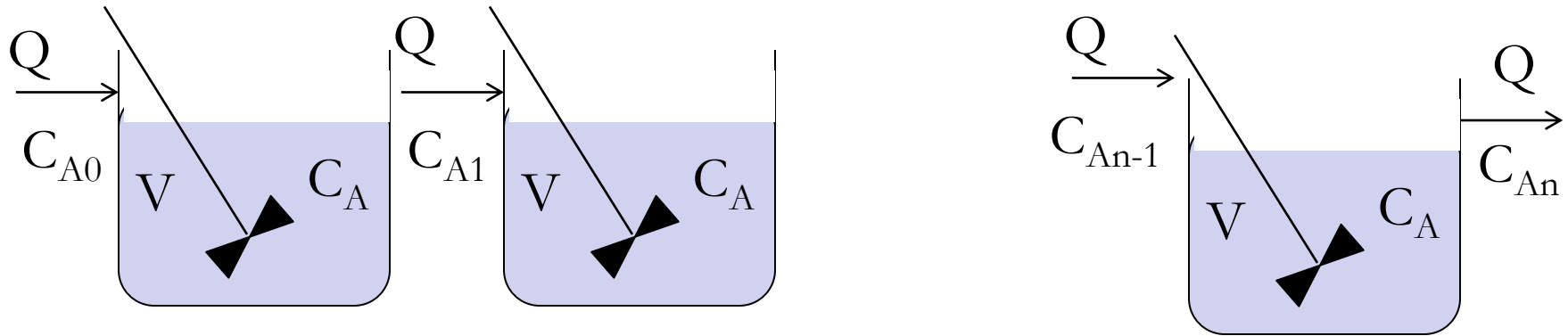
$$dC_{A1}V = C_{A0}Qdt - C_{A1}Qdt - kVC_{A1}dt$$

$$\frac{dC_{A1}}{dt} = C_{A0}\frac{Q}{V} - C_{A1}\frac{Q}{V} - kC_{A1}$$

$$0 = C_{A0}\frac{Q}{V} - C_{A1}\frac{Q}{V} - kC_{A1}$$

$$\theta = \frac{C_{A0} - C_{A1}}{kC_{A1}}$$

# Multiple CFSTRs at steady state



$$[Output] = [Input] - [Reaction]$$

$$C_{A1}Q = C_{A0}Q - kVC_{A1}$$

$$C_{A1} = C_{A0} - \theta r_{A1}$$

$$C_{Ai} = C_{Ai-1} - \theta r_{Ai}$$

# Dispersed Plug Flow Reactors

Flow pattern is considered as non-ideal-flow regime

$$\frac{C_{A1}}{C_{A0}} = \frac{4i \exp \left[ 1/2 \left( \frac{vL}{D} \right) \right]}{(1+i)^2 \exp \left[ i/2 \left( \frac{vL}{D} \right) \right] - (1-i)^2 \exp \left[ -i/2 \left( \frac{vL}{D} \right) \right]}$$

$$i = \left[ 1 + 4k\theta \left( \frac{D}{vL} \right) \right]^{0.5}, \text{ dimensionless}$$

v= velocity at the axial direction

L=reactor length

D=Longitudinal dispersion coeff (length<sup>2</sup>/time), relative to the degree of mixing

k=rate constant

θ=residence time