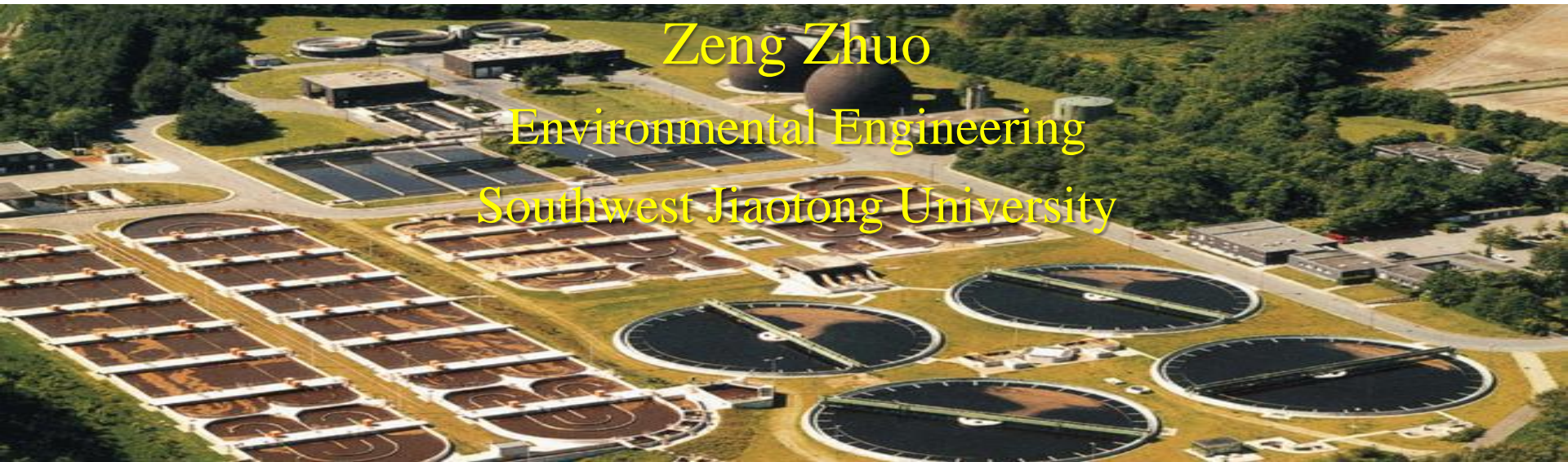


# Chapter Five

## Environmental systems: modeling and reactor design

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Environmental Engineering  
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- I. Overview
- II. Material balances
- III. Reaction kinetics
- IV. Flow regimes and reactor
- V. Energy balances



## Section 1

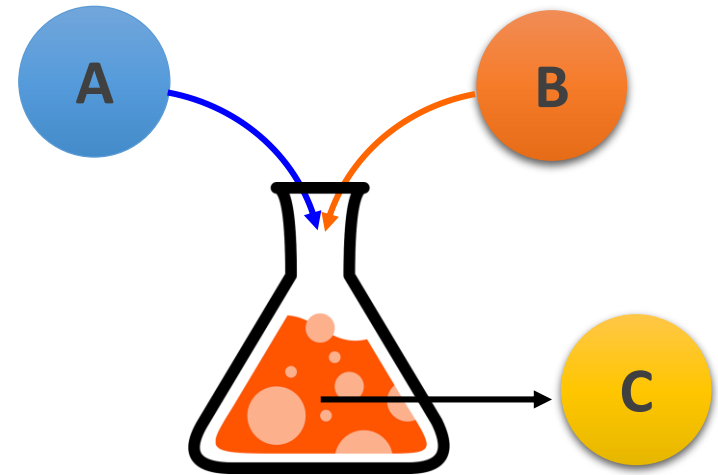
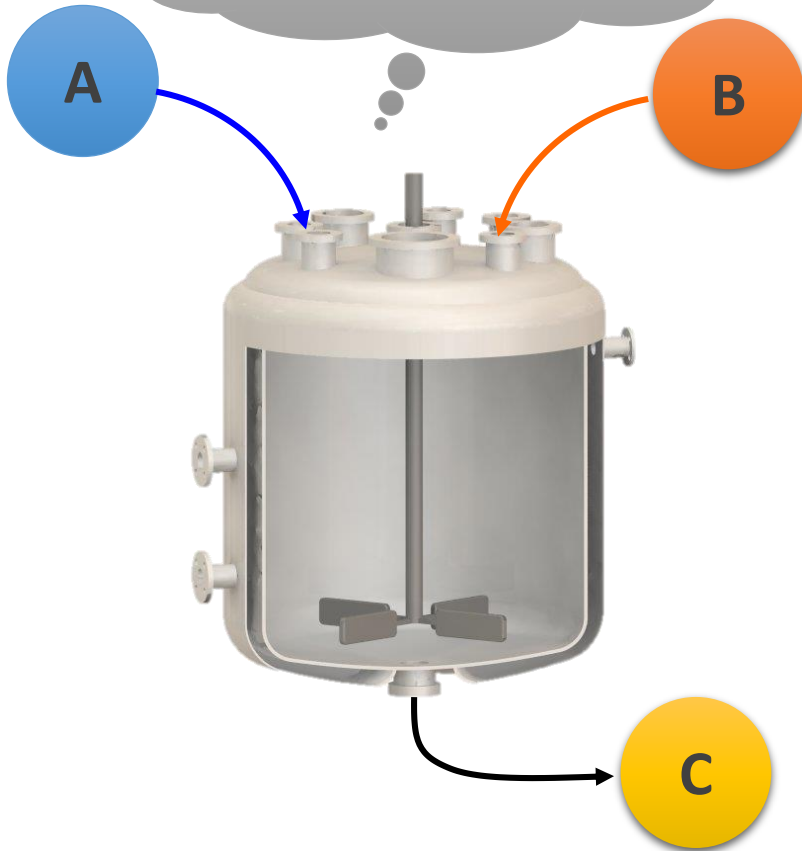
## Overview

# Overview



Think about:

1. If the flow rate of A and B is very high
2. If no mixture in reactor



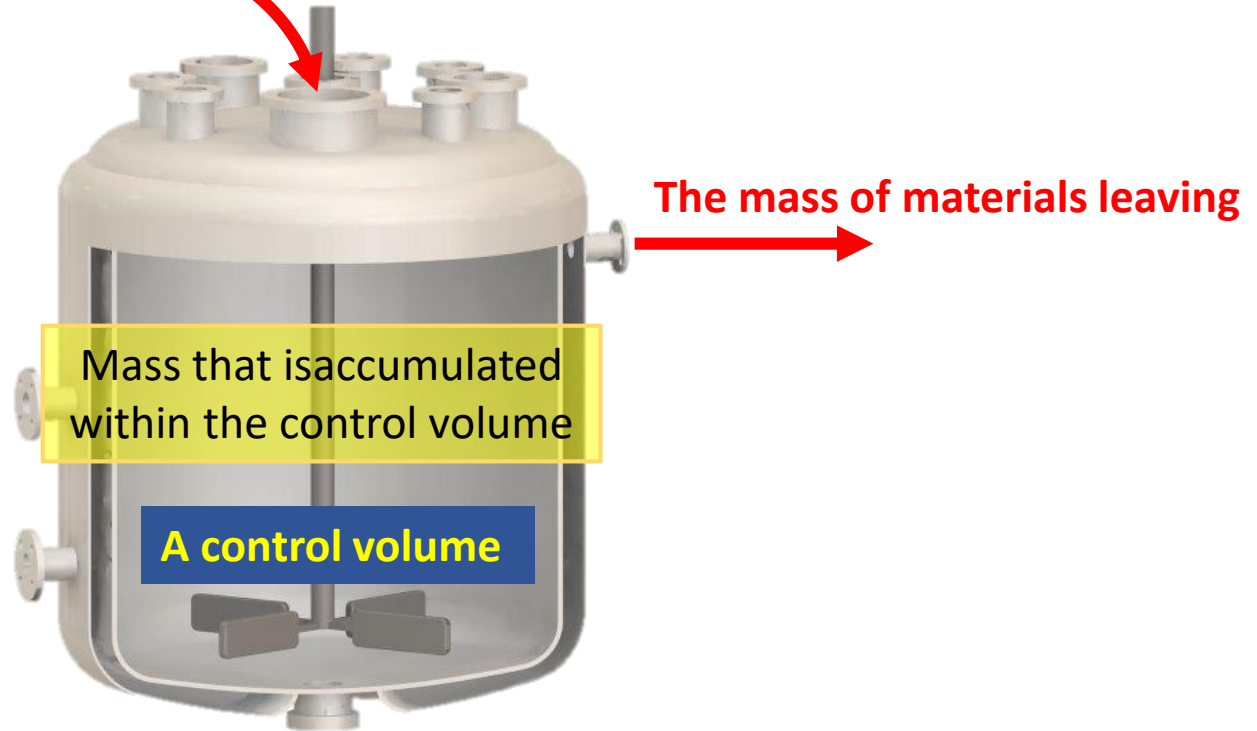
Chemical reactions in a beaker

Chemical reactions in a reactor

# Overview



The mass of materials entering



The mass of materials entering a control volume must be equal to the mass of materials leaving the control volume, plus any mass that is accumulated within the control volume.

# Overview



## Law of Conservation of Matter


Matter cannot be created nor destroyed.

## Law of Conservation of Energy


Energy cannot be created or destroyed

**Conservation of Matter**

In a chemical reaction, matter is neither created or destroyed.



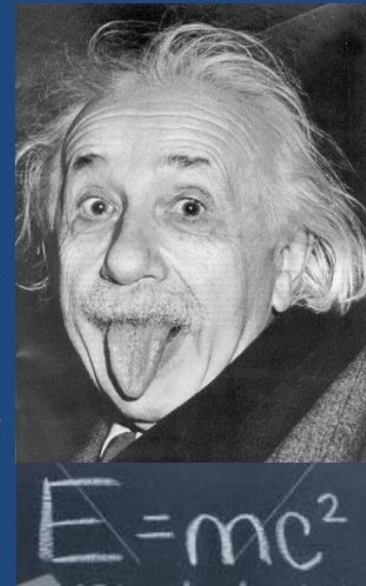
Antoine Laurent Lavoisier



A cartoon illustration of Antoine Lavoisier, a French chemist, holding a flask with a wavy line representing a chemical reaction. The text 'Conservation of Matter' is at the top, and 'In a chemical reaction, matter is neither created or destroyed.' is below it. The name 'Antoine Laurent Lavoisier' is at the bottom. A small 'Science & Steam' logo is in the bottom left corner.

## The Law of Conservation of Energy

- Law of Conservation of Energy-  
Energy cannot be created or destroyed, only transformed from one type to another
    - If energy seems to disappear, then scientists look for it – leading to many important discoveries.
  - In 1905, Albert Einstein said that mass and energy can be converted into each other
    - He showed that if matter is destroyed, energy is created, and if energy is destroyed mass is created.
- $E = mc^2$





# Overview

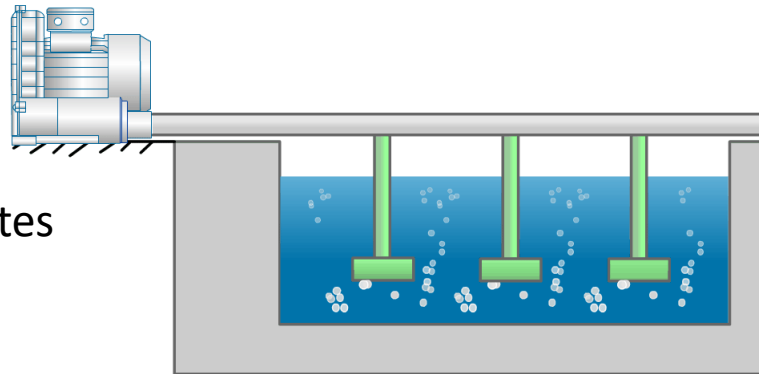


**The kinetics (how fast a reaction occurs)** of biological and chemical reactions that occur within a system will influence the efficiency and sizing of engineered systems.

Designing **an aeration basin** to treat municipal wastewater

Oxygen uptake rate

Substrate utilization rates



Size the aeration system

Dimensions of the reactor



## Section 2

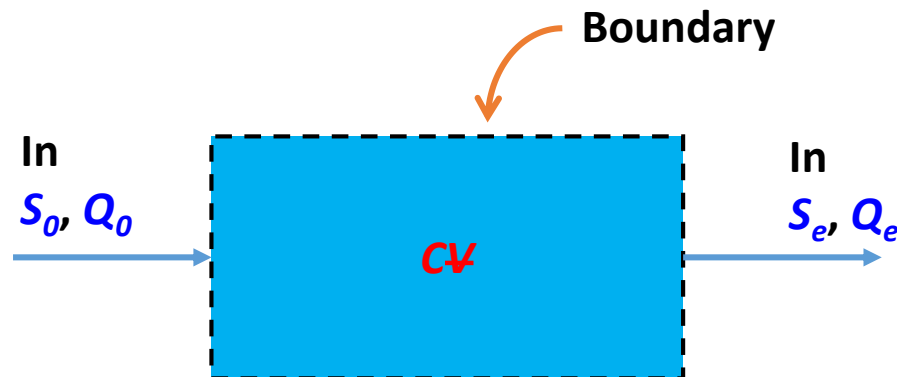
### Material balances



# Material balances



**Control volume (CV):** the specific region of space on which the mass balance is performed.

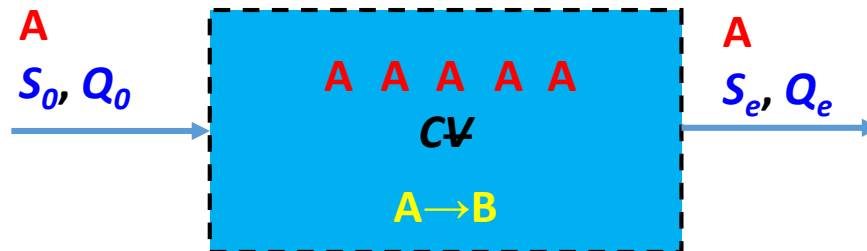


## Fates of an entering substance

Route 1: may **accumulate** within the control volume

Route 2: may be **transformed** into a different compound

Route 3: may **leave** the control volume without any change



In a non-reactive process

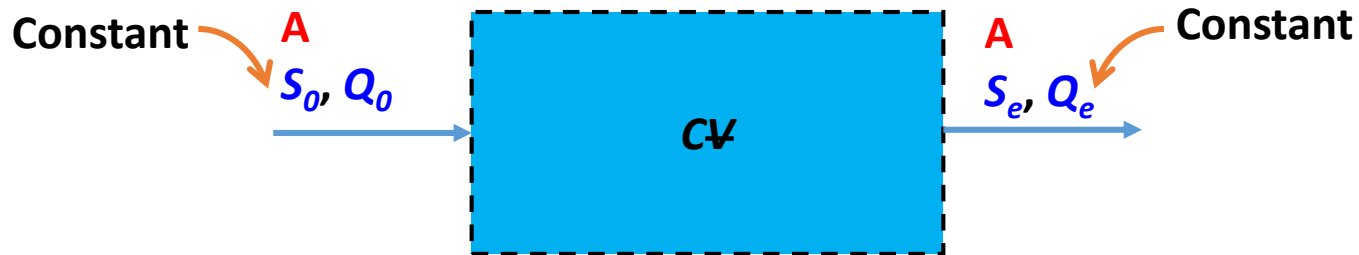
$$[accumulation] = [inputs] - [outputs]$$

# Material balances



## States

**Steady-state conditions:** the flow and concentration in each stream entering and exiting the control volume remain constant.



**In a non-reactive steady-state process**

$$[inputs] - [outputs] = [accumulation] = 0$$

**Nonsteady-state conditions:** the accumulation term will increase or decrease.

## Mass balance in a control volume

In a non-reactive process

$$[accumulation] = [inputs] - [outputs]$$



$$\left[ \begin{array}{c} \text{net change} \\ \text{in mass within CV} \end{array} \right] = \left[ \begin{array}{c} \text{total mass} \\ \text{entering CV} \end{array} \right] - \left[ \begin{array}{c} \text{total mass} \\ \text{exiting CV} \end{array} \right]$$



$$\frac{dm_{CV}}{dt} = \dot{m}_i - \dot{m}_e$$

**= 0, in steady-state**

**≠ 0, in unsteady-state**

$(dm_{CV}/dt)$  = net change of mass contained within the control volume, mass/time

$\dot{m}_i$  = mass flow rate across inlet, mass/time

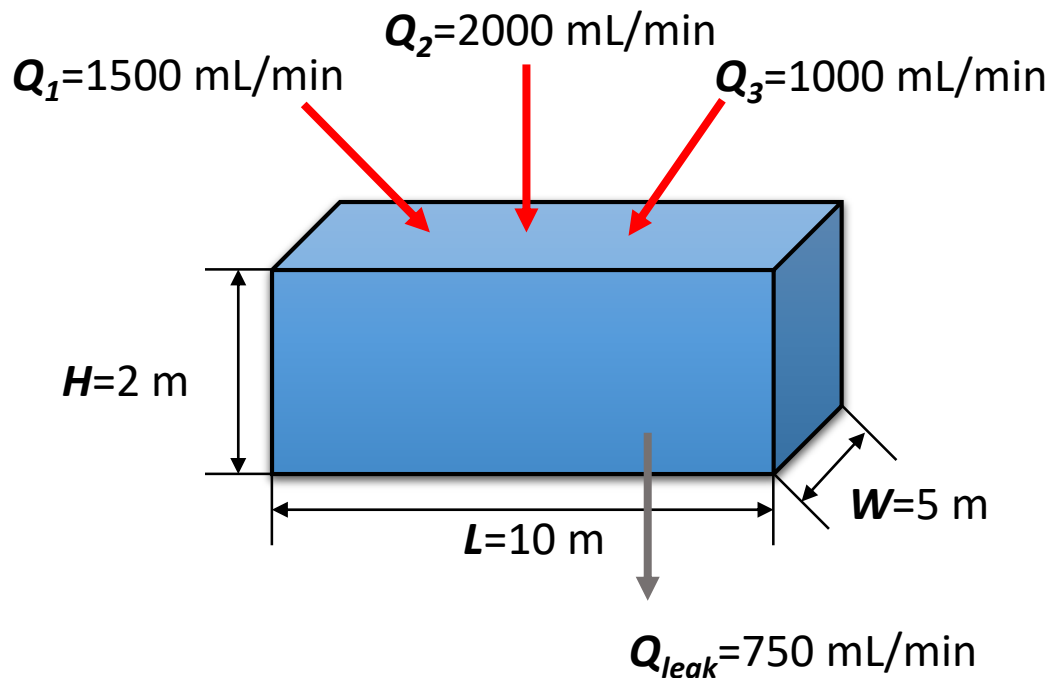
$\dot{m}_e$  = mass flow rate across outlet, mass/time

# Material balances



## Mass balance in a control volume

*How many hours it will take to fill the pool up?*



### Important parameters:

The volume of the pool,  $V$ ;  
The volumetric flow rate,  $Q$ ;  
The mass flow rate,  $\dot{m}$ ;  
The water density,  $\rho$ .

$$V = L \times W \times H$$

$$Q = V'/t$$

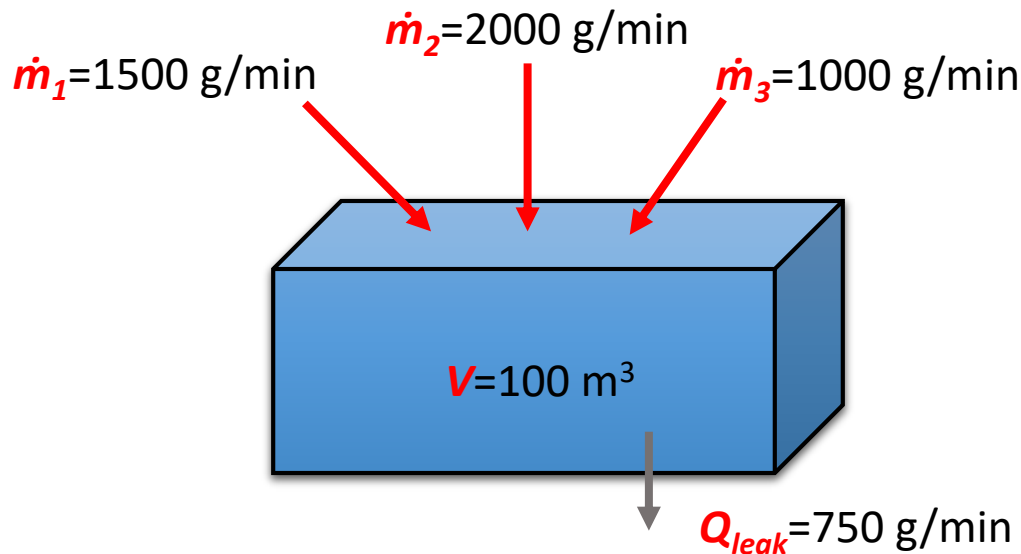
$$\dot{m} = \rho \times Q$$

# Material balances



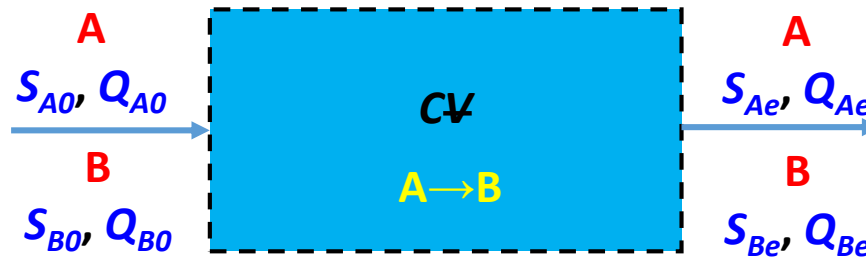
$$[accumulation] = [inputs] - [outputs]$$

- $m_{accum} = (\dot{m}_1 \times t) + (\dot{m}_2 \times t) + (\dot{m}_3 \times t) - (m_{leak} \times t)$
- $\rho \times V = (\dot{m}_1 + \dot{m}_2 + \dot{m}_3 - m_{leak}) \times t$
- $100 \text{ m}^3 \times 1000 \text{ kg/m}^3 = (1.5 \text{ kg/min} + 2 \text{ kg/min} + 1 \text{ kg/min} -$



- $1 \times 10^5 \text{ kg} = 3.75 \text{ kg/min} \times t$
- $t = 2.67 \times 10^4 \text{ min} = 18.5 \text{ d}$

## Reactions occurring in a control volume

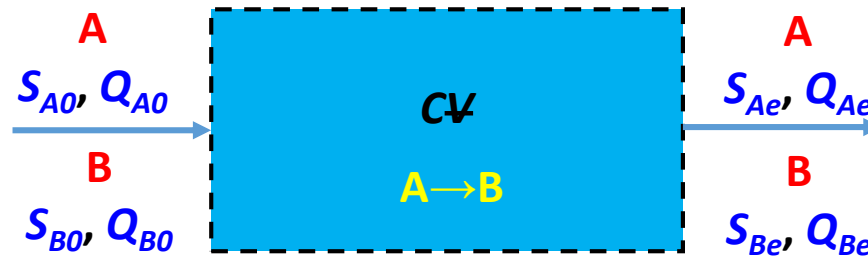


**A destructive type of reaction** results in the removal or reduction of a certain chemical or contaminant, so the concentration of the compound leaving the reactor will be less than the concentration entering it.  $S_{A0} > S_{Ae}$

**A production or synthesis reaction** will result in the production or synthesis of a compound, so the concentration of the compound leaving the reactor will be greater than the concentration entering it.  $S_{B0} < S_{Be}$



## Reactions occurring in a control volume



In a reactive process

$$[accumulation] = [inputs] - [outputs] + [reaction]$$

- If the reaction involves the **removal** or destruction of a constituent

$$[accumulation] = [inputs] - [outputs] - [reaction] \quad \text{BOD removal}$$

- If the reaction results in the **formation** of a product

$$[accumulation] = [inputs] - [outputs] + [reaction] \quad \text{Microorganisms growth}$$

## Steady-state modeling

In **steady-state**, all flow rates, concentrations, pressures, temperatures, etc. entering and exiting the control volume must **remain constant**.

In a non-reactive process

$$[accumulation] = [inputs] - [outputs] = 0$$



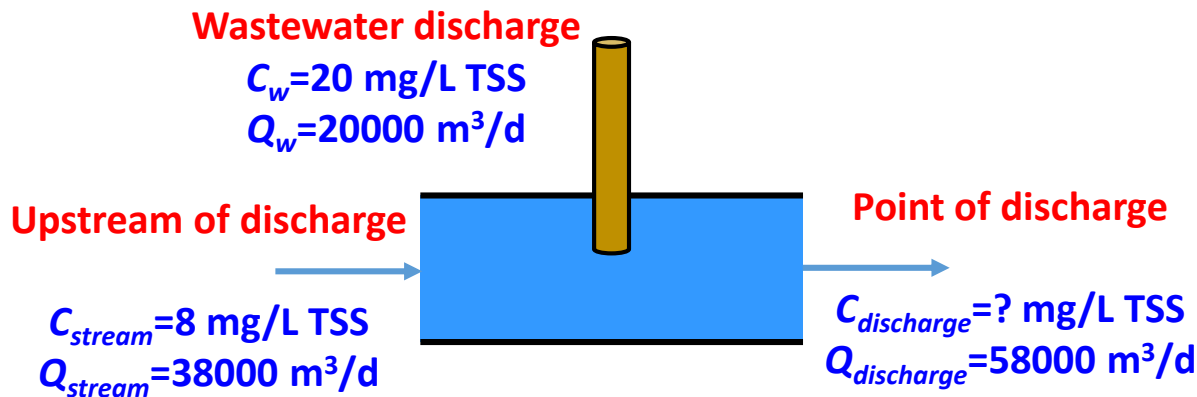
$$[inputs] = [outputs]$$



$$c_e = \frac{c_1 Q_1 + c_2 Q_2}{Q_1 + Q_2} = \frac{c_1 Q_1 + c_2 Q_2}{Q_e}$$

## Steady-state modeling

In the non-reactive process



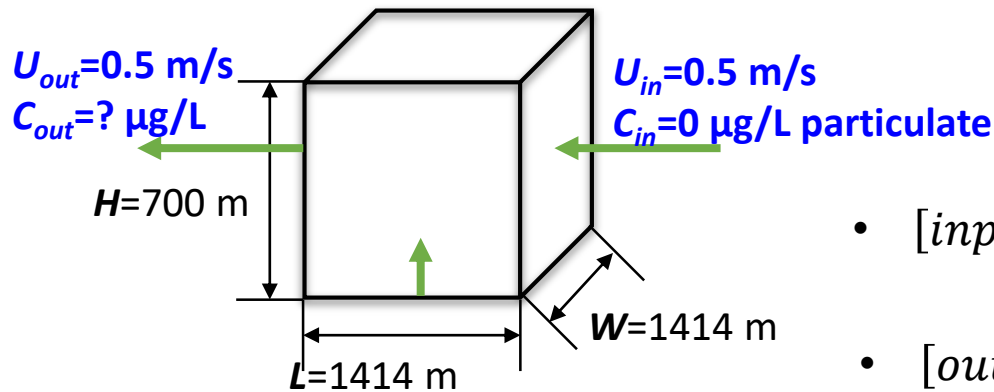
$$C_e = \frac{C_1 Q_1 + C_2 Q_2}{Q_1 + Q_2} = \frac{C_1 Q_1 + C_2 Q_2}{Q_e}$$

$$C_{\text{discharge}} = \frac{C_{\text{stream}} Q_{\text{stream}} + C_w Q_w}{Q_{\text{stream}} + Q_w} = \frac{8 \times 38000 + 20 \times 20000}{58000} = 12.1 \text{ mg/L}$$

## Steady-state modeling

### In the reactive process

$$[accum] = [inputs] - [outputs] + [reaction] = 0$$



**Rate of particulate generation**  
**4.7 kg/s**

### Assumption

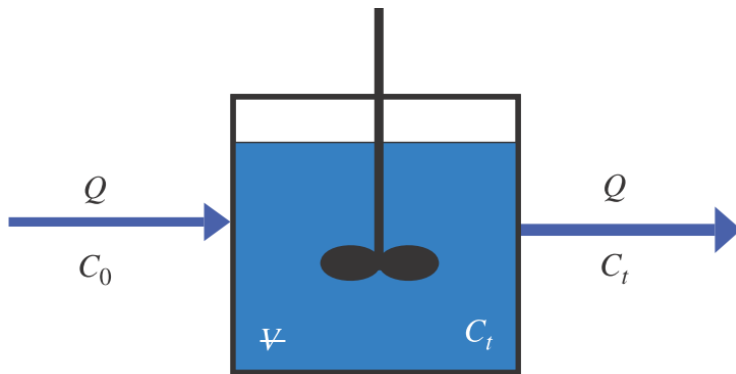
- The volume of air above the area is completely and uniformly mixed.
- Steady-state conditions prevail.

- $[inputs] = \dot{m}_{in} = U_{in} \times A \times C_{in}$   
 $= 0.5 \times 1414 \times 700 \times 0 = 0$
- $[outputs] = \dot{m}_{out} = U_{out} \times A \times C_{out}$   
 $= 0.5 \times 1414 \times 700 \times C_{out} = 4.95 \times 10^5 C_{out}$ 
  - $0 - 4.95 \times 10^5 C_{out} + 4.7 \times 10^9 = 0$
  - $C_{out} = 9494\text{ }\mu\text{g/L}$

## Dynamic (transient) modeling

In **dynamic-state**, any one of flow rates, concentrations, pressures, temperatures, etc. entering and exiting the control volume changes with time.

$$[accum] = [inputs] - [outputs] + [reaction]$$



$$\left(\frac{dC}{dt}\right)V = QC_0 - QC + rV \quad r = kC_t$$

$$\frac{dC}{dt} = \frac{QC_0 - QC}{V} + kC_t$$

## Brief summary

- Material balances** {
- Control volume
  - Mass balance in a control volume
  - Mass balance in steady-state (in non-reactive, reactive process)
  - Mass balance in dynamic-state





## Section 3

### Reaction kinetics



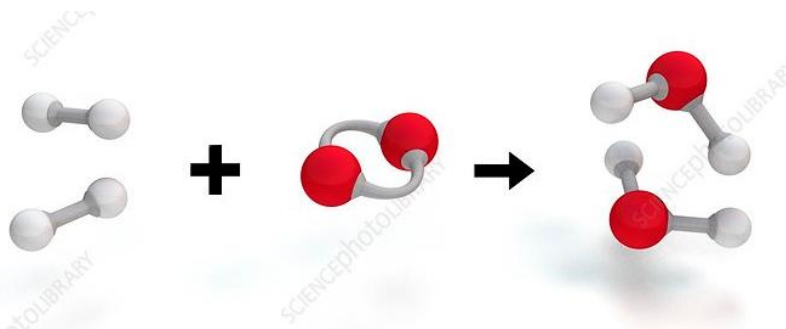
# Reaction kinetics



**Thermodynamic principles:** to determine which direction a process or reaction will proceed of its own accord.

**Chemical kinetics :** how fast a reaction occurs.

*Exergonic reaction*



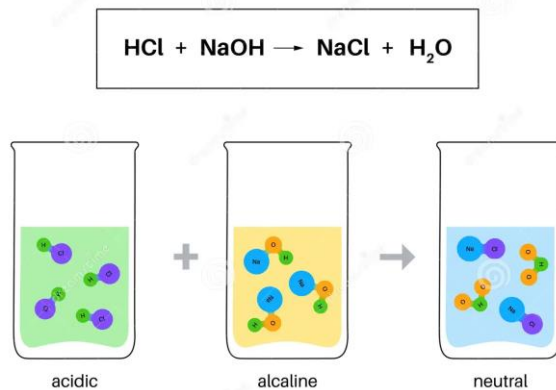
Do you know  
how fast this  
reaction going?

## Rates of reaction

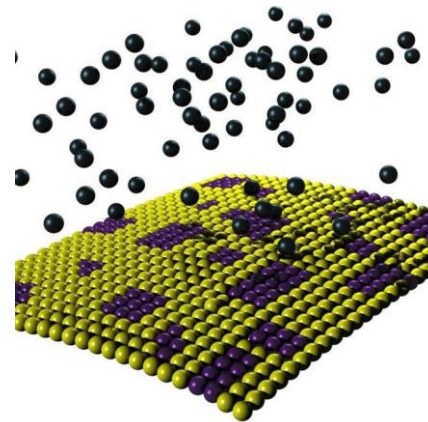
**The rate of a reaction ( $r$ )** is the rate of formation or disappearance of a chemical compound or species.

**Homogeneous reactions** are those that occur within a single phase.

**Heterogeneous reactions** occur between two phases.



*Neutralization reaction*




*Adsorption reaction*

## Rates of reaction



The chemical reaction rate ( $r$ ) can be expressed as the time rate of change of any of the reactants (-) or products (+).

*Stoichiometric relation*


$$r = -\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

The units for the rate of reaction( $r$ )  $\left\{ \begin{array}{l} \text{moles per unit of volume per unit time, mol/(L}\cdot\text{min)} \\ \text{mass per unit of volume per unit time, g/(L}\cdot\text{min)} \end{array} \right.$

## Rate law and order of reaction

The **rate law** expresses the mathematical relationship between the rate of the reaction and the concentration of species involved in the reaction.



$$r = -k[A]^{\alpha}[B]^{\beta} = k[C]^{\gamma}$$

*$\alpha$ -order respect to A*

*$\beta$ -order respect to B*

*$\gamma$ -order respect to C*

The overall order of the reaction based on the reactants A and B  *$\alpha + \beta$  order*

The overall order of the reaction based on the reactants C  *$\gamma$  order*

## Determination order of reaction

### *Elementary reactions*



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

First-order with respect to A  
The overall order of the reaction is first



$$r = -k[A]^1[B]^1$$

First-order with respect to A  
First-order with respect to B  
The overall order of the reaction is second



$$r = -k[A]^1[B]^2$$

First-order with respect to A  
Second-order with respect to B  
The overall order of the reaction is third

### *Complex reactions*

The rate law for any reaction must be determined by **experiment**.

## Zero-order reactions

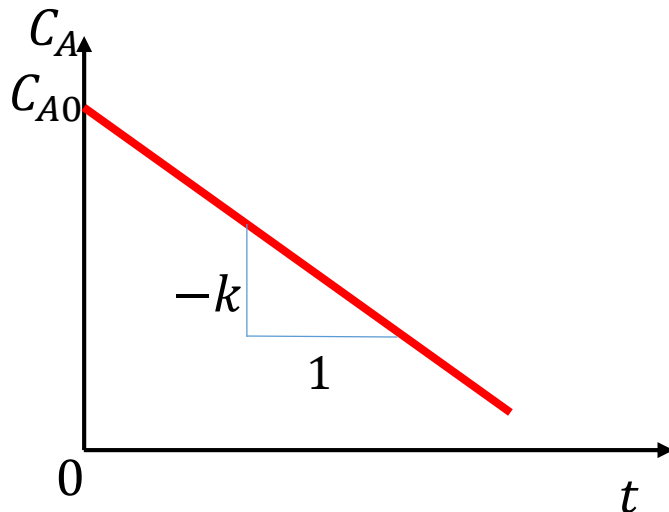
A zero-order removal reaction for A

$$r = -\frac{dC_A}{dt} = k \cdot C_A^0 = k$$

$$\int_{C_{A0}}^{C_{At}} dC = -k \int_0^t dt$$



$$C_{At} = C_{A0} - kt$$

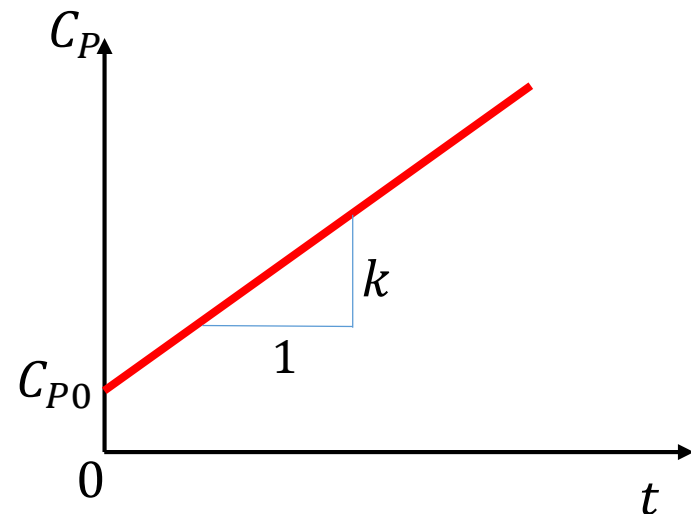


A zero-order production reaction for P

$$r = \frac{dC_P}{dt} = k \cdot C_P^0 = k$$

$$\int_{C_{P0}}^{C_{Pt}} dC = k \int_0^t dt$$

$$C_{Pt} = C_{P0} + kt$$

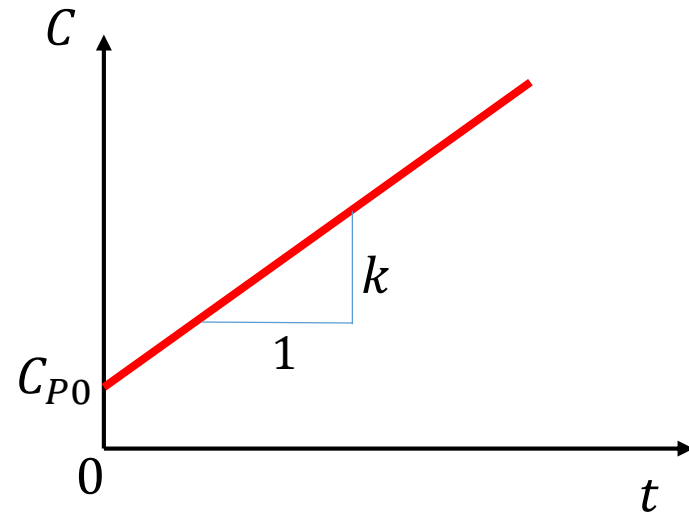
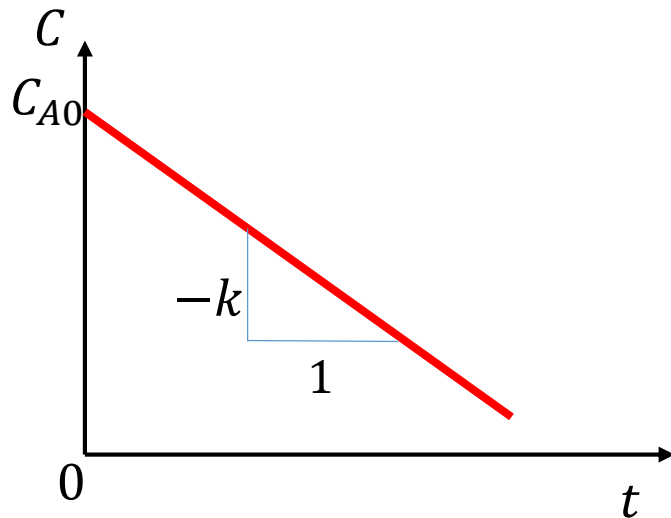


## Zero-order reactions



The characteristics of a zero-order reaction:

- **The rate is constant.**  $r = k \cdot C_A^0 = k$
- **The  $t$ - $C$  plot is a straight line.**





# Reaction kinetics



## First-order reactions



A first-order removal reaction for A

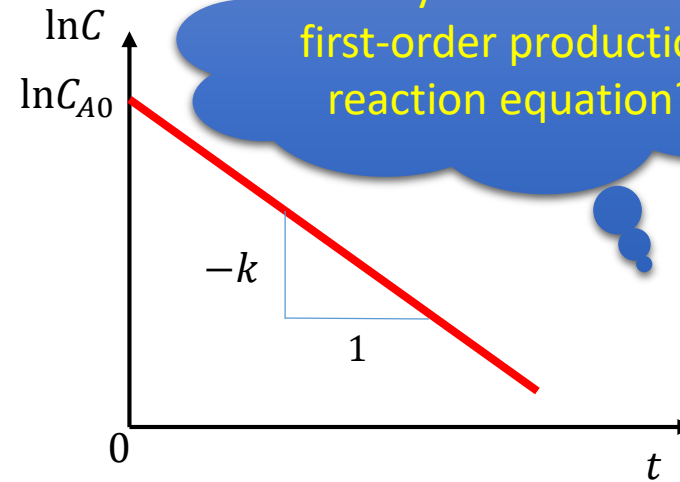
$$r = -\frac{dC_A}{dt} = k \cdot C_A^1 = kC_A$$

$$\int_{C_{A0}}^{C_{At}} \frac{dC}{C} = -k \int_0^t dt$$

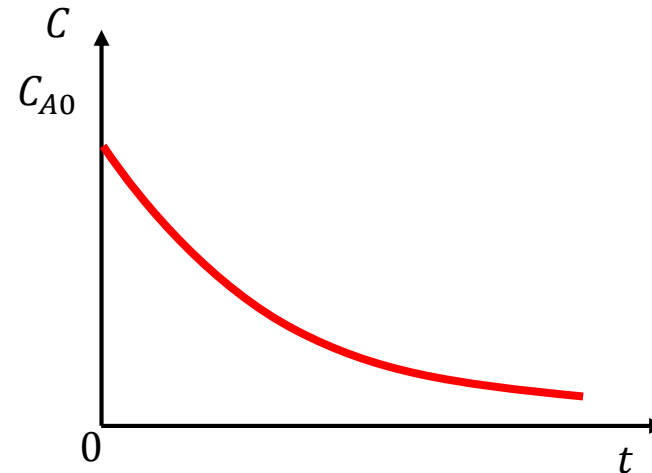
$$\ln(C_A) - \ln(C_{A0}) = -kt$$

$$\ln(C_A) = \ln(C_{A0}) - kt$$

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



Can you derive the first-order production reaction equation?

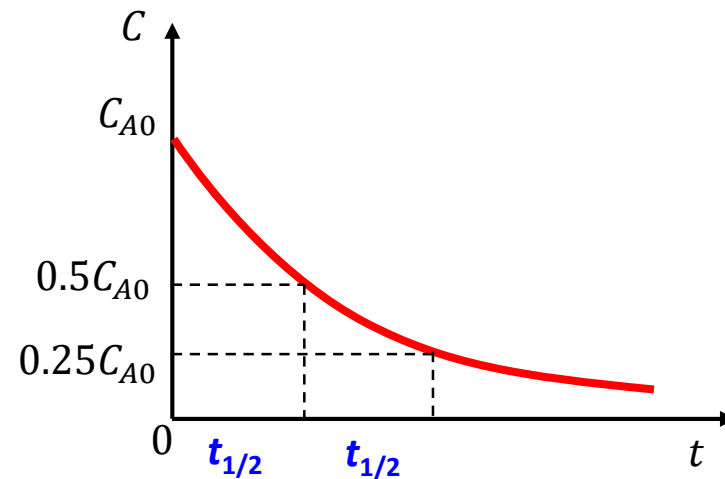
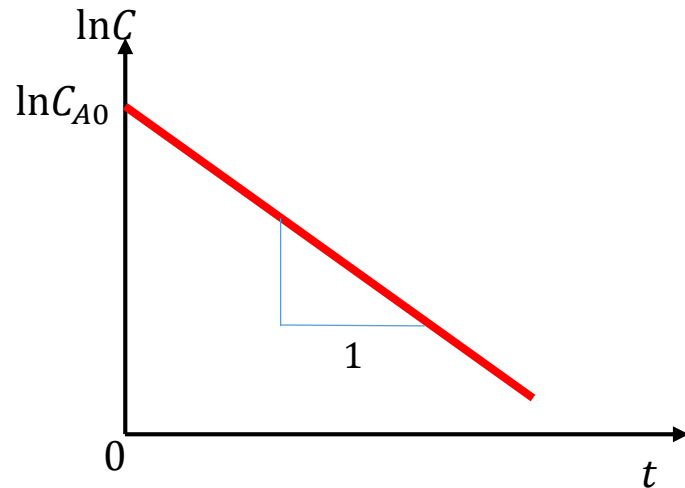


## First-order reactions



The characteristics of a first-order reaction:

- The rate is not a constant.  $r = k \cdot C_A^1 = kC_A$
- A plot of the natural log of  $C$ - $t$  for a first-order production reaction is a straight line.
- The half-life,  $t_{1/2}$ , is only related to  $k$ .  $t_{1/2} = \frac{0.693}{k}$



## Second-order reactions



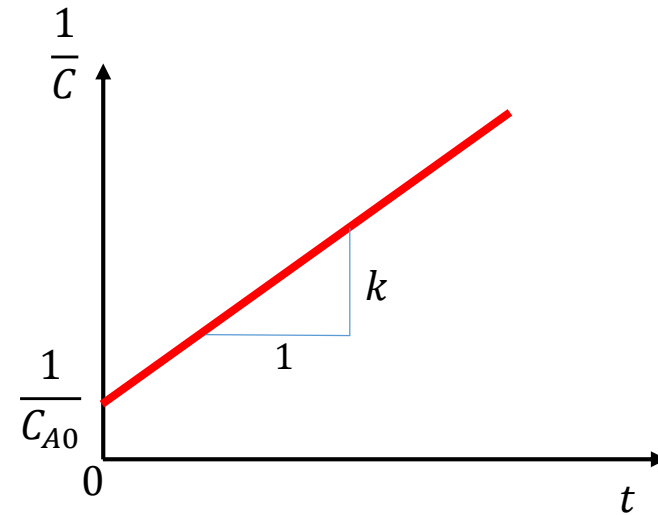
A second-order removal reaction for A

$$r = -\frac{dC_A}{dt} = k \cdot C_A^2 = kC_A^2$$

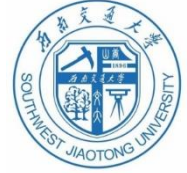
$$\int_{C_{A0}}^{C_{At}} \frac{dC}{C^2} = -k \int_0^t dt$$

$$\frac{1}{C_{A0}} - \frac{1}{C_{At}} = -kt$$

$$\frac{1}{C_{At}} = \frac{1}{C_{A0}} + kt$$

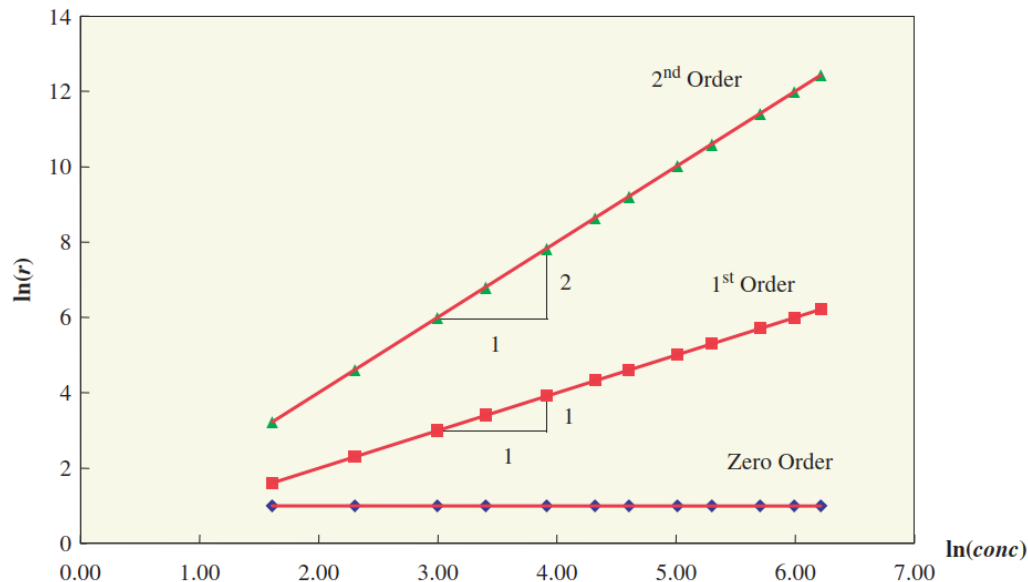


# Reaction kinetics



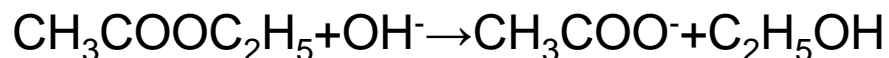
## Comparison of zero-, first-, second-order reactions

Order	Removal	Production	Reaction rate
Zero	$C_{At} = C_{A0} - kt$	$C_{Pt} = C_{P0} + kt$	$r = k$
First	$C_{At} = C_{A0}e^{-kt}$	$C_{Pt} = C_{P0}e^{kt}$	$r = kC_A$
Second	$\frac{1}{C_{At}} = \frac{1}{C_{A0}} + kt$	$\frac{1}{C_{Pt}} = \frac{1}{C_{P0}} - kt$	$r = kC_A^2$



## Determination of reaction order and $k$

**Ethyl acetate hydrolysis** reaction in alkaline solution as following:



The reaction is carried out at 25 °C. The initial concentrations of both reactants are 0.064 mol/L. The concentrations of  $\text{OH}^-$  measured by sampling at different times are shown in the following table.

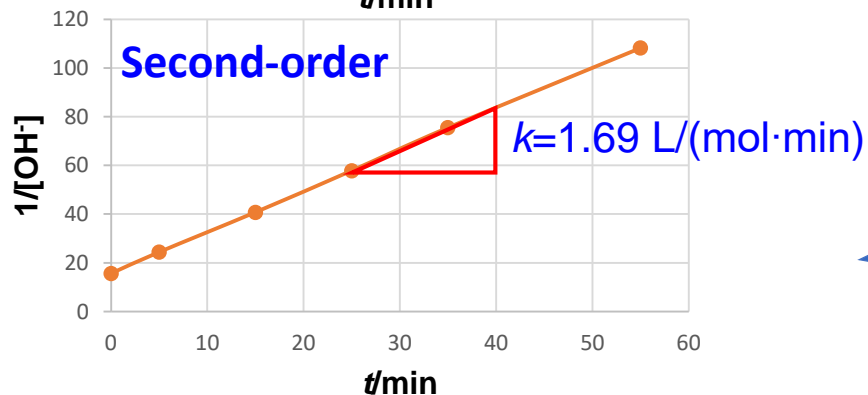
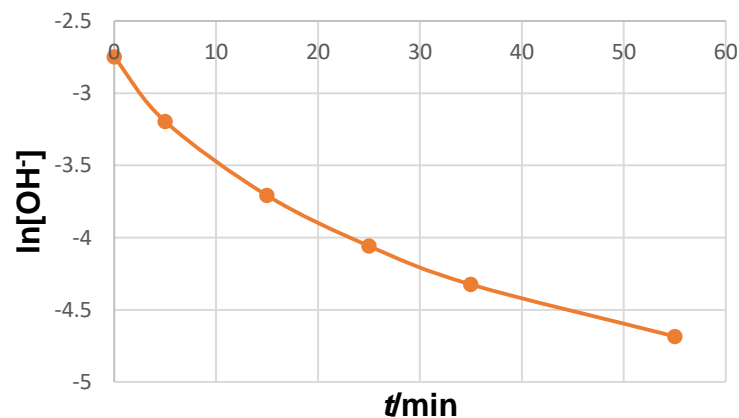
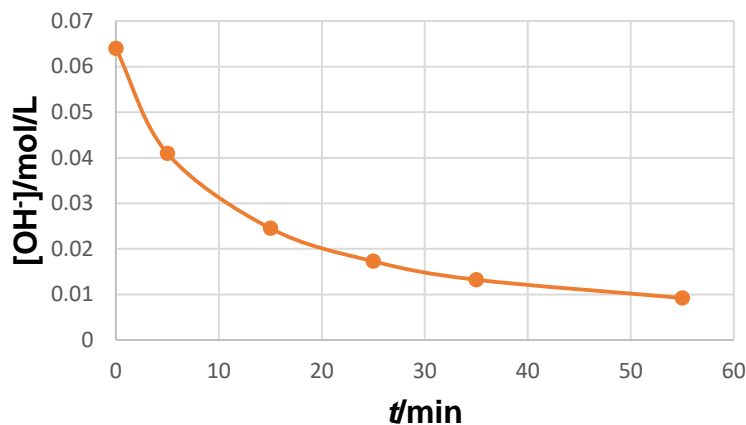
t/min	0	5	15	25	35	55	$\infty$
$[\text{OH}^-]/\text{mol}\cdot\text{L}^{-1}$	0.064	0.041	0.025	0.017	0.013	0.009	0

- (1) Determine the reaction order of this reaction.
- (2) Calculate the reaction rate constant  $k$ .

# Reaction kinetics



t/min	0	5	15	25	35	55	$\infty$
$[\text{OH}^-]/\text{mol}\cdot\text{L}^{-1}$	0.064	0.041	0.025	0.017	0.013	0.009	0
$\ln[\text{OH}^-]$	-2.749	-3.195	-3.708	-4.058	-4.325	-4.684	-
$1/[\text{OH}^-]$	15.6	24.4	40.8	57.9	75.5	108.2	-



**Plotting method:** plotting  $C_A-t$ ,  $\ln C_A-t$  and  $1/C_A-t$ , respectively, to find **straight line**.

## Temperature effects on rate constants

A temperature correction coefficient ( $\theta$ ) of 1.047 is typically used for making temperature corrections when performing biochemical oxygen demand (BOD) analyses. If the BOD rate constant,  $k$ , at 20 °C is 0.15 d<sup>-1</sup>.

Determine the value of  $k$  for a temperature of 25 °C.

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

$$k_{25^\circ\text{C}} = k_{20^\circ\text{C}} \theta^{(T_2 - T_1)}$$

$$k_{25^\circ\text{C}} = 0.15 \times 1.047^{(25^\circ\text{C} - 20^\circ\text{C})}$$

$$k_{25^\circ\text{C}} = 0.19 \text{ d}^{-1}$$



## Brief summary

### Reaction kinetics

- Rates of reactions
- Order of reaction
- Zero-order reaction
- First-order reaction
- Second-order reaction
- Temperature corrections





## Section 4

### Flow regimes and reactors

# Flow regimes and reactors



**Reactors** are tanks or vessels in which physical, chemical, and biological reactions occur.

**A flow regime** or flow model is used to evaluate the effects of detention time and flow rate on a given system

The ideal or theoretical detention time ( $\tau$ )

$$\tau = \frac{V}{Q}$$

The volume of the reactor ( $V$ )

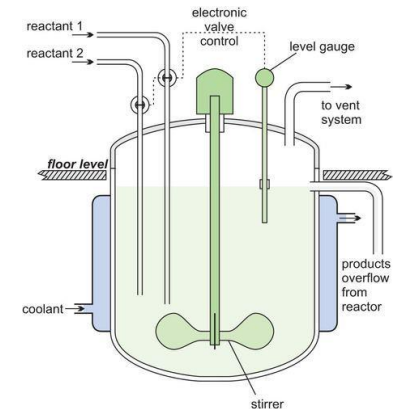
Volumetric flow rate ( $Q$ )



Sequencing batch reactor  
(SBR)

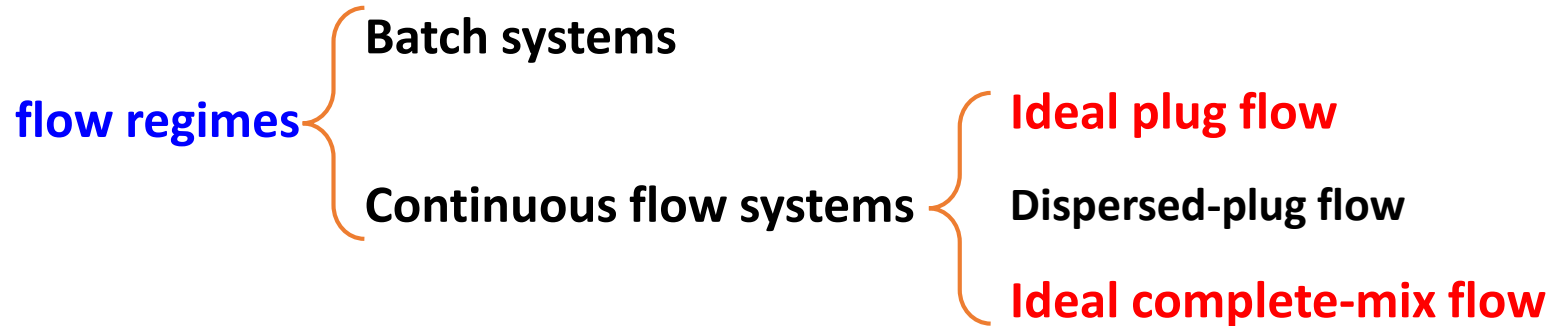


Plug-flow reactor



Mixed-flow reactor

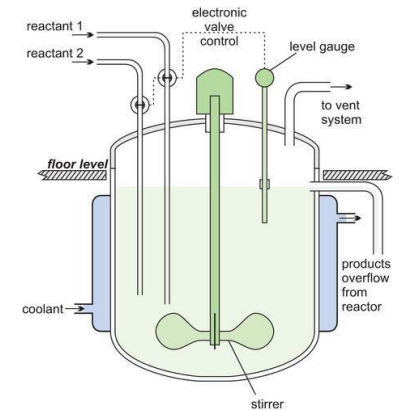
# Flow regimes and reactors



Sequencing batch reactor  
(SBR)



Plug-flow reactor



Mixed-flow reactor

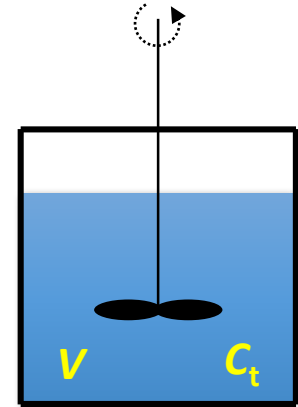
# Flow regimes and reactors



## Ideal Complete-Mix Batch Reactor

### Characteristics

- No continuous flow into and out of a batch reactor;
- The system operates under nonsteady-state conditions;
- The concentration of a substrate will decrease as reaction time increases.



### Operation steps

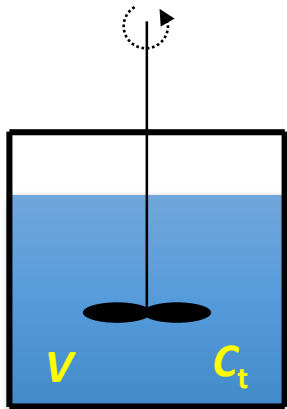
- I. The reactor is filled with the process stream containing the constituents to be processed;
- II. The flow to the reactor is stopped and air or chemicals are added to the reactor (treatment may begin);
- III. The reactor is operated until the desired degree of treatment or conversion has been accomplished;
- IV. Once processing or treatment of the flow has been accomplished, the contents of the reactor are drained and a new cycle will begin.

# Flow regimes and reactors



## Ideal Complete-Mix Batch Reactor

A zero-order removal reaction for a complete-mix batch reactor



Mass balance in this reactor

$$[accumulation] = [inputs] - [outputs] + [reaction]$$

$$V \left( \frac{dC}{dt} \right)_{accum} = QC_0 - QC_t + \left( \frac{dC}{dt} \right) V$$

Zero-order

$$V \left( \frac{dC}{dt} \right)_{accum} = 0 - 0 + (-k)V$$

$$-\frac{dC}{dt} = k \cdot C^0 = k$$

$$\left( \frac{dC}{dt} \right)_{accum} = -k \rightarrow C_t - C_0 = -kt \rightarrow t = \frac{C_t - C_0}{k}$$

## Ideal Complete-Mix Batch Reactor

### Example 5.9 Complete-mix batch reactor design

A CMBR is to be designed to pre-treat a food-processing wastewater that contains 500 mg/L of five-day biochemical oxygen demand ( $\text{BOD}_5$ ). A treatability study performed on the food-processing wastewater determined the kinetics for  $\text{BOD}_5$  removal to be zero-order with a rate constant of 40 mg/(L·h).

Determine:

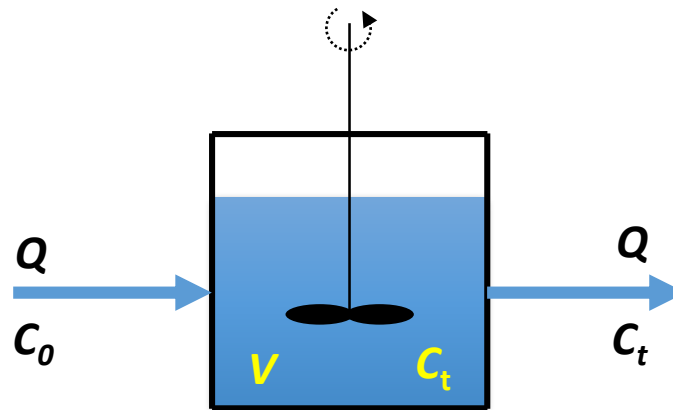
- a) Reaction or treatment time necessary to reduce the  $\text{BOD}_5$  of the wastewater to 100 mg/L.
- b) The volume of the reactor to treat 6,000 m<sup>3</sup> of wastewater daily.



## Ideal Complete-Mix flow Reactor

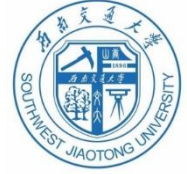
### Characteristics

- Complete and instantaneous mixing of the fluid particles occurs on entering the reactor;
- The composition of the effluent is the same as the composition within the reactor;
- **The steady-state assumption is made in the reactor.**



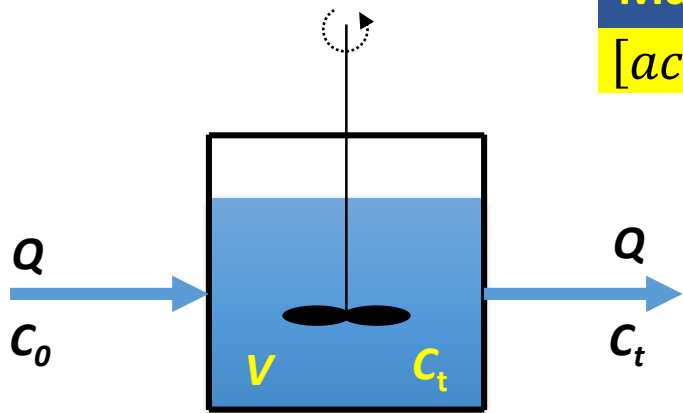


# Flow regimes and reactors



## Ideal Complete-Mix flow Reactor

A first-order removal reaction for a complete-mix flow reactor



Mass balance in this reactor

$$[accumulation] = [inputs] - [outputs] + [reaction]$$

$$V \left( \frac{dC}{dt} \right)_{accum} = QC_0 - QC_t + \left( \frac{dC}{dt} \right) V$$

In the steady-state, accumulation  $\rightarrow 0$

$$0 = QC_0 - QC_t - kC_tV$$

$$kC_tV = Q(C_0 - C_t)$$

$$\frac{V}{Q} = \frac{(C_0 - C_t)}{kC_t}$$

First-order

$$-\frac{dC}{dt} = kC$$

$$\tau = \frac{V}{Q} = \frac{\left(\frac{C_0}{C_t} - 1\right)}{k}$$

## Ideal Complete-Mix flow Reactor

### Example 5.10 Complete-mix flow reactor design

A complete-mix flow reactor is to be designed to treat an influent stream containing 200 mg/L of chemical oxygen demand (COD) at a flow rate of 200 gallons per minute (gpm). COD represents the total quantity of oxygen required to oxidize organic matter to carbon dioxide and water. COD removal follows a first-order removal reaction, with a rate constant  $k$  of  $0.45 \text{ h}^{-1}$ .

Determine:

- a) The detention time in hours if the effluent is to contain 15 mg/L of COD.
- b) The volume of the reactor in  $\text{ft}^3$  if the effluent is to contain 15 mg/L of COD.

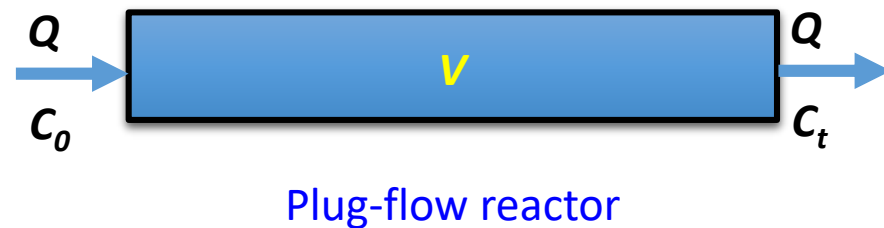


## Ideal Plug Flow Reactor

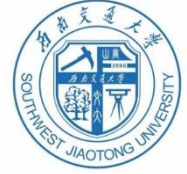
**In ideal plug flow regime**, all the elements of the fluid that enter the system (or control volume) at a given time pass through the system at the same velocity, remain in the system the same amount of time, and exit the system at the same time.

### Assumption

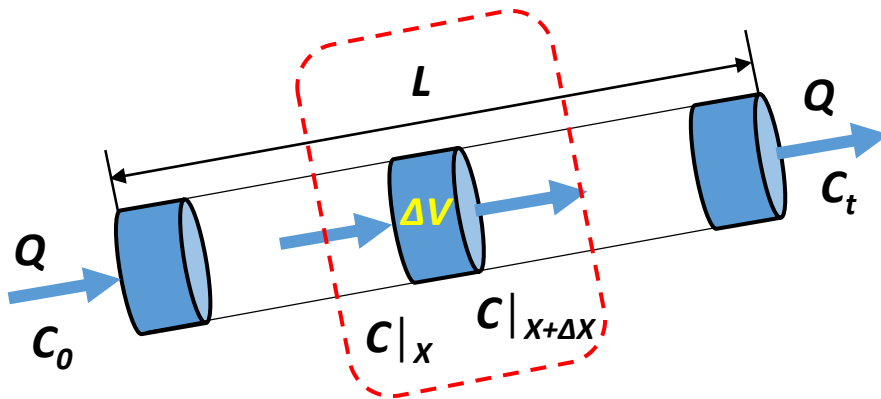
- no longitudinal mixing occurs between adjacent fluid elements.
- Each element of fluid varies as a function of time along the length of the reactor.



# Flow regimes and reactors



## Ideal Plug Flow Reactor



- Complete-mixed
- Steady-state

$$\Delta V = A\Delta X \longrightarrow$$

### Mass balance in this reactor

$$[accumulation] \\ = [inputs] - [outputs] + [reaction]$$

In this differential unit:

$$\left(\frac{\partial C}{\partial t}\right) \Delta V = QC|_x - QC|_{x+\Delta X} + r\Delta V$$

$$\left(\frac{\partial C}{\partial t}\right) \Delta V = QC - Q(C + \Delta C) + r\Delta V$$

$$\left(\frac{\partial C}{\partial t}\right) A\Delta X = QC - QC - Q\Delta C + rA\Delta X$$

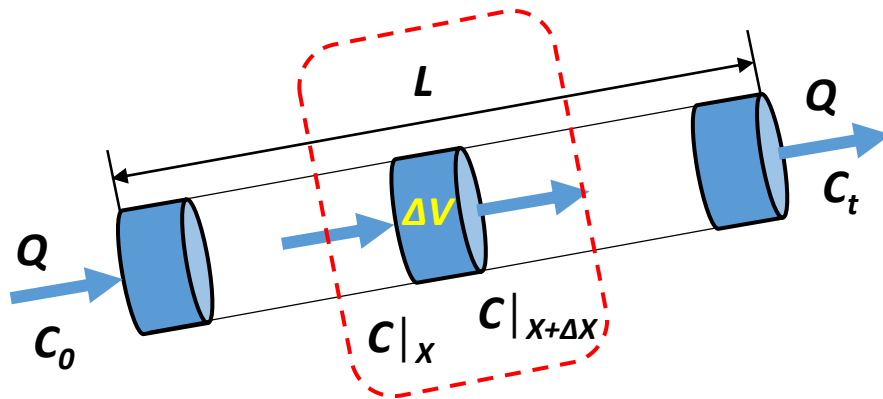
$$\left(\frac{\partial C}{\partial t}\right) = -\frac{Q\Delta C}{A\Delta X} + r \xrightarrow{\text{Steady-state}} \frac{Q\Delta C}{A\Delta X} = r$$

# Flow regimes and reactors



## Ideal Plug Flow Reactor

A first-order removal reaction for an ideal Plug Flow Reactor



- Complete-mixed
- Steady-state

First-order

$$\frac{Q\Delta C}{A\Delta X} = r$$

$$-\frac{dC}{dt} = kC$$

$$\frac{QdC}{AdX} = -kC \longrightarrow \frac{dC}{C} = -k\frac{A}{Q}dX$$

$$\int_{C_0}^{C_t} \frac{dC}{C} = -k\frac{A}{Q} \int_0^L dX$$

$$\ln(C_t) - \ln(C_0) = -k\frac{A}{Q}L = -k\frac{V}{Q} = -k\tau$$

$$\tau = \frac{1}{k} \ln\left(\frac{C_0}{C_t}\right)$$

# Summary

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1. Material or **mass balances** are used in modeling engineered and natural systems.
2. When systems operate at **steady-state**, wherein the influent and effluent concentrations of all parameters and flows remain constant, the accumulation term can be set equal to zero.
3. **Dynamic systems** are those that operate in a state of flux and where the mass balances yield differential equations that are more complex to solve.
4. **The rate of a reaction  $r$**  is the rate of formation or disappearance of a chemical compound or species.
5. **The order of the reaction** is related to the exponent of the chemical species given in the rate law.
6. Most biological and chemical reactions involved in environmental engineering are either **zero-, first-, or second-order reactions**.
7. **Complete-mix** refers to systems in which their contents are uniform throughout.
8. **Plug flow** systems are those that are not well-mixed; the fluid particles pass through with little to no longitudinal mixing.

# Homework



## Problem 14, Page 235

- 14** Consider the irreversible conversion of a single reactant (A) to a single product (P) for the following reaction:  $A \rightarrow P$ . Evaluate the following data to determine whether the reaction is zero-, first-, or second-order. Also, determine the magnitude of the rate constant  $k$  and list the appropriate units.

Time (minutes)	Concentration of A (g/L)
0	1.00
11	0.50
20	0.25
48	0.10
105	0.05

## Problem 29, Page 236

- 29** Several reactor configurations are to be considered for reducing the influent substrate concentration from 100 mg/L to 15 mg/L at a design flow rate of 5 million gallons per day (MGD). Assume that substrate removal follows first-order kinetics and the first-order rate constant  $k$  is  $8.0 \text{ d}^{-1}$ . Determine the reactor volume required for the following configurations operating at steady-state:
- One ideal plug flow reactor.
  - One ideal complete-mix reactor.
  - Three ideal complete-mix reactors in series.
  - Ten ideal complete-mix reactors in series.

## Problem 30, Page 236

- 30** A complete-mix flow reactor is designed to treat an influent waste stream containing 130 mg/L of casein at a flow rate of 380 liters per minute (Lpm). Assume that casein removal follows first-order removal kinetics with a rate constant  $k$  of  $0.5 \text{ h}^{-1}$  and that the effluent should contain 13 mg/L of casein at steady state. Determine:
- The detention time in hours.
  - The volume of the reactor in cubic meters.



*The end*

**Thank You!**

