

# ESE5001: Physical Principles

## Lecture 1

Material balance and reactor design

# Who am I?

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- Teaching: ESE5001 and ESE60001

# Learning outcome

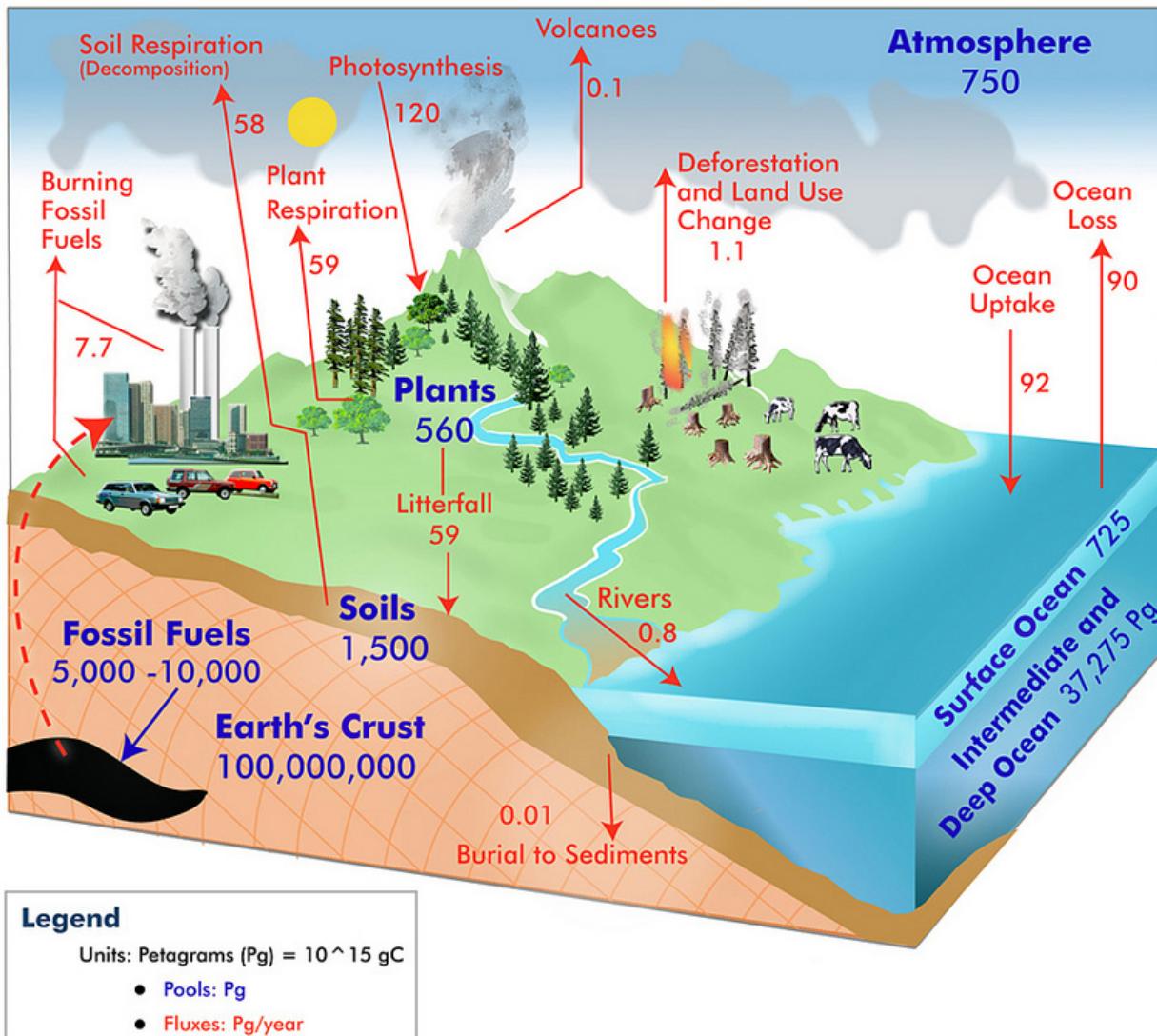
After this lecture, you would be able to

- construct and solve simple material (or mass) balance equations for different *environmental* and *engineering* systems
- 
- ✓ Environmental systems: Lake, river, air, etc.
  - ✓ Engineering systems: chemical reactor, treatment process, etc.

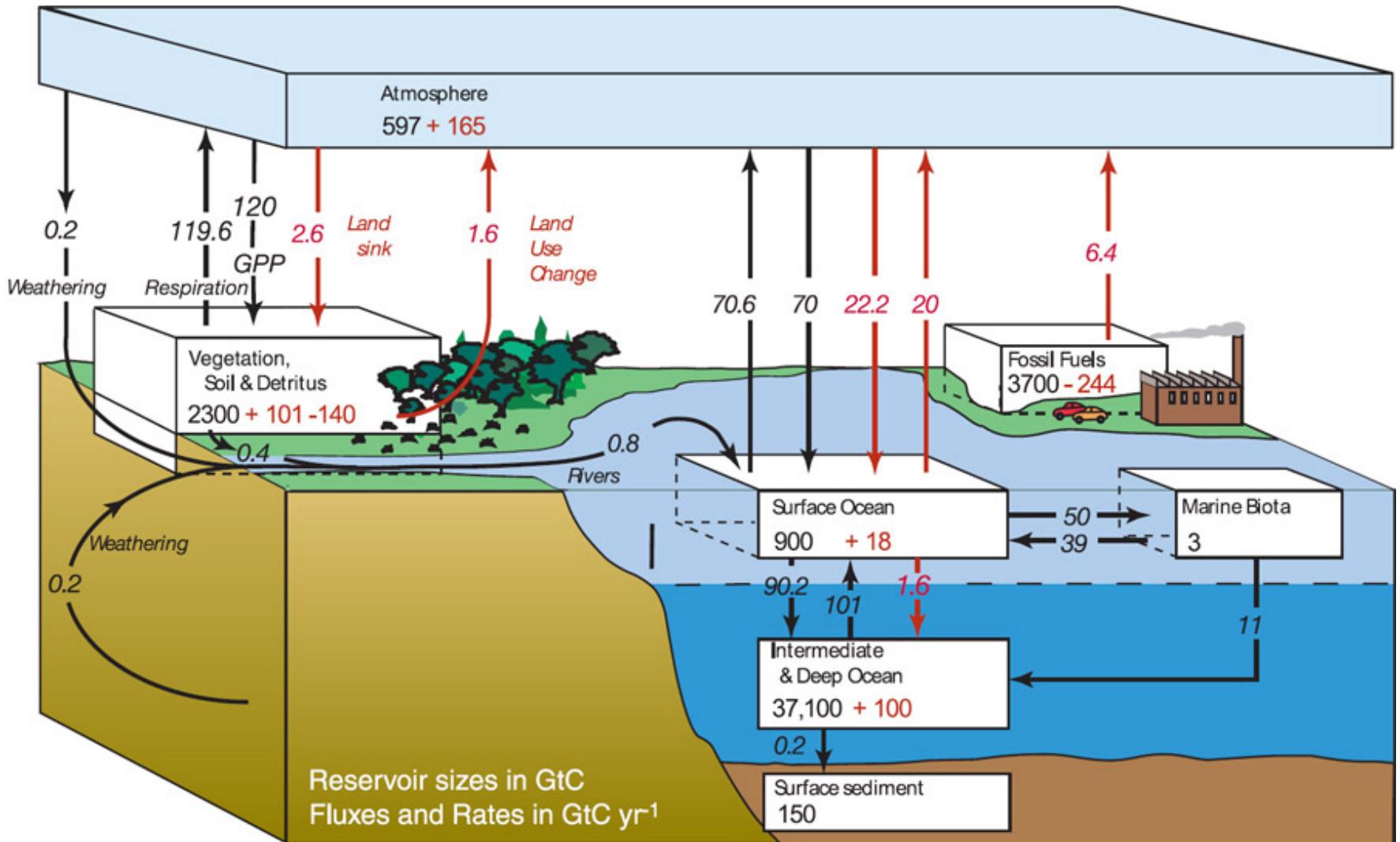
# What is material balance?

- Material balance is a key tool in *achieving quantitative understanding* of environmental and engineering systems (e.g. flow of materials into and out of the system).
- Material balance provides us with a tool for modeling the production, transport and fate of pollutants in environments and designing various treatment processes.

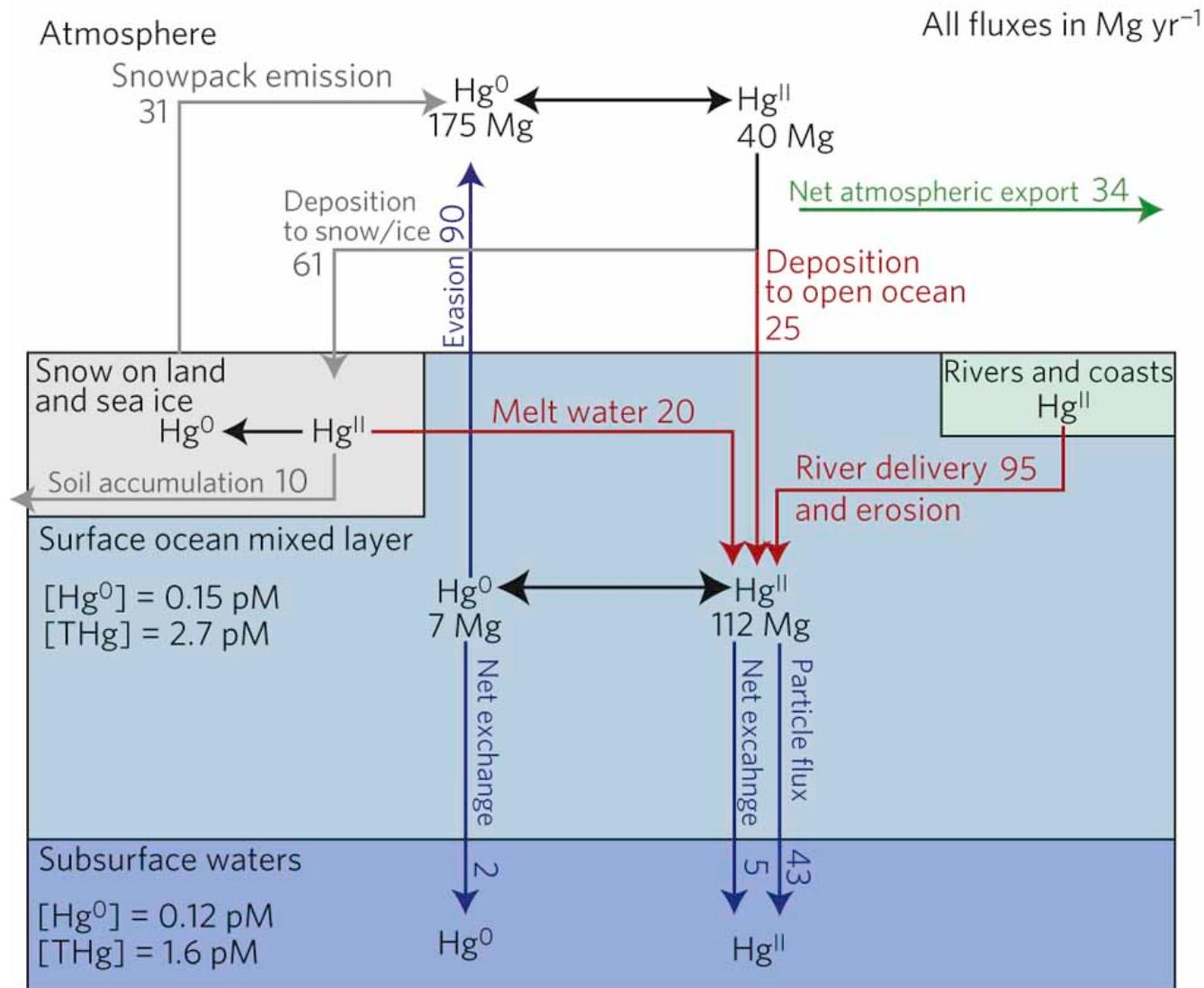
# Global carbon cycle (1)



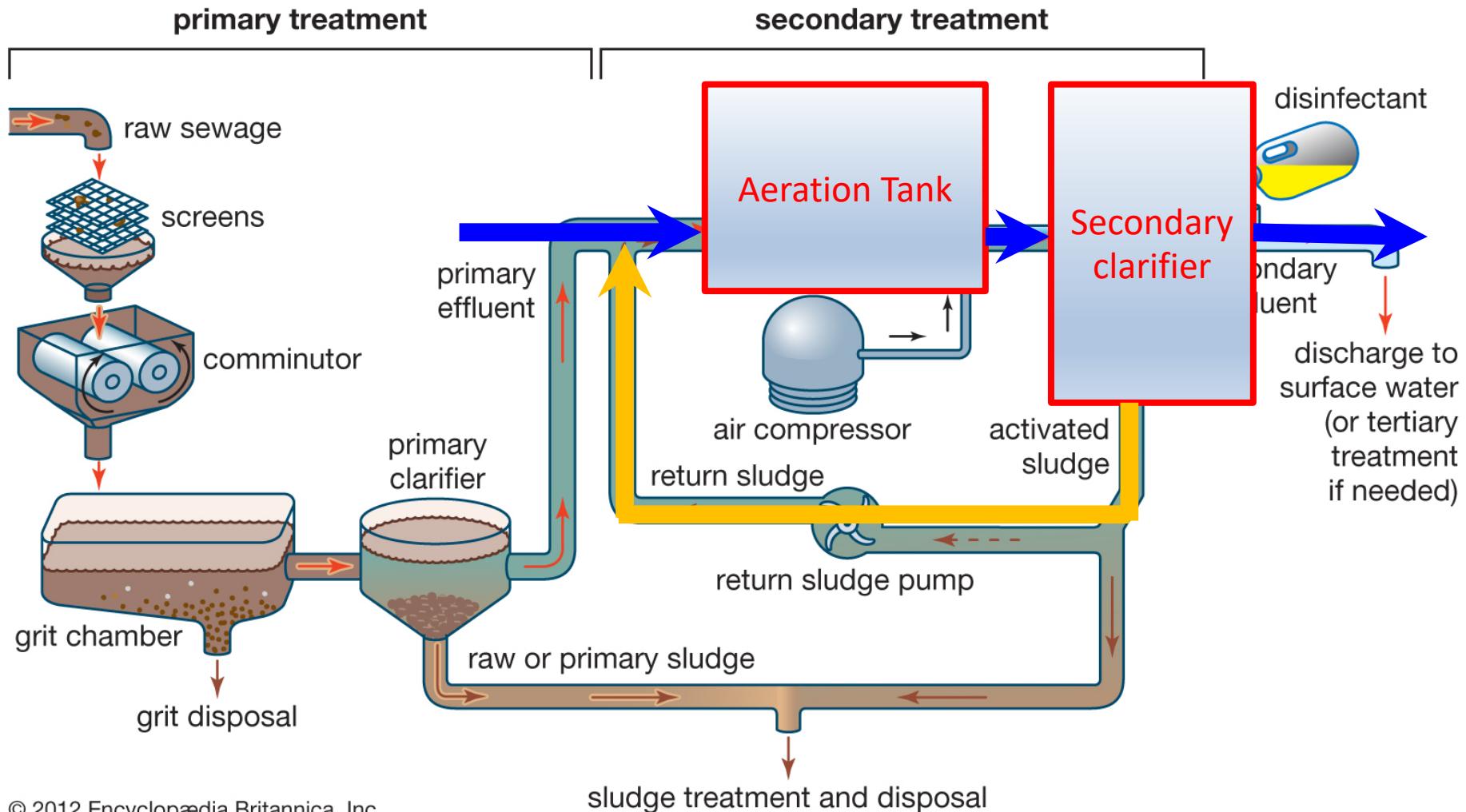
# Global carbon cycle (2)



# Fate & transport of pollutants - Mercury



# Wastewater treatment plant



# Basic theories

Conservation of matter: for material balance

- The law of conservation of matter states that *matter can neither be created or destroyed* (without nuclear reaction).

**“Everything has to go somewhere”**

Conservation of Energy: for energy balance

- The law of conservation of energy states that *energy cannot be created or destroyed.*

# Simple material balance equation

For a system without reactions,

$$\text{Accumulation} = \text{input} - \text{output}$$

where accumulation, input and output refer to the mass quantities accumulating, flowing into and out of the system (e.g. a pond, river, or a pollution control device), respectively.

$$\text{Accumulation Rate} = \text{input rate} - \text{output rate}$$

$$\frac{dM_{Acc}}{dt} = \frac{d(M_{in})}{dt} - \frac{d(M_{out})}{dt}$$

# I am thirsty!

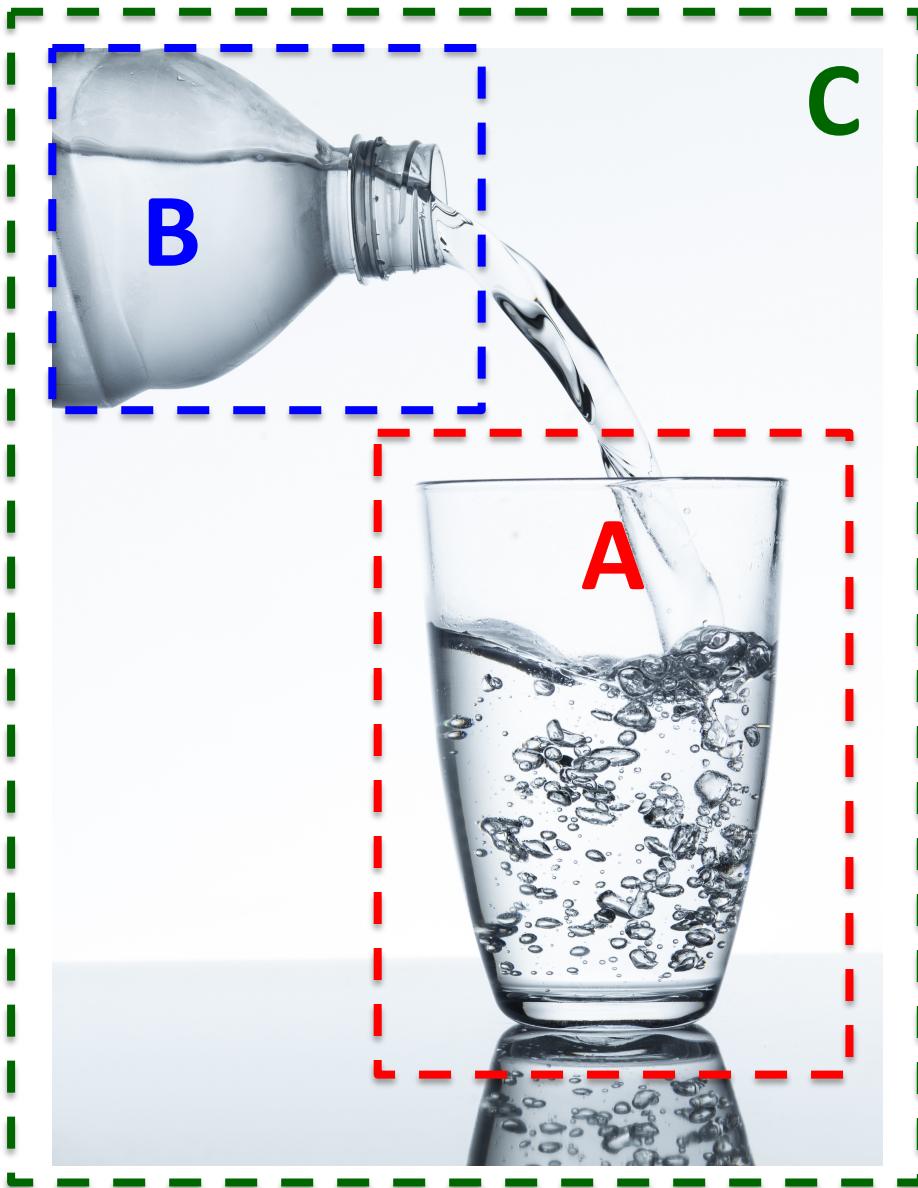


100g of water is transferred from a bottle to a glass. What is the mass accumulation in the system?

- A) 100 g
- B)-100 g
- C) 0 g



# I am thirsty!



C

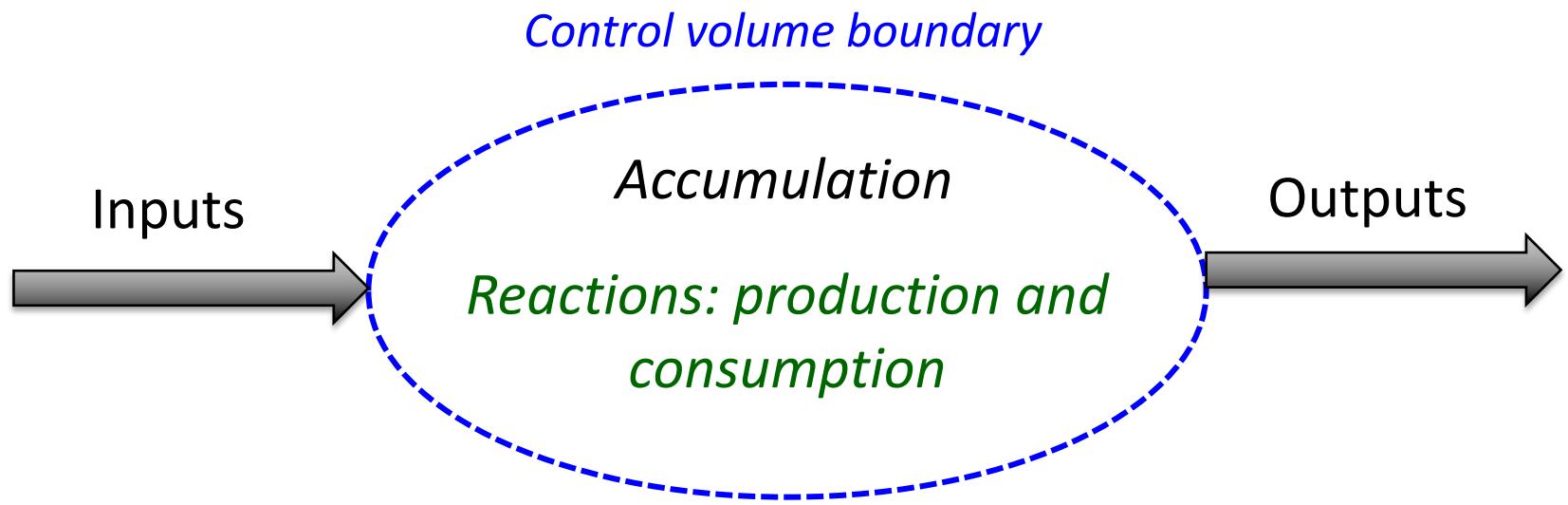
100g of water is transferred from a bottle to a glass. What is the mass accumulation in the system?

- A) 100 g
- B)-100 g
- C) 0 g



# Control volume

- The first step in mass balance analysis is to define the particular region (system boundary) in space that is to be analyzed. *The system within the boundaries is called the control volume.*



*Accumulation rate*

= *Input rate – Output rate + Production rate – Consumption rate*

# Material balance equation with a single material

*Basic mass balance equation:*

$$\left[ \begin{array}{c} \text{Mass per unit} \\ \text{time of } X \\ \text{ACCUMULATED} \end{array} \right] = \left[ \begin{array}{c} \text{Mass per unit} \\ \text{time of } X \\ \text{IN} \end{array} \right] - \left[ \begin{array}{c} \text{Mass per unit} \\ \text{time of } X \\ \text{OUT} \end{array} \right] + \left[ \begin{array}{c} \text{Mass per unit} \\ \text{time of } X \\ \text{PRODUCED} \end{array} \right] - \left[ \begin{array}{c} \text{Mass per unit} \\ \text{time of } X \\ \text{CONSUMED} \end{array} \right]$$

*if density of X remains constant*

$$\left[ \begin{array}{c} \text{Volume per unit} \\ \text{time of } X \\ \text{ACCUMULATED} \end{array} \right] = \left[ \begin{array}{c} \text{Vol. per unit} \\ \text{time of } X \\ \text{IN} \end{array} \right] - \left[ \begin{array}{c} \text{Vol. per unit} \\ \text{time of } X \\ \text{OUT} \end{array} \right] + \left[ \begin{array}{c} \text{Vol. per unit} \\ \text{time of } X \\ \text{PRODUCED} \end{array} \right] - \left[ \begin{array}{c} \text{Vol. per unit} \\ \text{time of } X \\ \text{CONSUMED} \end{array} \right]$$

*In terms of rate*

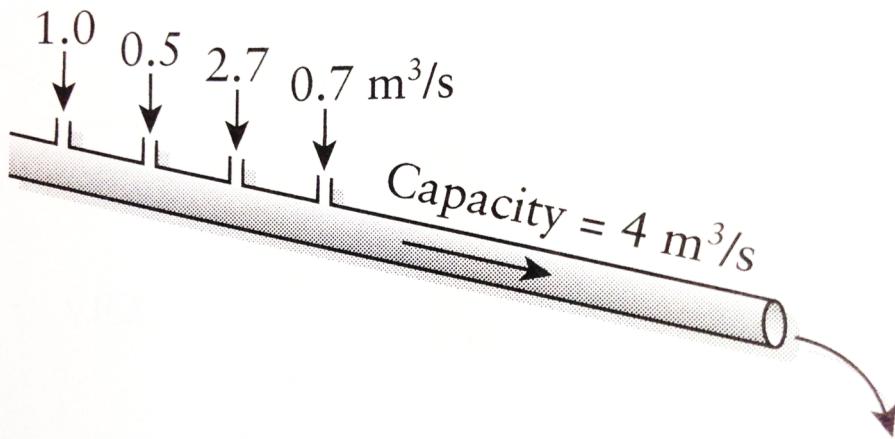
$$\left[ \begin{array}{c} \text{Rate} \\ \text{of } X \\ \text{ACCUMULATED} \end{array} \right] = \left[ \begin{array}{c} \text{Rate} \\ \text{of } X \\ \text{IN} \end{array} \right] - \left[ \begin{array}{c} \text{Rate} \\ \text{of } X \\ \text{OUT} \end{array} \right] + \left[ \begin{array}{c} \text{Rate} \\ \text{of } X \\ \text{PRODUCED} \end{array} \right] - \left[ \begin{array}{c} \text{Rate} \\ \text{of } X \\ \text{CONSUMED} \end{array} \right]$$

# Example (1)

**Example:** A trunk sewer has a flow capacity of  $4.0 \text{ m}^3/\text{s}$ . If the flow to the sewer is exceeded, it will not be able to transmit all the sewage through the pipe.

Currently, three neighborhoods contribute to the sewer, and the peak flows are  $1.0$ ,  $0.5$ , and  $2.7 \text{ m}^3/\text{s}$ . A builder wants to construct a house that will contribute a maximum flow of  $0.7 \text{ m}^3/\text{s}$ . to the trunk sewer.

Would this cause the sewer to exceed its capacity?



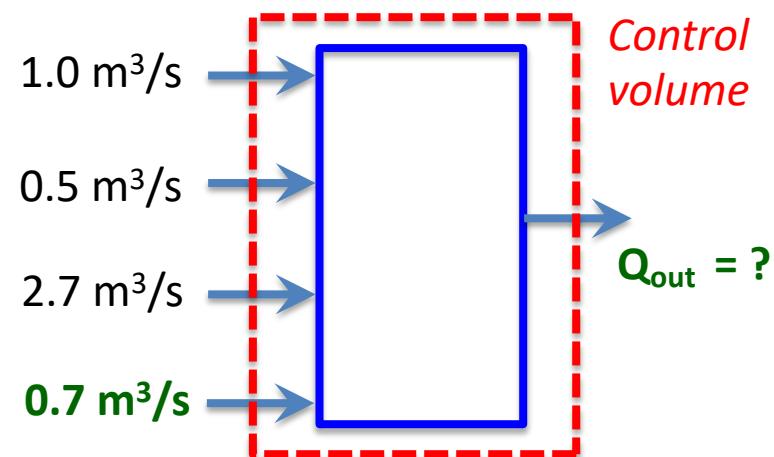
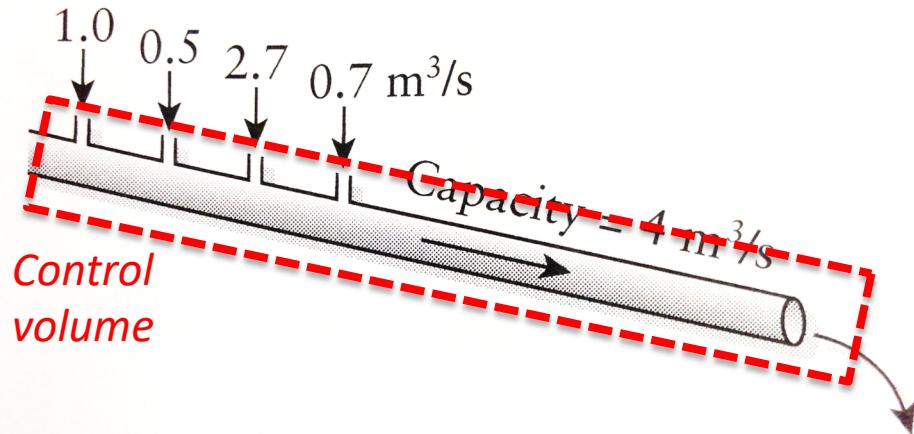
# Example (1)

- Solution:**
1. Define control volume (draw a block diagram)
  2. Assume: the densities of sewage in each flow are the same
  3. Set up the mass balance equation in terms of  $\text{m}^3/\text{s}$

$$[\text{Volume of sewage}]_{\text{ACCUMULATED}} = [\text{Volumetric flow of sewage IN}] - [\text{Volumetric flow of sewage OUT}] + [\text{Volume of sewage PRODUCED/COMSUMED}]$$

$$[\text{Volumetric flow of sewage OUT}] = [\text{Volumetric flow of sewage IN}]$$

$$Q_{\text{out}} = 1.0 + 0.5 + 2.7 + 0.7 = 4.9 \text{ m}^3\text{s}^{-1} > 4.0 \text{ m}^3\text{s}^{-1}$$



# I want to take a bath!

**Example:** Alex is filling his bathtub but he forgot to put the plug in. If the volume of water for a both is  $0.350 \text{ m}^3$  and the tap is flowing at  $1.32 \text{ L/min}$  and drain is running at  $0.32 \text{ L/min.}$ , **how long will it take to fully fill the bathtub?** Assume the density of water remains constant.



# Example (2)

- Solution:**
1. Define control volume (draw a block diagram)
  2. Given: the density of water remains constant
  3. Set up the mass balance equation

$$\text{Mass} = (\text{Volume}) (\text{density}) = V(\rho)$$

$$\text{Volume} = (\text{flow rate})(\text{time}) = Q(t)$$

$$\text{Unit conversion: } 0.350 \text{ m}^3 = 350 \text{ L}$$

Mass balance equation:

$$V(\rho) = Q_{in}(\rho)(t) - Q_{out}(\rho)(t)$$

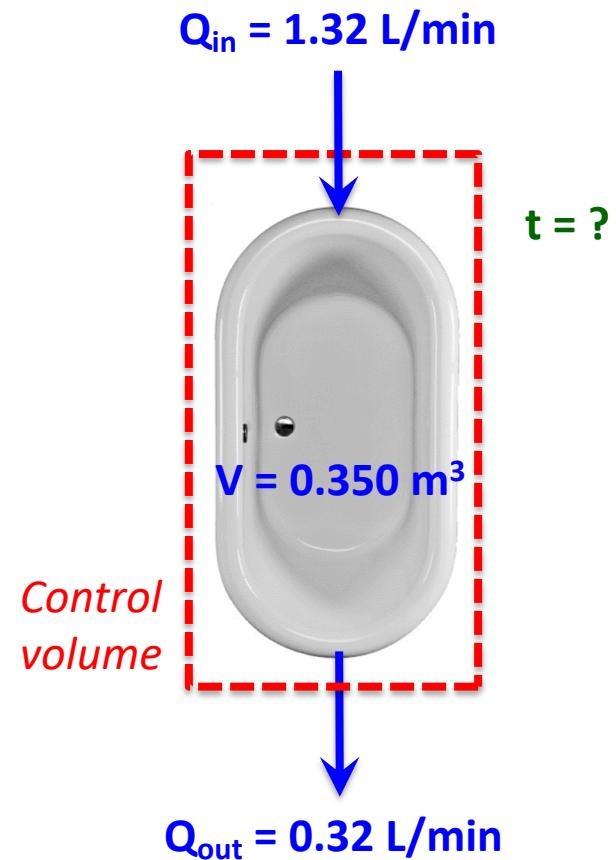
$$V = Q_{in}(t) - Q_{out}(t)$$

$$350 = 1.32(t) - 0.32(t)$$

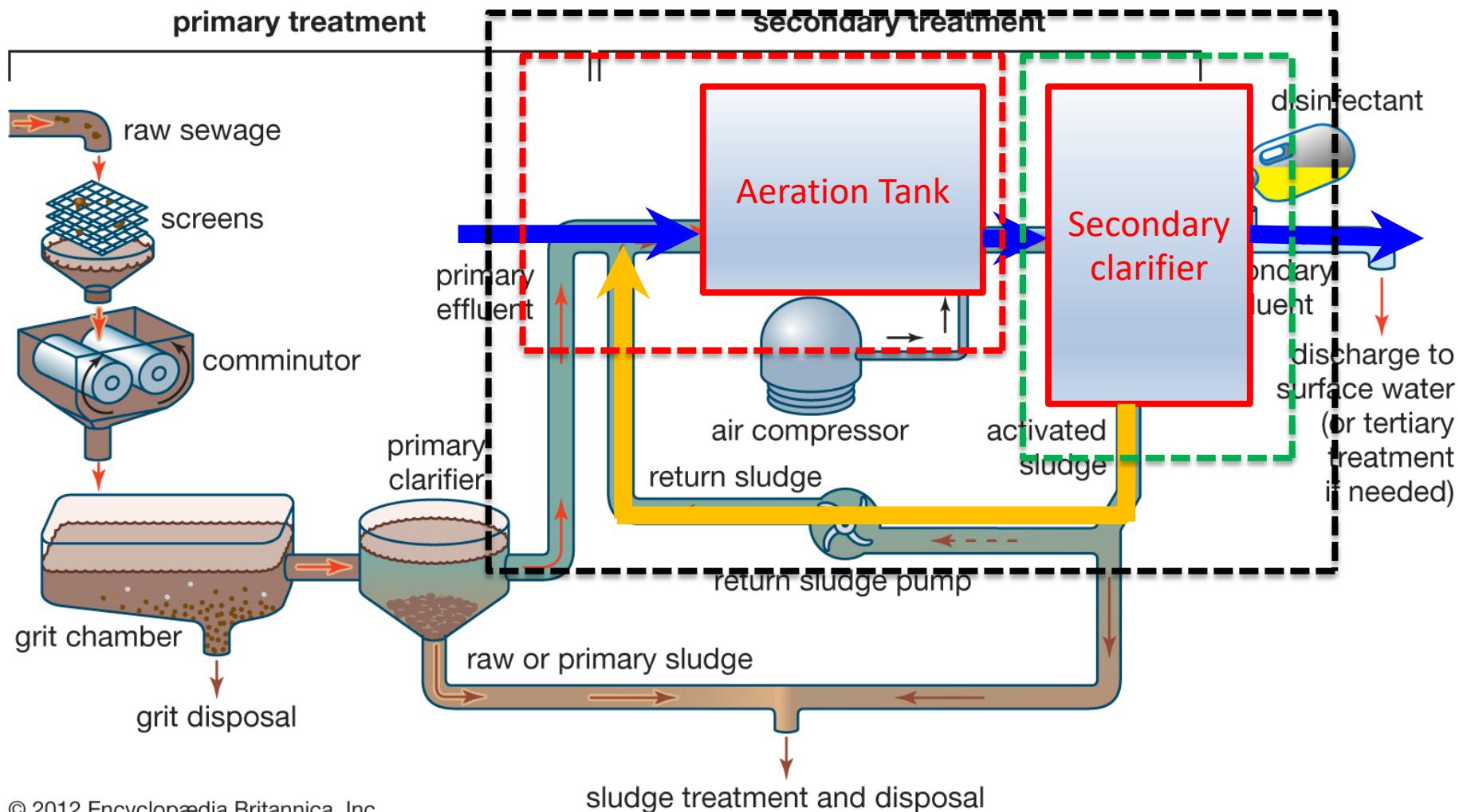
$$t = 350 \text{ min}$$

Volume of wasted water

$$= 0.32 \text{ L/min} (350 \text{ min}) = 112 \text{ L}$$



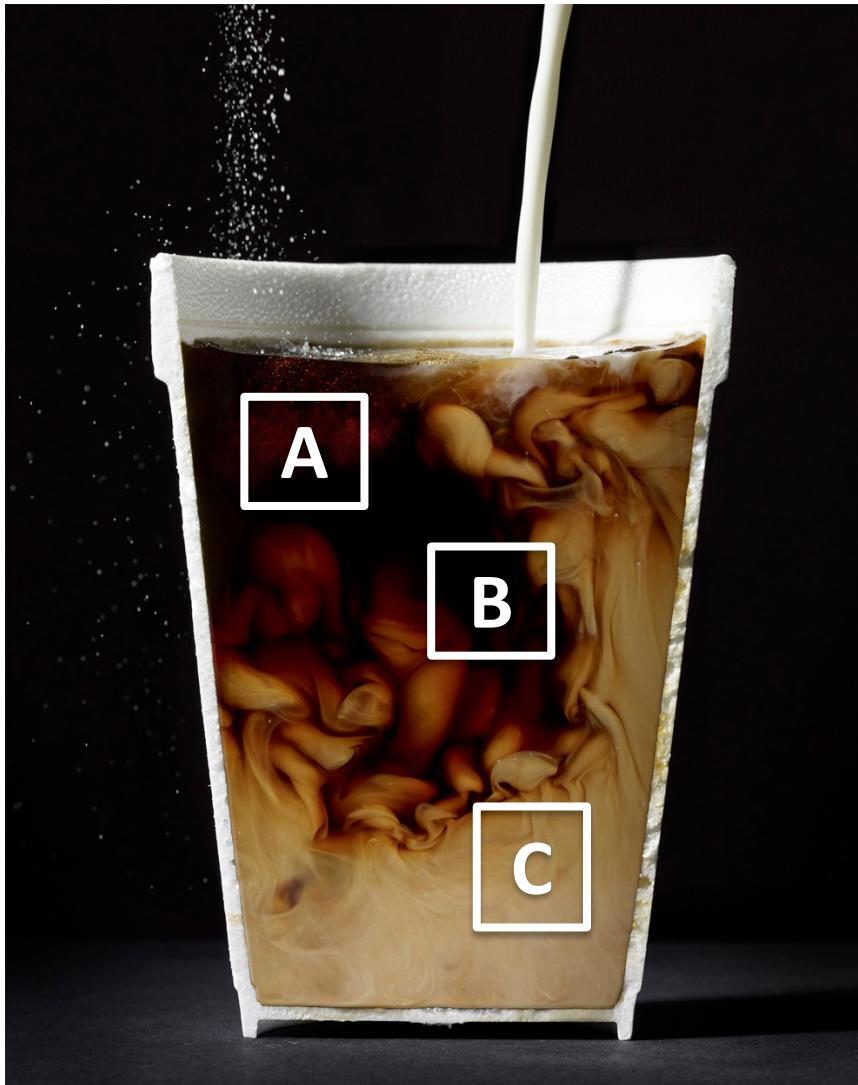
# Wastewater treatment plant



# General rules for solving material balance problems

1. Draw the system as a diagram, including all flows (inputs and outputs) as arrows.
2. Add the available information, such as flow rates and concentrations, and assign symbols to unknown variables.
3. Draw a continuous dashed line around the component or components that are to be balanced. This could be a unit operation, a junction, or a combination of these. Everything inside this dashed line becomes the black box.
4. Decide what material is to be balanced (Volumetric or mass flow rate).
5. Write the material balance equation.
6. If only one variable is unknown, solve for that variable.
7. If more than one variable is unknown, repeat the procedure, using a different black box or a different material for the same black box.

# I am still sleepy. I need coffee!



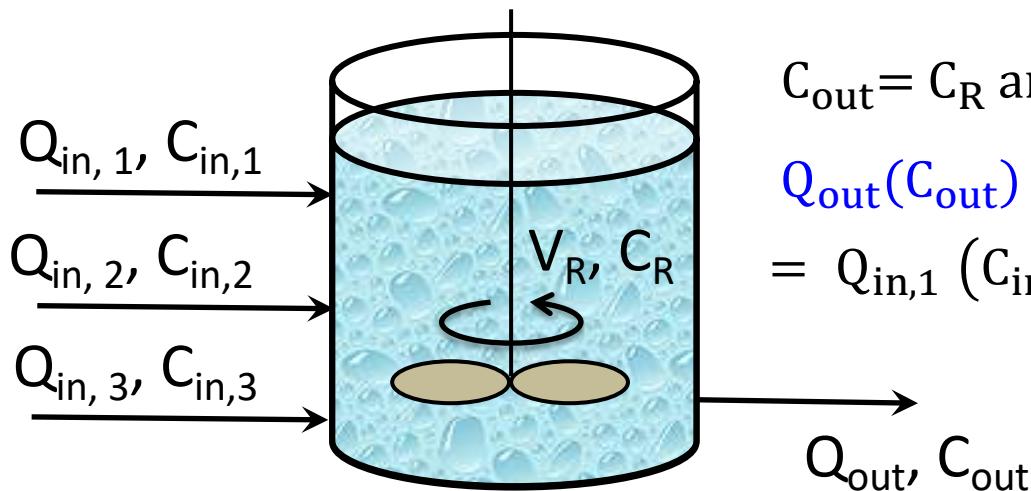
10 g of cream is added to 100 ml of black coffee. If I take a sample immediately at areas A, B and C, which is the best option to describe the system?

- A)  $C_A \approx C_B$
- B)  $C_B > C_C$
- C)  $C_C > C_A$



# State of mixing and steady state

- *Completely mixed system*: Every drop of fluid is homogeneous with every other drop (i.e. same material concentration and physical property). *The output is the same as the contents within the control volume.*
- *Steady state*: When the input and output rates are constant and equal, *the rate of accumulation is zero ( $dM/dt = 0$ ).*



$$C_{out} = C_R \text{ and } Q_{out} = \sum_{i=1}^n Q_{in,i}$$

$$\begin{aligned} Q_{out}(C_{out}) &= \sum_{i=1}^n Q_{in,i}(C_{in,i}) \\ &= Q_{in,1}(C_{in,1}) + Q_{in,2}(C_{in,2}) + Q_{in,3}(C_{in,3}) \end{aligned}$$

# Example (3)

**Exercise:** A storm sewer is carrying snow melt containing 1.2 g/L of sodium chloride (NaCl) into a small stream. The stream has naturally occurring NaCl concentration of 20 mg/L. If the storm sewer flow rate is 2000 L/min and stream flow rate is 2.0 m<sup>3</sup>/s, what is the concentration of NaCl in the stream after the discharge point?

**Solution:**

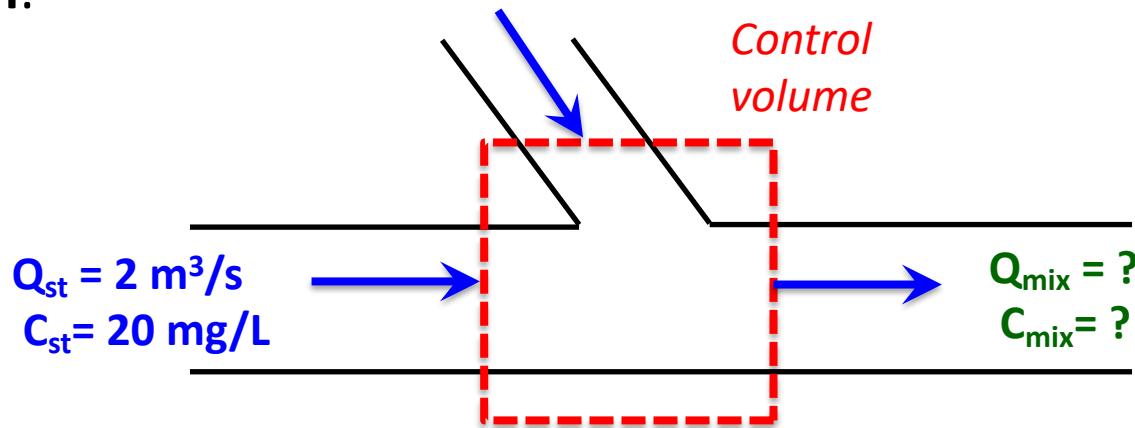
1. Define control volume (draw a block diagram)
2. Assumption: 1) completely mixed, 2) NaCl is a conservative substance, and 3) steady state
3. Set up the mass balance equation



# Example (3)

Solution:

$$Q_{se} = 2000 \text{ L/min}, C_{se} = 1.2 \text{ g/L}$$



Unit conversion:

$$C_{se} = (1.2 \text{ gL}^{-1})(1000 \text{ mg g}^{-1}) = 1200 \text{ mg L}^{-1}$$

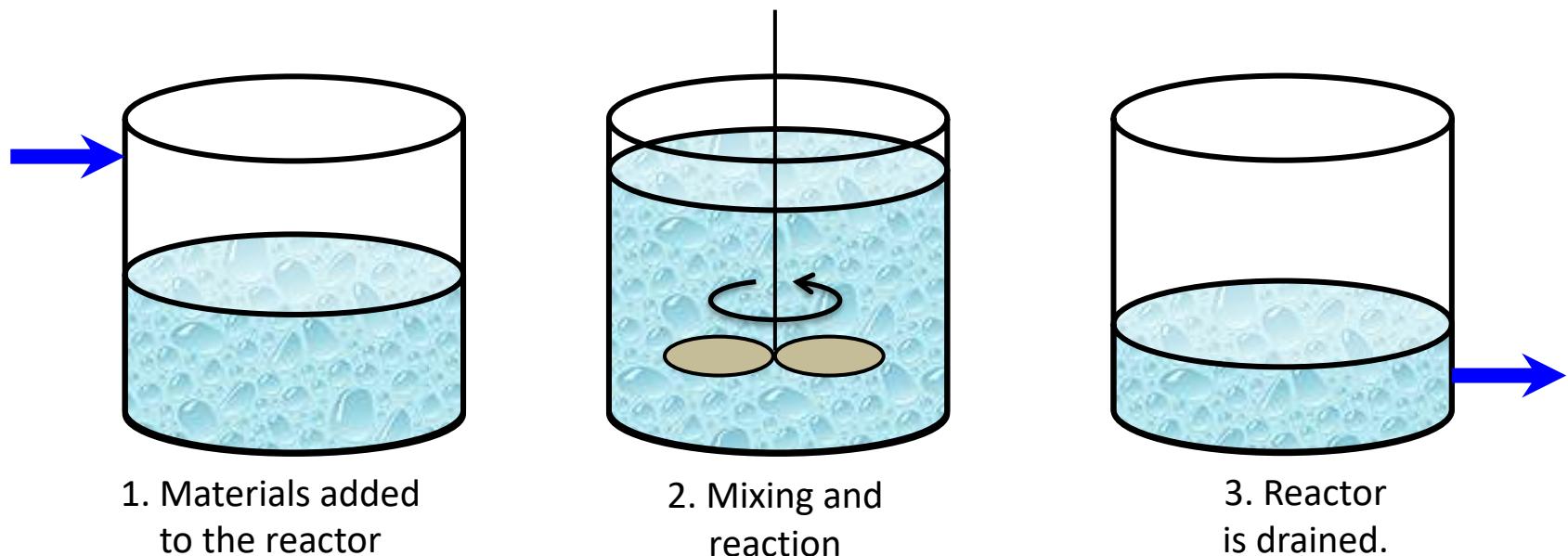
$$Q_{st} = 2 \text{ m}^3\text{s}^{-1}(1000 \text{ L m}^{-3})(60 \text{ s min}^{-1}) = 120,000 \text{ L min}^{-1}$$

$$Q_{mix} = Q_{se} + Q_{st} = 120,000 \text{ L min}^{-1} + 2000 \text{ L min}^{-1} = 122,000 \text{ L min}^{-1}$$

$$C_{mix} = \frac{C_{st}Q_{st} + C_{se}Q_{se}}{Q_{mix}} = \frac{20(120,000) + 1200(2000)}{122,000} = 39.34 \text{ mg L}^{-1}$$

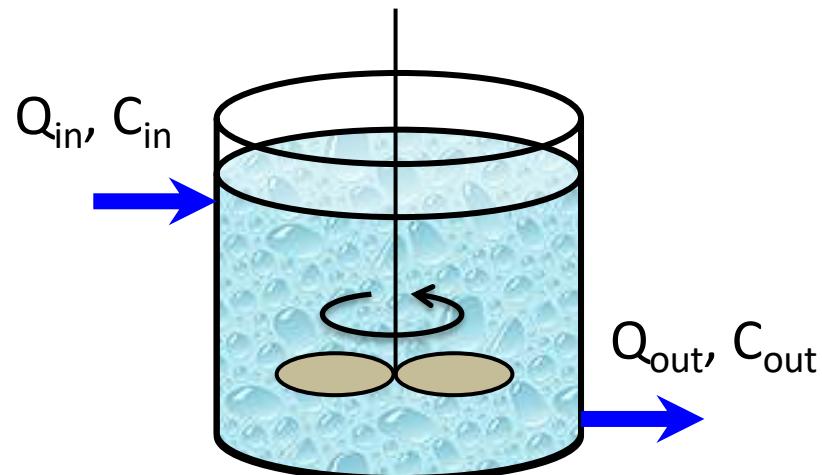
# Type of ideal reactors

- Many natural processes as well as engineered systems can be conveniently analyzed by using the notion of ideal reactors
  - 3 types of ideal reactors based on certain assumptions about their flow and mixing characteristics
1. *Batch reactor*: fully mixed and does not have flow into or out of the reactor (i.e.  $t$  increases, [pollutant] decreases)

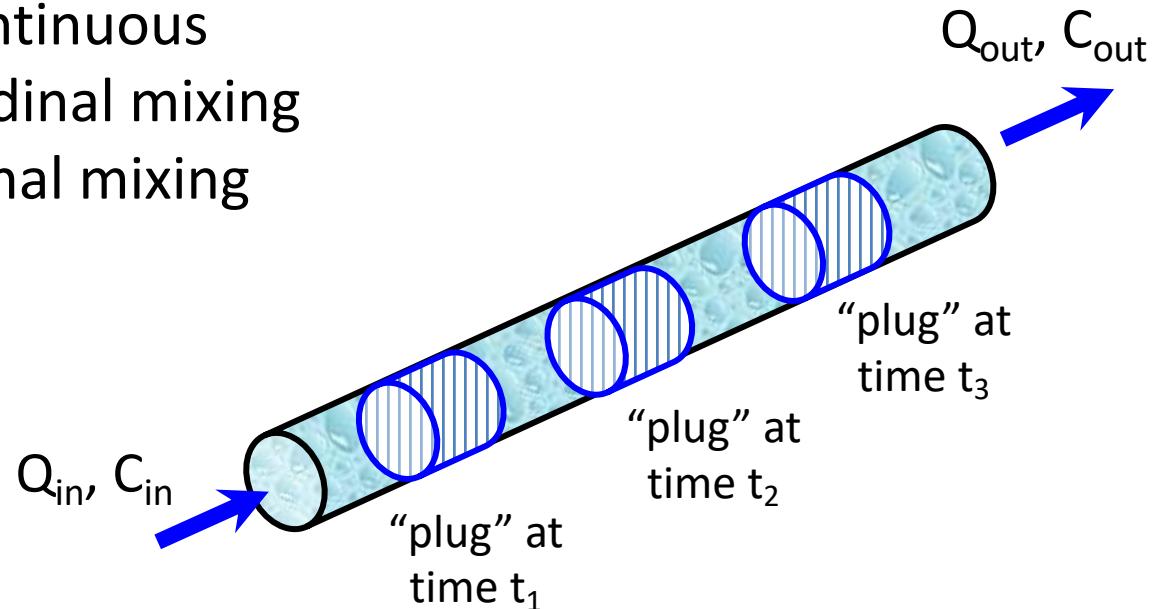


# Type of ideal reactors

- *Completely mixed-flow reactor* (CMFR, aka completely stirred tank reactor, CSTR): continuous operation and perfect mixing



- *Plug-flow reactor*: continuous operation, no longitudinal mixing but complete latitudinal mixing



# Retention time

- For time-dependent reactions, the time that fluid remains in the reactor obviously affects the degree to which the reaction goes to completion.
- In ideal reactors, the average time of species in the reactor (retention time) is defined as

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

where       $\theta$  = theoretical retention time (s)  
 $V$  = volume of fluid in reactor ( $m^3$ )  
 $Q$  = volumetric flow rate into reactor ( $m^3 s^{-1}$ )

# Reaction kinetics

- Most chemical and biochemical reaction rates can be approximated as either *zero, first, or second-order reaction rate*. (more detail in the section of chemical principles)



$$\text{overall reaction rate: } r = -\frac{r_A}{a} = -\frac{r_B}{b} = \frac{r_C}{c}$$

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

where k = rate constant, n = reaction order

Reaction Order	Rate Expression	Units on Rate Constant
Zero	$r_A = -k$	(concentration)(time) $^{-1}$
First	$r_A = -k[A]$	(time) $^{-1}$
Second	$r_A = -k[A]^2$	(concentration) $^{-1}$ (time) $^{-1}$

# Batch system – Zero-order decay

- Note: Laboratory experiments are often conducted in batch reactors because they are inexpensive and easy to build.
- Zero-order reaction: Many changes in nature occur at a constant rate

$$\mathbf{r} = -\mathbf{k}$$

where  $k$  = zero-order reaction rate constant ( $\text{g L}^{-1} \text{s}^{-1}$ )

Accumulation = Inputs – Outputs + Production – Consumption

$$\frac{dM}{dt} = -kV \quad \Rightarrow \quad V \frac{dC}{dt} = -Vk$$

$$\int_{C_0}^{C_t} dC = -k \int_0^t dt \quad \Rightarrow \quad C_t - C_0 = -kt \quad \Rightarrow \quad C_t = C_0 - kt$$

# Batch system – first-order decay

- First-order reaction: the change of concentration is proportional to the concentration itself

$$\mathbf{r} = -kC$$

where  $k$  = first-order reaction rate constant ( $s^{-1}$ )

$$\frac{dM}{dt} = -kVC \quad \Rightarrow \quad V \frac{dC}{dt} = -VkC$$

$$\int_{C_0}^{C_t} \frac{1}{C} dC = -k \int_0^t dt$$

$$\ln\left(\frac{C_t}{C_0}\right) = -kt \quad \Rightarrow \quad \ln(C_t) = \ln(C_0) - kt \quad \text{or} \quad C_t = C_0 e^{-kt}$$

# Batch system – second-order decay

- Second-order reaction: the change of concentration is proportional to the square of the component

$$r = -kC^2$$

where  $k$  = second-order reaction rate constant (  $\text{g}^{-1} \text{ L s}^{-1}$  )

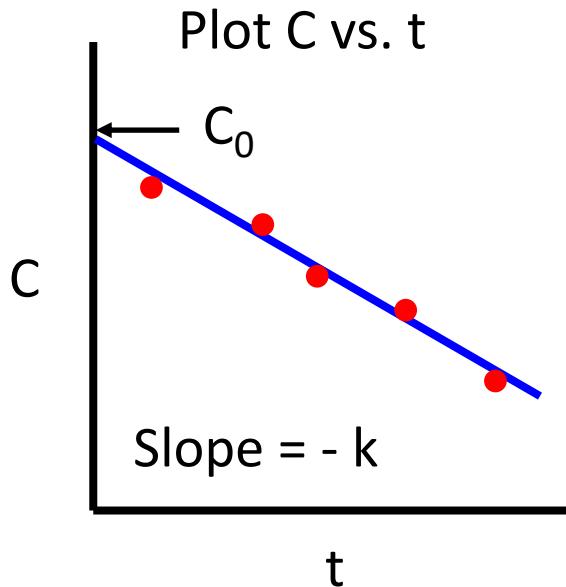
$$\frac{dM}{dt} = -kVC^2 \quad \Rightarrow \quad V \frac{dC}{dt} = -VkC^2$$
$$\int_{C_0}^{C_t} \frac{1}{C^2} dC = -k \int_0^t dt$$

$$\frac{1}{C_t} = \frac{1}{C_0} + kt \quad \text{or} \quad C_t = \frac{C_0}{1 + C_0 kt}$$

# Batch system – Different orders of decay

Zero-order decay

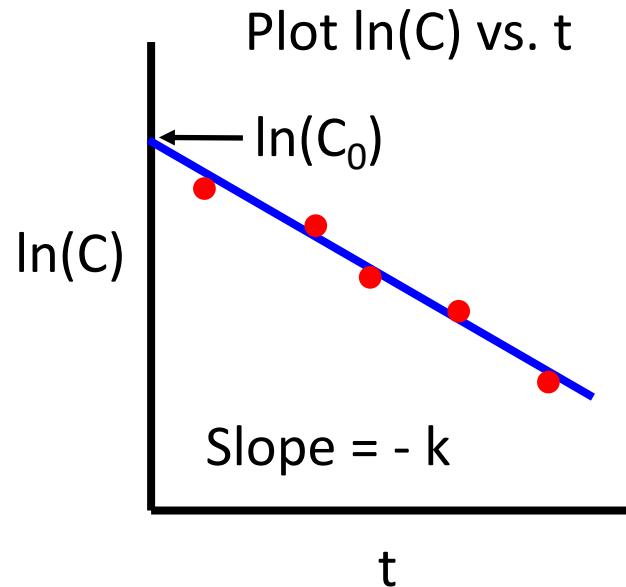
$$C_t = C_0 - kt$$



$$\text{Half-life } t_{1/2} = \frac{C_0}{2k}$$

First-order decay

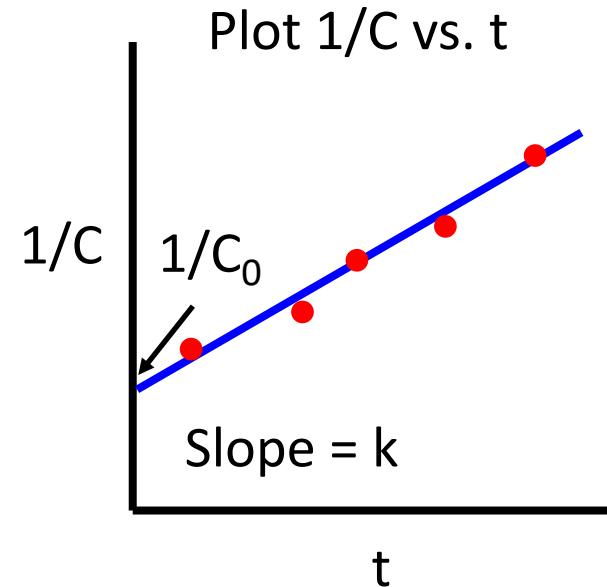
$$\ln(C_t) = \ln(C_0) - kt$$



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

Second-order decay

$$\frac{1}{C_t} = \frac{1}{C_0} + kt$$

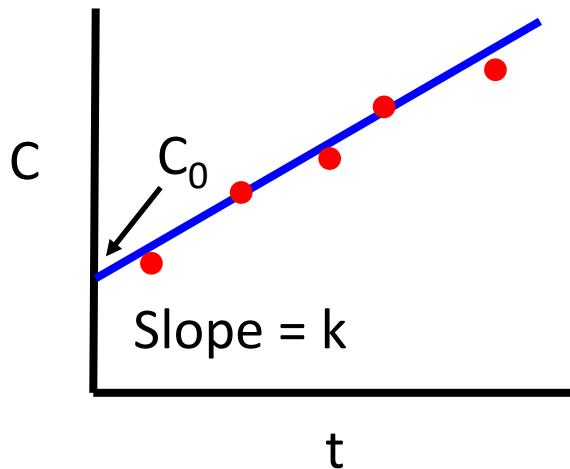


$$t_{1/2} = \frac{1}{kC_0}$$

# Batch system – Different orders of production

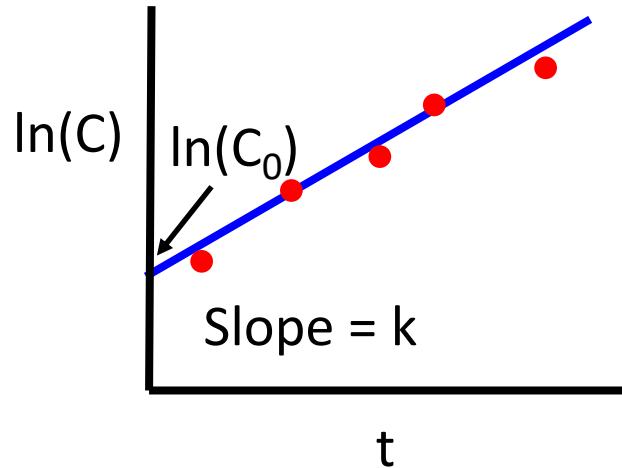
Zero-order production

$$C_t = C_0 + kt$$



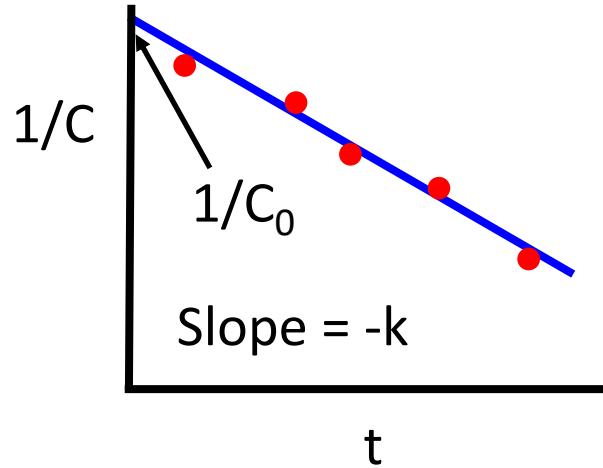
First-order production

$$\ln(C_t) = \ln(C_0) + kt$$



Second-order production

$$\frac{1}{C_t} = \frac{1}{C_0} - kt$$



Plotting Procedure to Determine Order of Reaction by Method of Integration

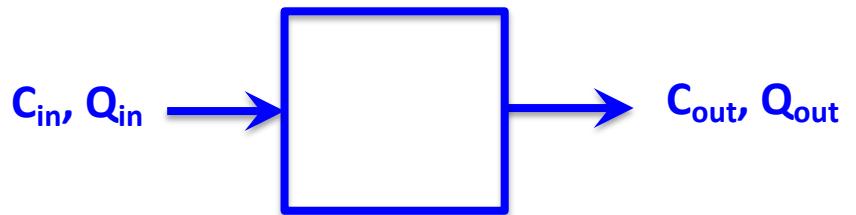
Order	Rate Equation	Integrated Equation	Linear Plot	Slope	Intercept
0	$d[A]/dt = -k$	$[A] - [A]_0 = -kt$	$[A]$ vs. $t$	$-k$	$[A]_0$
1	$d[A]/dt = -k[A]$	$\ln[A]/[A]_0 = -kt$	$\ln[A]$ vs. $t$	$-k$	$\ln[A]_0$
2	$d[A]/dt = -k[A]^2$	$1/[A] - 1/[A]_0 = kt$	$1/[A]$ vs. $t$	$k$	$1/[A]_0$

# Efficiency

- The effectiveness of an environmental process in removing a contaminant can be determined using the mass balance.

$$\frac{dM}{dt} = C_{in}Q_{in} - C_{out}Q_{out}$$

$$\frac{dM/dt}{C_{in}Q_{in}} = \frac{C_{in}Q_{in} - C_{out}Q_{out}}{C_{in}Q_{in}}$$



where    C<sub>in</sub>, C<sub>out</sub> = concentrations of contaminant into and out of the process  
            Q<sub>in</sub>, Q<sub>out</sub> = flow rate into and out of the process

$$\text{Efficiency} = \eta = \frac{M_{in} - M_{out}}{M_{in}} (100\%)$$

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} (100\%) \quad \text{if } Q_{in} = Q_{out}$$

# Example (4)

**Example:** A contaminated soil is to be excavated and treated in a completely mixed aerated lagoon at a Superfund site. To determine the time it will take to treat the contaminated soil, a laboratory completely mixed batch reactor is used to gather the following data.

Assuming a first-order reaction, estimate the rate constant,  $k$ , and determine the time to achieve 99% reduction in the original concentration.

Time (day)	Waste Concentration (mg L <sup>-1</sup> )
1	280
16	132



# Example (4)

Solution:

Time interval:  $t = 16 - 1 = 15$  days

$$C_t = C_0 e^{-kt} \Rightarrow \frac{132 \text{ mg L}^{-1}}{280 \text{ mg L}^{-1}} = \exp[-k(15d)] \Rightarrow 0.4714 = \exp[-k(15)]$$

Taking the natural logarithm (base e) of both sides of the equation, we obtain

$$\begin{aligned}-0.7520 &= -k(15) \\ k &= 0.05 \text{ d}^{-1}\end{aligned}$$

To achieve 99% reduction,  $C_t = 0.01(C_0)$       Recall:  $\eta = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} (100\%)$

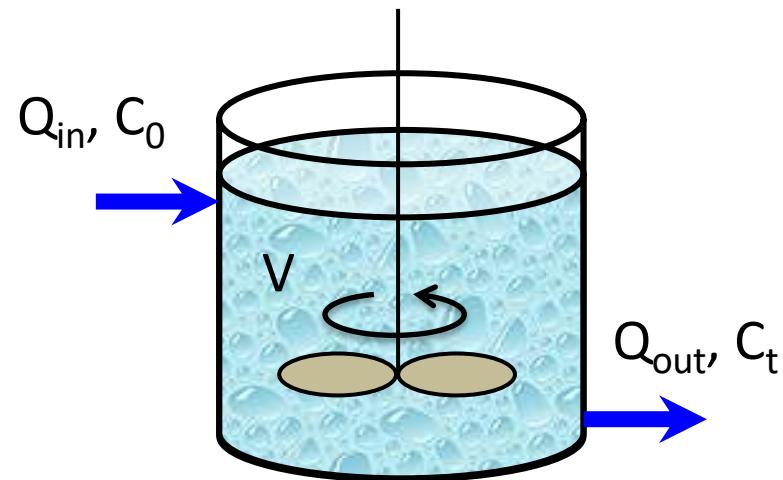
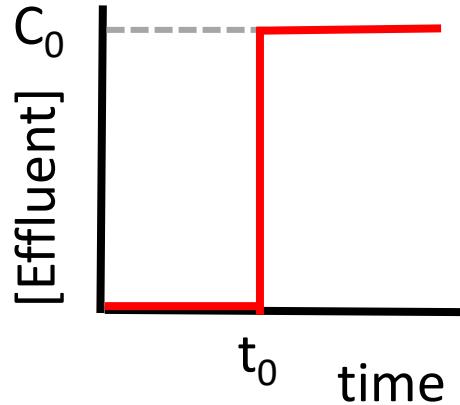
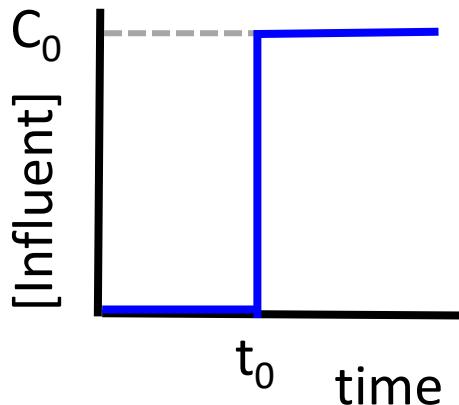
$$C_t = C_0 e^{-kt} \Rightarrow 0.01 = \exp[-0.05(t)]$$

Taking the logarithm of the both sides and solving for t, we get

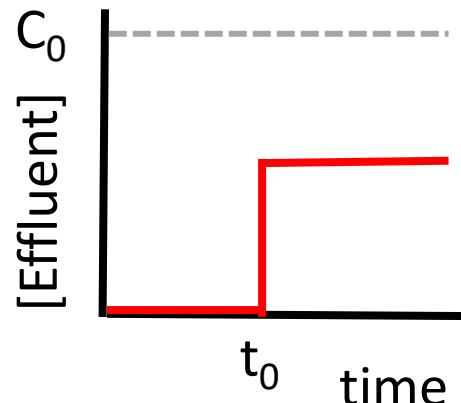
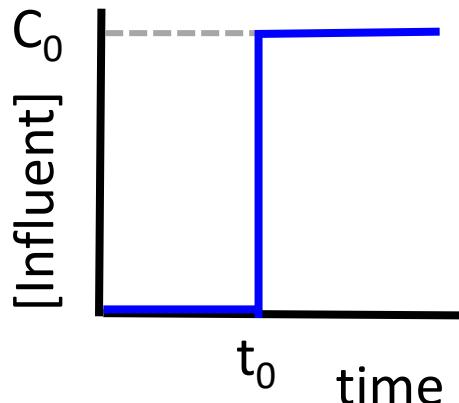
$$t = 92 \text{ days}$$

# Step response – CMFR (Steady state)

- NO reactions & steady state ( $C_{in} = C_{out}$ )



- First-order decay & steady state ( $C_{in} > C_{out}$ )



$$\frac{dM}{dt} = C_0 Q_{in} - C_t Q_{out} - k C_t V$$

$$\frac{dC}{dt} = \frac{1}{\theta} (C_0 - C_t) - k C_t$$

$$C_t = \frac{C_0}{1 + k\theta} \quad \text{and} \quad \theta = \frac{V}{Q_{in}}$$

$$\text{if } \theta = \frac{1}{k} \Rightarrow C_t = \frac{1}{2} C_0$$

# Step response – CMFR (non-steady state)

Assume first-order decay and zero-order production of a pollutant in the environment

$$V \frac{dC}{dt} = QC_{in} - QC - k_d V C + k_g V$$

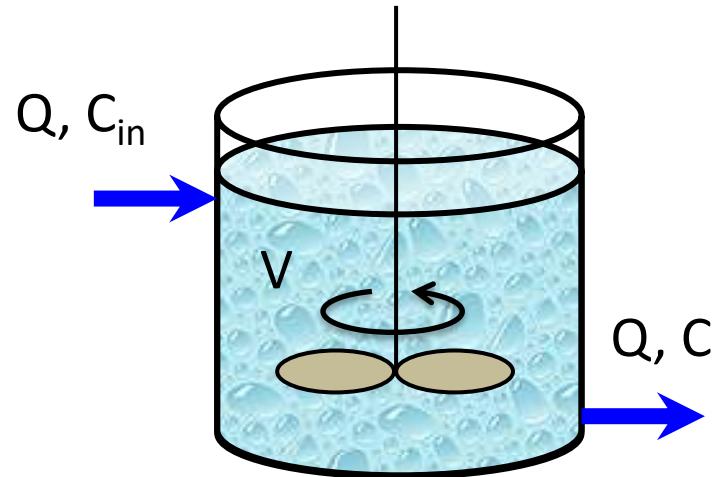
Steady state solution, at  $t = \infty$ ,

$$QC_{in} - QC_{\infty} - k_d V C_{\infty} + k_g V = 0$$

$$C_{\infty} = \frac{QC_{in} + k_g V}{Q + k_d V}$$

Non-steady state solution

$$\frac{dC}{dt} = - \left( \frac{Q}{V} + k_d \right) \left( C - \frac{QC_{in} + k_g V}{Q + k_d V} \right) \Rightarrow \frac{dC}{dt} = - \left( \frac{Q}{V} + k_d \right) (C - C_{\infty})$$



$k_d$  = First-order decay rate const.

$k_g$  = Zero-order production rate const.

# Step response – CMFR (non-steady state)

To solve this differential equation: make a change of variable

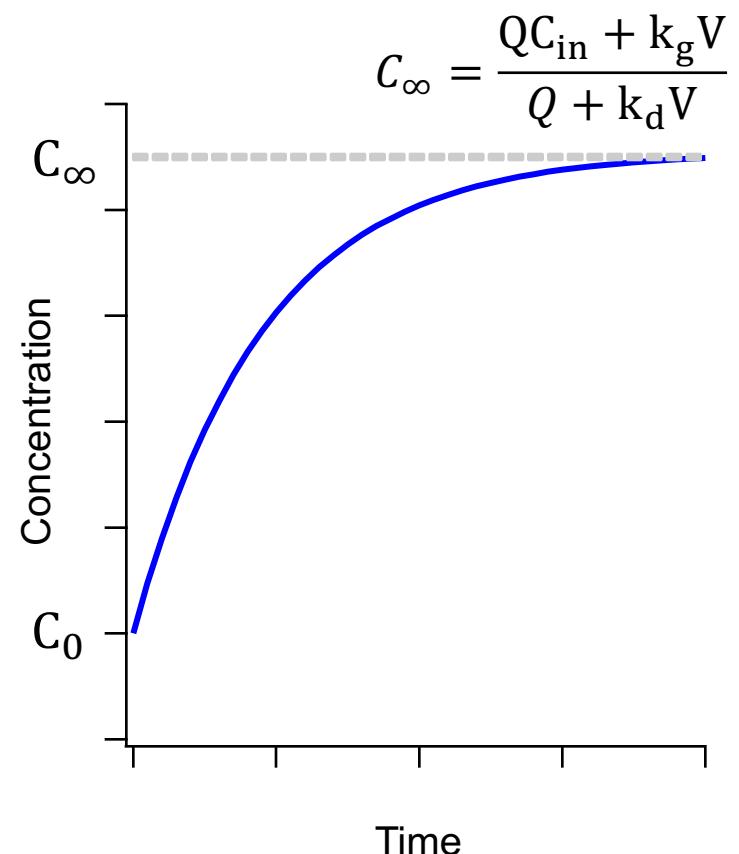
$$y = C - C_\infty \Rightarrow \frac{dy}{dt} = \frac{dC}{dt} \Rightarrow \frac{dy}{dt} = -\left(\frac{Q}{V} + k_d\right)y$$

$$\int_{y_0}^y \frac{1}{y} dy = -\left(\frac{Q}{V} + k_d\right) \int_0^t dt$$

$$y = y_0 \exp \left[ -\left( k_d + \frac{Q}{V} \right) t \right]$$

At time = 0,  $y = C_0 - C_\infty$

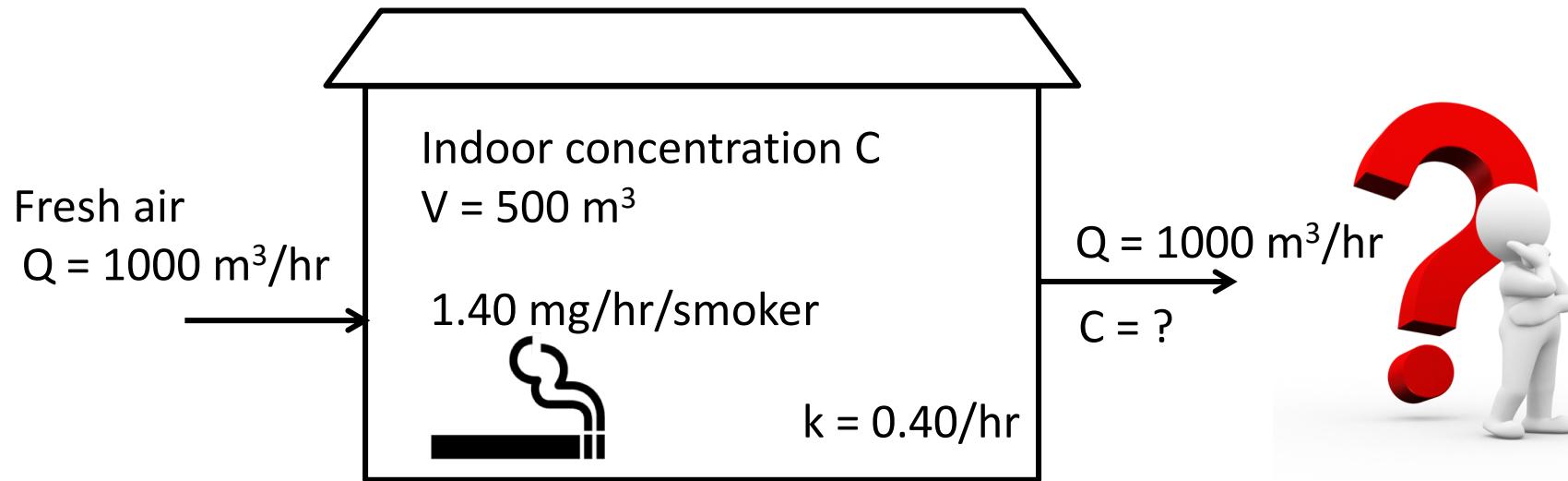
$$C_t = C_\infty + (C_0 - C_\infty) \exp \left[ -\left( k_d + \frac{Q}{V} \right) t \right]$$



# Arr...I am not a smoker, but please solve this

**Example:** A bar with volume  $500 \text{ m}^3$  has 50 smokers in it, each smoking 2 cigarettes per hour. An individual cigarette emits, among other things, about 1.4 mg of formaldehyde (HCHO).

Formaldehyde converts to carbon dioxide with a reaction rate coefficient  $k = 0.40/\text{hr}$ . Fresh air enters the bar at the rate of  $1,000 \text{ m}^3/\text{hr}$ , and stale air leaves at the same rate. Assuming complete mixing, estimate the steady-state concentration of formaldehyde in the air. How does the result compare with the threshold for eye irritation of  $0.06 \text{ mg/m}^3$ ?



# Example (5)

**Solution:** Accumulation= Inputs – Outputs + Production – Decay

$$\frac{dM}{dt} = C_0 Q_{in} - C_t Q_{out} + P - kC_t V$$

$$C_t Q_{out} = P - kC_t V$$

$$P = 50 \text{ smokers} \times 2 \frac{\text{cigs}}{\text{hr}} \times \frac{1.4 \text{ mg}}{\text{cig}} = 140 \text{ mg/hr}$$

$$C_t = \frac{P}{Q_{out} + kV} = \frac{140 \text{ mg/hr}}{1,000 \text{ m}^3/\text{hr} + (0.40/\text{hr}) \times 500 \text{ m}^3} = 0.117 \text{ mg/m}^3$$

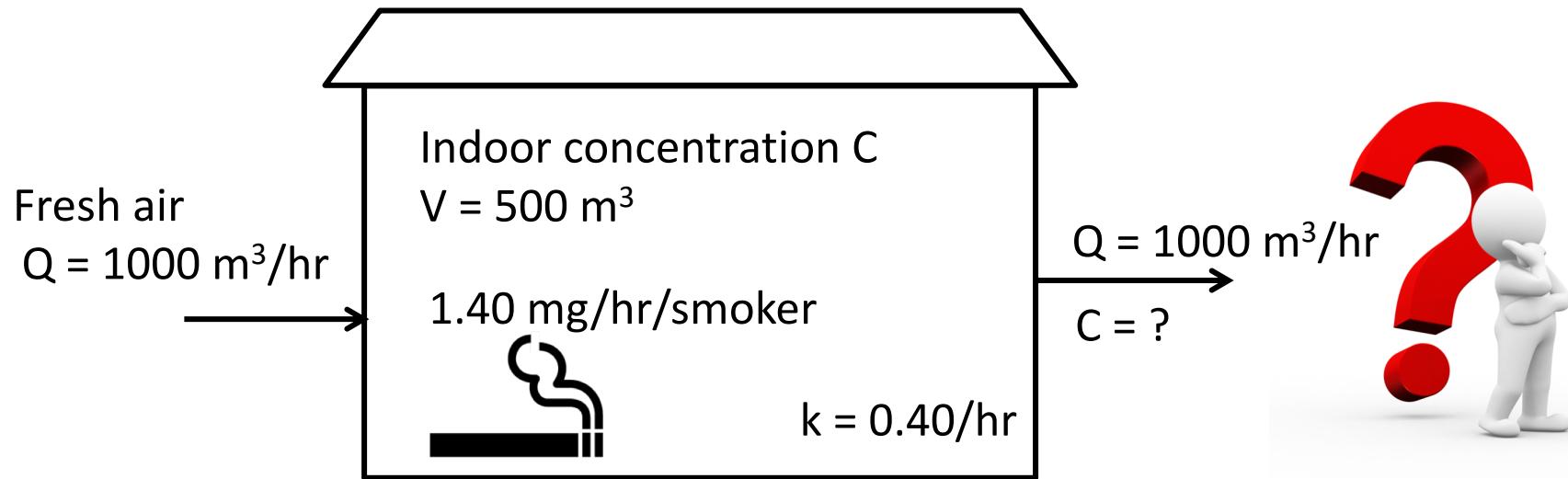
This is nearly double the 0.06 mg/m<sup>3</sup> threshold for eye irritation.

# Revisit Example (5)

**Example:** The bar in Example 5 had volume  $500 \text{ m}^3$  with fresh air entering at the rate of  $1,000 \text{ m}^3/\text{hr}$ . Suppose when the bar opens at 5 p.m., the air is clean. If formaldehyde, with decay rate  $k_d = 0.40/\text{hr}$ , is emitted from cigarette smoke at the constant rate of  $140 \text{ mg/hr}$  starting at 5 p.m., what would the concentration be at 6 p.m.?

$$C_\infty = \frac{QC_{\text{in}} + k_g V}{Q + k_d V}$$

$$C_t = C_\infty + (C_0 - C_\infty) \exp \left[ - \left( k_d + \frac{Q}{V} \right) t \right]$$



# Revisit Example (5)

**Solution:**

$$C_{\infty} = \frac{QC_i + k_g V}{Q + k_d V} = \frac{P}{Q + k_d V} = \frac{140 \text{ mg/hr}}{1,000 \text{ m}^3/\text{hr} + 0.40/\text{hr} \times 500 \text{ m}^3} = 0.117 \text{ mg/m}^3$$

This agrees with the result obtained in Example 5. To find the concentration at any time after 5 p.m.,

$$C_t = C_{\infty} + (C_0 - C_{\infty}) \exp \left[ - \left( k_d + \frac{Q}{V} \right) t \right]$$

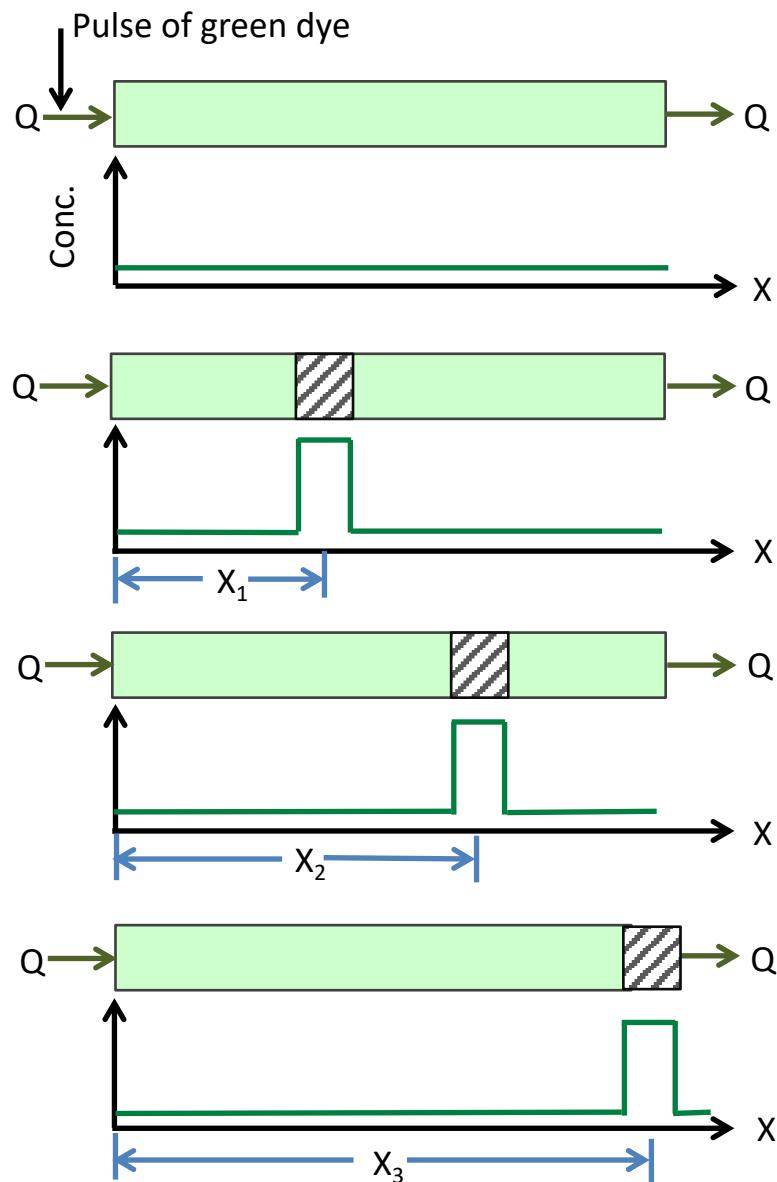
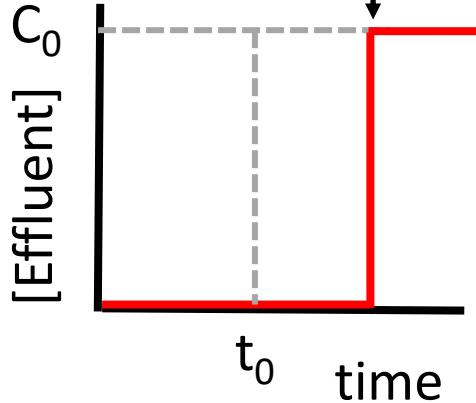
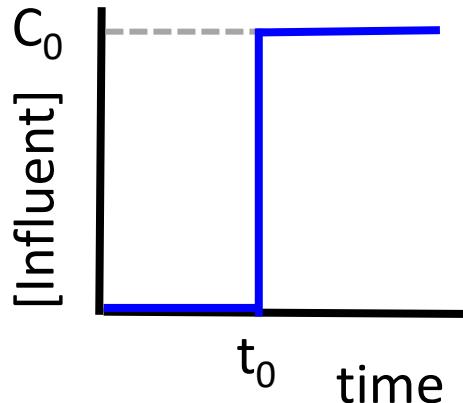
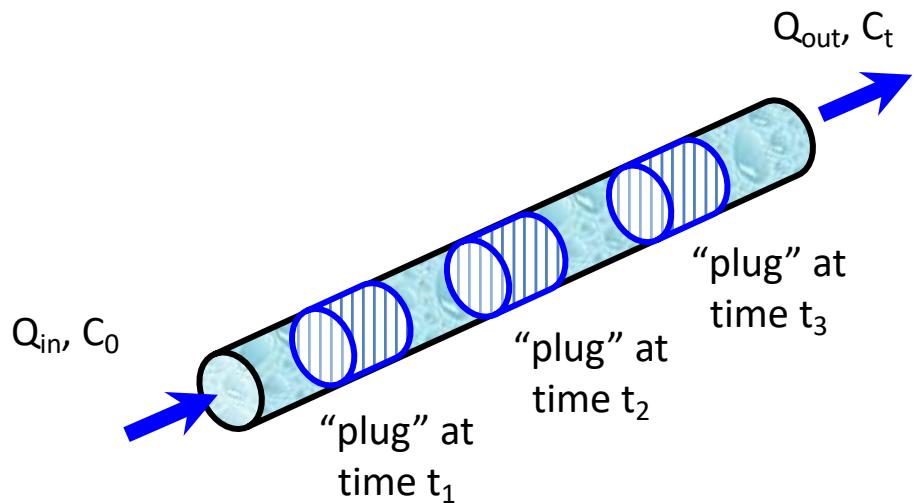
$$C(t) = C_{\infty} \left\{ 1 - \exp \left[ - \left( k_d + \frac{Q}{V} \right) t \right] \right\} = 0.117 \left\{ 1 - \exp [ - (0.40 + 1,000/500)t ] \right\}$$

at 6 p.m.,  $t = 1\text{hr}$ , so

$$C(1\text{ hr}) = 0.117 [1 - \exp(-2.4 \times 1)] = 0.106 \text{ mg/m}^3 = 0.9 C_{\infty}$$

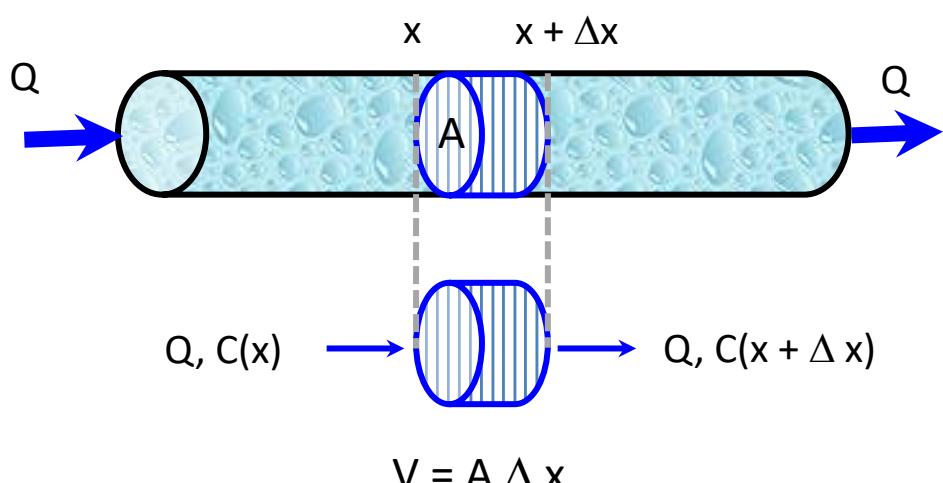
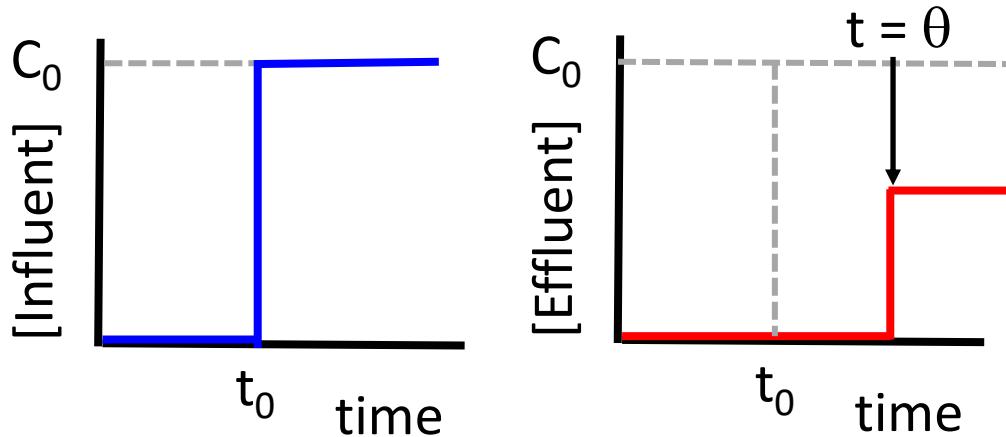
# Step response - Plug-flow reactor (Steady State)

- NO reactions & steady state ( $C_{in} = C_{out}$ )



# Step response - Plug-flow reactor (Steady State)

- First-order decay & steady state ( $C_{in} > C_{out}$ )



$$\frac{dM}{dt} = QC(x) - QC(x + \Delta x) + rV$$

$$-rA = -\left[ \frac{QC(x + \Delta x) - QC(x)}{\Delta x} \right]$$

$$\frac{dQC}{dx} = \lim_{\Delta x \rightarrow 0} \left[ \frac{QC(x + \Delta x) - QC(x)}{\Delta x} \right]$$

$$\frac{dQC}{dx} = rA \Rightarrow \frac{dQC}{dV} = r \Rightarrow Q \frac{dC}{dV} = -kC$$

$$\int_{C_0}^{C_t} \frac{1}{C} dC = -\frac{k}{Q} \int_0^V dV$$

$$\ln\left(\frac{C_t}{C_0}\right) = -k\theta \Rightarrow C_t = C_0 e^{-k\theta}$$

$$\text{if } \theta = \frac{1}{k} \Rightarrow C_t = 0.368C_0$$

# Performance characteristics of reactors - $C_t$

## Decay reactions:

Reaction Order	$r$	Equations for $C_t$		
		Ideal Batch	Ideal Plug Flow	Ideal CMFR
Zero <sup>b</sup>	$t \leq C_0/k$	$C_0 - kt$	$C_0 - k\theta$	$C_0 - k\theta$
	$t > C_0/k$	0		
First	$-kC$	$C_0[\exp(-kt)]$	$C_0[\exp(-k\theta)]$	$\frac{C_0}{1 + k\theta}$
Second	$-kC^2$	$\frac{C_0}{1 + ktC_0}$	$\frac{C_0}{1 + k\theta C_0}$	$\frac{(4k\theta C_0 + 1)^{1/2} - 1}{2k\theta}$

$C_0$  = initial concentration or influent concentration

$C_t$  = final condition or effluent concentration

$\theta$  = Retention time ( $V/Q$ )

<sup>b</sup> Time conditions are for ideal batch reactor only

# Performance characteristics of reactors - θ

## Decay reactions:

Equations for Mean Retention Times ( $\theta$ )				
Reaction Order	$r$	Ideal Batch	Ideal Plug Flow	Ideal CMFR
Zero <sup>b</sup>	$-k$	$\frac{(C_0 - C_t)}{k}$	$\frac{(C_0 - C_t)}{k}$	$\frac{(C_0 - C_t)}{k}$
First	$-kC$	$\frac{\ln(C_0/C_t)}{k}$	$\frac{\ln(C_0/C_t)}{k}$	$\frac{(C_0/C_t) - 1}{k}$
Second	$-kC^2$	$\frac{(C_0/C_t) - 1}{kC_0}$	$\frac{(C_0/C_t) - 1}{kC_0}$	$\frac{(C_0/C_t) - 1}{kC_t}$

$C_0$  = initial concentration or influent concentration;

$C_t$  = final condition or effluent concentration.

<sup>b</sup> Expressions are valid for  $k\theta \leq C_0$ ; otherwise  $C_t = 0$ .

# Performance characteristics of reactors - V

**Decay reactions:**

Reaction Order	CMF	Plug-Flow Reactor
Zero	$V = \frac{Q}{k}(C_0 - C)$	$V = \frac{Q}{k}(C_0 - C)$
First	$V = \frac{Q}{k} \left( \frac{C_0}{C} - 1 \right)$	$V = \frac{Q}{k} \ln \frac{C_0}{C}$
Second	$V = \frac{Q}{k} \left( \frac{C_0}{C} - 1 \right) \frac{1}{C}$	$V = \frac{Q}{k} \left( \frac{1}{C} - \frac{1}{C_0} \right)$

For example: CSTR, steady state and first-order decay

$$\frac{dM}{dt} = C_0 Q_{in} - C_t Q_{out} - k C_t V$$

$$\frac{dC}{dt} = \frac{Q}{V} (C_0 - C_t) - k C_t$$

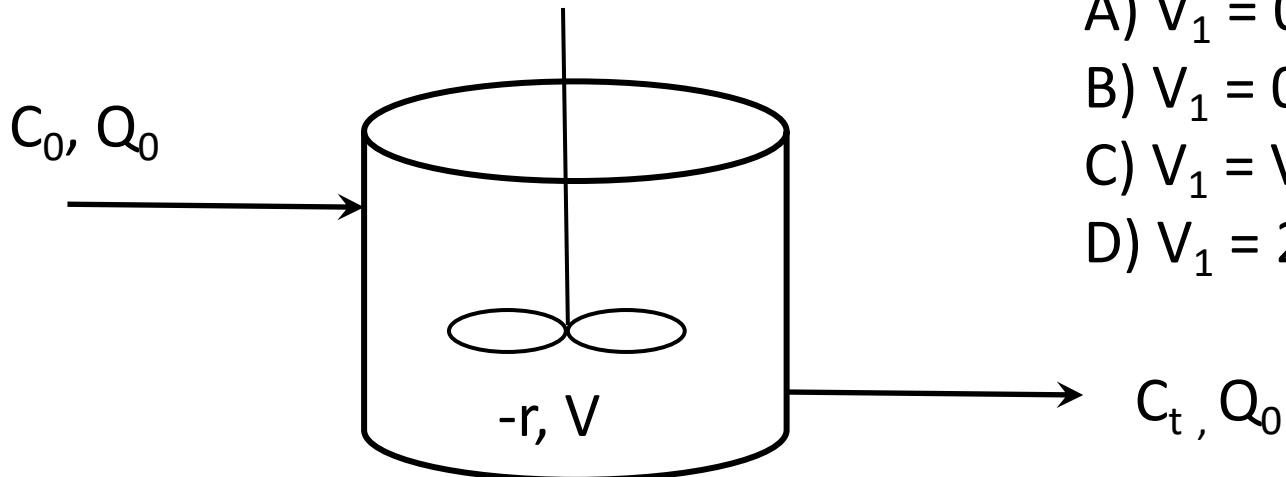
$$V = \frac{Q(C_0 - C_t)}{k C_t}$$

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

$$\text{and } \frac{C_0}{C_t} = 1 + \frac{kV}{Q}$$

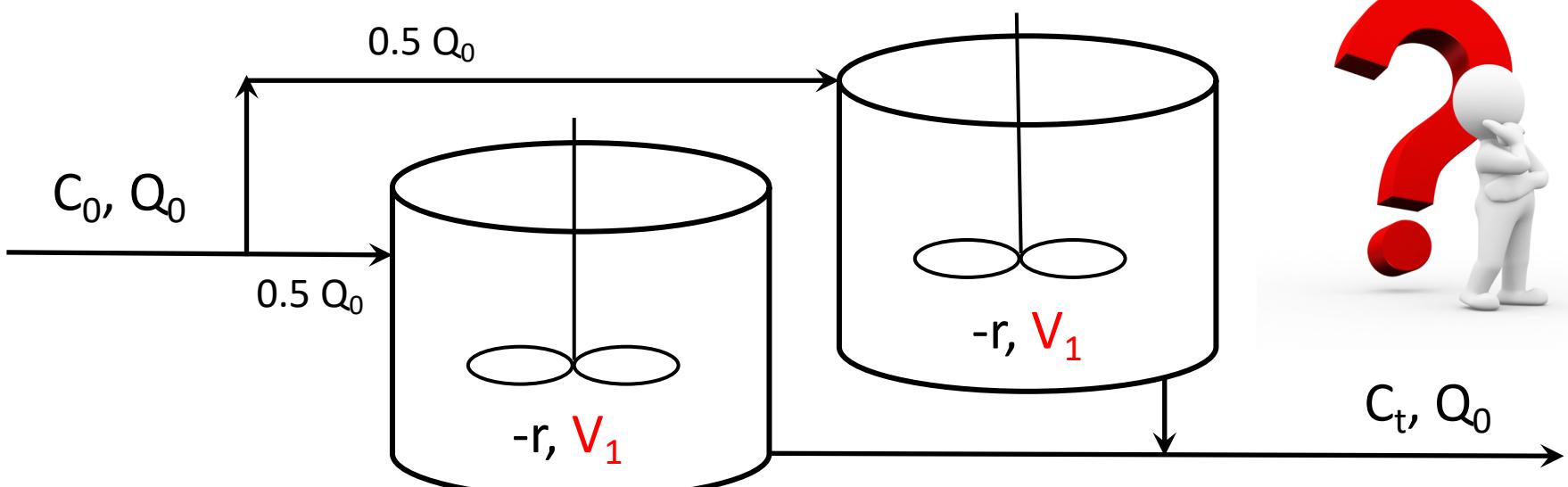
# CSTR in parallel

Case 1



- A)  $V_1 = 0.5V$
- B)  $V_1 = 0.75V$
- C)  $V_1 = V$
- D)  $V_1 = 2V$

Case 2:  $V_1 = ?$  (in terms of  $V$ )



# Example (6)

**Example:** Consider a first-order reaction, requiring 50% reduction in concentration. Would a plug-flow or completely mixed-flow reactor require least volume?

Reaction Order	CMF	Plug-Flow Reactor
Zero	$V = \frac{Q}{k}(C_0 - C)$	$V = \frac{Q}{k}(C_0 - C)$
First	$V = \frac{Q}{k} \left( \frac{C_0}{C} - 1 \right)$	$V = \frac{Q}{k} \ln \frac{C_0}{C}$
Second	$V = \frac{Q}{k} \left( \frac{C_0}{C} - 1 \right) \frac{1}{C}$	$V = \frac{Q}{k} \left( \frac{1}{C} - \frac{1}{C_0} \right)$



# Example (6)

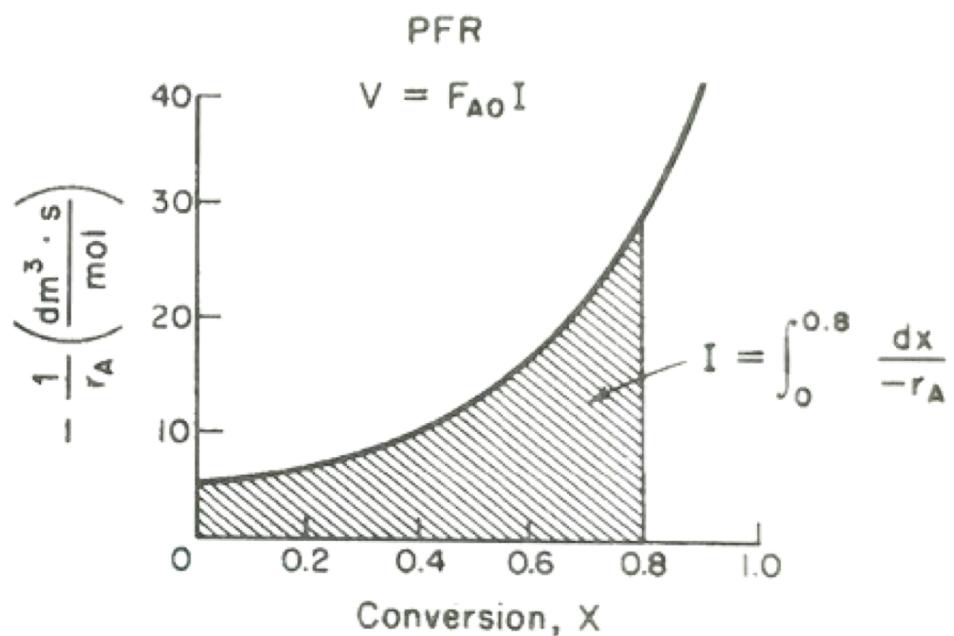
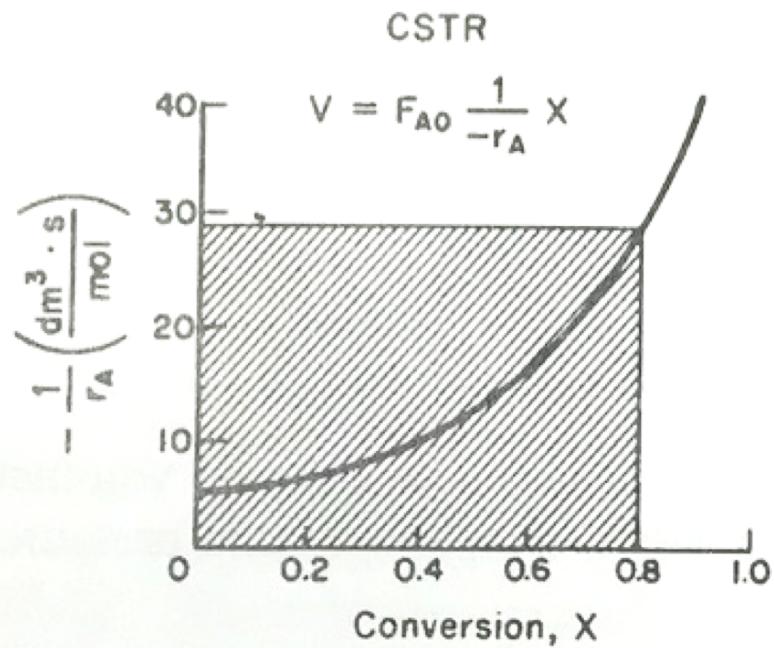
**Solution:**

$$\frac{V_{CMF}}{V_{PFR}} = \frac{\frac{Q}{k} \left( \frac{C_0}{C_t} - 1 \right)}{\frac{Q}{k} \left( \ln \frac{C_0}{C_t} \right)} \quad \text{and} \quad \frac{C_0}{C_t} = 2$$

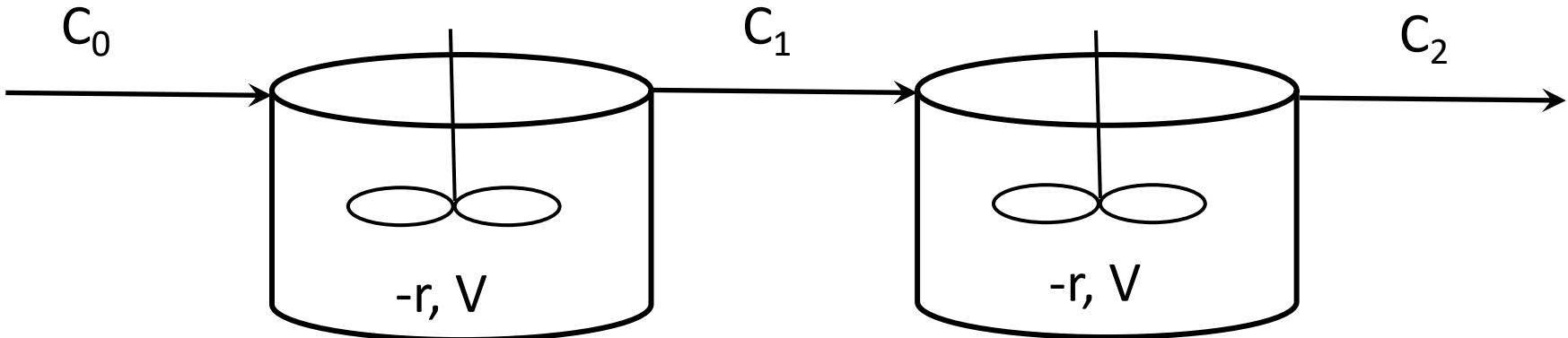
$$\frac{V_{CMF}}{V_{PFR}} = \frac{(2 - 1)}{(\ln 2)} = 1.44$$

A CMF reactor would require 44% more volume than a PFR. Stated generally, for reactions orders  $\geq 1$ , the ideal plug-flow reactor will always outperform the ideal completely mixed-flow reactor. This fact is a powerful tool in the design and operation of treatment systems

# Reactor volume: CSTR vs. PFR



# CSTR in series



For first order reaction and single reactor, recall  $\frac{C_0}{C_t} = 1 + \frac{kV}{Q}$

$$\frac{C_0}{C_1} = 1 + \frac{kV}{Q} \quad \text{and} \quad \frac{C_1}{C_2} = 1 + \frac{kV}{Q} \quad \Rightarrow \quad \frac{C_0}{C_1} \left( \frac{C_1}{C_2} \right) = \frac{C_0}{C_2} = \left[ 1 + \frac{kV}{Q} \right]^2$$

For any number of reactors in series,

$$\frac{C_0}{C_n} = \left[ 1 + \frac{kV}{Q} \right]^n \quad \Rightarrow \quad \left( \frac{C_0}{C_n} \right)^{1/n} = \left[ 1 + \frac{kV}{Q} \right] \quad \Rightarrow \quad V = \frac{Q}{k} \left[ \left( \frac{C_0}{C_n} \right)^{1/n} - 1 \right]$$

# Revisit example (6)

**Example:** Consider a first-order reaction, requiring 50% reduction in concentration. Compare the total volume of 5 completely mixed-flow reactors connected in series to the volume of a plug-flow reactor.

$$\frac{C_0}{C_n} = \left[1 + \frac{kV}{Q}\right]^n \Rightarrow \left(\frac{C_0}{C_n}\right)^{1/n} = \left[1 + \frac{kV}{Q}\right] \Rightarrow V = \frac{Q}{k} \left[ \left(\frac{C_0}{C_n}\right)^{1/n} - 1 \right]$$

- A) CSTR
- B) PFR



# Revisit example (6)

**Solution:**

Total volume of 5 CMF connected in series

$$nV = \frac{nQ}{k} \left[ \left( \frac{C_0}{C_n} \right)^{1/n} - 1 \right] = \frac{5Q}{k} [(2)^{1/5} - 1]$$

$$\frac{V_{CMF}}{V_{PFR}} = \frac{\frac{5Q}{k} [(2)^{1/5} - 1]}{\frac{Q}{k} (\ln 2)} = \frac{5[(2)^{1/5} - 1]}{\ln 2} = 1.07$$

Five CMF reactors connected in series would require 7% more volume than a PFR and the volume of each CMF becomes smaller when the number of reactors increases.