

AOS 104

Fundamentals of Air and Water Pollution

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MS1961
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TuTh 1:00-3:05
MS 7124A

Grades

Homework	160 pts
2 Midterms	290 pts
Final Exam	550 pts
Total	1000 pts

Homework

- **There will be 4 homework sets**
- **Homework is due by the end of business (~ 5 pm) on the due date**
- **Late homework will receive partial credit as outlined in the syllabus**
- **You are encouraged to work together and discuss approaches to solving problems, but must turn in your own work**

Lecture Notes

AOS 104 Fundamentals of Air and Water Pollution

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TuTh 2:00-3:15
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Grades

Homework	20%
Exam I	25%
Exam II	25%
Final Exam	30%
Total	100%

Homework

- There will be 6 homework sets
- Homework is due at the beginning of class
- Late homework will receive partial credit as outlined in the syllabus
- You are encouraged to work together and discuss approaches to solving problems, but must turn in your own work

Overview of Topics

- Calculating pollution concentration
- Effects of pollution on acidity (pH)—acid rain
- Types of water pollution
 - Health effects from water pollution
- Types of air pollution
 - Health effects of air pollution
- Urban air pollution—bad ozone
- Stratospheric air pollution—depletion of good ozone

Topics of the course

- **Calculating pollution concentration**
- **Effects of pollution on acidity (pH)—acid rain**
- **Types of water pollution**
 - **Health effects from water pollution**
- **Types of air pollution**
 - **Health effects of air pollution**
- **Urban air pollution—bad ozone**
- **Stratospheric air pollution—depletion of good ozone**
- **Global climate change**

Introduction

- **Measurement of Concentration**
 - **Liquids**
 - **Air**
 - **Conversions Involving the Ideal Gas Law**
- **Material Balance Models**
 - **Basics**
 - **Steady-state Model With Conservative Pollutants**
 - **Residence Time**
 - **Steady and Non-steady Models With Non-conservative Pollutants**

Units of Measurement

- **Both SI and British units used**
 - **Be able to convert between these two standards**
 - **Examples**

Quantity	SI	British
Length	m	ft
Volume	m ³	ft ³
Power	watt	BTU/hr
Density	kg/m ³	lb/ft ³

Concentration

- **The amount of a specified substance in a unit amount of another substance**
 - **Usually, the amount of a substance dissolved in water or mixed with the atmosphere**
- **Can be expressed as...**

Mass/Mass	g/kg, lb/ton, ppmm, ppbm
Mass/Volume	g/L, $\mu\text{g}/\text{m}^3$
Volume/Volume	mL/L, ppmv, ppbv
Volume/Mass	L/kg
Moles/Volume	molarity, M, mol/L

Liquids

Concentrations of substances dissolved in water are generally given as mass per unit volume.

e.g., milligrams/liter (mg/L) or micrograms/liter ($\mu\text{g/L}$)

Concentrations may also be expressed as a mass ratio, for example:

7 mass units of substance A per million mass units of substance B is 7 ppm.

Example 1

23 μg of sodium bicarbonate are added to 3 liters of water.

What is the concentration in $\mu\text{g/L}$ and in ppb (parts per billion) and in moles/L?

$$\frac{23 \mu\text{g}}{3 \text{ L}} = 7.7 \frac{\mu\text{g}}{\text{L}}$$

To find the concentration in ppb we need the weight of the water.

Standard assumption: density of water is 1g/ml or 1000 g/L (at 4°C).

$$\frac{7.7 \times 10^{-6} \text{ g}}{1 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ g}} = 7.7 \times 10^{-9} = \frac{7.7}{10^9} = \frac{7.7}{\text{billion}} = 7.7 \text{ ppbm}$$

⇒ **For density of water is 1000 g/L,**

$$\mathbf{1 \mu\text{g/L} = 1 \text{ ppbm}}$$

$$\mathbf{1 \text{ mg/L} = 1 \text{ ppm}}$$

Sometimes, liquid concentrations are expressed as mole/L (M).

e.g., concentration of sodium bicarbonate (NaHCO₃) is 7.7 μg/L

$$\begin{aligned}\text{Molecular Weight} &= [23 + 1 + 12 + (3 \times 16)] \frac{\text{g}}{\text{mol}} \\ &= 84 \frac{\text{g}}{\text{mol}}\end{aligned}$$

$$\begin{aligned}\text{Molar Concentration} &= \frac{7.7 \mu\text{g}}{1 \text{ L}} \times \frac{1 \text{ mol}}{84 \text{ g}} \times \frac{1 \text{ g}}{1 \times 10^6 \mu\text{g}} \\ &= 9.2 \times 10^{-8} \frac{\text{mol}}{\text{L}}\end{aligned}$$

Air

**Gaseous pollutants—use volume ratios:
ppmv, ppbv**

**Or, mass/volume concentrations—use m^3
for volume**

Example 2

A car is running in a closed garage. Over 3 minutes, it expels 85 L of CO. The garage is 6 m \times 5 m \times 4 m. What is the resulting concentration of CO? Assume that the temperature in the room is 25°C.

Solution:

The volume of CO is 85 L and

$$\begin{aligned}\text{Volume of room} &= 6 \text{ m} \times 5 \text{ m} \times 4 \text{ m} \\ &= 120 \text{ m}^3 \\ &= 120000 \text{ L}\end{aligned}$$

$$\begin{aligned}\text{Concentration} &= \frac{85 \text{ L}}{120000 \text{ L}} = 0.000708 = 708 \times 10^{-6} \\ &= 708 \text{ ppmv}\end{aligned}$$

Example 2 Cont.

Instead of 85 L of CO, let's say 3 moles of CO were emitted.

We need to find the volume occupied by three moles of CO.

IDEAL GAS LAW: $PV = nRT$

P = Pressure (atm)

V = Volume (L)

n = Number of moles

R = Ideal Gas Constant = $0.08206 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

T = Temperature (K)

**To remember the units it's
All Lovers Must Kiss
(atm, L, mol, K)**

**This law tells you how a gas responds to a
change in its physical conditions. Change P,
V or T, and the others adjust**

The Ideal Gas Law

$$PV = nRT$$

so $P_1V_1 = nRT_1$ $P_2V_2 = nRT_2$ etc.

Can rearrange to get the equality,

$$\frac{P_1V_1}{T_1} = nR = \frac{P_2V_2}{T_2}$$

The ideal gas law also tells you that:

- ▶ **at 0°C (273 K) and 1 atm (STP),
1 mole occupies 22.4 L**
- ▶ **at 25°C (298 K) (about room temperature)
and 1 atm,
1 mole occupies 24.5 L**

Back to Example 2

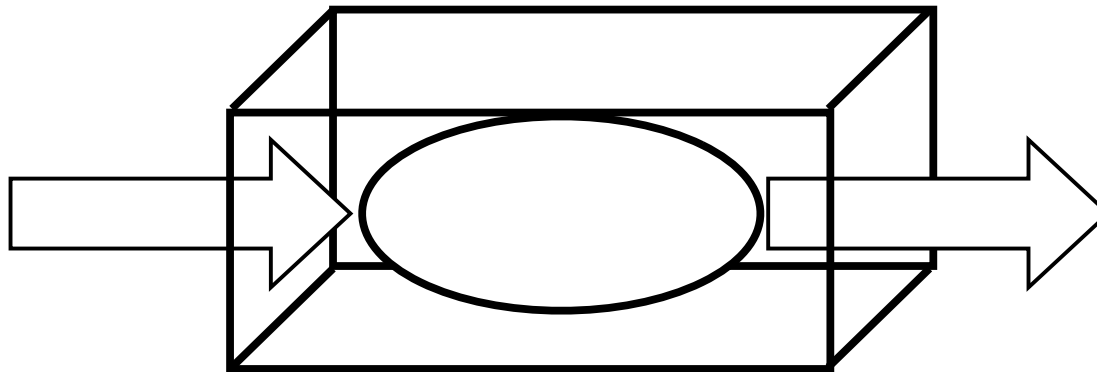
$$\text{Volume of CO} = (3 \text{ mol}) \left(24.5 \frac{\text{L}}{\text{mol}} \right) = 73.5 \text{ L}$$

$$\begin{aligned} \text{Volume of room} &= 6 \text{ m} \times 5 \text{ m} \times 4 \text{ m} \\ &= 120 \text{ m}^3 = 120000 \text{ L} \end{aligned}$$

$$\begin{aligned} \text{Concentration} &= \frac{73.5 \text{ L}}{120000 \text{ L}} \\ &= 0.000613 \\ &= 613 \times 10^{-6} = 613 \text{ ppmv} \end{aligned}$$

Material Balances

- Expresses *Law of Conservation of Mass*
- Material balances can be applied to many systems—organic, inorganic, steady-state, financial, etc.



Basic equation of material balance

$$\text{Input} = \text{Output} - \text{Decay} + \text{Accumulation}$$

(eq. 1.11)

Input, output, etc. are usually given as rates, but may also be quantities (i.e. masses).

- ➔ **This equation may be written for the overall system, or a series of equations may be written for each component and the equations solved simultaneously.**

Steady-state (or equilibrium), conservative systems are the simplest

- ➔ **Accumulation rate = 0, decay rate = 0**

Example 3

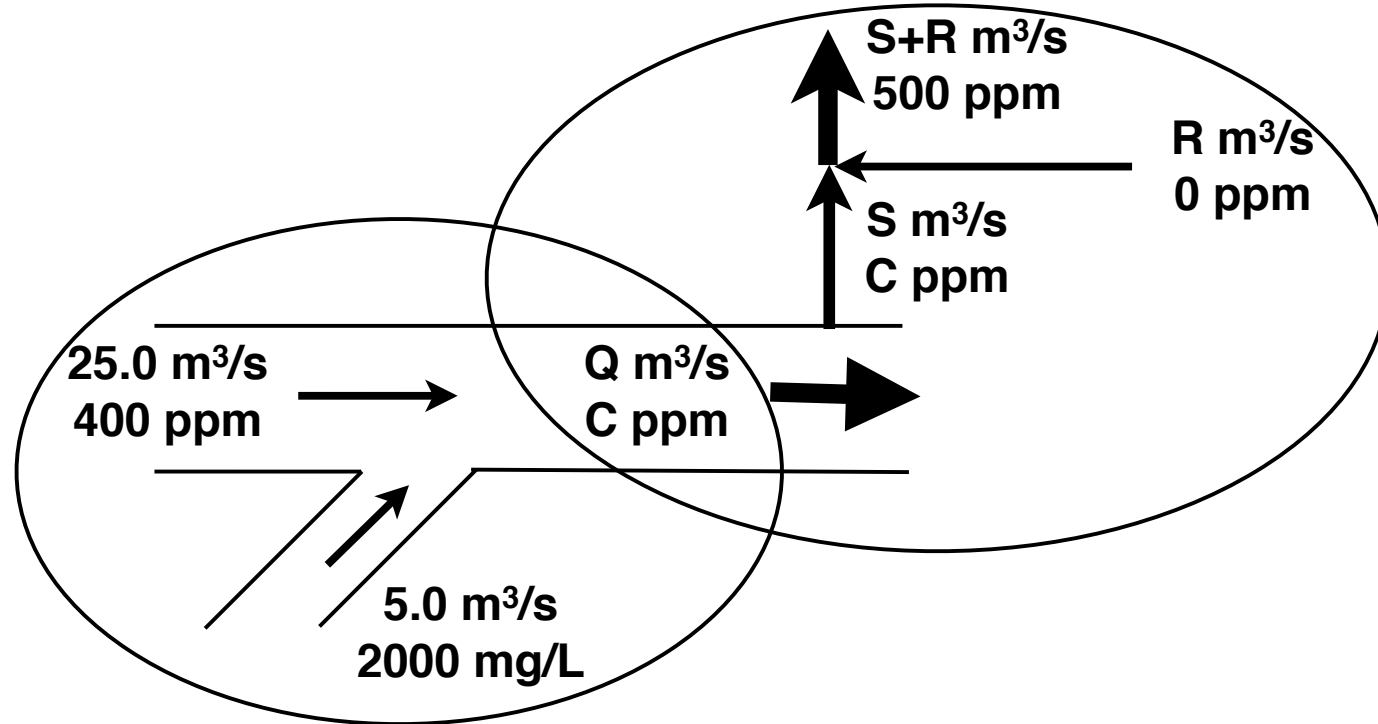
Problem 1.7 – Agricultural discharge containing 2000 mg/L of salt is released into a river that already has 400 ppm of salt. A town downstream needs water with <500 ppm of salt to drink. How much clean water do they need to add?

Maximum recommended level of salts for drinking water = 500 ppm.

Brackish waters have > 1500 ppm salts.

Saline waters have > 5000 ppm salts.

Sea water has 30,000–34,000 ppm salts.

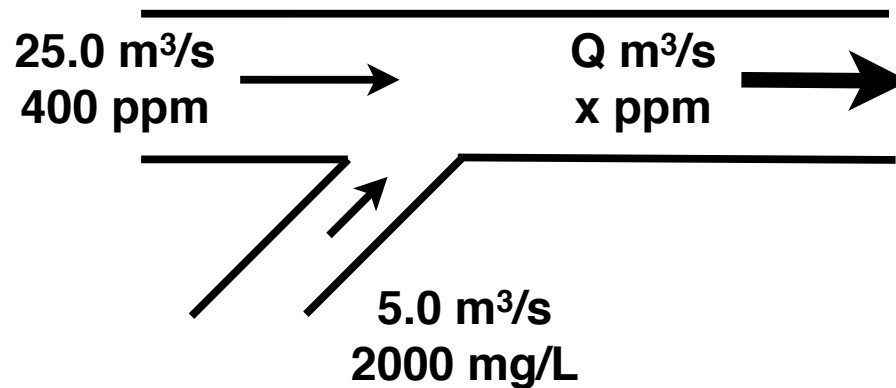


What is the concentration in flow Q?

What flow of clean water (R) must be mixed to achieve 500 ppm?

(What is the ratio of R/S?)

To simplify, we can break this into two systems—first (remembering that 1 ppm = 1 mg/L)



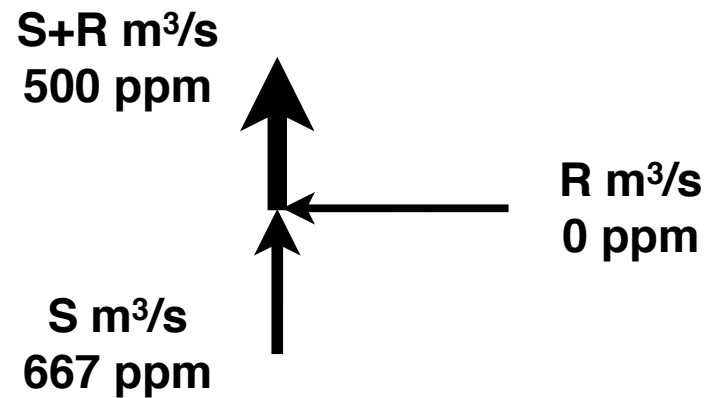
Basic equation: input = output

$$\left(25.0 \frac{\text{m}^3}{\text{s}} \times 400 \text{ ppm}\right) + \left(5.0 \frac{\text{m}^3}{\text{s}} \times 2000 \text{ ppm}\right) = \left(Q \frac{\text{m}^3}{\text{s}} \times C \text{ ppm}\right)$$

$$Q = \text{Total flow} = 25.0 \frac{\text{m}^3}{\text{s}} + 5.0 \frac{\text{m}^3}{\text{s}} = 30.0 \frac{\text{m}^3}{\text{s}}$$

Thus, C = the salt concentration at the take-out from the river = 667 ppm

Solve the other part of the system:



$$\left[S \frac{\text{m}^3}{\text{s}} \times 667 \text{ ppm} \right] + \left[R \frac{\text{m}^3}{\text{s}} \times 0 \text{ ppm} \right] = (S + R) \frac{\text{m}^3}{\text{s}} \times 500 \text{ ppm}$$

$$667S = 500S + 500R$$

$$\frac{R}{S} = \frac{667 - 500}{500} = 0.33$$

Residence Time

- **Lifetime or residence time of substance**
≡ amount / rate of consumption

- **Lifetime of Earth's petroleum resources:**

$$1.0 \times 10^{22} \text{ J} / 1.35 \times 10^{20} \text{ J/yr} = 74 \text{ years}$$

ANWR has ~5.7 to 16.3×10^9 barrels of oil; best guess is 10×10^9 . The US consumes 19 million barrels/day of oil. How much time does this give us?



- **The residence time may be defined for a system in *steady-state* as:**

$$\frac{\text{Stock (material in system)}}{\text{Flow rate (in or out)}}$$

- **Residence time in a lake: The average time water spends in the lake**
 - **Some water may spend years in the lake**
 - **Some may flow through in a few days**
 - ➔ **Depends on mixing.**

- **In the first approximation, consider only stream flow in and stream flow out.**

$$\mathbf{T = M/F_{in} = M/F_{out}}$$

For this very simple steady state system, we calculate the residence time

Ex. The volume of a lake fed by a stream flowing at $7 \times 10^5 \text{ m}^3/\text{day}$ is $3 \times 10^8 \text{ m}^3$. What is the residence time of the water in the lake?

$$\frac{3 \times 10^8 \text{ m}^3}{7 \times 10^5 \frac{\text{m}^3}{\text{day}}} = 430 \text{ days}$$

More Material Balances

- **What if a substance is removed by chemical, biological or nuclear processes?**
 - **The material is still in steady-state if its concentration is not changing.**
- **Steady-state for a non-conservative pollutant:**
 - **We now need to include the decay rate in our material balance expression:**
Input rate = Output rate + Decay rate

Assume decay is proportional to concentration (“1st order decay”).

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

where k = reaction rate coefficient, in units of 1/time.

C = concentration of pollutant

Separate variables and integrate:

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

Solution: $\ln(C) - \ln(C_0) = -kt - \cancel{kt_0}$

$$\ln(C) - \ln(C_0) = \ln\left(\frac{C}{C_0}\right) = -kt$$

Take the exponential of each side:

$$C = C_0 e^{-kt}$$

For a particular system (i.e., a lake), we can write a total mass decay rate (mass/time), that we can compare with the input and output rates:

$$= kCV \Rightarrow \text{mass removal rate}$$

k has units of 1/time

C has units of mass/volume

V has units of volume

Thus the decay rate = kCV (mass/time)

Material Balance Equation

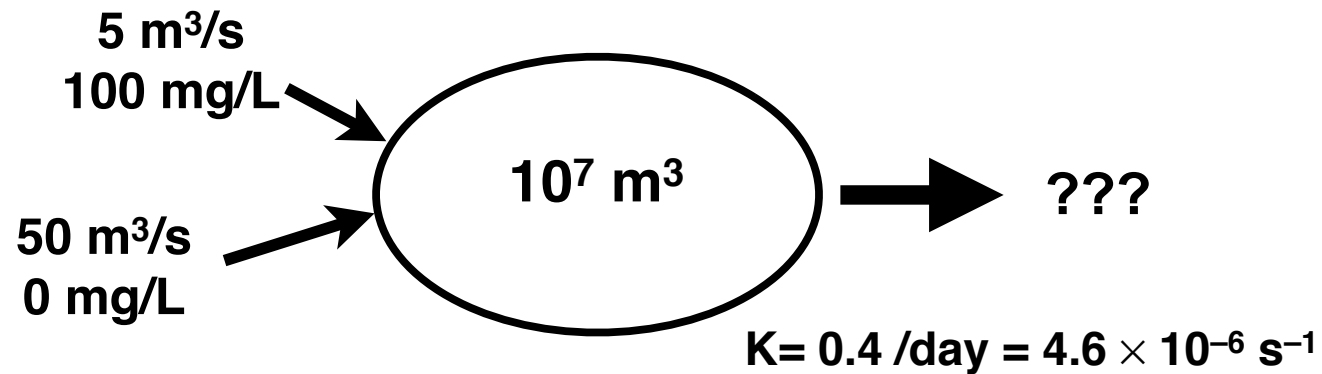
Steady state with decay

$$\text{Input rate} = \text{Output rate} + kCV$$

Example 4

A lake with a constant volume of 10^7 m^3 is fed by a clean stream at a flow of $50 \text{ m}^3/\text{s}$. A factory dumps $5.0 \text{ m}^3/\text{s}$ of a non-conservative pollutant with a concentration of 100 mg/L into the lake. The pollutant has a reaction (decay) rate coefficient of $0.4/\text{day}$ ($= 4.6 \times 10^{-6} \text{ s}^{-1}$). Find the steady-state concentration of the pollutant in the lake.

Start by drawing a diagram of the problem statement.



Solution:

Assume the volume of the lake is constant, so the outflow is equal to the inflow, or

Water outflow rate = 55 m³/s

For the pollutant:

Input rate = Output rate + Decay rate

Variation—Non-steady situation

Consider a lake that initially had zero concentration of the pollutant, and then a pollutant was introduced. How is the concentration changing with time? (i.e., a transient phenomenon—*not steady-state*)

👉 **Step function response**

Mass balance:

**Accumulation rate = Input rate
- Output rate
- Decay rate**

$$V \frac{dC}{dt} = S - QC - kCV$$

Eventually system reaches a steady-state concentration, $C(\infty)$ (i.e., when $dC/dt = 0$)

$$C(\infty) = C_{\infty} = \frac{S}{Q + kV}$$

Concentration as a function of time (before steady-state is reached) is given by the transient equation:

$$\frac{dC}{dt} = \frac{S}{V} - \frac{QC}{V} - kC$$

which can be rearranged to give:

$$\frac{dC}{dt} = -\left(k + \frac{Q}{V}\right)\left[C - \frac{S}{Q + kV}\right]$$

So we can substitute for C_∞ :

$$\frac{dC}{dt} = -\left(k + \frac{Q}{V}\right)[C - C_\infty]$$

To integrate, we simplify the $C - C_\infty$ term:

$$y = C - C_\infty \Rightarrow \frac{dy}{dt} = \frac{dC}{dt}$$

$$\frac{dy}{dt} = -\left(k + \frac{Q}{V}\right)y$$

⇒ **a familiar, separable differential equation ($k+Q/V$ is a constant!), with a solution of the form:**

$$y = y_0 e^{-\left(k + \frac{Q}{V}\right)t} \text{ where } y_0 = C_0 - C_\infty$$

Substituting and rearranging,

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

At $t = 0$, $\exp = 1$

$t = \infty$, $\exp = 0$

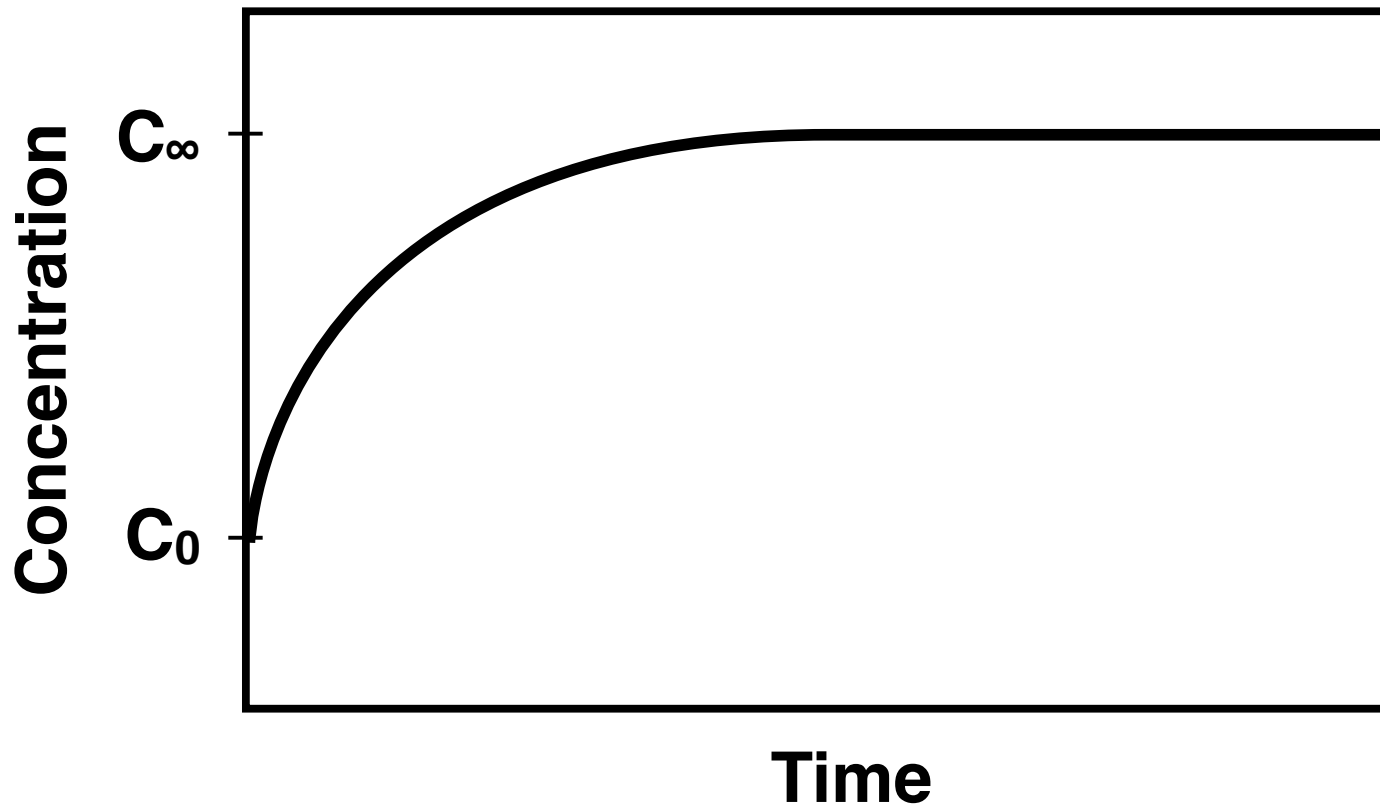
$$C(t) = C_{\infty} + (C_0 - C_{\infty}) \exp \left[- \left(k + \frac{Q}{V} \right) t \right]$$

What is the general behavior of this equation?

At time = 0, the exponential term goes to 1 so

$$\mathbf{C = C(0)}$$

At time = ∞ , exp goes to 0 \Rightarrow $\mathbf{C = C_{\infty}}$



Example 5

Bar with volume of 500 m³

Fresh air enters at a rate of 1000 m³/hr

Bar is clean when it opens at 5 PM

Formaldehyde is emitted at 140 mg/hr after 5 PM by smokers

k = the formaldehyde removal rate coeff. = 0.40/hr

What is the concentration at 6 PM?

$$C(t) = (C(0) - C_{\infty}) \exp \left[- \left(k + \frac{Q}{V} \right) t \right] + C_{\infty}$$

Solution—First we need C_∞

**$Q = 1000 \text{ m}^3/\text{hr}$; $V = 500 \text{ m}^3$; $S=140 \text{ mg/hr}$;
 $k = 0.40 \text{ /hr}$**

$$C_{\infty} = \frac{S}{Q + kV} = \frac{140.0 \text{ mg/hr}}{1000.0 \text{ m}^3/\text{hr} + (0.4/\text{hr} \times 500 \text{ m}^3)}$$

$$C_{\infty} = 0.117 \text{ mg/m}^3$$

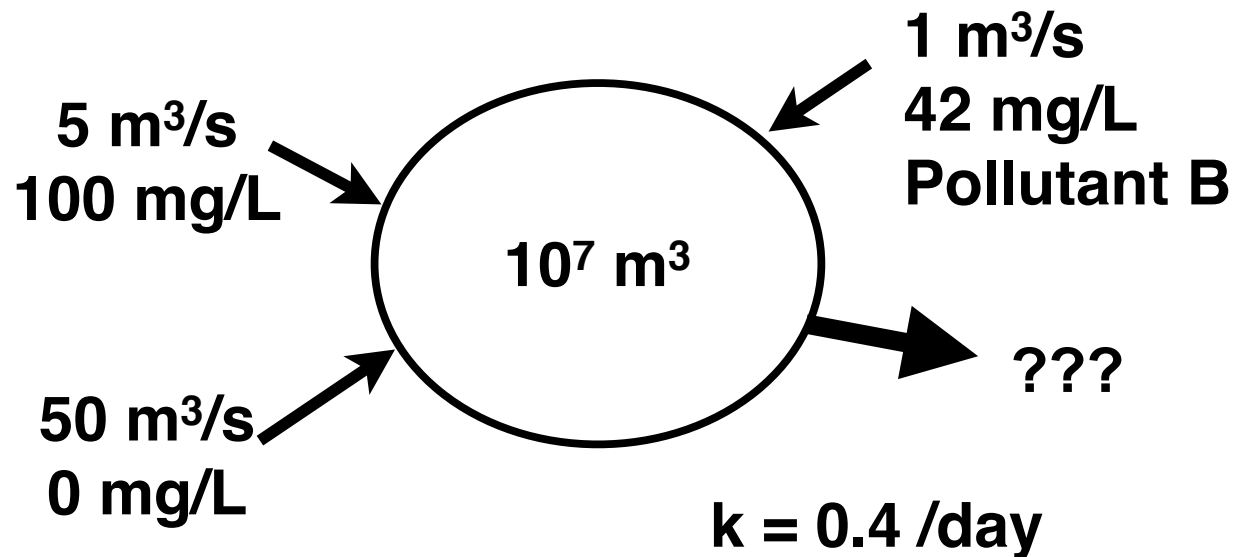
For the concentration at 6 PM, one hour after the bar opens, substitute known values into:

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

$$C(t) = \left(0 - 0.117 \frac{\text{mg}}{\text{m}^3} \right) \exp \left[- \left(0.40 \frac{1}{\text{hr}} + \frac{1000.0 \frac{\text{m}^3}{\text{hr}}}{500.0 \text{m}^3} \right) t \right] + 0.117 \frac{\text{mg}}{\text{m}^3}$$

$$C(t) = 0.117 \frac{\text{mg}}{\text{m}^3} (1 - e^{-2.4t})$$

$$C(1 \text{ hr}) = 0.117 \frac{\text{mg}}{\text{m}^3} (1 - e^{-2.4}) = 0.106 \text{ mg/m}^3$$



New factory opens, discharging pollutant B. If k is $0.4/\text{day}$, what is the concentration after 2 days of discharges?

$$S = \left(1 \frac{\text{m}^3}{\text{s}} \right) \left(1000 \frac{\text{L}}{\text{m}^3} \right) \left(86400 \frac{\text{s}}{\text{day}} \right) \left(42 \frac{\text{mg}}{\text{L}} \right) = 3.628 \times 10^9 \frac{\text{mg}}{\text{day}}$$

$$Q = \left((50 + 5 + 1) \frac{\text{m}^3}{\text{s}} \right) \left(1000 \frac{\text{L}}{\text{m}^3} \right) \left(86400 \frac{\text{s}}{\text{day}} \right) = 4.838 \times 10^9 \frac{\text{L}}{\text{day}}$$

$$V = 10^7 \text{ m}^3$$

$$Q = 4.838 \times 10^9 \text{ L/day}$$

$$S = 3.628 \times 10^9 \text{ mg/day}$$

$$k = 0.4/\text{day}$$

$$C = \underline{\hspace{2cm}}$$

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

$$C_{\infty} = \frac{S}{Q + kV}$$

First step:

$$\begin{aligned}C_{\infty} &= \frac{S}{Q + KV} \\&= \frac{3.628 \times 10^9 \frac{\text{mg}}{\text{day}}}{4.838 \times 10^9 \frac{\text{L}}{\text{day}} + 0.4 \frac{1}{\text{day}} \times 10^{10} \text{ L}} \\&= 0.410 \text{ mg/L}\end{aligned}$$

Now use step function to find concentration at 2 days

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

$$C_0 = 0;$$

$$C(t) = \left[1 - \exp \left[- \left(k + \frac{Q}{V} \right) t \right] \right] C_{\infty}$$

$$= \left[1 - \exp \left[- \left(0.4 \frac{1}{\text{day}} + \frac{4.84 \times 10^9 \frac{\text{m}^3}{\text{day}}}{10^{10} \text{m}^3} \right) 2 \text{ days} \right] \right] \left(0.41 \frac{\text{mg}}{\text{L}} \right)$$

$$= (0.829) 0.41 \frac{\text{mg}}{\text{L}}$$

$$= 0.34 \text{ mg/L}$$