Materials Balance
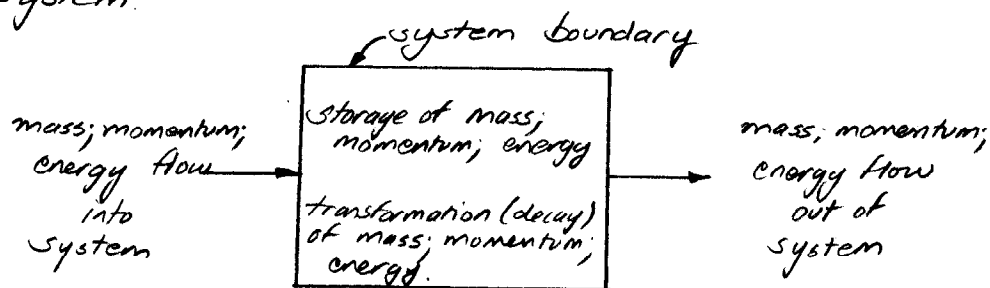
Fundamental tool in environmental engineering analysis

Based on conservation laws

    i) conservation of mass   ii) conservation of momentum

    iii) conservation of energy

Used to track quantities of (mass, momentum, energy) throughout a system.

Mass Balance

A mass balance is usually written as a mass flow _rate_ equation. Conservation of mass for a system says:

$$\frac{dm}{dt}\bigg|_{system} = 0 \quad \text{or} \quad \dot{m}_{system} = 0$$

In words: rate of storage — rate of transformation — rate entering + rate exiting = 0

$$\dot{m}_{storage} - \dot{m}_{trans} - \dot{m}_{input} + \dot{m}_{output} = 0$$

Typically the rate balance is written as

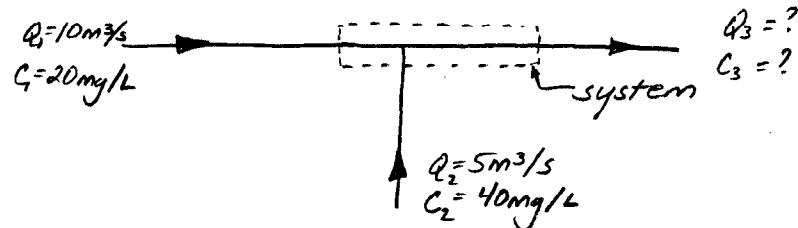$$\dot{m}_{in} - \dot{m}_{out} = \dot{m}_{storage} - \dot{m}_{trans}$$

Common simplifications

   i) Equilibrium $\Rightarrow$ usually means that $\dot{m}_{storage} = 0$

     $\therefore \dot{m}_{in} - \dot{m}_{out} = 0 - \dot{m}_{trans}$

   ii) Conservative $\Rightarrow$ usually means that $\dot{m}_{trans} = 0$

     $\therefore \dot{m}_{in} - \dot{m}_{out} = \dot{m}_{out}$

Consider two streams.

Main stream $Q = 10 m^3/s$; Tributary $Q = 5 m^3/s$.

$[Cl^-] = 20 mg/L$; $[Cl^-] = 40 mg/L$

Estimate $[Cl^-]$ downstream of confluence

$Q_1 = 10 m^3/s$ $Q_3 = ?$
$C_1 = 20 mg/L$ $C_3 = ?$

system

$Q_2 = 5 m^3/s$
$C_2 = 40 mg/L$

Assume complete mixing in system.

$$\dot{m}_{in} - \dot{m}_{out} = \underset{=0}{\underset{equilibrium}{\dot{m}_{stor}}} - \underset{=0 \; conservative}{\dot{m}_{tran}}$$

$$\therefore \dot{m}_{in} = \dot{m}_{out}$$

1) hydraulic mass flow: $\rho Q_1 + \rho Q_2 = \rho Q_3$

$$\therefore Q_3 = Q_1 + Q_2$$

2) chemical mass flow: $C_1 Q_1 + C_2 Q_2 = C_3 Q_3 = C_3 (Q_1 + Q_2)$

$$C_3 = \frac{C_1 Q_1 + C_2 Q_2}{Q_1 + Q_2} = \frac{(20)(10) + (40)(5)}{10+5} = 26.6 mg/L$$

This example has a practical application for measuring flow:

   Dye Dilution Method: Inject dye of known concentration & flow
   into an unknown flow. Sample downstream to infer unknown
   flow.

Q_d, C_0 sample downstream far enough for complete mixing

$Q_1 = ?$
C_1 $Q + Q_d , C_2$
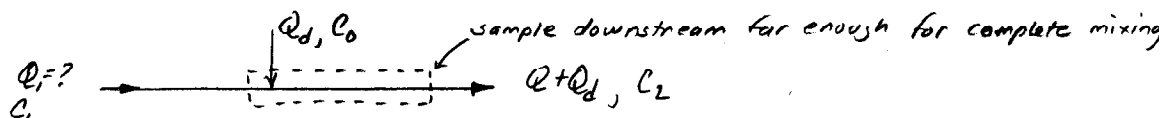
   Solve chemical mass flow for Q_1

$$C_1 Q_1 + C_0 Q_d = C_2 (Q_1 + Q_d) = C_2 Q_1 + C_2 Q_d$$

$$C_1 Q_1 - C_2 Q_1 = C_2 Q_d - C_0 Q_d$$

$$Q_1 = \frac{(C_2 - C_0) Q_d}{C_1 - C_2} = \frac{C_0 - C_2}{C_2 - C_1} Q_d$$

   Ideally $C_1 = 0$ so the result is $Q_1 = \frac{C_0 - C_2}{C_2} Q_d$

Many compounds undergo changes within a system so that the transfer term is not negligible. A variety of processes can occur — one possible process is a first-order decay type of transfer.

$$\dot{m}_{transfer} = -Km$$

(mass transfer rate is proportional to the mass in the system)

$$\frac{dm}{dt}\bigg|_{transfer} = -Km$$

separation and integration can be used to find the solution to this equation

$$dm = -Km\,dt$$

$$\frac{dm}{m} = -K\,dt$$

$$\int \frac{dm}{m} = -\int K\,dt \quad \rightarrow \quad \ln|m| = -Kt + c \quad \rightarrow \quad m = e^{-Kt} \cdot \underbrace{e^c}_{m_0}$$

$$\therefore \quad m = m_0\, e^{-Kt}$$

If first-order decay is appropriate for a particular system then the balance expression can be written as

$$\dot{m}_{in} - \dot{m}_{out} = \dot{m}_{storage} + Km$$

If the mass is uniformly distributed throughout the system, and the system has constant volume V, then the balance equation can be expressed in concentration units as

$$\frac{d}{dt}(cV)_{in} - \frac{d}{dt}(cV)_{out} = \frac{d}{dt}(cV)_{storage} + KcV$$

Expressed in this fashion, one has assumed complete mixing. When applied to reactor vessels such a system is called a $\Big\{$ CSTR — continuously stirred tank reactor

$\quad\quad$ CMFR — completely mixed flow reactor

$Q_1 C_1$

$\forall, C$

$\rightarrow Q_2 C_2$
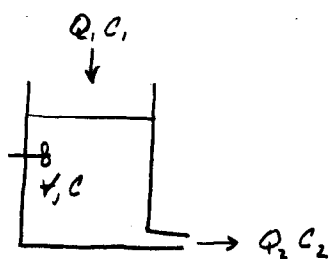
Complete mixing means that $C_2 = C$

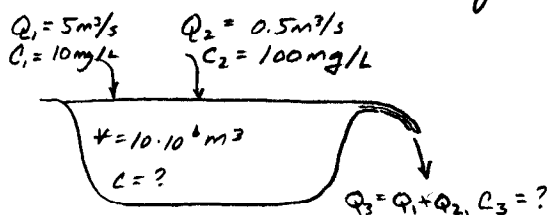The balance expression for this fixed volume reactor is

$$\dot{m}_{in} - \dot{m}_{out} = \dot{m}_{stor} - \dot{m}_{tran}$$

$$C_1 Q_1 - C_2 Q_2 = \forall \frac{dC_2}{dt} + K C_2 \forall$$

Example: $10 \cdot 10^6 m^3$ lake. Stream supplies $Q = 5 m^3/s$, $Toc = 10 mg/L$.
Sewage outfall supplies $Q = 0.5 m^3/s$, $Toc = 100 mg/L$.
Lake has intrinsic assimilation capacity to degrade Toc
by first-order model of $0.2/day$. Estimate _equilibrium_ Toc.

$Q_1 = 5 m^3/s$ $Q_2 = 0.5 m^3/s$
$C_1 = 10 mg/L$ $C_2 = 100 mg/L$

$\forall = 10 \cdot 10^6 m^3$
$C = ?$

$Q_3 = Q_1 + Q_2, C_3 = ?$

① Assume complete mixing

② Hydraulic mass balance: $Q_3 = Q_1 + Q_2$

③ Chemical mass balance

$$\dot{m}_{in} - \dot{m}_{out} = \forall \frac{dC_3}{dt} + K C_3 \forall$$

$$= 0 \text{ equilibrium}$$

$$\underbrace{Q_1 C_1 + Q_2 C_2}_{known} - \underbrace{Q_3 C_3}_{known} = \underbrace{K C_3 \forall}_{known} \qquad \text{solve for } C_3$$

$$C_3 (-Q_1 - Q_2 - K\forall) = -C_1 Q_1 - C_2 Q_2$$

$$C_3 = \frac{C_1 Q_1 + C_2 Q_2}{Q_1 + Q_2 + K\forall} = \frac{(10)(5) + (100)(.5)}{5 + 0.5 + 0.2(10 \cdot 10^6)(\frac{1}{86400})} = 3.49 mg/L$$

$$\rightarrow 1 \text{ day} = 86400 \text{ seconds}$$

Non-equilibrium analysis is concerned with the response of the system over some time period. One response of interest is the response to a step-function change in input. The response to a step change gives a lot of information regarding the degree of mixing in a system
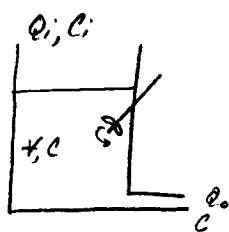
Consider a completely mixed reactor with 1-st order decay. Balance expression is

$$\dot{m}_{in} - \dot{m}_{out} = \dot{m}_{stor} - \dot{m}_{tran}$$

$$Q_i C_i - Q_o C = V \frac{dc}{dt} + KcV$$

At equilibrium $\frac{dc}{dt} = 0$ and solution is $\quad c = \dfrac{C_i Q_i}{Q_o + KV}$

If C_i is changed to C_k then new __equilibrium__ solution is

$$c = \frac{C_k Q_i}{Q_o + KV}$$

But often one is interested in behavior of system as it progresses to the new equilibrium. — to study this behavior one needs to solve the differential equation

$$V \frac{dc}{dt} = Q_i C_i - Q_o C - KcV = C_i Q_i - C(Q + KV); \quad \frac{C_i Q_i}{V} - \frac{c}{V}(Q + KV) = \frac{dc}{dt}$$

$$\frac{dc}{dt} = \frac{C_i Q_i}{V} \frac{(Q+KV)}{(Q+KV)} - c \frac{(Q+KV)}{V} = \frac{Q+KV}{V}\left(\frac{C_i Q_i}{Q+KV} - c\right)$$

Now let $\quad U = \dfrac{C_i Q_i}{Q+KV} - c \qquad dU = -dc \; ; \; thus \quad \dfrac{dc}{dt} = -\dfrac{dU}{dt}$

Now substitute: $\quad -\dfrac{dU}{dt} = \dfrac{Q+KV}{V} U$

Separate & integrate: $\quad -\displaystyle\int \frac{dU}{U} = \int \frac{Q+KV}{V} dt$

$$\ln|U| = -\frac{Q+KV}{V} t + c$$

$$\therefore \quad U = e^{-\frac{Q+KV}{V}t} \cdot \underbrace{e^{C}}_{U_0} \quad \rightarrow \quad U = U_0 e^{-\frac{Q+KV}{V}t}$$
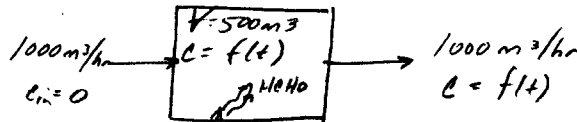
Now substitute original variables back into equation

$$\frac{c_i Q_i}{Q+KV} - c = \left(\frac{c_i Q_i}{Q+KV} - c_0\right)e^{-\frac{Q+KV}{V}t}$$

Rearrange:

$$c = \frac{c_i Q_i}{Q+KV} + \left(c_0 - \frac{c_i Q_i}{Q+KV}\right)e^{-\left(\frac{Q+KV}{V}\right)t}$$

Example: 500 m³ room with burning substance that emits HCHO at rate 140 mg/hr. Fresh air enters at $Q = 1000$ m³/hr. HCHO converts to CO_2 at first-order rate 0.40/hr. Plot conc. history of HCHO; in hours after ignition
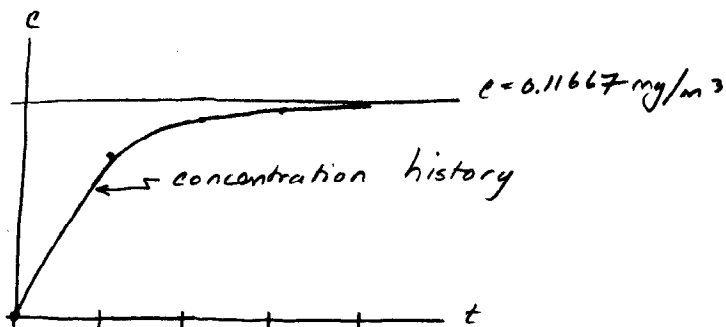

$$V\frac{dc}{dt} = \overset{0}{\cancel{c_{in}Q}} - cQ + \underbrace{\dot{m}_{combustion}}_{c_i Q_i} - \underbrace{\dot{m}_{transfer}}_{KcV} \quad \Bigg\} \text{same structure as step-function}$$

$$\therefore \quad c = \frac{c_i Q_i}{Q+KV} + \left(c_0 - \frac{c_i Q_i}{Q+KV}\right)e^{-\left(\frac{Q+KV}{V}\right)t}$$

$c_i Q_i = 140$ mg/hr $\quad KV = 200$ m³/hr

$Q = 1000$ m³/hr $\quad c_0 = 0$

t	c
0	0
1	0.106
2	0.115
3	0.1165
4	0.1166

$c = 0.11667$ mg/m³

concentration history

Cascade Models

One need not study a single reactor - a feed-forward series or cascade model can be used to i) study a single, poorly mixed reactor ii) a series of well mixed reactors
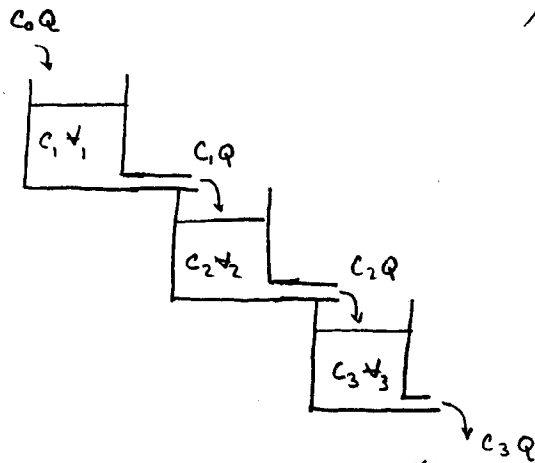
$$c_1 = \frac{c_0 Q}{Q + K_1 V_1} + \left(c_1(0) - \frac{c_0 Q}{Q + K_1 V_1}\right) e^{-\left(\frac{Q + K_1 V_1}{V_1}\right)t}$$

$$c_2 = \frac{c_1 Q}{Q + K_2 V_2} + \left(c_2(0) - \frac{c_1 Q}{Q + K_2 V_2}\right) e^{-\left(\frac{Q + K_2 V_2}{V_2}\right)t}$$

$$c_3 = \frac{c_2 Q}{Q + K_3 V_3} + \left(c_3(0) - \frac{c_2 Q}{Q + K_3 V_3}\right) e^{-\left(\frac{Q + K_3 V_3}{V_3}\right)t}$$

these can be simplified by substituting the RHS of c_1 into c_2 and c_2 into c_3

Using a computer makes the substitution unnecessary.

Now if a step-response for a single reactor is best modeled by N smaller reactors of equal volume, whose total volume (sum) is the same as the single reactor - this is an indication of poor mixing — most real systems are not perfectly mixed, but many are well modeled by complete mixing

For most of this course we will assume complete mixing, but keep in mind that cascade models can be used to explain more complex situations