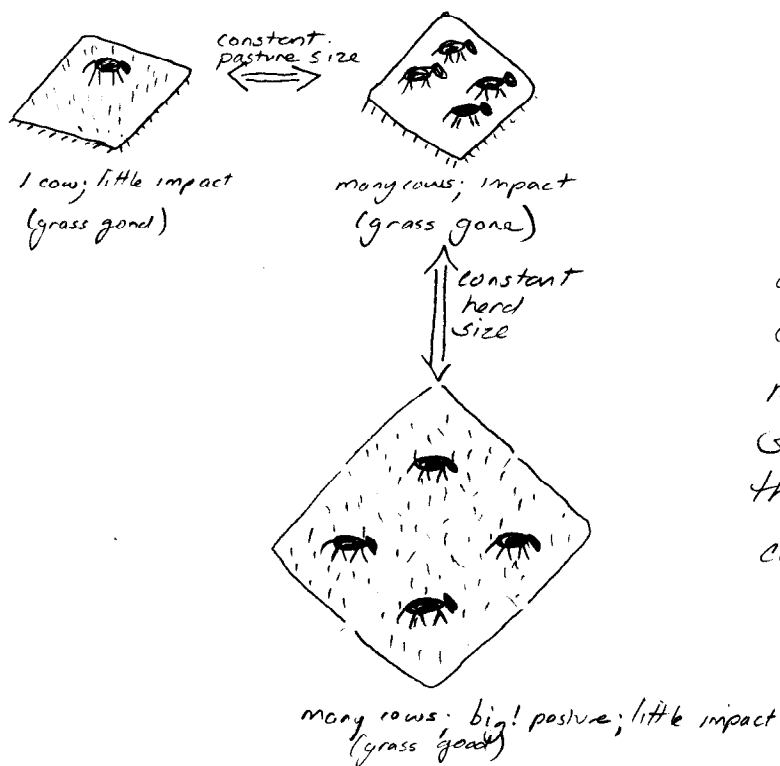


Concentration

Consider a cow in a pasture - a single cow may place a very small burden on the pasture. Likewise the waste of a single person discharged into a lake may be unnoticeable. However when the number of cattle or number of people is increased then the impact can be significant.

If the volume of the lake is changed, or the size of pasture changed the impact may also change - thus both the number of cattle and pasture size is important in predicting impact.



A uniform way to express the relationship is the concept of concentration. In terms of cattle, the number of cattle per hectare is a more useful measure of stress on the pasture than the absolute number of cattle.

Chemical concentration is critical in environmental engineering because it is the driving force that controls the movement of chemicals within and between environmental compartments, as well as the driving forces that controls many chemical reactions.

Concentrations of chemicals are routinely expressed in a variety of units depending on where the chemical is located (soil, water, air) and how the measurement will be used.

Typical concentration units

Representation	Example	Typical Units
mass/mass	mg/kg in soil	mg/kg; ppm _m
mass/volume	mg/L in water	mg/L; µg/m ³
volume/volume	volume fraction in air	ppmv
moles/volume	moles/L in water	M
equivalents/volume	eq/L in water	eq/L, meq/L

Mass-Mass Units

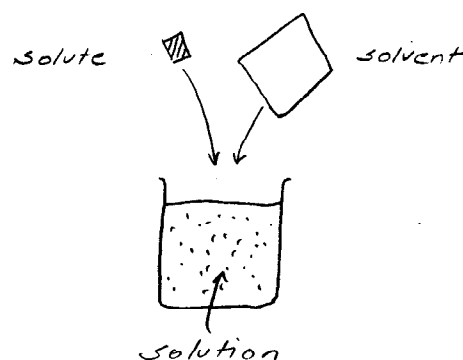
$$\text{mass fraction} = \frac{\text{mass solute}}{\text{mass solution}} = \frac{m_i}{m_b}$$

$$\text{parts per million} = \frac{m_i}{m_b} \times 10^6$$

$$\text{parts per billion} = \frac{m_i}{m_b} \times 10^9$$

$$\text{parts per trillion} = \frac{m_i}{m_b} \times 10^{12}$$

$$\text{parts per hundred (per cent)} = \frac{m_i}{m_b} \times 10^2$$



Example 5mg TCE in soil. 1 kg soil sample. What is [TCE]?

$$[\text{TCE}] = \frac{5\text{mg TCE}}{1\text{kg soil}} = \frac{0.005\text{g}}{1000\text{g}} = 5 \cdot 10^{-6} [\text{TCE}] \text{ (mass fraction)}$$

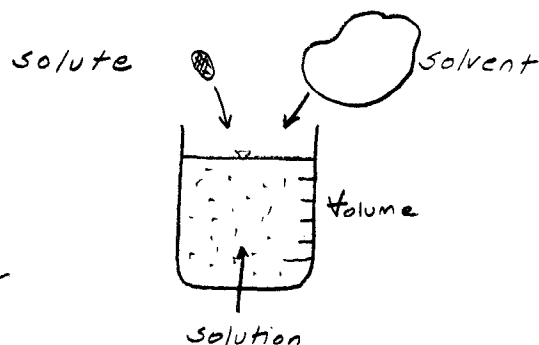
$$\left. \begin{array}{l} \text{all the same massic} \\ \text{concentration expressed} \\ \text{on different basis.} \end{array} \right\} \begin{array}{l} 5 \cdot 10^{-6} \times 10^2 = 0.0005\% \\ 5 \cdot 10^{-6} \times 10^6 = 5 \text{ ppm} \\ 5 \cdot 10^{-6} \times 10^9 = 5000 \text{ ppb} \end{array}$$

Mass-Volume Units

$$\text{Solute density} = \frac{\text{mass solute}}{\text{volume solution}}$$

Typical units are mg/m^3 , $\mu\text{g}/\text{m}^3$ } air

mg/L , $\mu\text{g}/\text{L}$ } water



In dilute aqueous systems $1\text{mg}/\text{L} \approx 1\text{ppm}$.

Example 1 L of water sample has 5.0mg TCE. What is [TCE] in mg/L and ppm at 20°C ?

$$[\text{TCE}] = \frac{5\text{mg TCE}}{1\text{L solution}} = 5\text{mg}/\text{L}$$

$$\frac{5\text{mg}/\text{L TCE}}{1\text{L H}_2\text{O}} \cdot \frac{1\text{L H}_2\text{O}}{998.2\text{g}} = \frac{0.005\text{g}}{998.2\text{g}} = 5.009 \cdot 10^{-6} \times 10^6 = 5.009\text{ppm}$$

Water density @ 20°C

less than 1% error in using $1\text{mg}/\text{L} \approx 1\text{ppm}$ in this system!

Use care when converting dilute systems as temperature will have an effect on water density!

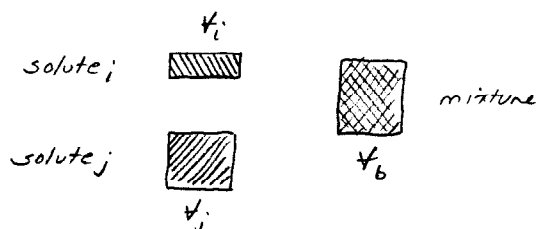
Volume-Volume; Mole-Mole Units

Volume fraction units are used for gas concentrations

Mole fraction units are used for gases & hydrocarbon mixtures

$$\text{Volume fraction} = \frac{\text{solute volume}}{\text{mixture volume}} = \frac{V_i}{V_b}$$

$$\text{parts per million} = \frac{V_i}{V_b} \times 10^6$$



$$\text{parts per billion} = \frac{V_i}{V_b} \times 10^9$$

Volume fractions are used for gas concentrations because the concentrations do not change as the gas is compressed or expanded. The ideal gas law is used to convert between mass/volume and volume/volume units

$$pV = nRT \quad \text{or} \quad pV = \frac{m}{M}RT$$

$$R = 0.08205 \frac{\text{L-atm}}{\text{K-mole}} ; 8.314 \frac{\text{J}}{\text{K-mole}} ; 1.987 \frac{\text{cal}}{\text{K-mole}}$$

Example Gas mixture of 0.001 mole SO_2 and 0.999 mole air. What is $[\text{SO}_2]$ in ppm?

$$\begin{aligned} [\text{SO}_2] &= \frac{V_{\text{SO}_2}}{V_b} \times 10^6 & V_{\text{SO}_2} &= 0.001 \text{ mole SO}_2 \times \frac{RT}{P} \\ &= \frac{0.001 \frac{RT}{P}}{1.000 \frac{RT}{P}} \times 10^6 = 1000 \text{ ppm}_v & V_b &= (0.999 + 0.001) \text{ mole} \times \frac{RT}{P} \end{aligned}$$

For gasses, volume ratios and mole ratios are equivalent

Partial Pressure Units

Often concentrations of gasses and volatile compounds in air are expressed as partial pressures. Total pressure in a gas is the sum of all the partial pressures of each component. The partial pressure of a component is the pressure that component would exert in the absence of other gasses.

Typical notation is P_i where i is the component of interest. Eg. $P_{\text{O}_2} = 0.21 \text{ atm}$
(Air is approx 21% oxygen)

$$P_i = \frac{V_i}{V_b} \cdot P_b \quad \text{ppm} = \frac{P_i}{P_b} \times 10^6$$

Mole/Volume (Molarity)

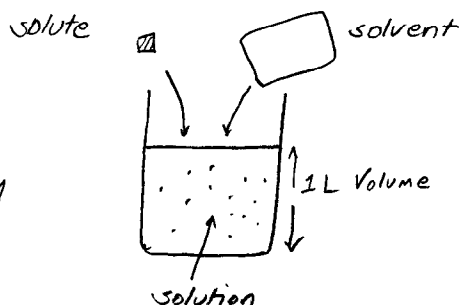
Moles per liter are used to report compounds in water. It is especially important for compounds that react.

5/5

$$\text{Molarity} = \frac{\text{moles}_i}{L_b} = \text{Molar, M}$$

$$\frac{\text{moles}_i}{L_b} \times 10^3 = \text{millimolar, mM}$$

$$\frac{\text{moles}_i}{L_b} \times 10^6 = \text{micromolar, } \mu\text{M}$$



Normality; Equivalents

Normality (equivalents/L) are used in aqueous acid-base and oxidation-reduction reactions. Used when two species react and the two species reacting have the same activity on an equivalent basis.

Acid-base

*equivalents per mole (acid) = moles H^+ that the acid can donate

*equivalents per mole (base) = moles H^+ that the base can accept

Oxidation-reduction

*equivalents per mole = moles e^- that the reactant can donate or accept
(oxidize) (reduce)

Equivalent weight is molecular weight of a species divided by the number of equivalents in the species.

Equivalent weight

Examples: Equivalents/mole of H_2SO_4 , $NaOH$, $CaCO_3$

$$H_2SO_4 \leftrightarrow 2H^+ + SO_4^{2-} \quad \frac{2 \text{ mole } H^+}{1 \text{ mole } H_2SO_4} = \frac{2 \text{ eq}}{\text{mol}} \quad \times \frac{1 \text{ mol}}{98 \text{ g}} = \frac{2 \text{ eq}}{98 \text{ g}} \text{ or } 49 \text{ g/eq}$$

$$NaOH \leftrightarrow Na^+ + OH^- \quad \frac{1 \text{ mole } H^+(OH^-)}{1 \text{ mole } NaOH} = \frac{1 \text{ eq}}{\text{mol}} \quad \times \frac{1 \text{ mol}}{40 \text{ g}} = \frac{1 \text{ eq}}{40 \text{ g}} \text{ or } 40 \text{ g/eq}$$

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \quad \frac{2 \text{ mole } H^+(CO_3^{2-})}{1 \text{ mole } CaCO_3} = \frac{2 \text{ eq}}{\text{mol}} \quad \times \frac{1 \text{ mol}}{100 \text{ g}} = \frac{2 \text{ eq}}{100 \text{ g}} \text{ or } 50 \text{ g/eq}$$

Materials Balance

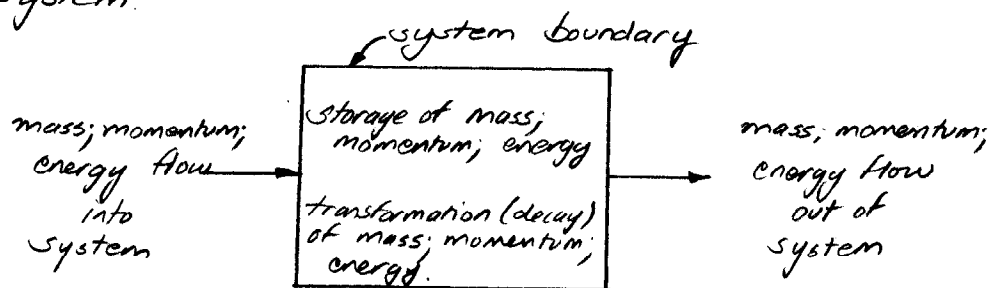
1/7

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:

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

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

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

Typically the rate balance is written as

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

Common simplifications

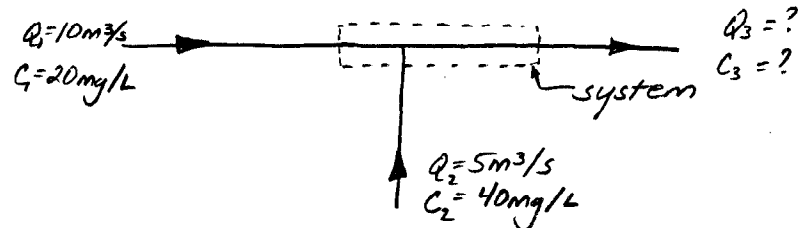
i) Equilibrium \Rightarrow usually means that $\dot{m}_{\text{storage}} = 0$
 $\therefore \dot{m}_{\text{in}} - \dot{m}_{\text{out}} = 0 - \dot{m}_{\text{trans}}$

ii) Conservative \Rightarrow usually means that $\dot{m}_{\text{trans}} = 0$
 $\therefore \dot{m}_{\text{in}} - \dot{m}_{\text{out}} = \dot{m}_{\text{storage}}$

Consider two streams.

Main stream $Q = 10 \text{ m}^3/\text{s}$; Tributary $Q = 5 \text{ m}^3/\text{s}$.
 $[Cl^-] = 20 \text{ mg/L}$; $[Cl^-] = 40 \text{ mg/L}$

Estimate $[Cl^-]$ downstream of confluence



Assume complete mixing in system.

$$\dot{m}_{in} - \dot{m}_{out} = \underbrace{\dot{m}_{stor}}_{\substack{=0 \\ \text{equilibrium}}} - \underbrace{\dot{m}_{tran}}_{\substack{=0 \\ \text{conservative}}}$$

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

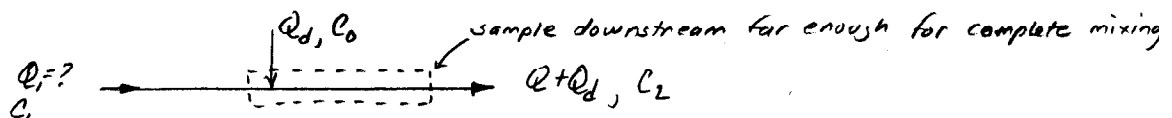
1) hydraulic mass flow: $\rho Q_1 + \rho Q_2 = \rho Q_3$
 $\therefore Q_3 = Q_1 + Q_2$

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

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

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.



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 $Q_1 = \frac{C_0 - C_2}{C_2} Q_d$

3/7

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.

$$\dot{m}_{\text{transfer}} = -Km \quad (\text{mass transfer rate is proportional to the mass in the system})$$

$$\frac{dm}{dt}_{\text{transfer}} = -Km \quad \text{separation and integration can be used to find the solution to this equation}$$

$$dm = -Kmdt$$

$$\frac{dm}{m} = -Kdt$$

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

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

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

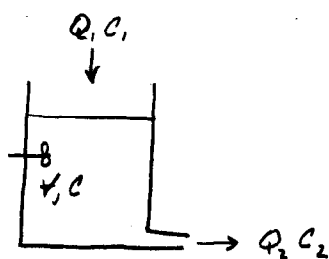
$$\dot{m}_{\text{in}} - \dot{m}_{\text{out}} = \dot{m}_{\text{storage}} + Km$$

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

$$\frac{d}{dt}(Ct)_{\text{in}} - \frac{d}{dt}(Ct)_{\text{out}} = \frac{d}{dt}(Ct)_{\text{storage}} + KCt$$

Expressed in this fashion, one has assumed complete mixing. When applied to reactor vessels such a system is called a { CSTR — continuously stirred tank reactor
CMFR — completely mixed flow reactor

4/7



Complete mixing means that $C_2 = C$

The balance expression for this fixed volume reactor is

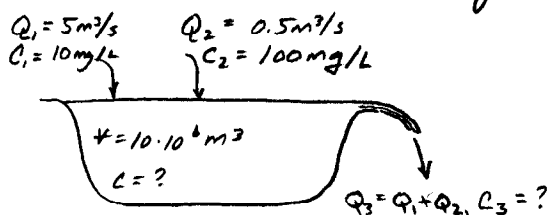
$$\dot{m}_{in} - \dot{m}_{out} = \dot{m}_{stor} - \dot{m}_{tran}$$

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

Example: $10 \cdot 10^6 \text{ m}^3$ lake. Stream supplies $Q = 5 \text{ m}^3/\text{s}$, $\text{TOC} = 10 \text{ mg/L}$.

Sewage outfall supplies $Q = 0.5 \text{ m}^3/\text{s}$, $\text{TOC} = 100 \text{ mg/L}$.

Lake has intrinsic assimilation capacity to degrade TOC by first-order model of $0.2/\text{day}$. Estimate equilibrium TOC.



- ① Assume complete mixing
- ② Hydraulic mass balance: $Q_3 = Q_1 + Q_2$
- ③ Chemical mass balance

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

$= 0$ equilibrium

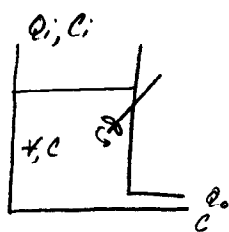
$$\underbrace{Q_1 C_1 + Q_2 C_2}_{\text{known}} - \underbrace{Q_3 C_3}_{\text{known}} = - \underbrace{K C_3 V}_{\text{known}} \quad \text{solve for } C_3$$

$$C_3 (-Q_1 - Q_2 - K V) = -C_1 Q_1 - C_2 Q_2$$

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

→ 1 day = 86400 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 1st 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 $C = \frac{C_i Q_i}{Q_o + KV}$

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

$$V \frac{dC}{dt} = Q_i C_i - Q_o C - KCV = C_i Q_i - C(Q_o + KV); \quad \frac{C_i Q_i}{V} - \frac{C}{V} (Q_o + KV) = \frac{dC}{dt}$$

$$\frac{dC}{dt} = \frac{C_i Q_i}{V} \frac{(Q_o + KV)}{(Q_o + KV)} - \frac{C (Q_o + KV)}{V} = \frac{Q_o + KV}{V} \left(\frac{C_i Q_i}{Q_o + KV} - C \right)$$

Now let $U = \frac{C_i Q_i}{Q_o + KV} - C$ $dU = -dC$; thus $\frac{dC}{dt} = -\frac{dU}{dt}$

Now substitute: $-\frac{dU}{dt} = \frac{Q_o + KV}{V} U$

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

$$\ln|U| = -\frac{Q_o + KV}{V} t + C$$

6/7

$$\therefore U = e^{-\frac{Q+K_v}{V}t} \cdot \underbrace{e^c}_{U_0} \rightarrow U = U_0 e^{-\frac{Q+K_v}{V}t}$$

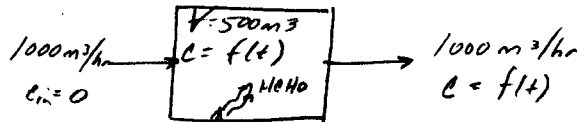
Now substitute original variables back into equation

$$\frac{C_i Q_i}{Q+K_v} - C = \left(\frac{C_i Q_i}{Q+K_v} - C_0 \right) e^{-\frac{Q+K_v}{V}t}$$

Rearrange:

$$C = \frac{C_i Q_i}{Q+K_v} + \left(C_0 - \frac{C_i Q_i}{Q+K_v} \right) e^{-\left(\frac{Q+K_v}{V} \right) t}$$

Example: 500m³ room with burning substance that emits MeHO at rate 140mg/hr. Fresh air enters at $Q = 1000\text{m}^3/\text{hr}$. MeHO converts to CO₂ at first-order rate 0.40/hr. Plot conc. history of MeHO; in hours after ignition

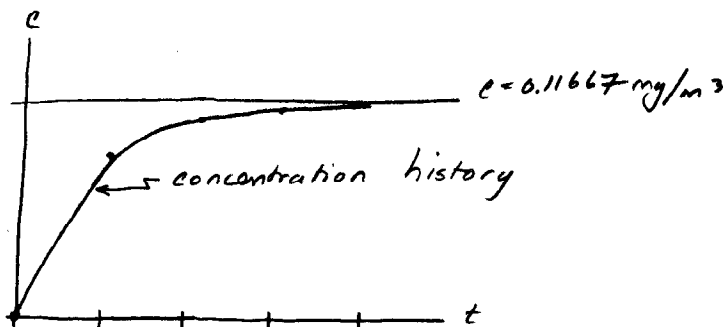


$$V \frac{dC}{dt} = \underbrace{C_i Q_i}_{\text{in combustion}} - \underbrace{C Q}_{\text{out transfer}} + \underbrace{\dot{m}_{\text{combustion}}}_{C_i Q_i} - \underbrace{\dot{m}_{\text{transfer}}}_{K_v C} \quad \left. \vphantom{\frac{dC}{dt}} \right\} \text{same structure as step-function}$$

$$\therefore C = \frac{C_i Q_i}{Q+K_v} + \left(C_0 - \frac{C_i Q_i}{Q+K_v} \right) e^{-\left(\frac{Q+K_v}{V} \right) t}$$

$$\begin{aligned} C_i Q_i &= 140 \text{ mg/hr} & K_v &= 200 \text{ m}^3/\text{hr} \\ Q &= 1000 \text{ m}^3/\text{hr} & C_0 &= 0 \end{aligned}$$

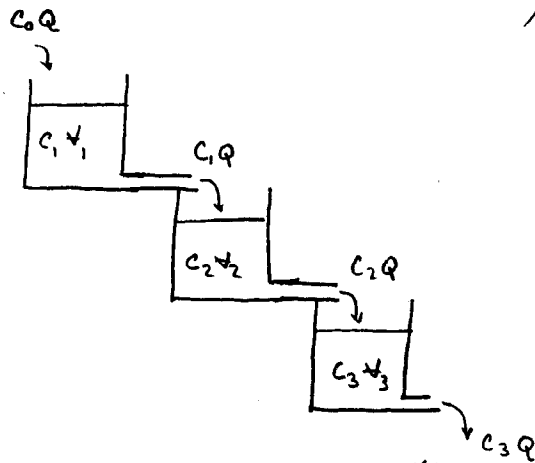
t	C
0	0
1	0.106
2	0.115
3	0.1165
4	0.1166



Cascade Models

One need not study a single reactor - a feed-forward series or cascade model can be used to

- study a single, poorly mixed reactor
- 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.

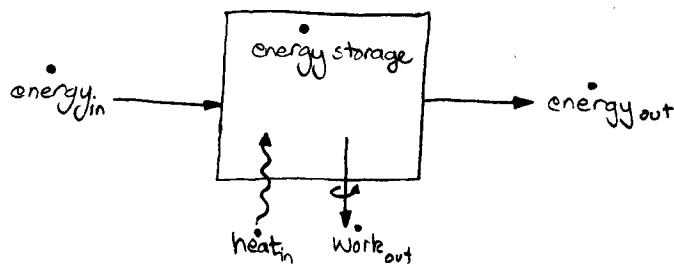
Now if a step-response for a single reactor is best modeled by N smaller reactors of equal volume, whose total volume (sum) is the same as the single reactor - this is an indication of poor mixing - most real systems are not perfectly mixed, but many are well modeled by complete mixing

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

Materials Balance

Energy balance is based on the conservation of energy (first law of thermodynamics) and the net growth of entropy (second law of thermodynamics)

Energy balance is used to track energy through a system. It is a little more complicated than the mass balance because the "transfer" term involves heat and work



The energy balance is usually written as an energy flow rate equation. Conservation of energy for a system says:

$$\left. \frac{dE}{dt} \right|_{\text{system}} = \underbrace{\frac{dQ}{dt}}_{\text{heat}_{in}} - \underbrace{\frac{dW}{dt}}_{\text{work}_{out}}$$

In words: rate of energy accumulated - rate entering + rate exiting =
rate of heat entering - rate of work (done by system) out.

Using e as a symbol for energy, the balance can be arranged as

$$\underbrace{\dot{e}_{in} - \dot{e}_{out}}_{\text{usually associated with mass flows}} = \dot{e}_{storage} - \underbrace{\dot{q}_{in}}_{\text{heat flow into system}} + \underbrace{\dot{w}_{out}}_{\text{work done by system}}$$

2/7

An open system will usually have both mass & energy flows.

A closed system will have only heat (and possibly) work flows.

Energy is the ability to do work. There are different "kinds" of energy based on the kind of work performed

kinetic energy - momentum
potential energy - position in gravitational, electrical or magnetic field

internal energy - microscopic level associated with KE & PE and thermal energy of a molecule. Often expressed as pressure in gases & liquids - temperature in solids

chemical energy - energy associated with chemical bonds

Total energy is sum of all relevant types of energy for a fixed quantity of mass. $E = KE + PE + U$. Thus the energy in the balance expression includes all types of energy.

Adding energy to a system often raises its temperature (think of a teapot). The amount of heat added (thermal energy) to raise the temperature of a unit mass of a substance by 1 degree is called the specific heat of the substance.

Btu - energy to heat 1 lb water, 1°F @ 59°F .
kcal - energy to heat 1 kg water, 1°C @ 15°C
cal - " " 1 g water, 1°C @ 15°C

The preferred unit is kJ/kg. For water the specific heat is 4.184 kJ/kg. For substances that remain as liquids or solids during the entire heating event (no phase change), the specific heats are essentially constant.

Gases expand during heating unless their volume is fixed. Specific heats are determined either at constant volume, constant pressure, or both c_v - constant volume sp. heat; c_p - constant pressure sp. heat.

Enthalpy of a substance is the sum of its internal energy and its "state" (pV).

$$H = \underbrace{U}_{\text{internal energy}} + \underbrace{pV}_{\text{"compression" energy}}$$

When heat is added to a substance, the change in enthalpy is given by

$$\frac{dH}{dT} = \frac{dU}{dT} + \frac{d(pV)}{dT} = \frac{dU}{dT} + p \frac{dV}{dT} + V \frac{dp}{dT}$$

For solids & liquids the pV term is relatively constant ($\frac{d(pV)}{dT} \sim \text{small}$) so that $\frac{dH}{dT} \approx \frac{dU}{dT}$.

For a gas either $p = \text{const.}$ (balloon) or $V = \text{const.}$ (gas cylinder)

$$H = U + pV = U + mRT$$

$$\left. \frac{dH}{dT} \right|_{V=\text{const.}} = \frac{dU}{dT} + V \frac{dp}{dT} = m c_v \quad \text{(Although pressure changes, it cannot do any work; work = force * distance)}$$

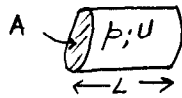
$$\left. \frac{dH}{dT} \right|_{p=\text{const.}} = \frac{dU}{dT} + p \frac{dV}{dT} = m c_p$$

Work - some thermal energy is lost.

In many systems of interest, the system is a fluid or solid - or behavior is isovolumetric so that the change in stored energy is mostly internal and can be represented as

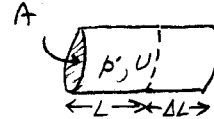
$$\Delta E_{\text{stored}} = m c \Delta T$$

Constant pressure heating



$$H_1 = U_1 + p_1 A L$$

Now add heat



$$H_2 = U_2 + p_2 A (L + \Delta L)$$

$$\begin{aligned} \Delta H = H_2 - H_1 &= U_2 - U_1 + p_2 A (L + \Delta L) - p_1 A L \quad \text{but } p_1 = p_2 \text{ so} \\ &= U_2 - U_1 + \underbrace{p_1 A \Delta L}_{\text{force} \times \text{distance} = \text{work}} \end{aligned}$$

$$\therefore \Delta H = \Delta U + \text{Work to expand}$$

Constant volume heating



$$H_1 = U_1 + p_1 A L$$



$$H_2 = U_2 + p_2 A L$$

$$\Delta H = H_2 - H_1 = U_2 - U_1 + (p_2 - p_1) A L$$

$$\Delta H = \Delta U + \underbrace{\Delta p A L}_{\text{No work because } V = \text{const.}}$$

Heat transfer

Stored energy from heat transfer is $m c \Delta T$; the expression assumes $c = \text{constant}$ and that there is no phase change.

Phases: gas, liquid, solid.
 fluids

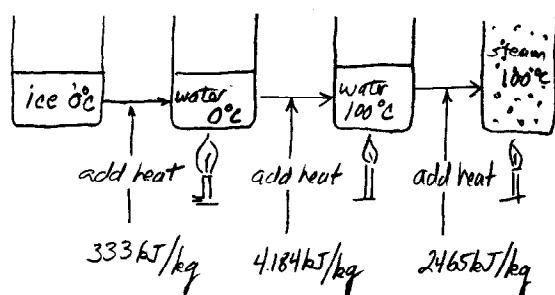
When a phase change occurs, energy is absorbed or released without a change in temperature (water freezes at 0°C ; ice melts at 0°C)

fusion fusion
(water boils at 100°C ; steam condenses at 100°C)
vaporization vaporization

Constant pressure sp. ^{energy} ~~heat~~ required to change from solid to liquid (or reverse) is called the enthalpy of fusion (latent heat of fusion).

Constant pressure sp. energy required to change from liquid to gas (or reverse) is called the enthalpy of vaporization.

5/7



Total energy to convert
1 kg ice at 0°C to 1 kg steam at 100°C
is

$$\begin{array}{r}
 333 \text{ kJ/kg} \quad (\text{ice to water}) \\
 4184 \text{ kJ/kg} \quad (\text{water } 0^\circ\text{C to water } 100^\circ\text{C}) \\
 2465 \text{ kJ/kg} \quad (\text{water } 100^\circ\text{C to steam } 100^\circ\text{C}) \\
 \hline
 3216 \text{ kJ/kg}
 \end{array}$$

To reverse process remove
energy in equal amounts

Phase change energies can be represented as $\Delta e_{\text{phase change}} = mL$

Many problems involve the flow of both mass and energy across
the system boundary. In such cases we might write

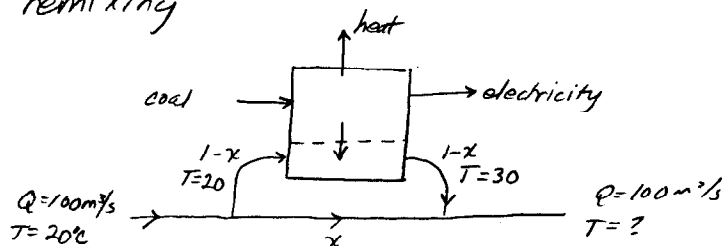
$$\dot{e}_{\text{stored}} = \dot{m} c \Delta T \quad \dot{m} \text{ is } \dot{m}_{\text{net}} \text{ mass flow rate.}$$

\dot{e} has units of power (kJ/sec; Btu/hr; $\frac{\text{work}}{\text{time}}$; $\frac{\text{force} \cdot \text{distance}}{\text{time}}$; force \cdot velocity)

A typical ^{integrated} energy balance might be expressed as

$$(U_{\text{in}} + KE_{\text{in}} + PE_{\text{in}}) - (U_{\text{out}} + KE_{\text{out}} + PE_{\text{out}}) + \text{HEAT}_{\text{in}} = \Delta E_{\text{SYSTEM}}$$

Example: coal fired 1000 MW power plant. 33% efficient. Remaining power lost as
heat; 15% to atmosphere; 85% to cooling water. Cooling water from
river $Q = 100 \text{ m}^3/\text{s}$, $T = 20^\circ\text{C}$. How much flow is diverted from
river if ΔT cooling water is 10°C ? What is temp. of river
after remixing



6/7

$$\eta = \frac{P_{out}}{P_{in}} = \frac{1}{3} \quad \therefore \text{coal } P_{in} = \frac{P_{out}}{\frac{1}{3}} = 3P_{out} = 3000 \text{ MW.}$$

$$P_{lost} = P_{in} - P_{out} = 2000 \text{ MW}$$

$$P_{ATM} = (0.15)(2000 \text{ MW}) = 300 \text{ MW} ; P_{RIVER} = (0.85)(2000 \text{ MW}) = 1700 \text{ MW}$$

Overall energy balance

$$\dot{e}_{in} - \dot{e}_{out} = \dot{e}_{storage} - \dot{q}_{in} + \dot{w}_{out}$$

$$\dot{e}_{in} = P_{in, coal} + P_{in, cooling, water}$$

$$\dot{e}_{out} = P_{out, elec} + P_{out, cooling, water}$$

$$\dot{e}_{storage} = 0$$

$$\dot{w}_{out} = 0$$

$$\dot{q}_{in} = -P_{ATM}$$

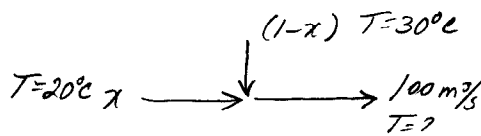
$$3000 \text{ MW} + p(1-x)cT_{in} - 1000 \text{ MW} - p(1-x)cT_{out} = 300 \text{ MW}$$

$$2000 \text{ MW} - p(1-x)c\Delta T = 300 \text{ MW}$$

$$p(1-x)c\Delta T = 1700 \text{ MW}$$

$$(1-x) = \frac{1700 \cdot 10^6 \text{ J/sec}}{4184 \text{ J/kg}^\circ\text{C} \cdot 10^\circ\text{C} \cdot 1000 \text{ kg/m}^3} = 40.63 \text{ m}^3/\text{sec}$$

Downstream temperature



$$\dot{e}_{in} - \dot{e}_{out} = \dot{e}_{stor} - \dot{q}_{in} + \dot{w}_{out}$$

$$\dot{e}_{in} = \dot{e}_{out}$$

$$p x \cdot 20^\circ\text{C} + p(1-x) \cdot 30^\circ\text{C} = p \cdot 100 \text{ m}^3/\text{s} \cdot T^\circ\text{C}$$

$$\frac{59.47(20) + 40.63(30)}{100} = 24.1^\circ\text{C}$$

Second law

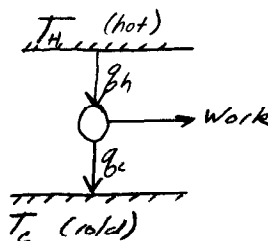
The second law of thermodynamics states that the rate of change of entropy in the system plus net rate of entropy flow out of the system is at least equal to overall heat transfer across the boundary and the internal heat production.

Entropy is roughly analogous to the reciprocal of "useful fuel".

As entropy decreases, a system can do more useful work. As entropy increases, a system does less useful work and generates more waste heat.

Carnot cycle heat engine

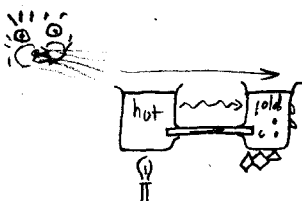
$$\eta = \frac{\text{Work out}}{\text{Work in}} = 1 - \frac{T_c}{T_h}$$



Maximum possible $\eta = 1$ when $T_c \rightarrow 0$ or $T_h \rightarrow \infty$. \therefore All real systems have $\eta < 1$

- Component efficiencies can be very high, but overall η is what counts
- waste heat is wasted \$, but if a 1% increase in η costs more than the \$ saved, the efficiency will not be improved (economics)
- waste is unavoidable - finding use for waste is beneficial and increases overall efficiency.

Heat transfer concepts



Two objects at different T . Heat will transfer from hot to cold object.

conduction - transfer by direct physical contact
convection - transfer by host fluid that carries heat

radiation - transfer by heat acting as e-m wave.