CIVE 3331 - ENVIRONMENTAL ENGINEERING
Spring 2003

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Precision and Accuracy

The concepts of precision and accuracy are important in all quantitative aspects of engineering. These are distinct ideas that express the degree that our information about a system represents the truth. Information is precise if it can be determined repeatedly with little variation (precision is associated with repeatability). Information is accurate if the average (some averaging scheme, not necessarily an arithmetic mean) of repeated measurements is close to the true value.

Inaccuracy and imprecision are grouped under the heading of “errors” reflecting a limit on the quantity of knowledge. (These “errors” do not necessarily imply mistakes, although mistakes can certainly produce huge error.) Improved precision and accuracy are desirable goals that usually require greater expense. Engineers generally aim for answers that are accurate and precise enough for the application at hand (consequences of failure need consideration here). The need to keep costs under control means that engineers do not generally seek accuracy or precision much greater than necessary (engineering science on the other hand is always striving to increase accuracy and precision).

By convention, the precision of a numerical result is conveyed by how it is written. For example the numbers 1.0 and 1.000 are mathematically equivalent, but the implied precision of the second number is 100 times greater than the first. That is 1.0 implies that the result is between 0.95 and 1.05, while 1.000 implies the result is between 0.9995 and 1.0005. The uncertainty is much greater in the first case.

As a guideline, quantitative results in engineering seldom have less than 1% error, consequently it makes little sense for a result to have more than three significant figures, thus results in this course should adhere to this guideline.

Concentration

Recall the fable of the commons. A single cow in a pasture placed 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 is increased or the number of people discharging increases, then the impact can be a problem. Now if the size of the lake or pasture is increased, then the impact may change - thus not only is the number of cattle important, the size of the pasture is important too.

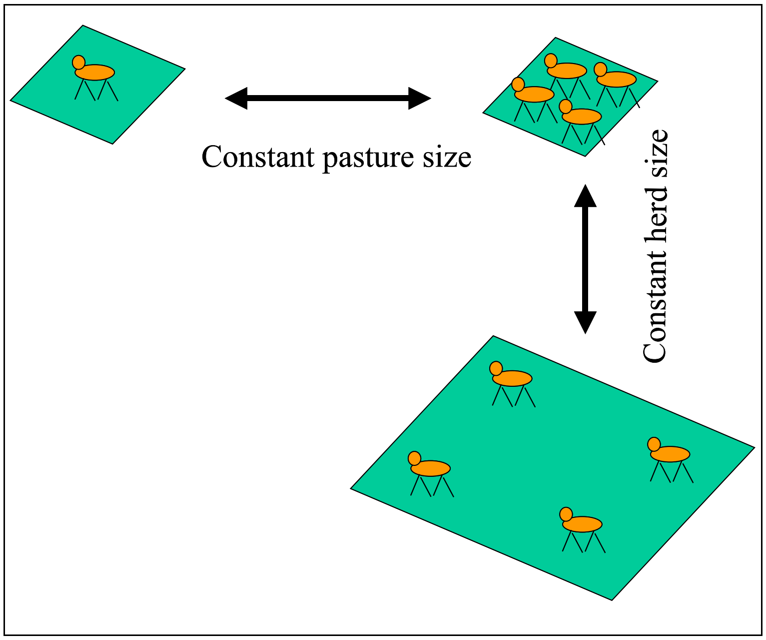


Figure 1. Herd size and pasture sixe relationships

One uniform way to express this idea is the concept of concentration. In terms of cattle, the number of cattle per acre is a more useful measure of stress on the pasture than is the absolute number of cattle. The concept of concentration is vital in engineering (and medicine). Very small concentrations of poison (drugs) are therapeutic. Large concentrations of the same materials can be quite lethal.

Chemical concentration is critical in environmental engineering because it is the driving force that controls the movement of chemicals within and between different 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, fire, and air) and how often the measurement will be used.

Table 1. Various Concentration Units in Environmental Engineering

Representation	Example	Typical Units
mass/mass	mg/kg in soil	mg/kg, ppm_m
mass/volume	mg/L in water	mg/L,$\mu g/m^3$
volume/volume	volume fraction in air	ppm_v
moles/volume	moles/L in water	M
equivalents/volume	eq/L in water	eq/L, meq/L

Mass/Mass

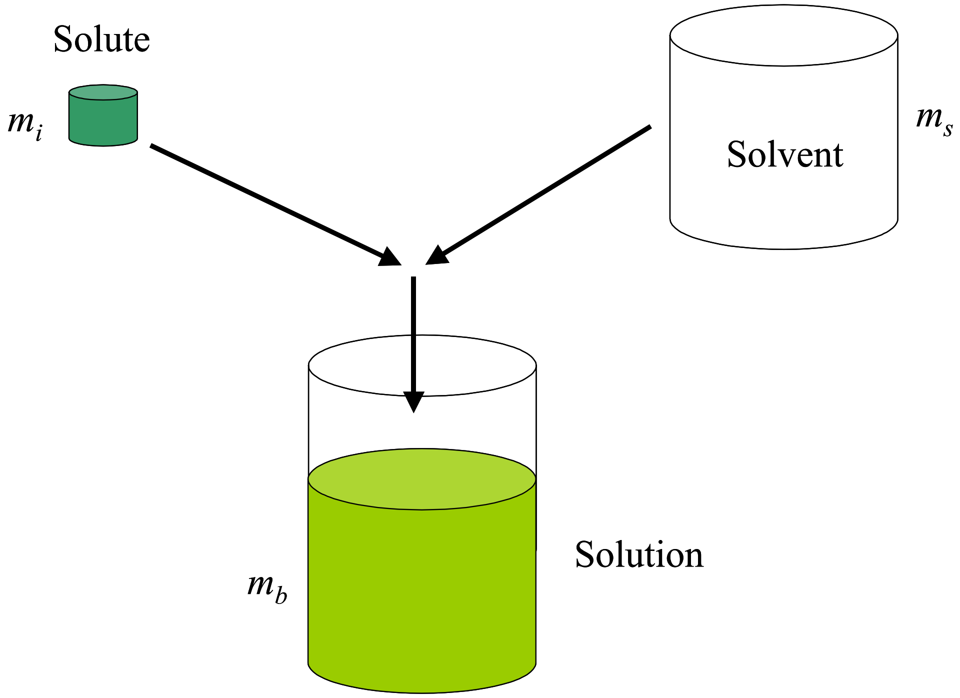


Figure 2. Mass-Mass Concentration Concept

Mass/mass concentrations are commonly expressed in parts per million, parts per billion, and so on. For example 1 milligram of solute placed into 1 kg of solvent produces a concentration of the solute of 1mg/kg = 1ppm.

A general formula for parts per million mass/mass concentrations is

$$ppm_m = \frac{m_i}{m} \times 10^6$$

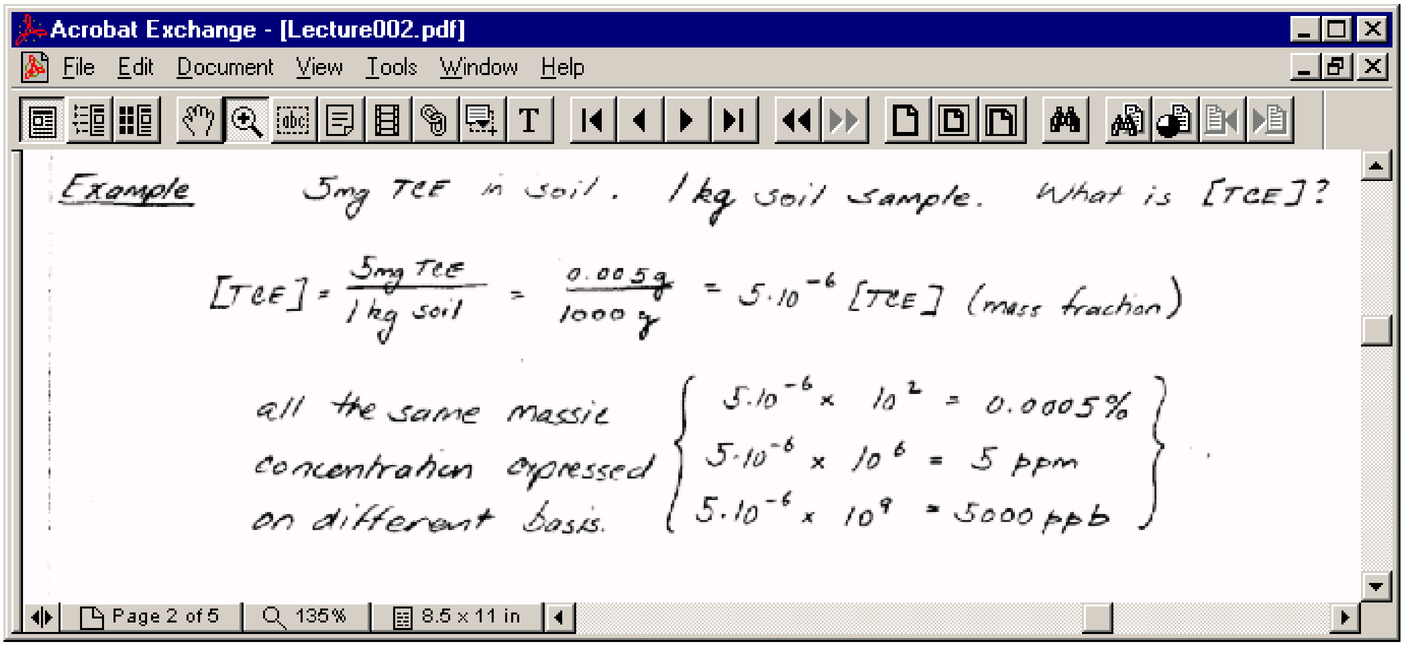
A general formula for parts per million mass/mass concentrations is

$$ppb_m = \frac{m_i}{m} \times 10^9$$

Similar relationships can be expressed for other mass/mass units. The notation ppt can refer to either parts per thousand or parts per trillion. Salinity concentrations are often expressed in parts per thousand, abbreviated as ppt.

Problem:

A one-kg sample of soil is analyzed for the chemical solvent TCE. The analysis indicates that the sample contains 5.0 mg of TCE. What is the TCE concentration in ppm and ppb?



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

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

all the same massic concentration expressed on different basis.

$$\left\{ \begin{array}{l} 5 \cdot 10^{-6} \times 10^{2} = 0.0005\% \\ 5 \cdot 10^{-6} \times 10^{6} = 5\ ppm \\ 5 \cdot 10^{-6} \times 10^{9} = 5000\ ppb \end{array} \right\}$$

Figure 3. Calculations for TCE in soil.

Problem:

A mass of one gram of solids is added to one kilogram of water. What is the concentration of the solids in %-solids?

Mass/Volume

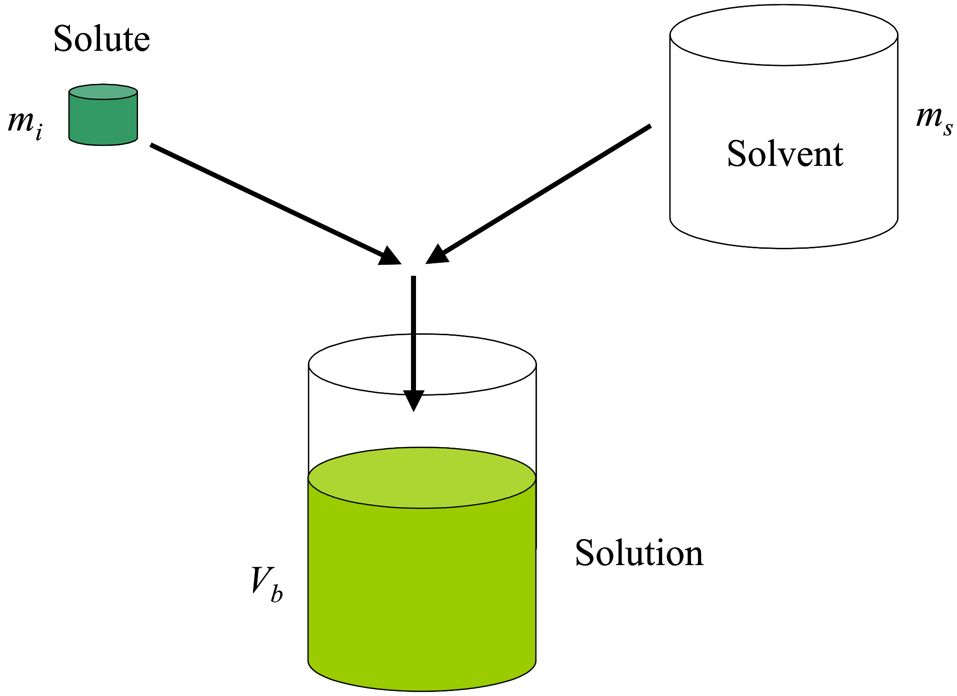
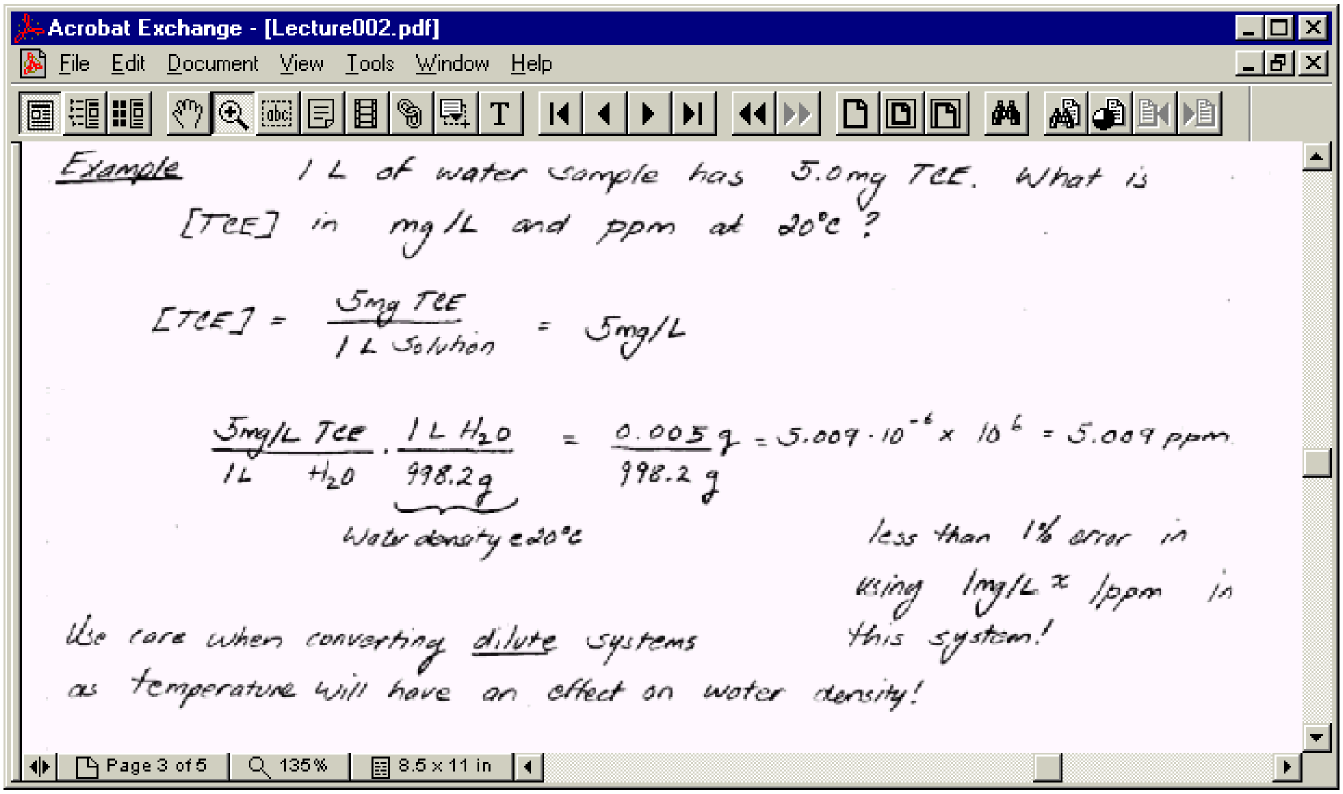


Figure 4. Mass-Volume Concentration Concept

Mass/volume units are commonly used in air and water descriptions. For example if 1 mg of salt is added to one liter of water, the salt concentration is 1 mg/L. In dilute aqueous systems, 1 mg/L ~ 1 ppm.

Problem:

One liter of water is analyzed and found to contain 5.0 mg TCE. What is the TCE concentration in mg/L and ppm?



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

$$[TCE] = \frac{5\,mg\ TCE}{1\,L\ Solution} = 5\,mg/L$$

$$\frac{5\,mg/L\ TCE}{1L\quad H_2O} \cdot \underbrace{\frac{1\,L\ H_2O}{998.2\,g}}_{\text{Water density @ 20°C}} = \frac{0.005\,g}{998.2\,g} = 5.009 \cdot 10^{-6} \times 10^{6} = 5.009\ ppm$$

less than 1% error in using 1 mg/L ≈ 1 ppm in this system!

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

Figure 5. Calculations for TCE in water.

Problem:

What is the CO concentration in µg/m^3 of a 10-L gas sample that contains 10^{-6} mole of CO?

V*olume/Volume and Mole/Mol*e

Units of volume fraction and mole fraction are frequently used for gas concentrations, and for hydrocarbon mixtures. The common volume fraction units are ppm and ppb.

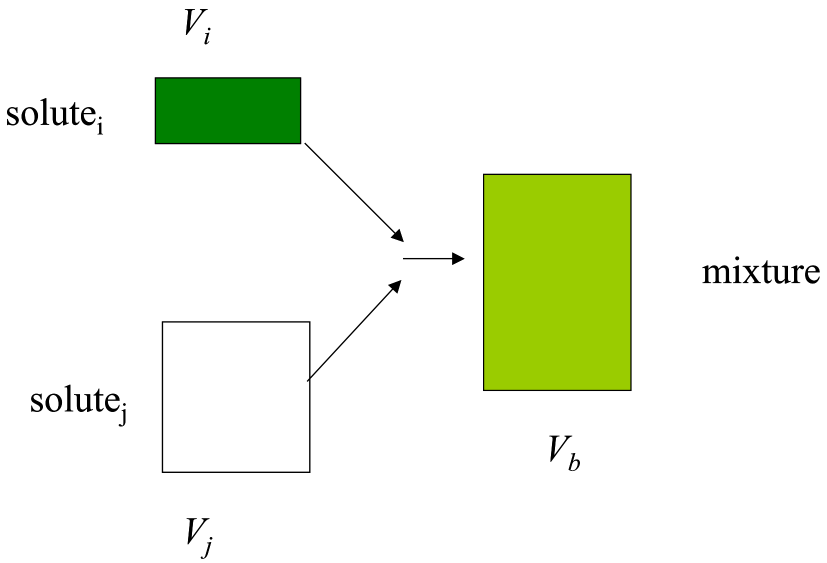


Figure 6. Volume-Volume Concentration Concept

A general formula for parts per million volume/volume concentrations is

$$ppm_v = \frac{V_i}{V} \times 10^6$$

A general formula for parts per million volume/volume concentrations is

$$ppm_v = \frac{V_i}{V} \times 10^9$$

Volume fraction units are used in gasses because the units do not change as the gas is compressed or expanded, while mass/volume units do change with compression or expansion. The Ideal Gas Law can be used to convert gaseous concentrations between mass/volume and volume/volume.

$$pV = nRT \quad \text{or} \quad pV = (m/M)\,RT$$

R = 0.08205 (L-atm)/(K-mole) ; 8.314 (J)/(K-mole) ; 1.987 (cal)/(K-mole)

Example:

Gas mixture of 0.001 mole of SO_2 and 0.999 mole air. What is $[SO_2]$ in ppm?

$$ppm_v = \frac{V_i}{V} \times 10^6 \quad ; \quad [SO_2] = \frac{V_{so_2}}{V_b} \times 10^6$$

$$V_{so_2} = 0.001 \text{ mole } SO_2 \cdot \frac{RT}{P} ; \; V_b = (0.999 + 0.001) \text{ mole } (SO_2 + air) \cdot \frac{RT}{P}$$

$$[SO_2] = \frac{0.001 \cdot \frac{RT}{P}}{1.000 \cdot \frac{RT}{P}} \times 10^6 = 1000 \;\; ppm[SO_2]$$

Partial Pressure Units

Often concentrations of gasses and volatile compounds are expressed as partial pressures. Total pressure in a gas is the sum of all the partial pressures of each component of the gas (a gas is treated as a mixture). The partial pressure of a component is the pressure that component exerts in the absence of the other gasses.

Typical notation is Pi where I is the component of interest. For instance, P_{O2} = 0.21 atm. (Air is approximately 21% oxygen).

$$P_i = \frac{V_i}{V_b} \times P_b \quad ; \quad ppm_v = \frac{P_i}{P_b} \times 10^6$$

Mole-Volume (molarity) Units

Moles per liter are used to report compounds in water, especially for compounds that are expected to react. The name of the concentration unit is this case is molarity.

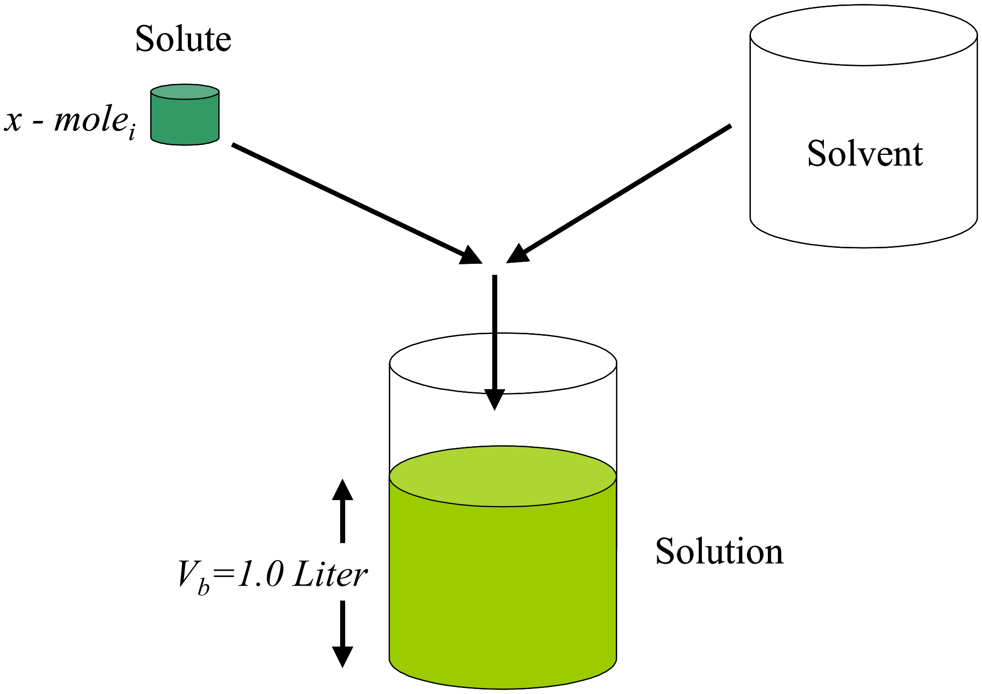


Figure 7. Molarity Concentration(s)

$$\frac{moles_{\mathrm{i}}}{V_b} = \text{molar}, M$$

$$\frac{moles_i}{V_b} \times 10^3 = \text{millimolar}, mM$$

$$\frac{moles_i}{V_b} \times 10^6 = \text{micromolar}, \mu M$$

Normality and Equivalents

Normality (equivalents/L) are used in aqueous acid-base and oxidation-reduction systems for quantifying how much of a particular chemical species is present. This type of concentration expression is most useful when two species react and the species reacting have the same activity on an equivalent basis.

Acid-Base

#equivalents per mole (acid) = moles H^+ that the acid can donate (produce).
#equivalents per mole (base) = moles H^+ that the base can accept (consume).

Oxidation-Reduction

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

Equivalent weights

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

Examples:

Equivalents/mole of H_2SO_4 ; NaOH ; $CaCO_3$

$H_2SO_4 \Leftrightarrow 2H^+ + SO_4^{2-}$

$$\frac{2H^+}{1H_2SO_4} = \frac{2eq}{mole} \times \frac{1H_2SO_4}{98g} = \frac{2eq}{98g} \text{ or } \frac{98g}{2eq} = \frac{49g}{eq.}$$

$NaOH \Leftrightarrow Na^+ + OH^-$

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

$CaCO_3 \Leftrightarrow Ca^+ + CO_3^{2-}$

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

Materials Balance

A material balance is the fundamental tool used in environmental engineering analysis. In its simplest form it is an accounting procedure. Your checkbook is an example:

$$\textit{Balance} = \textit{Deposits} - \textit{Withdrawls}$$

In an environmental system the accounting equation (for Mass) would be written as:

$$\textit{Accumulation of Mass} = \textit{Input of Mass} - \textit{Output of Mass}$$

The Accumulation, Input, and Output refer to important quantities flowing into or out of the system.

In environmental engineering the balance concept is usually based on two conservation laws:

1. conservation of mass
2. conservation of energy

The conservation of linear and angular momentum is sometimes important when dealing with fluid systems, but these balances will be examined in your hydraulics class, so we will not talk much about them in this class.

The balance process is used to track materials of interest throughout a system.

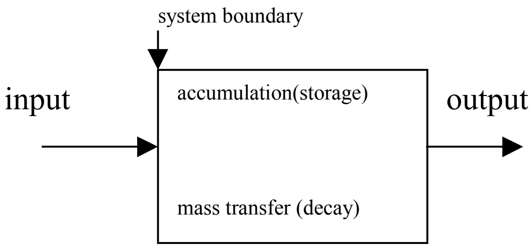


Figure 8. System Diagram

For the general accounting procedure the materials of interest have the attribute of identity (e.g. chemical species, direct revenue, etc.).

Mass Balance

Usually the balance is written as a mass flow rate equation:

Input Mass Flow Rate - Output Mass Flow Rate = Mass Accumulation Rate – Mass Transfer Rate

Although the fundamental equation looks simple, it is remarkable useful. Often the individual terms of the equation are very complicated, but not always. Using the language of calculus the balance equation is expressed as:

$$\left.\frac{dm}{dt}\right|_{input} - \left.\frac{dm}{dt}\right|_{output} = \left.\frac{dm}{dt}\right|_{accumulation} - \left.\frac{dm}{dt}\right|_{transfer}$$

Generally inputs and outputs refer to mass that enters in some flow stream, while transfer may be distributed across the boundary or into an internal compartment or simply a change in identity of the mass (radioactive decay). The above equation is intended as a memory device – it simply tells us that after we draw a boundary around a system for analysis or design, we need to identify inputs to the system, outputs from the system, a way of expressing accumulation within the system, and any mass transfer terms that occur across the system boundary or internally that are not associated with flows in the input and output streams.

Important simplifications

<u>Equilibrium</u> - Sometimes called steady state, equilibrium usually means that there is no apparent accumulation within the boundary of the system.

Thus we set $\left.\frac{dm}{dt}\right|_{accumulation} = 0$ and we solve for the remaining terms.

For example the balance is expressed as: $\left.\frac{dm}{dt}\right|_{input} - \left.\frac{dm}{dt}\right|_{output} + \left.\frac{dm}{dt}\right|_{transfer} = 0$

<u>Conservative</u> - Often means that the mass transfer term is zero (the materials do not interact within the system). In this situation the balance is

$$\left.\frac{dm}{dt}\right|_{input} - \left.\frac{dm}{dt}\right|_{output} = \left.\frac{dm}{dt}\right|_{accumulation}$$

<u>Conservative properties in equilibrium</u> - This system has both zero accumulation and mass transfer. The balance expression is

$$\left.\frac{dm}{dt}\right|_{input} = \left.\frac{dm}{dt}\right|_{output}$$

Example - Equilibrium, Conservative

Consider two streams, the main stream has a volumetric flow rate of 10 m^3/sec, and its tributary has a volumetric flow rate of 5m^3/sec. The main stream has chloride concentration of 20 mg/L upstream of the confluence while the tributary has concentration of 40 mg/L. Estimate the concentration of chloride downstream of the confluence.

Sketch the system.

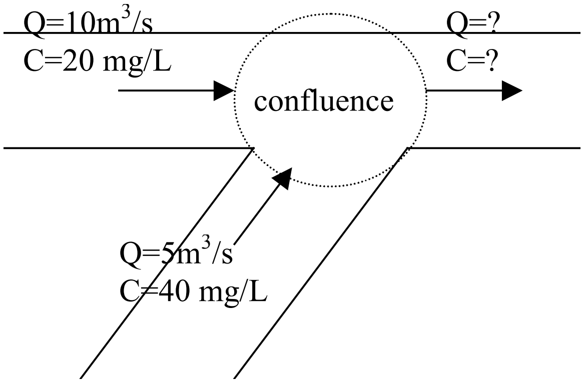


Figure 9. Sketch of Stream Confluence

1) Assume complete mixing in the confluence

2) Write a hydraulic mass balance:

Mass Flow Rate In - Mass Flow Rate Out = Mass Accumulated Rate

Mass Accumulated Rate = 0

$$\rho Q_{main-in} + \rho Q_{trib-in} - \rho Q_{main-out} = 0$$

3) Solve the balance equation for the unknown volumetric flow rate:

$$Q_{main-out} = \frac{\rho Q_{trib-in} + \rho Q_{main-out}}{\rho} = 10m^3/s + 5m^3/s = 15m^3/s$$

4) Write a chemical mass balance

Mass Flow Rate In - Mass Flow Rate Out = Mass Accumulated Rate

Mass Accumulated Rate = 0

$$C_{main-in}Q_{main-in} + C_{trib-in}Q_{trib-in} - C_{main-out}Q_{main-out} = 0$$

5) Solve the balance equation for the unknown concentration

$$C_{main-out} = \frac{C_{trib-in}Q_{trib-in} + C_{main-in}Q_{main-in}}{Q_{main-out}} =$$

$$\frac{(20mg/L)(10m^3/s) + (40mg/L)(5m^3/s)}{15m^3/s} = 26.6mg/L$$

This particular example has a practical application. One method of measuring flow rate is called the dye dilution method. A tracer (dye, chloride, etc.) is injected into a flow, usually the injection flow rate is small relative to the main flow. The downstream concentration is measured and from its value the main flow can be inferred.

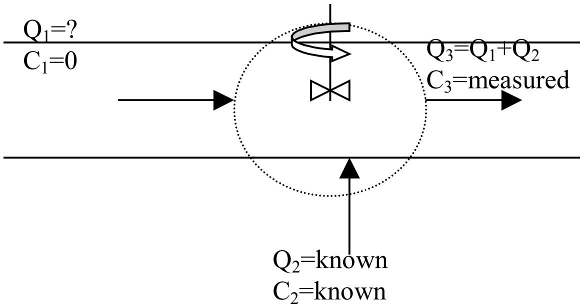


Figure 10. Dye Dilution Schematic

The method assumes complete mixing at the measurement location. The hydraulic mass balance is

$Q_3=Q_1+Q_3$

The tracer mass balance is

$C_3Q_3=C_1Q_1+C_2Q_2$

Solving for Q1 we obtain

$Q_1=(C_2-C_3)Q_2/(C_3-C_1)$

A good tracer is usually absent from the upstream flow so that $C_1=0$ and the formula is

$Q_1=(C_2-C_3)Q_2/C_3$

Equilibrium, non-conservative systems

Many chemical species undergo change as they traverse a system so that the internal mass transfer term cannot be treated as negligible. The balance expression in such a case (recall we are still in equilibrium) is

$$\left.\frac{dm}{dt}\right|_{input} - \left.\frac{dm}{dt}\right|_{output} + \left.\frac{dm}{dt}\right|_{transfer} = 0$$

The internal mass transfer term covers a variety of possible processes (reactions). Often a first order decay function is used to model this term.

$$\left.\frac{dm}{dt}\right|_{transfer} = -Km$$

This expression states that the mass transfer is proportional to the mass in the system. The mass transfer term does not mean that mass is destroyed, it means that the nature of the mass changes so that it is no longer involved in the process.

Separation and integration can be used to find the solution to this differential equation:

$$\int\frac{dm}{m} = \int -Kdt \rightarrow \ln(m) = -Kt + c$$
$$\rightarrow m = e^c e^{-Kt} = m_o e^{-Kt}$$

If first-order decay is the appropriate description of internal mass transfer then the balance equation is

$$\left.\frac{dm}{dt}\right|_{input} - \left.\frac{dm}{dt}\right|_{output} - Km = 0$$

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

$$\left.\frac{dCV}{dt}\right|_{input} - \left.\frac{dCV}{dt}\right|_{output} - KCV = 0$$

This particular representation assumes complete mixing. When it is applied to reactor vessels such a system is called a continuously stirred tank reactor (CSTR) or a completely mixed flow reactor (CMFR).

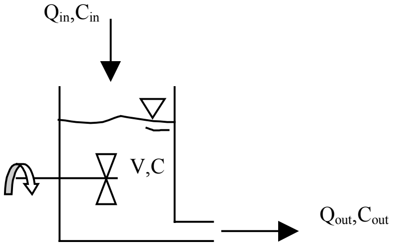


Figure 11. Schematic of Mixed System

Complete mixing means that C_{out}=C.

Example

A 10 x 10^6 cubic meter lake is supplied by a stream with Q=5 cms and a TOC (Total Organic Carbon) load of 10 mg/L. A sewage outfall discharges into the lake with Q=0.5 cms and a TOC of 100mg/L. The lake has an intrinsic assimilation capacity (ability to transfer TOC into other materials) of 0.20/day. The assimilation process is approximately first-order. Estimate the average equilibrium concentration of TOC in the lake.

1) Sketch the system, label relevant features

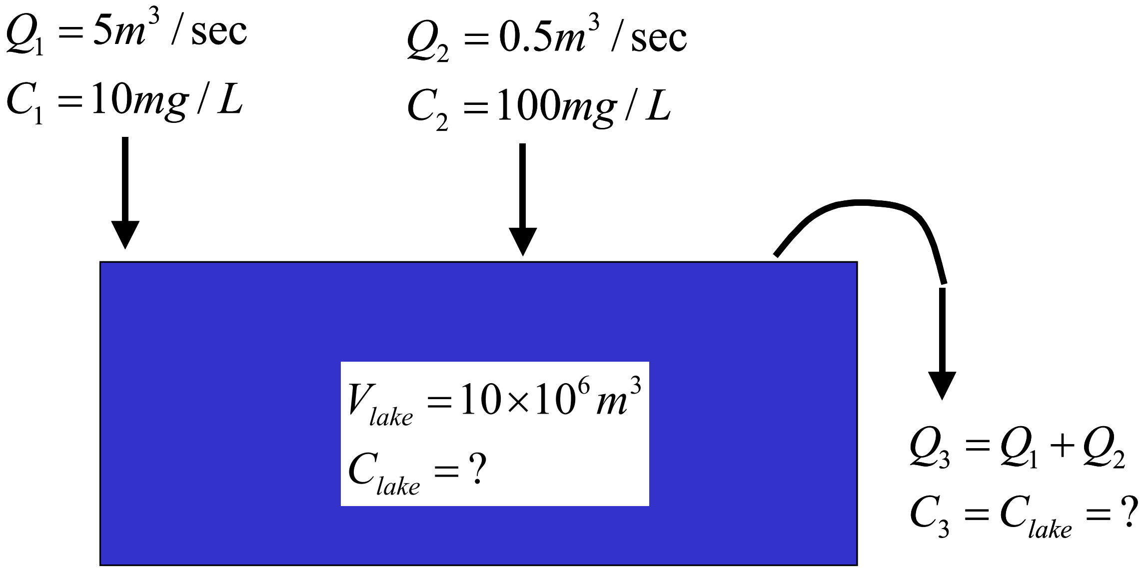


Figure 12. Lake Balance Model Sketch

2) Assume lake is completely mixed (only way we know right now).

3) Hydraulic mass balance:

$$Q_3 = Q_1 + Q_2$$

4) Chemical mass balance.

$$\dot{m}_{\inf low} - \dot{m}_{outflow} = \frac{dm_{storage}}{dt} + \dot{m}_{decay} = (Q_1C_1 + Q_2C_2) - (Q_3C_{lake}) = \frac{dC_{lake}V_{lake}}{dt} + \dot{m}_{decay}$$

5) Apply first-order mass transfer term.

$$(Q_1C_1 + Q_2C_2) - (Q_3C_{lake}) = \frac{dC_{lake}V_{lake}}{dt} + KC_{lake}V_{lake}$$

6) Equilibrium conditions (accumulation = 0)

$$(Q_1C_1 + Q_2C_2) - (Q_3C_{lake}) = 0 + KC_{lake}V_{lake}$$

Solve resulting equation(s).

$$(Q_1C_1 + Q_2C_2) - (Q_3C_{lake}) = 0 + KC_{lake}V_{lake}$$

$$(Q_1C_1 + Q_2C_2) = C_{lake}(KV_{lake} + Q_3)$$

$$\frac{(Q_1C_1 + Q_2C_2)}{(KV_{lake} + Q_3)} = C_{lake}$$

$$C_{lake} = \frac{(5m^3/s)(10mg/L) + (0.5m^3/s)(100mg/L)}{5.5m^3/s + (0.2/day)(10\times10^6\,m^3)(\frac{1day}{86400s})} = 3.49mg/L$$

Non-equilibrium response.

Non-equilibrium analysis is concerned with the response of the system over some specified time period. One response of great importance is the step-function response. This response provides information about mixing in the system.

Consider a completely mixed reactor as shown

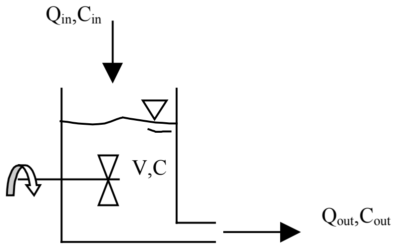


Figure 13. Completley Mixed Reactor

Assume first-order internal mass transfer. Consider a chemical mass balance.

$$\left.\frac{dm}{dt}\right|_{accumulation} = \left.\frac{dCV}{dt}\right|_{system} = V\left.\frac{dC}{dt}\right|_{system}$$

$$\left.\frac{dm}{dt}\right|_{input} = C_{in}Q_{in}$$

$$\left.\frac{dm}{dt}\right|_{output} = CQ \text{ (complete mixing)}$$

$$\left.\frac{dm}{dt}\right|_{transfer} = -KCV$$

The balance expression for this reactor is

$$V\frac{dC}{dt} = C_{in}Q_{in} - CQ - KCV$$

The equilibrium solution is

$$C = \frac{C_{in} Q_{in}}{Q + KV}$$

If the source concentration were changed from C_{in} to C_{new} then the new equilibrium concentration is

$$C = \frac{C_{new} Q_{in}}{Q + KV}$$

However we are often interested in the behavior of the system while it is changing from one equilibrium condition to another – to study this behavior one needs to solve the differential equation associated with the problem. The non-equilibrium (transient) solution is obtained by calculus using a substitution.

$$V\frac{dC}{dt} = C_{in}Q_{in} - CQ - KCV = C_{in}Q - C(Q + KV)$$

$$\frac{dC}{dt} = \frac{C_{in}Q}{V} - \frac{C(Q + KV)}{V} = \frac{C_{in}Q}{V}\frac{Q + KV}{Q + KV} - \frac{C(Q + KV)}{V}$$

$$\frac{dC}{dt} = \left(\frac{Q + KV}{V}\right)\left(\frac{C_{in}Q}{Q + KV} - C\right);$$

$$\text{let } u = \frac{C_{in}Q}{Q + KV} - C; du = -dC$$

This substitution allows one to simplify the differential equation to

$$\frac{dC}{dt} = -\frac{du}{dt} = \left(\frac{Q + KV}{V}\right)u$$

$$-\frac{du}{u} = \left(\frac{Q + KV}{V}\right)dt$$

Next one integrates (finds antiderivative) of both sides of the equation. Note the constant of integration can be carried on either side of the expression.

$$-\int \frac{du}{u} = \int \left(\frac{Q+KV}{V} \right) dt \rightarrow$$

$$-\ln(u) = \left(\frac{Q+KV}{V} \right) t + c$$

$$u = e^{-\left(\frac{Q+KV}{V}\right)t} e^{-c} \rightarrow u_o e^{-\left(\frac{Q+KV}{V}\right)t}$$

The constant of integration is evaluated from known conditions (if there are any), in this case one has assumed that conditions are known at time zero. Next we substitute back the original variables to obtain a solution to our particular problem

$$\frac{C_{in}Q}{Q+KV} - C = (\frac{C_{in}Q}{Q+KV} - C_o)e^{-\left(\frac{Q+KV}{V}\right)t}$$

$$C = \frac{C_{in}Q}{Q+KV} + (C_o - \frac{C_{in}Q}{Q+KV})e^{-\left(\frac{Q+KV}{V}\right)t}$$

Example:

Consider a chamber of volume 500 m3 with fresh air entering at a rate of 1000 m3/hr. Material in the chamber is ignited and burns to emit formaldehyde (HCHO) at a rate of 140 mg/hr. Formaldehyde reacts with air and converts to CO_2 at a first order rate of K=0.40/hr. Assume the chamber is completely mixed. Plot a concentration history of the average formaldehyde concentration in the chamber, in hours from initial ignition.

(1) Sketch the situation, and label relevant features.

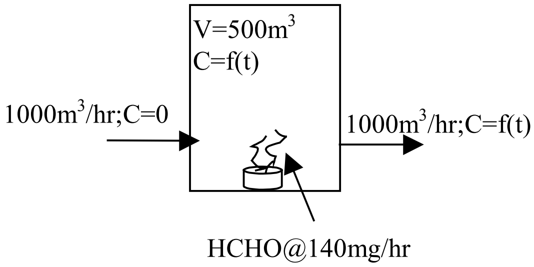


Figure 14. Schematic of Smoking Fire

(2) Write an appropriate balance equation. (For some problems this portion could be quite involved, especially if you have to do the analysis from first principles, in this example the balance equation is pretty simple).

$$V\frac{dC}{dt} = C_{in}Q_{in} + CQ + \dot{m}_{combustion} - \dot{m}_{co2}$$

$$\rightarrow V\frac{dC}{dt} = CQ + (CQ)_{combustion} - KCV$$

(3) Use calculus, algebra, etc. to solve for unknown value/function

$$C = \frac{(CQ_{combustion})}{Q+KV} + (C_o - \frac{(CQ_{combustion})}{Q+KV})e^{-\left(\frac{Q+KV}{V}\right)t}$$

(4) Substitute numerical values into the "model" equation for the problem.

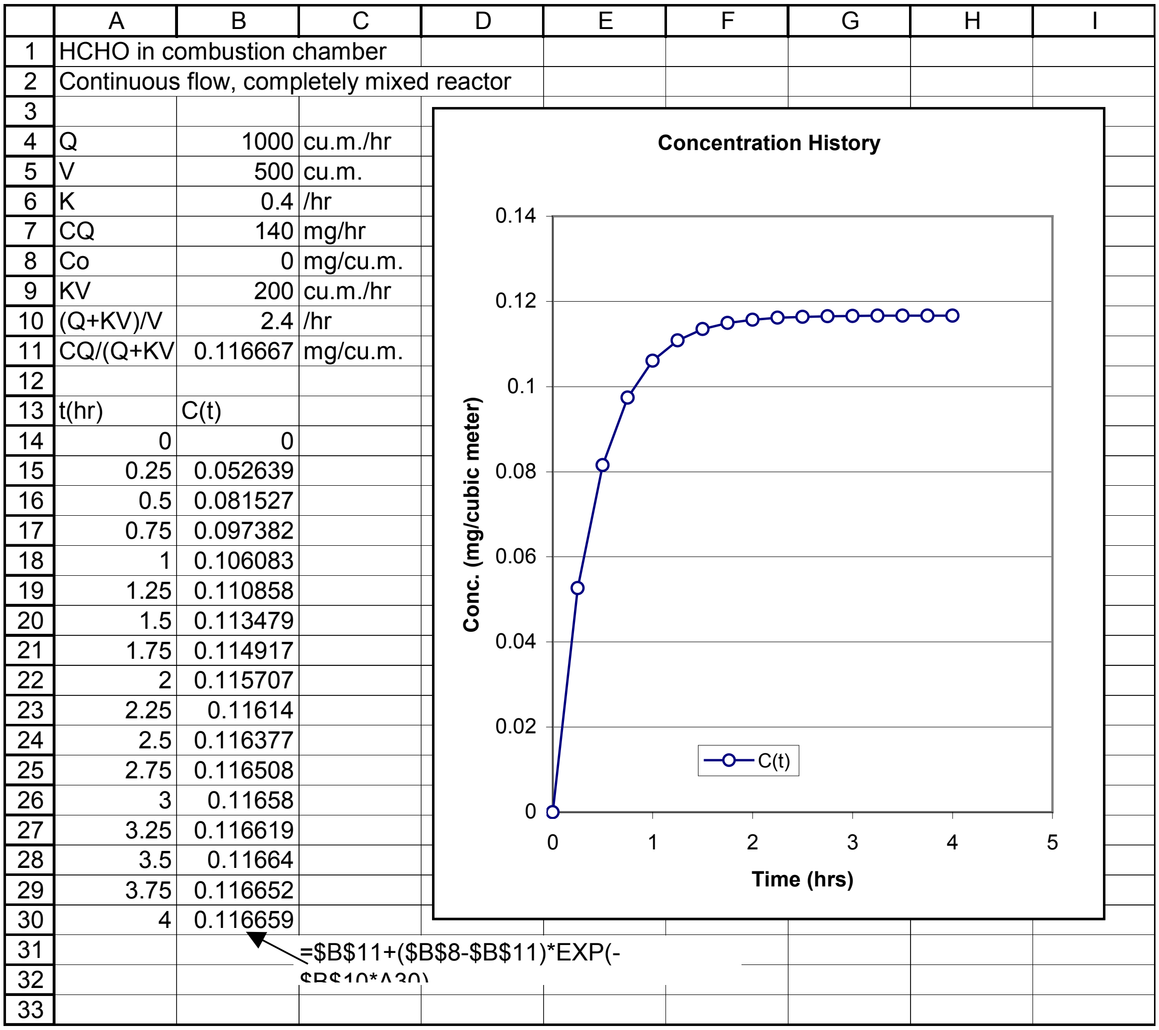
$$(CQ)_{combustion} = 140mg/hr$$

$$Q = 1000m^3/hr$$

$$KV = (0.4/hr)(500m^3) = 200m^3/hr$$

$$C(t) = 0.11667\tfrac{mg}{m^3} + (C_o - 0.11667\tfrac{mg}{m^3})e^{-2.4t}$$

If you were using a calculator, you would then evaluate C(t) at different values of t and plot the results on graph paper. Using a spreadsheet such as EXCEL, you can directly enter the formula, and instruct the software to prepare a plot .



	A	B	C
1	HCHO in combustion chamber		
2	Continuous flow, completely mixed reactor		
3			
4	Q	1000	cu.m./hr
5	V	500	cu.m.
6	K	0.4	/hr
7	CQ	140	mg/hr
8	Co	0	mg/cu.m.
9	KV	200	cu.m./hr
10	(Q+KV)/V	2.4	/hr
11	CQ/(Q+KV	0.116667	mg/cu.m.
12			
13	t(hr)	C(t)	
14	0	0	
15	0.25	0.052639	
16	0.5	0.081527	
17	0.75	0.097382	
18	1	0.106083	
19	1.25	0.110858	
20	1.5	0.113479	
21	1.75	0.114917	
22	2	0.115707	
23	2.25	0.11614	
24	2.5	0.116377	
25	2.75	0.116508	
26	3	0.11658	
27	3.25	0.116619	
28	3.5	0.11664	
29	3.75	0.116652	
30	4	0.116659	
31			=B11+(B8-B11)*EXP(-
32			B10*A30)
33			

Figure 15. Concentration history of HCHO.

Cascade Models

One is not constrained to study a single reactor – the engineer can link reactors to simulate spatial variation in real systems. Typically, cascades are used to study single, poorly mixed systems and/or a series of well-mixed systems. The cascade approach can also include feedback mechanisms to simulate certain kinds of engineering flow processes.

To illustrate a simple cascade, consider three reactors in series without feedback.

A schematic is

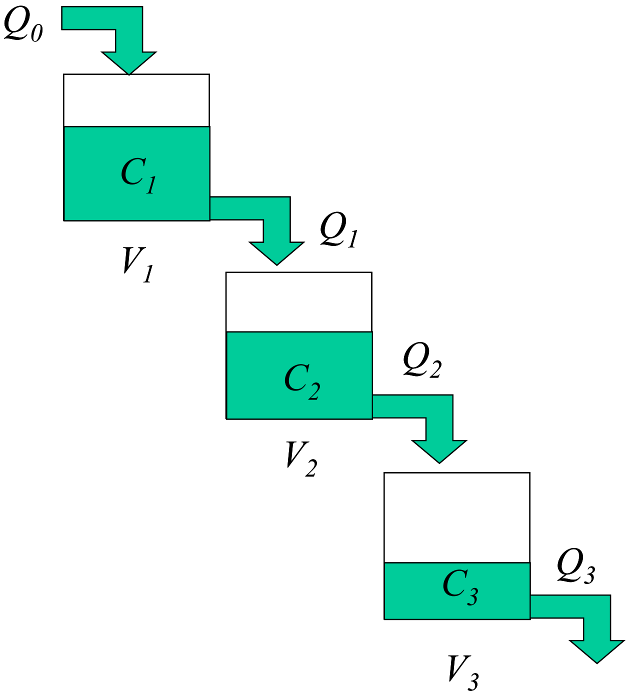


Figure 16. Cascade of Reactors

We simple write a mass balance for each reactor, and remember that the output of one reactor is input to the next. Once the mass balances for the entire set of reactors is assembled, simultaneous solution provides the unknown concentrations in each reactor and at the output. For the schematic in Figure 16, the system of equation(s) is

$$C_1(t) = \frac{C_0Q_0}{Q_1 + K_1V_1} + (C_1(0) - \frac{C_0Q_0}{Q_1 + K_1V_1})e^{-(\frac{Q_1+K_1V_1}{V_1})t}$$

$$C_2(t) = \frac{C_1Q_1}{Q_2 + K_2V_2} + (C_2(0) - \frac{C_1Q_1}{Q_2 + K_2V_2})e^{-(\frac{Q_2+K_2V_2}{V_2})t}$$

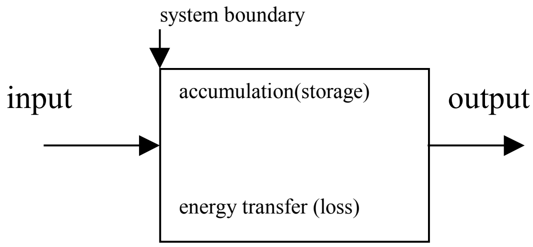
$$C_3(t) = \frac{C_2Q_2}{Q_3 + K_3V_3} + (C_3(0) - \frac{C_2Q_2}{Q_3 + K_3V_3})e^{-(\frac{Q_3+K_3V_3}{V_3})t}$$

Inclusion of feedback paths requires one to start with the basic mass balance and formulate the equations to include influences from reactors upstream and downstream of the reactor of interest. While the algebra is more complicated, the concept is identical to the above schematic.

Energy Balance

An energy balance, like the materials balance is another fundamental tool used in engineering analysis. It is based on the conservation of energy (first law of thermodynamics) and the net growth of entropy (second law of thermodynamics).

An energy balance is used to track energy throughout a system.



The energy balance is nearly the same as the mass balance except some of the terms are associated with mass flows, while some terms are not.

$$\text{Energy}_{IN}\text{-Energy}_{OUT} = \text{Energy}_{ACC} - \text{Energy}_{TRAN}$$

The left hand side is usually associated with mass flows, while the transfer term is associated with heat flow only.

When written as a flow rate equation using conventional thermodynamic terms the energy balance is:

Rate of energy entering the system – Rate of energy leaving the system = Rate of energy accumulating + Rate of heat transfer into the system – Rate of Work done by the system.

- An open system (for the energy balance) will have both energy and mass flows.
- A closed system will only have energy (heat) flows.

Energy is defined as the ability to do work. There are different "kinds" of energy based on the kind of work it can perform.

- *kinetic energy* is energy associated with momentum.
- *potential energy* is energy associated with position in a gravitational, electrical, and/or magnetic field.
- *internal energy* is energy at a microscopic level associated with the KE and PE of individual atoms as well as thermal energy.
- *chemical energy* is energy associated with the breaking of chemical bonds. It is often normalized and expressed as a chemical potential (energy per unit weight of material). The remainder of this discussion will ignore chemical energy.

Total energy is the sum of all the types of energy for a fixed quantity of mass

$$E = KE + PE + U$$

In terms of total energy the energy balance can be written as

$$E_{in}-E_{out}-\Delta E_{sys} - E_{tran}$$

Adding energy to a system often raises its temperature. (Think of a teapot). The amount of heat added (thermal energy) needed to raise the temperature of a unit mass of substance by 1 degree is called the specific heat of the substance. For water two units are in common use.

Btu (British thermal unit) - energy needed to heat 1 lb of water, 1 degree F , at 59F.

kilocalorie = energy needed to heat 1 kg of water, 1 degree C, at 15 C.

The preferred SI unit of specific heat is kJ/kg.

For water the specific heat is 4.184 kJ/kg ^{o}C

For substances that remain liquid or solid during heating (no phase change) the specific heats are relatively constant.

Gasses expand during heating unless their volume is fixed. Usually specific heats are determined for materials at either constant volume of constant pressure (or both).

Cv is the symbol for sp. heat at constant volume.

Cp is the symbol for sp. heat at constant pressure.

The enthalpy of a substance is the sum of its internal energy and a term related to its pressure and volume.

H = U + PV

The first term on the right represents energy stored internally, the second term represents energy lost/gained by work done to expand/compress the mass. When heat is added to a substance, the change in enthalpy is given by

$$\frac{dH}{dT} = \frac{dU}{dT} + \frac{dPV}{dT} = \frac{dU}{dT} + P\frac{dV}{dT} + V\frac{dP}{dT}$$

For solids and liquids, PV ~ constant so that

$$\frac{dH}{dT} \approx \frac{dU}{dT}$$

For gasses heating can occur at constant volume (a butane cylinder) or at constant pressure (a balloon)

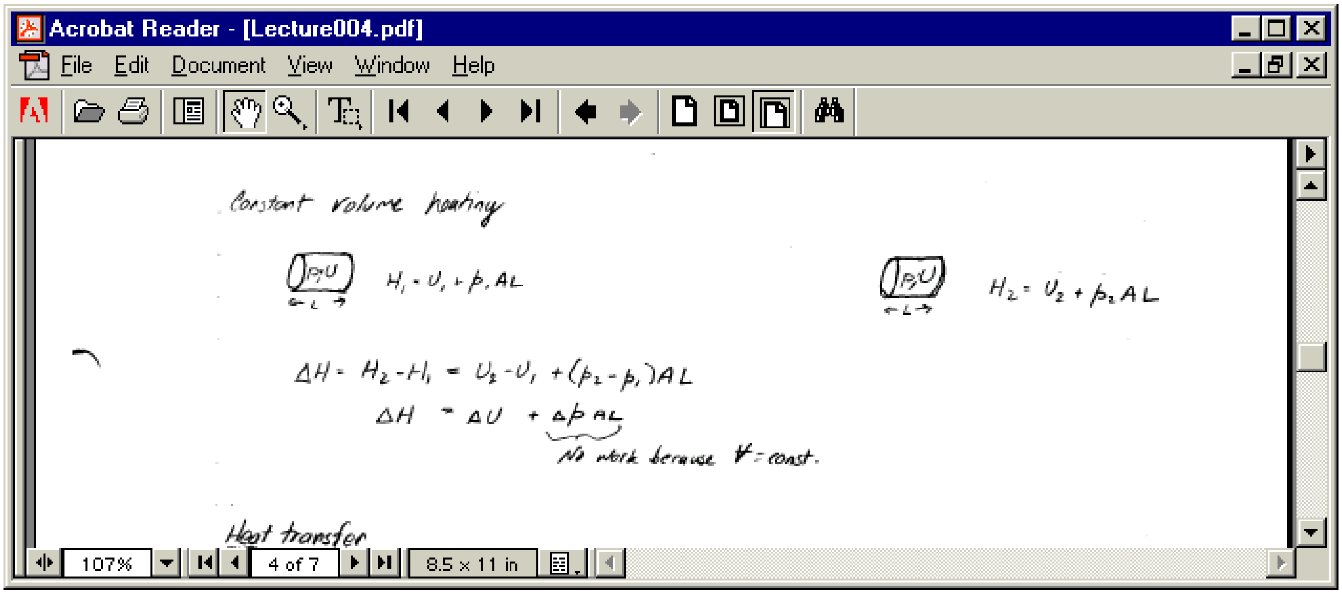
H = U+PV = U + mRT

$$\left(\frac{\partial H}{\partial T}\right)\bigg|_{V=const} = \left(\frac{\partial U}{\partial T}\right)\bigg|_{V=const} + \left(\frac{\partial PV}{\partial T}\right)\bigg|_{V=const}$$

or

$$\left(\frac{\partial H}{\partial T}\right)\bigg|_{P=const} = \left(\frac{\partial U}{\partial T}\right)\bigg|_{P=const} + \left(\frac{\partial PV}{\partial T}\right)\bigg|_{P=const}$$

When volume is held constant, although pressure increases it cannot do any work (Work = Force * Distance). Thus all the thermal energy is stored as internal energy and



Constant volume heating

$H_1 = U_1 + p_1 A L$

$H_2 = U_2 + p_2 A L$

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

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

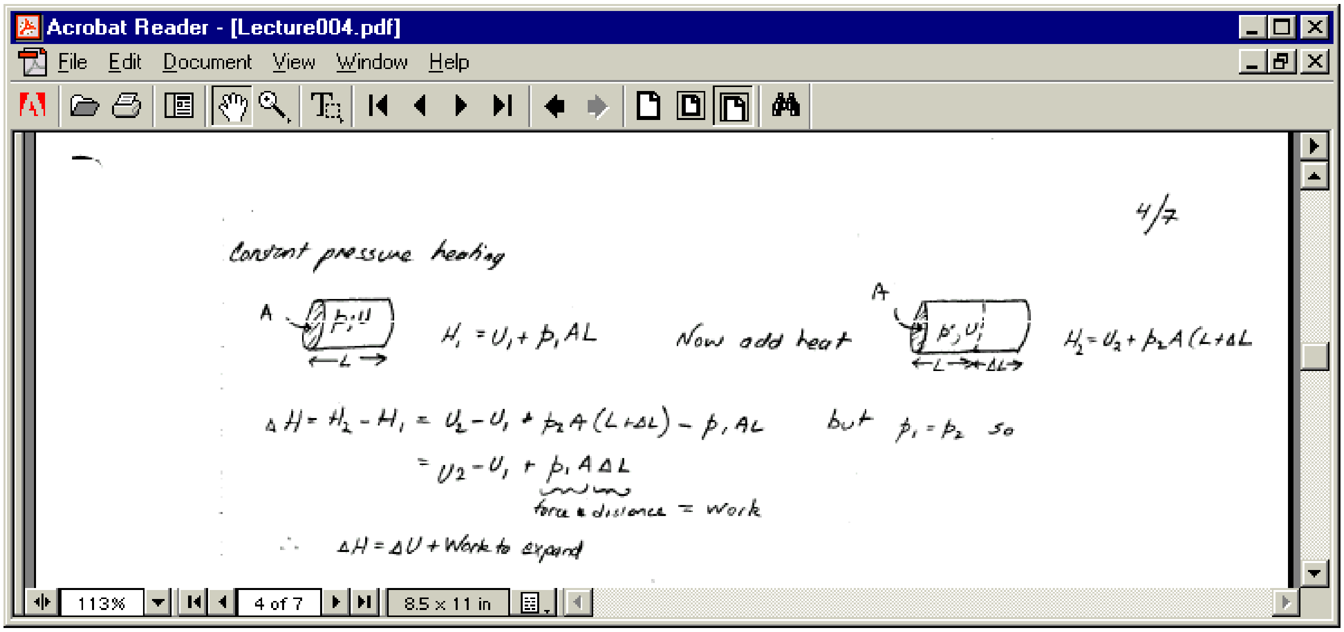
Heat transfer

Figure 17. Constant Volume Heating

$\Delta H = \Delta U$ so that $\left(\frac{dU}{dT}\right)_{V=const} = mC_v$

Cv is the constant volume specific heat.

When pressure is held constant, but volume changes thermal energy is lost as work done to expand against the pressure force so that



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Constant pressure heating

$H_1 = U_1 + p_1 AL$ Now add heat $H_2 = U_2 + p_2 A(L + \Delta L$

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

$= U_2 - U_1 + \underbrace{p_1 A \Delta L}_{\text{force * distance = work}}$

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

Figure 18. Constant Pressure Heating

$\Delta H = \Delta U + \Delta PV$ and $\left(\frac{dH}{dT}\right)_{P=const} = mC_P$

In many environmental systems of practical interest, the system is a fluid or solid, or the behavior is nearly isovolumetric so that stored energy is mostly internal and the change in stored energy from added heat can be represented as $mc\Delta T$ where c is the specific heat of the substance.

Energy Transfer

Stored energy from heat transfer is $mc\Delta T$; the expression assumes that the specific heat is constant during the energy transfer and that there is no phase change. The phases of matter are gas, liquid, and solid. The first two phases are “fluids.”

When a pahse change occurs, energy is absorbed or released without a change in temperature, and this phenomenon is accounted for with enthalpies associated with phase change. Water freezes and ice melts at 0 ^{o}C, the process is called “fusion.” Water boils and steam condenses at 100 oC, this process is called “vaporization.” The constant pressure specific energy required to change from solid to liquid is called the enthalpy of fusion, and the constant pressure specific energy required to change from liquid to gas is called the enthalpy of vaporization.

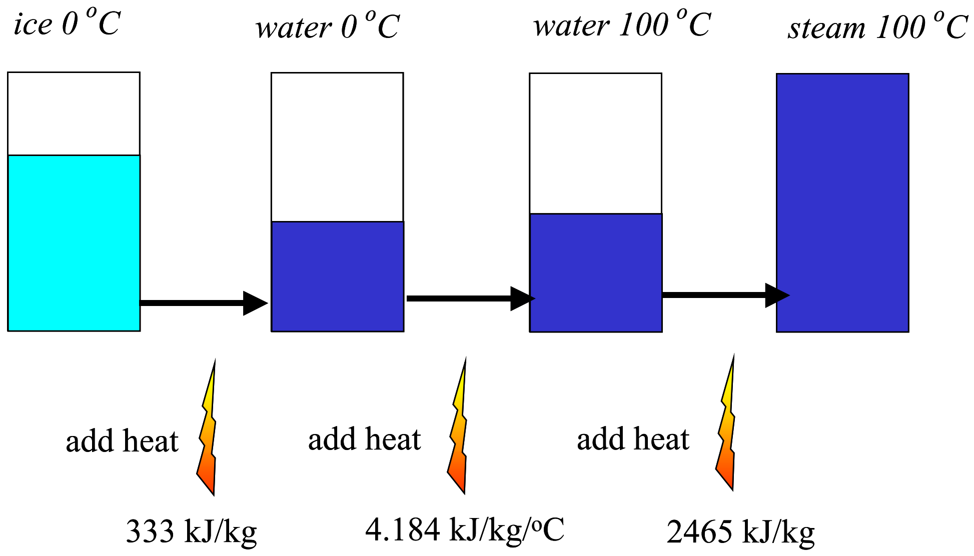

Figure 19. Heats required to take ice to steam.

Figure 17 is a cartoon illustrating the concepts of various enthalpies. The left most element is ice at zero degrees. The addition of 333 kJ/kg does not change the temperature, but the ice becomes water at zero degrees. The addition of 418 kJ/kg does raise the temperature 100 degrees (constant pressure heating). At 100 degrees, the addition of 2645 kJ/kg, does not change the temperature any further, but the water now becomes water vapor (steam). The entire process takes 3216 kJ/kg, of which less than 20% goes to changing temperature, the rest to melting and vaporization.

Phase change energies can be represented in our formula(s) as mL, where L is the phase change enthalpy value of interest. Many problems involve the flow of both mass and energy across the system boundary. In such cases we might write

$$\dot{e}_{stored} = \dot{m}c\Delta T$$

where the change in stored energy is primarily because of the accumulation of mass within the system boundary. The change in energy in this case has units of power (work/time). Typical units are: kJ/sec; Btu/hr; force*distance/time; force*velocity.

An integrated energy balance using the concepts in the chapter can then be written as

$$(U_{in} + KE_{in} + PE_{in}) - (U_{out} + KE_{out} + PE_{out}) + Heat_{IN} - Work_{out} = \Delta Energy$$

Second law

The second law of thermodynamics states that the rate of change of entropy in the system plus the net rate of entropy flow out of the system is at least equal to the overall heat transfer across the boundary and the internal heat production. Entropy is roughly analogous to "useful fuel" – the amount of energy that can be exploited to do work.

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

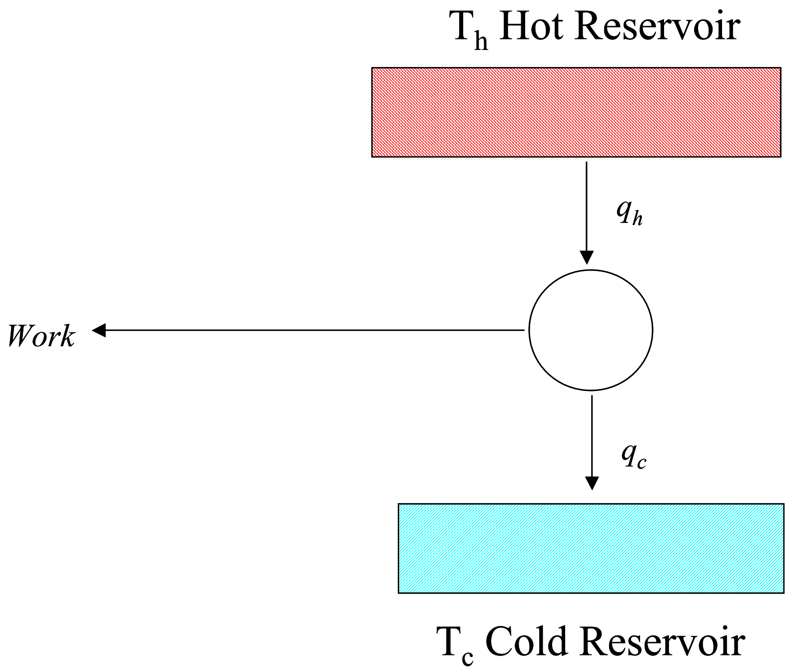

Figure 20. Carnot cycle heat engine

The efficiency for a Carnot cycle heat engine provides an idea of the limitations of real systems.

$$\text{Efficiency} = \eta = \frac{WorkOut}{WorkIn} = 1 - \frac{T_c}{T_h}$$

The best efficiency is 1.0, but it can only be achieved when the $T_c \Leftrightarrow 0$ or $T_h \Leftrightarrow$ *inifinte value*; thus all real systems have efficiencies less than 1.0. Some implications are:

1. Component efficiencies can be really high, but overall eff. is what counts.
2. Waste heat is wasted $, but if a 1% increase in eff costs more than the $ saved, economics considerations will overrule the improved efficiency.
3. Waste is unavoidable – finding uses for the waste is beneficial (because it is no longer waste) and increases the overall efficiency.

Heat Transfer Concepts

Two objects at different temperatures will try to equilibrate by various heat transfer processes. Heat will transfer from the hot to the cold object until the temperatures are the same.

1. Conduction – transfer by direct physical contact.
2. Convection – transfer by a host fluid that carries heat.
3. Radiation – heat transfer as an electromagnetic wave.

Insulation is an engineering tool to reduce heat transfer by these mechanisms.

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