

Introduction to Chemical Engineering Processes/Print Version

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[[edit](#)] Chapter 1: Prerequisites

[[edit](#)] Consistency of units

Any value that you'll run across as an engineer will either be *unitless* or, more commonly, will have specific types of units attached to it. In order to solve a problem effectively, all the types of units should be consistent with each other, or should be in the same *system*. A system of units defines each of the basic unit types with respect to some measurement that can be easily duplicated, so that for example 5 ft. is the same length in Australia as it is in the United States. There are five commonly-used base unit types or *dimensions* that one might encounter (shown with their abbreviated forms for the purpose of dimensional analysis):

Length (L), or the physical distance between two objects with respect to some standard distance

Time (t), or how long something takes with respect to how long some natural phenomenon takes to occur

Mass (M), a measure of the inertia of a material relative to that of a standard

Temperature (T), a measure of the average kinetic energy of the molecules in a material relative to a standard

Electric Current (E), a measure of the total charge that moves in a certain amount of time

There are several different consistent systems of units one can choose from. Which one should be used depends on the data available.

[[edit](#)] Units of Common Physical Properties

Every system of units has a large number of *derived* units which are, as the name implies, derived from the base units. The new units are based on the physical definitions of other quantities which involve the combination of different variables. Below is a list of several common derived system properties and the corresponding dimensions ($\stackrel{\cdot}{=}$ denotes unit equivalence). If you don't know what one of these properties is, you will learn it eventually

Mass $\stackrel{\cdot}{=}$ M

Area $\stackrel{\cdot}{=}$ L²

Velocity $\stackrel{\cdot}{=}$ L/t

Force $\stackrel{\cdot}{=}$ M*L/t²

Power $\stackrel{\cdot}{=}$ M*L²/t³

Density $\stackrel{\cdot}{=}$ M/L³

Diffusivity $\stackrel{\cdot}{=}$ L²/s

Specific Heat Capacity $\stackrel{\cdot}{=}$ L²/(T*t²)

Specific Enthalpy, Gibbs Energy $\stackrel{\cdot}{=}$ L²/t²

Specific Entropy $\stackrel{\cdot}{=}$ L²/(t²*T)

Length $\stackrel{\cdot}{=}$ L

Volume $\stackrel{\cdot}{=}$ L³

Acceleration $\stackrel{\cdot}{=}$ L/t²

Energy/Work/Heat $\stackrel{\cdot}{=}$ M*L²/t²

Pressure $\stackrel{\cdot}{=}$ M/(L*t²)

Viscosity $\stackrel{\cdot}{=}$ M/(L*t)

Thermal conductivity $\stackrel{\cdot}{=}$ M*L/(t³*T)

[\[edit\]](#) SI (kg-m-s) System

This is the most commonly-used system of units in the world, and is based heavily on units of 10. It was originally based on the properties of water, though currently there are more precise standards in place. The major dimensions are:

L $\stackrel{\cdot}{\equiv}$ meters, m t $\stackrel{\cdot}{\equiv}$ seconds, s M $\stackrel{\cdot}{\equiv}$ kilograms, kg
T $\stackrel{\cdot}{\equiv}$ degrees Celsius, °C E $\stackrel{\cdot}{\equiv}$ Amperes, A

where $\stackrel{\cdot}{\equiv}$ denotes unit equivalence. The close relationship to water is that one m³ of water weighs (approximately) 1000 kg at 0°C.

Each of these base units can be made smaller or larger in units of ten by adding the appropriate **metric prefixes**. The specific meanings are (from the [SI](#) page on Wikipedia):

SI Prefixes

Name yotta zetta exa peta tera giga mega kilo hecto deca

Symbol Y Z E P T G M k h da

Factor 10²⁴ 10²¹ 10¹⁸ 10¹⁵ 10¹² 10⁹ 10⁶ 10³ 10² 10¹

Name deci centi milli micro nano pico femto atto zepto yocto

Symbol d c m μ n p f a z y

Factor 10⁻¹ 10⁻² 10⁻³ 10⁻⁶ 10⁻⁹ 10⁻¹² 10⁻¹⁵ 10⁻¹⁸ 10⁻²¹ 10⁻²⁴

If you see a length of 1 km, according to the chart, the prefix "k" means there are 10³ of something, and the following "m" means that it is meters. So 1 km = 10³ meters.

It is very important that you are familiar with this table, or at least as large as mega (M), and as small as nano (n). The relationship between different sizes of metric units was deliberately made simple because you will have to do it all of the time. You may feel uncomfortable with it at first if you're from the U.S. but trust me, after working with the English system you'll learn to appreciate the simplicity of the Metric system.

[\[edit\]](#) Derived units from the SI system

Imagine if every time you calculated a pressure, you would have to write the units in $\text{kg}/(\text{m}\cdot\text{s}^2)$. This would become cumbersome quickly, so the SI people set up **derived units** to use as shorthand for such combinations as these. The most common ones used by chemical engineers are as follows:

Force: $1 \text{ kg}/(\text{m}\cdot\text{s}^2) = 1 \text{ Newton, N}$ Energy: $1 \text{ N}\cdot\text{m} = 1 \text{ J}$
Power: $1 \text{ J}/\text{s} = 1 \text{ Watt, W}$ Pressure: $1 \text{ N}/\text{m}^2 = 1 \text{ Pa}$
Volume: $1 \text{ m}^3 = 1000 \text{ Liters, L}$ Thermodynamic temperature: $1 \text{ }^\circ\text{C} = \text{K} - 273.15$, K is Kelvin

Another derived unit is the *mole*. A mole represents $6.022\cdot 10^{23}$ molecules of *any substance*. This number, which is known as the **Avogadro constant**, is used because it is the number of molecules that are found in 12 grams of the ^{12}C isotope. Whenever we have a reaction, as you learned in chemistry, you have to do stoichiometry calculations based on moles rather than on grams, because *the number of grams of a substance does not only depend on the number of molecules present but also on their size*, whereas the stoichiometry of a chemical reaction only depends on the number of molecules that react, not on their size. Converting units from grams to moles eliminates the size dependency.

[\[edit\]](#) CGS (cm-g-s) system

The so-called CGS system *uses the same base units as the SI system but expresses masses and grams in terms of cm and g instead of kg and m*. The CGS system has its own set of derived units (see [w:cgs](#)), but commonly basic units are expressed in terms of cm and g, and then the derived units from the SI system are used. In order to use the SI units, the masses *must* be in kilograms, and the distances *must* be in meters. This is a very important thing to remember, especially when dealing with force, energy, and pressure equations.

[\[edit\]](#) English system

The English system is fundamentally different from the Metric system in that *the fundamental inertial quantity is a force, not a mass*. In addition, units of different sizes do not typically have prefixes and have more complex conversion factors than those of the metric system.

The base units of the English system are somewhat debatable but these are the ones I've seen most often:

Length: $L \stackrel{\cdot}{=} \text{feet, ft}$ $t \stackrel{\cdot}{=} \text{seconds, s}$
 $F \stackrel{\cdot}{=} \text{pounds-force, lb(f)}$ $T \stackrel{\cdot}{=} \text{degrees Fahrenheit, }^\circ\text{F}$

The base unit of electric current remains the Ampere.

There are several derived units in the English system but, unlike the Metric system, the conversions are not neat at all, so it is best to consult a conversion table or program for the necessary changes. It is especially important to keep good track of the units in the English

system because if they're not on the same basis, you'll end up with a mess of units as a result of your calculations, i.e. for a force you'll end up with units like Btu/in instead of just pounds, lb. This is why it's helpful to know the derived units in terms of the base units: it allows you to make sure everything is in terms of the same base units. *If every value is written in terms of the same base units, and the equation that is used is correct, then the units of the answer will be consistent and in terms of the same base units.*

[\[edit\]](#) How to convert between units

[\[edit\]](#) Finding equivalences

The first thing you need in order to convert between units is the equivalence between the units you want and the units you have. To do this use a **conversion table**. See [w:Conversion of units](#) for a fairly extensive (but not exhaustive) list of common units and their equivalences.

Conversions within the metric system usually are not listed, because it is assumed that one can use the prefixes and the fact that $1 \text{ mL} = 1 \text{ cm}^3$ to convert anything that is desired.

Conversions within the English system and especially between the English and metric system are sometimes (but not on Wikipedia) written in the form:

$$1(\textit{unit1}) = (\textit{number})(\textit{unit2}) = (\textit{number})(\textit{unit3}) = \dots$$

For example, you might recall the following conversion from chemistry class:

$$1 \text{ atm} = 760 \text{ mmHg} = 1.013 * 10^5 \text{ Pa} = 1.013 \text{ bar} = \dots$$

The table on Wikipedia takes a slightly different approach: the column on the far left side is the unit we have 1 of, the middle is the definition of the unit on the left, and on the far right-hand column we have the metric equivalent. One listing is the conversion from feet to meters:

$$\text{foot (International) ft} = 1/3 \text{ yd} = 0.3048 \text{ m}$$

Both methods are common and one should be able to use either to look up conversions.

[\[edit\]](#) Using the equivalences

Once the equivalences are determined, use the general form:

$$\text{What you want} = \text{What you have} * \frac{\text{What you want}}{\text{What you have}}$$

The fraction on the right comes directly from the conversion tables.



Example:

Convert 800 mmHg into bars

Solution If you wanted to convert 800 mmHg to bars, using the horizontal list, you could do it directly:

$$\text{bars} = 800 \text{ mmHg} * \frac{1.013 \text{ bar}}{760 \text{ mmHg}} = 1.066 \text{ bar}$$

Using the tables from Wikipedia, you need to convert to an *intermediate* (the metric unit) and then convert from the intermediate to the desired unit. We would find that

$$1 \text{ mmHg} = 133.322 \text{ Pa} \text{ and } 1 \text{ bar} = 10^5 \text{ Pa}$$

Again, we have to set it up using the same general form, just we have to do it twice:

$$\text{bars} = 800 \text{ mmHg} * \frac{133.322 \text{ Pa}}{1 \text{ mmHg}} * \frac{1 \text{ bar}}{10^5 \text{ Pa}} = 1.066 \text{ bar}$$

Setting these up takes practice, there will be some examples at the end of the section on this. It's a **very important** skill for any engineer.

One way to keep from avoiding "doing it backwards" is to write everything out and make sure your units cancel out as they should! If you try to do it backwards you'll end up with something like this:

$$\text{bars} = 800 \text{ mmHg} * \frac{760 \text{ mmHg}}{1.013 \text{ bar}} = 6.0 * 10^5 \frac{\text{mmHg}^2}{\text{bar}}$$

If you write everything (even conversions within the metric system!) out, and make sure that everything cancels, you'll help mitigate unit-changing errors. About 30-40% of all mistakes I've seen have been unit-related, which is why there is such a long section in here about it. Remember them well.

[edit] Dimensional analysis as a check on equations

Since we know what the units of velocity, pressure, energy, force, and so on should be in terms of the base units L, M, t, T, and E, we can use this knowledge to check the feasibility of equations that involve these quantities.



Example:

Analyze the following equation for dimensional consistency: $P = g * h$ where g is the gravitational acceleration and h is the height of the fluid

Solution We could check this equation by plugging in our units:

$$P \doteq M/(L * t^2) , h \doteq L , g \doteq L/t^2$$
$$g * h \doteq L^2/t^2 \neq M/(L * t^2)$$

Since $g*h$ doesn't have the same units as P , the equation must be wrong *regardless of the system of units we are using!* The correct equation, in fact, is:

$$P = \rho * g * h$$

where ρ is the density of the fluid. Density has base units of M/L^3 so

$$\rho * g * h \doteq L^2/t^2 * M/L^3 \doteq M/(L * t^2)$$
 which are the units of pressure.

This does not tell us the equation is correct but it *does* tell us that the units are consistent, which is necessary though not sufficient to obtain a correct equation. *This is a useful way to detect algebraic mistakes that would otherwise be hard to find.* The ability to do this with an algebraic equation is a good argument against plugging in numbers too soon!

[edit] Chapter 1 Practice Problems



Problem:

1. Perform the following conversions, using the appropriate number of significant figures in your answer:

a) $1.5 \frac{g}{s} \rightarrow \frac{lb}{hr}$

b) $4.5 * 10^2 W \rightarrow \frac{btu}{min}$

c) $34 \frac{\mu g}{\mu m^3} \rightarrow \frac{oz}{in^3}$

d) $4.18 \frac{J}{g * oC} \rightarrow \frac{kWh}{lb * oF}$ (note: kWh means kilowatt-hour)

e) $1.00 m^3 \rightarrow L \rightarrow dm^3 \rightarrow mL \rightarrow cm^3$



Problem:

2. Perform a dimensional analysis on the following equations to determine if they are reasonable:

a) $v = dt$, where v is velocity, d is distance, and t is time.

b) $F = \frac{m * v^2}{r}$ where F is force, m is mass, v is velocity, and r is radius (a distance).

c) $F_{bouy} = \rho * V * g$ where ρ is density, V is volume, and g is gravitational acceleration.

d) $\dot{m} = \frac{\dot{V}}{\rho}$ where \dot{m} is mass flow rate, \dot{V} is volumetric flow rate, and ρ is density.



Problem:

3. Recall that the ideal gas law is $PV = nRT$ where P is pressure, V is volume, n is number of moles, R is a constant, and T is the temperature.

a) What are the units of R in terms of the base unit types (length, time, mass, and temperature)?

b) Show how these two values of R are equivalent:

$$R = 0.0821 \frac{L \cdot atm}{mol \cdot K} = 8.31 \frac{J}{mol \cdot K}$$

c) If an ideal gas exists in a closed container with a molar density of $0.03 \frac{mol}{L}$ at a pressure of $0.96 \cdot 10^5 Pa$, what temperature is the container held at?

d) What is the molar concentration of an ideal gas with a partial pressure of $4.5 \cdot 10^5 Pa$ if the total pressure in the container is $6 atm$?

e) At what temperatures and pressures is a gas most and least likely to be ideal? (hint: you can't use it when you have a liquid)

f) Suppose you want to mix ideal gasses in two separate tanks together. The first tank is held at a pressure of 500 Torr and contains 50 moles of water vapor and 30 moles of water at 70°C. The second is held at 400 Torr and 70°C. The volume of the second tank is the same as that of the first, and the ratio of moles water vapor to moles of water is the same in both tanks.

You recombine the gasses into a single tank the same size as the first two. Assuming that the temperature remains constant, what is the pressure in the final tank? If the tank can withstand 1 atm pressure, will it blow up?



Problem:

4. Consider the reaction $H_2O_2 \rightleftharpoons H_2O + \frac{1}{2}O_2$, which is carried out by many organisms as a way to eliminate hydrogen peroxide.

a). What is the standard enthalpy of this reaction? Under what conditions does it hold?

b). What is the standard Gibbs energy change of this reaction? Under what conditions does it hold? In what direction is the reaction spontaneous at standard conditions?

c). What is the Gibbs energy change at biological conditions (1 atm and 37°C) if the initial hydrogen peroxide concentration is 0.01M? Assume oxygen is the only gas present in the cell.

d). What is the equilibrium constant under the conditions in part c? Under the conditions in part b)? What is the constant independent of?

e). Repeat parts a through d for the alternative reaction $H_2O_2 \rightarrow H_2 + O_2$. Why isn't this reaction used instead?



Problem:

5. Two ideal gasses A and B combine to form a third ideal gas, C, in the reaction $A + B \rightarrow C$. Suppose that the reaction is irreversible and occurs at a constant temperature of 25°C in a 5L container. If you start with 0.2 moles of A and 0.5 moles of B at a total pressure of 1.04 atm, what will the pressure be when the reaction is completed?



Problem:

6. How much heat is released when 45 grams of methane are burned in excess air under standard conditions? How about when the same mass of glucose is burned? What is one possible reason why most heterotrophic organisms use glucose instead of methane as a fuel? Assume that the combustion is complete, i.e. no carbon monoxide is formed.



Problem:

7. Suppose that you have carbon monoxide and water in a tank in a 1.5:1 ratio.

a) In the literature, find the reaction that these two compounds undergo (hint: look for the *water gas shift* reaction). Why is it an important reaction?

b) Using a table of Gibbs energies of formation, calculate the equilibrium constant for the reaction.

c) How much hydrogen can be produced from this initial mixture?

d) What are some ways in which the yield of hydrogen can be increased? (hint: recall Le Chatelier's principle for equilibrium).

e) What factors do you think may influence how long it takes for the reaction to reach equilibrium?

[[edit](#)] Chapter 2: Elementary mass balances

[[edit](#)] The "Black Box" approach to problem-solving

In this book, all the problems you'll solve will be "black-box" problems. This means that we take a look at a unit operation *from the outside*, looking at what goes into the system and what leaves, and extrapolating data about the properties of the entrance and exit streams from this. This type of analysis is important because it does not depend on the specific type of unit operation that is performed. *When doing a black-box analysis, we don't care about how the unit operation is designed, only what the net result is.* Let's look at an example:



Example:

Suppose that you pour 1L of water into the top end of a funnel, and that funnel leads into a large flask, and you measure that the entire liter of water enters the flask. If the funnel had no water in it to begin with, how much is left over after the process is completed?

Solution The answer, of course, is 0, because you only put 1L of water in, and 1L of water came out the other end. The answer to this does not depend on the how large the funnel is, the slope of the sides, or any other design aspect of the funnel, which is why it is a black-box problem.

[[edit](#)] Conservation equations

The formal mathematical way of describing the black-box approach is with **conservation equations** which explicitly state that what goes into the system must either come out of the system somewhere else, get used up or generated by the system, or remain in the system and **accumulate**. The relationship between these is simple:

1. The streams entering the system cause an increase of the substance (mass, energy, momentum, etc.) in the system.
2. The streams leaving the system decrease the amount of the substance in the system.
3. Generating or consuming mechanisms (such as chemical reactions) can either increase or decrease the stuff in the system.
4. What's left over is the amount of stuff in the system

With these four statements we can state the following very important general principle:

$$Accumulation = In - Out + Generation$$

It's so important, in fact, that you'll see it a million times or so, including a few in this book, and it is used to derive a variety of forms of conservation equations.

[\[edit\]](#) Common assumptions on the conservation equation

The conservation equation is very general and applies to any property a system can have. However, it can also lead to complicated equations, and so in order to simplify calculations when appropriate, it is useful to apply assumptions to the problem.

- **Closed system:** A closed system is one which does not have flows in or out of the substance. Almost always, when one refers to a closed system it is implied to be closed to *mass flow* but not to other flows such as energy or momentum. The equation for a closed system is:

$$Accumulation = Generation$$

The opposite of a closed system is an **open system** in which the substance is allowed to enter and/or leave the system. The funnel in the example was an open system because mass flowed in and out of it.

- **No generation:** Certain quantities are always **conserved** in the strict sense that they are never created or destroyed. These are the most useful quantities to do balances on because then the user does not need to worry about a generation term.

$$Accumulation = In - Out$$

The most commonly-used conserved quantities are **mass** and **energy**. It is important to note, however, that though the *total* mass and *total* energy in a system are conserved, the mass of a single species is *not* (since it may be changed into something else). Neither is the "heat" in a system if a so-called "heat-balance" is performed. Therefore one must be careful when deciding whether to discard the generation term.

- **Steady State:** A system which does not accumulate a substance is said to be at steady-state. Often times, this allows the engineer to avoid having to solve differential equations and instead use algebra.

$$In - Out + Generation = 0$$

All problems in this text assume steady state but it is not always a valid assumption. It is mostly valid after a process has been running for long enough that all the flow rates, temperatures, pressures, and other system parameters have reached equilibrium values. It is not valid when a process is first warming up and the parameters wobble significantly. How they wobble is a subject for another course.

[[edit](#)] Conservation of mass

TOTAL mass is a conserved quantity (except in nuclear reactions, let's not go there), as is the mass of any individual species if there is no chemical reaction occurring in the system. Let us write the conservation equation *at steady state* for such a case (with no reaction):

$$In - Out = 0$$

Now, there are two major ways in which mass can enter or leave a system: diffusion and convection. However, for large-scale systems such as the ones considered here, in which the velocity entering the unit operations is fairly large and the concentration gradient is fairly small, diffusion can be neglected and the only mass entering or leaving the system is due to convective flow:

$$Mass_{in} = \dot{m}_{in} = \rho * v * A$$

A similar equation apply for the mass out. In this book generally we use the symbol \dot{m} to signify a convective mass flow rate, in units of *mass/time*. Since the total flow in is the sum of individual flows, and the same with the flow out, the following **steady state mass balance** is obtained for the overall mass in the system:

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

If it is a *batch* system, or if we're looking at how much has entered and left in a given period of time (rather than instantaneously), we can apply the same mass balance without the time component. In this book, a value without the dot signifies a value without a time component:

$$\sum m_{out} - \sum m_{in} = 0$$



Example:

Let's work out the previous example (the funnel) but explicitly state the mass balance. We're given the following information:

1. $m_{in} = 1L$
2. $m_{out} = 1L$

From the general balance equation,

$$In - Out = Accumulation$$

Therefore, $Accumulation = 1L - 1L = 0$.

Since the accumulation is 0, the system is at steady state.

This is a fairly trivial example, but it gets the concepts of "in", "out", and "accumulation" on a physical basis, which is important for setting up problems. In the next section, it will be shown how to apply the mass balance to solve more complex problems with only one component.

[\[edit\]](#) Converting Information into Mass Flows - Introduction

In any system there will be certain parameters that are (often considerably) easier to measure and/or control than others. When you are solving any problem and trying to use a mass balance or any other equation, *it is important to recognize what pieces of information can be interconverted*. The purpose of this section is to show some of the more common alternative ways that mass flow rates are expressed, mostly because it is easier to, for example, [measure a velocity](#) than it is to measure a mass flow rate directly.

[\[edit\]](#) Volumetric Flow rates

A **volumetric flow rate** is a relation of how much volume of a gas or liquid solution passes through a fixed point in a system (typically the entrance or exit point of a process) in a given amount of time. It is denoted as:

$$\dot{V}_n \doteq \frac{\text{Volume}}{\text{time}} \text{ in stream } n$$

Volume in the metric system is typically expressed either in L (dm³), mL (cm³), or m³. Note that a cubic meter is very large; a cubic meter of water weighs about 1000kg (2200 pounds) at room temperature!

[\[edit\]](#) Why they're useful

Volumetric flowrates can be measured directly using **flowmeters**. They are especially useful for gases since the volume of a gas is one of the found properties that are needed in order to use an *equation of state* (discussed later in the book) to calculate the molar flow rate. Of the other three, two (pressure, and temperature) can be specified by the reactor design and control systems, while

one (compressibility) is strictly a function of temperature and pressure for any gas or gaseous mixture.

[\[edit\]](#) Limitations

Volumetric Flowrates are Not Conserved. We can write a balance on volume like anything else, but the "volume generation" term would be a complex function of system properties. Therefore if we are given a volumetric flow rate we should change it into a mass (or mole) flow rate before applying the balance equations.

Volumetric flowrates also do not lend themselves to splitting into components, since when we speak of volumes in practical terms we generally think of the total solution volume, not the partial volume of each component (the latter is a useful tool for thermodynamics, but that's another course entirely). There **are** some things that are measured in volume fractions, but this is relatively uncommon.

[\[edit\]](#) How to convert volumetric flow rates to mass flow rates

Volumetric flowrates are related to mass flow rates by a relatively easy-to-measure physical property. Since $\dot{m} = \text{mass}/\text{time}$ and $\dot{V} = \text{volume}/\text{time}$, we need a property with units of $\text{mass}/\text{volume}$ in order to convert them. The **density** serves this purpose nicely!

$$\dot{V}_n * \rho_n = \dot{m}_{n \text{ in stream } n}$$

The "i" indicates that we're talking about one particular flow stream here, since each flow may have a different density, mass flow rate, or volumetric flow rate.

[\[edit\]](#) Velocities

The velocity of a bulk fluid is *how much lateral distance along the system (usually a pipe) it passes per unit time*. The velocity of a bulk fluid, like any other, has units of:

$$v_n = \frac{\text{distance}}{\text{time}} \text{ in stream } n$$

By definition, the bulk velocity of a fluid is related to the volumetric flow rate by:

$$v_n = \frac{\dot{V}_n}{A_n \text{ in stream n}}$$

This distinguishes it from the velocity of the fluid at a certain point (since fluids flow faster in the center of a pipe). The bulk velocity is about the same as the instantaneous velocity for relatively fast flow, or especially for flow of gasses.

For purposes of this class, all velocities given will be bulk velocities, not instantaneous velocities.

[\[edit\]](#) Why they're useful

(Bulk) Velocities are useful because, like volumetric flow rates, they are relatively easy to measure. They are especially useful for liquids since they have constant density (and therefore a constant pressure drop at steady state) as they pass through the orifice or other similar instruments. This is a necessary prerequisite to use the design equations for these instruments.

[\[edit\]](#) Limitations

Like volumetric flowrates, **velocity is not conserved**. Like volumetric flowrate, velocity changes with temperature and pressure of a gas, though for a liquid velocity is generally constant along the length of a pipe.

Also, velocities can't be split into the flows of individual components, since all of the components will generally flow at the same speed. They need to be converted into something that can be split (mass flow rate, molar flow rate, or pressure for a gas) before concentrations can be applied.

[\[edit\]](#) How to convert velocity into mass flow rate

In order to convert the velocity of a fluid stream into a mass flow rate, you need two pieces of information:

1. The **cross sectional area** of the pipe.
2. The **density** of the fluid.

In order to convert, first use the definition of bulk velocity to convert it into a volumetric flow rate:

$$\dot{V}_n = v_n * A_n$$

Then use the density to convert the volumetric flow rate into a mass flow rate.

$$\dot{m}_n = \dot{V}_n * \rho_n$$

The combination of these two equations is useful:

$$\dot{m}_n = \dot{V}_n * \rho_n * A_{n \text{ in stream n}}$$

[\[edit\]](#) Molar Flow Rates

The concept of a molar flow rate is similar to that of a mass flow rate, it is the number of moles of a solution (or mixture) that pass a fixed point per unit time:

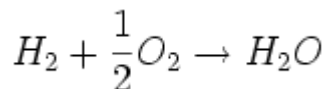
$$\dot{n}_n \doteq \frac{\text{moles}}{\text{time in stream n}}$$

[\[edit\]](#) Why they're useful

Molar flow rates are mostly useful because *using moles instead of mass allows you to write material balances in terms of reaction conversion and stoichiometry*. In other words, there are a lot less unknowns when you use a mole balance, since the stoichiometry allows you to consolidate all of the changes in the reactant and product concentrations in terms of one variable. This will be discussed more in a later chapter.

[\[edit\]](#) Limitations

Unlike mass, **total moles are not conserved**. Total mass flow rate is conserved whether there is a reaction or not, but the same is not true for the number of moles. For example, consider the reaction between hydrogen and oxygen gasses to form water:



This reaction consumes 1.5 moles of reactants for every mole of products produced, and therefore the total number of moles entering the reactor will be more than the number leaving it.

However, since neither mass nor moles of individual components is conserved in a reacting system, it's better to use moles so that the stoichiometry can be exploited, as described later.

The molar flows are also somewhat less practical than mass flow rates, since you can't measure moles directly but you can measure the mass of something, and then convert it to moles using the molar flow rate.

[\[edit\]](#) How to Change from Molar Flow Rate to Mass Flow Rate

Molar flow rates and mass flow rates are related by the **molecular weight** (also known as the **molar mass**) of the solution. In order to convert the mass and molar flow rates of the *entire solution*, we need to know the **average molecular weight** of the solution. This can be calculated from the molecular weights and mole fractions of the components using the formula:

$$\bar{M}W_n = [\sum(MW_i * y_i)]_n$$

where i is an index of *components* and n is the *stream* number. y_i signifies *mole fraction* of each component (this will all be defined and derived later).

Once this is known it can be used as you would use a molar mass for a single component to find the total molar flow rate.

$$\dot{m}_n = \dot{n}_n * \bar{M}W_n \text{ in stream } n$$

[\[edit\]](#) A Typical Type of Problem

Most problems you will face are significantly more complicated than the previous problem and the following one. In the engineering world, problems are presented as so-called "word problems", in which a system is described and the problem must be set up and solved (if possible) from the description. This section will attempt to illustrate through example, step by step, some common techniques and pitfalls in setting up mass balances. Some of the steps may seem somewhat excessive at this point, but if you follow them carefully on this relatively simple problem, you will certainly have an easier time following later steps.

[\[edit\]](#) Single Component in Multiple Processes: a Steam Process



Example:

A feed stream of pure liquid water enters an evaporator at a rate of 0.5 kg/s. Three streams come from the evaporator: a vapor stream and two liquid streams. The flowrate of the vapor

stream was measured to be 4×10^6 L/min and its density was 4 g/m^3 . The vapor stream enters a turbine, where it loses enough energy to condense fully and leave as a single stream. One of the liquid streams is discharged as waste, the other is fed into a heat exchanger, where it is cooled. This stream leaves the heat exchanger at a rate of 1500 pounds per hour. Calculate the flow rate of the discharge and the efficiency of the evaporator.

Note that one way to define efficiency is in terms of conversion, which is intended here:

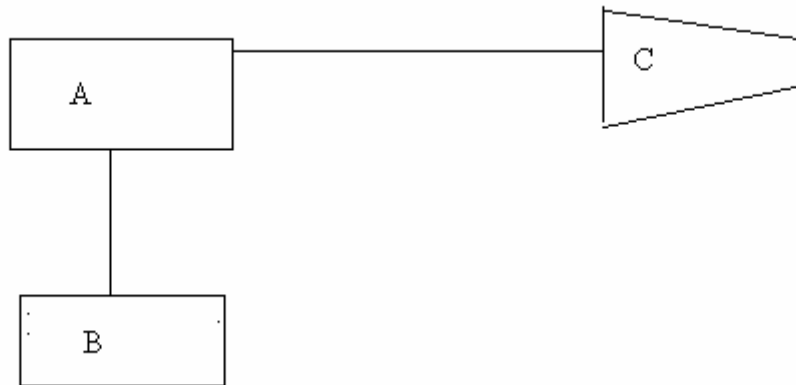
$$\text{efficiency} = \frac{\dot{m}_{\text{vapor}}}{\dot{m}_{\text{feed}}}$$

[edit] Step 1: Draw a Flowchart

The problem as it stands contains an awful lot of text, but it won't mean much until you *draw what is given to you*. First, ask yourself, what processes are in use in this problem? **Make a list** of the processes in the problem:

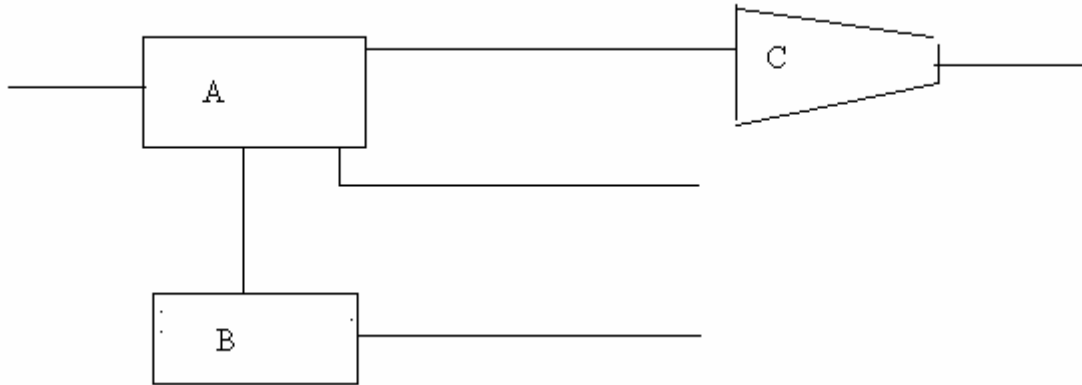
1. Evaporator (A)
2. Heat Exchanger (B)
3. Turbine (C)

Once you have a list of all the processes, you need to **find out how they are connected** (it'll tell you something like "the vapor stream enters a turbine"). Draw a basic sketch of the processes and their connections, and label the processes. It should look something like this:



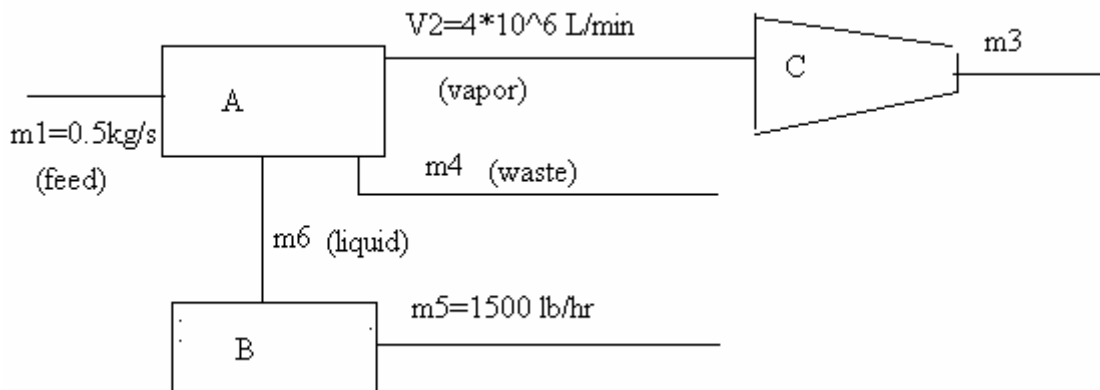
Remember, we don't care what the actual processes look like, or how they're designed. At this point, we only really label what they are so that we can go back to the problem and know which process they're talking about.

Once all your processes are connected, **find any streams that are not yet accounted for**. In this case, we have not drawn the feed stream into the evaporator, the waste stream from the evaporator, or the exit streams from the turbine and heat exchanger.



The third step is to **Label all your flows**. Label them with any information you are given. Any information you are not given, and even information you are given should be given a different variable. It is usually easiest to give them the same variable as is found in the equation you will be using (for example, if you have an unknown flow rate, call it \dot{m} so it remains clear what the unknown value is physically. Give each a different subscript corresponding to the number of the feed stream (such as \dot{m}_1 for the feed stream that you call "stream 1"). Make sure you **include all units** on the given values!

In the example problem, the flowchart I drew with all flows labeled looked like this:



Notice that for one of the streams, a *volume* flow rate is given rather than a *mass* flow rate, so it is labeled as such. This is very important, so that you avoid using a value in an equation that isn't valid (for example, there's no such thing as "conservation of volume" for most cases)!

The final step in drawing the flowchart is to **write down any additional given information in terms of the variables you have defined**. In this problem, the density of the water in the vapor stream is given, so write this on the side for future reference.

Carefully drawn flowcharts and diagrams are half of the key to solving any mass balance, or really a lot of other types of engineering problems. They are just as important as having the right units to getting the right answer.

[\[edit\]](#) Step 2: Make sure your units are consistent

The second step is to make sure all your units are consistent and, if not, to convert everything so that it is. In this case, since the principle that we'll need to use to solve for the flow rate of the waste stream (\dot{m}_3) is conservation of mass, everything will need to be on a mass-flow basis, and also in the *same* mass-flow units.

In this problem, since two of our flow rates are given in metric units (though one is a volumetric flow rate rather than a mass flow rate, so we'll need to change that) and only one in English units, it would save time and minimize mistakes to convert \dot{V}_2 and \dot{m}_5 to kg/s.

From the previous section, the equation relating volumetric flowrate to mass flow rate is:

$$\dot{V}_i * \rho_i = \dot{m}_i$$

Therefore, we need the density of water vapor in order to calculate the mass flow rate from the volumetric flow rate. Since the density is provided in the problem statement (if it wasn't, we'd need to calculate it with methods described later), the mass flow rate can be calculated:

$$\dot{V}_2 = \frac{4 * 10^6 \text{ L}}{1 \text{ min}} * \frac{1 \text{ m}^3}{1000 \text{ L}} * \frac{1 \text{ min}}{60 \text{ s}} = 66.67 \frac{\text{m}^3}{\text{s}}$$

$$\rho_2 = 4 \frac{\text{g}}{\text{m}^3} * \frac{1 \text{ kg}}{1000 \text{ g}} = 0.004 \frac{\text{kg}}{\text{m}^3}$$

$$\dot{m}_2 = 66.67 \frac{\text{m}^3}{\text{s}} * 0.004 \frac{\text{kg}}{\text{m}^3} = 0.2666 \frac{\text{kg}}{\text{s}}$$

Note that since the density of a gas is so small, a huge volumetric flow rate is necessary to achieve any significant mass flow rate. This is fairly typical and is a practical problem when dealing with gas-phase processes.

The mass flow rate \dot{m}_5 can be changed in a similar manner, but since it is already in terms of mass (or weight technically), we don't need to apply a density:

$$\dot{m}_5 = 1500 \frac{\text{lb}}{\text{hr}} * \frac{1 \text{ kg}}{2.2 \text{ lb}} * \frac{1 \text{ hr}}{3600 \text{ s}} = 0.1893 \frac{\text{kg}}{\text{s}}$$

Now that everything is in the same system of units, we can proceed to the next step.

[edit] Step 3: Relate your variables

Since we have the mass flow rate of the vapor stream we can calculate the efficiency of the evaporator directly:

$$efficiency = \frac{\dot{m}_2}{\dot{m}_1} = \frac{0.2666 \frac{kg}{s}}{0.5 \frac{kg}{s}} = 53.3\%$$

Finding \dot{m}_4 , as asked for in the problem, will be somewhat more difficult. One place to start is to write the mass balance on the evaporator, since that will certainly contain the unknown we seek. Assuming that the process is steady state we can write:

$$In - Out = 0$$

$$\dot{m}_1 - \dot{m}_2 - \dot{m}_4 - \dot{m}_6 = 0$$

Problem: we don't know \dot{m}_6 so with only this equation we cannot solve for \dot{m}_4 . Have no fear, however, because there is another way to figure out what \dot{m}_6 is... can you figure it out? Try to do so before you move on.

[edit] So you want to check your guess? Alright then read on.

The way to find \dot{m}_6 is to do a mass balance on the heat exchanger, because the mass balance for the heat exchanger is simply:

$$\dot{m}_6 - \dot{m}_5 = 0$$

Since we know \dot{m}_5 we can calculate \dot{m}_6 and thus the waste stream flowrate \dot{m}_4 .

NOTE:

Notice the strategy here: we first start with a balance on the operation containing the stream we need information about. Then we move to balances on other operations in order to garner additional information about the unknowns in the process. This takes **practice** to figure out when you have enough information to solve the problem or you need to do more balances or look up information.

It is also of note that **any process has a limited number of independent balances you can perform**. This is not as much of an issue with a relatively simple problem like this, but will become an issue with more complex problems. Therefore, a step-by-step method exists to tell you exactly how many independent mass balances you can write on any given process, and therefore how many total independent equations you can use to help you solve problems.

[edit] Step 4: Calculate your unknowns.

Carrying out the plan on this problem:

$$\dot{m}_6 - 0.1893 \frac{kg}{s} = 0$$

$$\dot{m}_6 = 0.1893 \frac{kg}{s}$$

Hence, from the mass balance on the evaporator:

$$\dot{m}_4 = \dot{m}_1 - \dot{m}_2 - \dot{m}_6 = (0.5 - 0.2666 - 0.1893) \frac{kg}{s} = 0.0441 \frac{kg}{s}$$

So the final answers are:

Evaporator Efficiency = 53.3%

Waste stream rate = $0.0441 \frac{kg}{s}$

[edit] Step 5: Check your work.

Ask: Do these answers make sense? Check for things like negative flow rates, efficiencies higher than 100%, or other physically impossible happenings; if something like this happens (and it will), you did something wrong. Is your exit rate higher than the total inlet rate (since no water is created in the processes, it is impossible for this to occur)?

In this case, the values make physical sense, so they may be right. It's always good to go back and check the math *and* the setup to make sure you didn't forget to convert any units or anything like that.

[[edit](#)] Chapter 2 Practice Problems



Problem:

1. *a)* A salt solution is to be concentrated by evaporating the water in a salt pan, with a condensing surface above it to gather the evaporated water. Suppose 1200g of salt solution are emptied into the pan. Once all the water is evaporated, the salt is weighed and found to weigh 100g. What percent of the original solution was water?
- b)* Now suppose that 0.1 L of the evaporated water was added back to the salt, to bring it to the desired concentration. How much water remains to be used elsewhere?
- c)* Do you think the salt solution would be safe to drink? Why or why not?



Problem:

2. *a)* In a stone quarry, limestone is to be crushed and poured into molds for manufacture of floor tiles. Suppose that a limestone company uses three trucks, each of which is capable of carrying 3000 kg of limestone. The quarry itself is 20 miles away from the processing plant, and the trucks get there at an average speed of 30 miles/hour. Once at the plant, the limestone is ground into fine powder and then melted and poured into the molds. If each of the resulting slabs weighs 2 kg and the plant operates 24 hours a day, how many slabs can the company make in a day?
- b)* How could this plant become more efficient? Plot the number of slabs the company can make as a function of distance from the quarry and capacity of the trucks. What factors might keep the company from simply moving as close to the quarry as possible and using the largest trucks possible?



Problem:

3. What is the volumetric flowrate of a solution with density 1.5 kg/m^3 flowing at a velocity of 5 m/s and a mass flow rate of 500 g/min? What is the area of the pipe? If it is circular, what is the radius?



Problem:

4. Suppose you have a pipe that constricts halfway through from a radius of 0.5 cm to a radius of 0.2 cm. A liquid approaches the constriction at a velocity of 0.5 m/s. What is the velocity of the fluid after the constriction? (Hint: Apply conservation of mass on both sides of the constriction).

Challenge: What kind of energy does the fluid gain? Energy is never created or destroyed, so where does it come from?



Problem:

5. Suppose that a river with a molar flow rate of 10000 mol/s meets another, larger river flowing at 500000 m³/s at room temperature. What is the mass flow rate of the river downstream of the intersection if you assume steady state?

b) Evaluate the feasibility of the steady state assumption in this situation. Also qualitatively evaluate the probability that the flowrates are actually constant.



Problem:

6. Suppose that the population of a certain country n years after year 2000 if there is no emigration can be modeled with the equation:

$$P = 2.5 * 10^8 * e^{0.045*n}$$

Also, suppose that in the country, a net emigration of 100,000 people per month actually occurs. What is the total accumulation of people in this country from year 2000 to 2003?

b) What was the population of people in 2002, according to this model?

c) What are some possible problems with this model? For example, what doesn't it take into account? What happens when n is 100? Where did those constants come from? Would they be the same for every country, or for the same country across generations?

[\[edit\]](#) Chapter 3: Mass balances on multicomponent systems

[\[edit\]](#) Component Mass Balance

Most processes, of course, involve more than one input and/or output, and therefore it must be learned how to perform mass balances on this type of system. The basic idea remains the same though. We can write a mass balance in the same form as the overall balance for each component:

$$In - Out + Generation = Accumulation$$

For **steady state** processes, this becomes:

$$In - Out + Generation = 0$$

The **overall** mass balance at steady state, recall, is:

$$\Sigma \dot{m}_{in} - \Sigma \dot{m}_{out} + m_{gen} = 0$$

The mass of each component can be described by a similar balance.

$$\Sigma \dot{m}_{A,in} - \Sigma \dot{m}_{A,out} + m_{A,gen} = 0$$

The biggest difference between these two equations is that **The total generation of mass m_{gen} is zero due to conservation of mass, but since individual species can be consumed in a reaction, $m_{A,gen} \neq 0$ for a reacting system**

[\[edit\]](#) Concentration Measurements

You may recall from general chemistry that a **concentration** is a measure of the amount of some species in a mixture relative to the total amount of material, or relative to the amount of another species. Several different measurements of concentration come up over and over, so they were given special names.

[\[edit\]](#) Molarity

The first major concentration unit is the **molarity** which relates the moles of one particular species to the total volume of the solution.

$$\text{Molarity}(A) = [A] = \frac{n_A}{V_{\text{soln}}} \text{ where } n \doteq \text{mol}, V \doteq L$$

A more useful definition for flow systems that is equally valid is:

$$[A] = \frac{\dot{n}_A}{\dot{V}_n} \text{ where } \dot{n}_A \doteq \text{mol/s}, \dot{V}_n \doteq L/s$$

Molarity is a useful measure of concentration because it takes into account the volumetric changes that can occur when one creates a mixture from pure substances. Thus it is a very practical unit of concentration. However, since it involves volume, it can change with temperature so *molarity should always be given at a specific temperature*. Molarity of a gaseous mixture can also change with pressure, so it is not usually used for gasses.

[\[edit\]](#) Mole Fraction

The **mole fraction** is one of the most useful units of concentration, since it allows one to directly determine the molar flow rate of any component from the total flowrate. It also conveniently is *always* between 0 and 1, which is a good check on your work as well as an additional equation that you can always use to help you solve problems.

The mole fraction of a component A in a mixture is defined as:

$$y_A = \frac{n_A}{n_n}$$

where n_A signifies moles of A. Like molarity, a definition in terms of flowrates is also possible:

$$y_A = \frac{\dot{n}_A}{\dot{n}_n}$$

As mentioned before, if you add up all mole fractions in a mixture, you should always obtain 1 (within calculation and measurement error):

$$\sum y_i = 1$$

Note that **each stream has its own independent set of concentrations.**

[\[edit\]](#) Mass Fraction

Since mass is a more practical property to measure than moles, flowrates are often given as *mass* flowrates rather than *molar* flowrates. When this occurs, it is convenient to express concentrations in terms of **mass fractions** defined similarly to mole fractions:

$$x_A = \frac{m_A}{m_n} \text{ for batch systems}$$

$$x_A = \frac{\dot{m}_A}{\dot{m}_n}$$

where m_A is the mass of A. It doesn't matter what the units of the mass are as long as they are the same as the units of the total mass of solution.

Like the mole fraction, the total mass fraction in any stream should always add up to 1.

$$\sum x_i = 1$$

[\[edit\]](#) Calculations on Multi-component streams

Various conversions must be done with multiple-component streams just as they must for single-component streams. This section shows some methods to combine the properties of single-component streams into something usable for multiple-component streams (with some assumptions).

[\[edit\]](#) Average Molecular Weight

The *average molecular weight* of a mixture (gas or liquid) is the multicomponent equivalent to the molecular weight of a pure species. It allows you to convert between the mass of a mixture

and the number of moles, which is important for reacting systems especially because balances must usually be done in moles, but measurements are generally in grams.

To find the value of $\bar{M}W_n = \frac{g \text{ sln}}{\text{mole sln}}$, we split the solution up into its components as follows, for k components:

$$\begin{aligned} \frac{g \text{ sln}}{\text{mole sln}} &= \frac{\sum m_i}{n_n} = \sum \frac{m_i}{n_n} \\ &= \sum \left(\frac{m_i}{n_i} * \frac{n_i}{n_n} \right) = \sum (MW_i * y_i) \end{aligned}$$

Therefore, we have the following formula:

$$\bar{M}W_n = \sum (MW_i * y_i)_n$$

This derivation only assumes that **mass is additive**, which is, so this equation is valid for *any* mixture.

[\[edit\]](#) Density of Liquid Mixtures

Let us attempt to calculate the density of a liquid mixture from the density of its components, similar to how we calculated the average molecular weight. This time, however, we will notice one critical difference in the assumptions we have to make. We'll also notice that there are **two** different equations we could come up with, depending on the assumptions we make.

[\[edit\]](#) First Equation

By definition, the density of a single component i is: $\rho_i = \frac{m_i}{V_i}$ The corresponding definition for

a solution is $\rho = \frac{m \text{ sln}}{V \text{ sln}}$. Following a similar derivation to the above for average molecular weight:

$$\begin{aligned} \frac{m \text{ sln}}{V \text{ sln}} &= \frac{\sum m_i}{V_n} = \sum \frac{m_i}{V_n} \\ &= \sum \frac{m_i}{V_i} * \frac{V_i}{V_n} = \sum \left(\rho_i * \frac{V_i}{V_n} \right) \end{aligned}$$

Now we make the assumption that **The volume of the solution is proportional to the mass**. This is true for any pure substance (the proportionality constant is the density), but it is further assumed that **the proportionality constant is the same for both pure k and the solution**. This equation is therefore useful for two substances with similar pure densities. If this is true then:

$$\frac{V_i}{V} = \frac{m_i}{m_n} = x_i \quad \text{and:}$$

$$\rho_n = \sum(x_i * \rho_i)_n$$

[\[edit\]](#) Second Equation

This equation is easier to derive if we assume the equation will have a form similar to that of average molar mass. Since density is given in terms of mass, it makes sense to try using mass fractions:

$$x_k = \frac{m_i}{m_n}$$

To get this in terms of only solution properties, we need to get rid of m_A . We do this first by dividing by the density:

$$\begin{aligned} \frac{x_i}{\rho_i} &= \frac{m_i}{m_n} * \frac{V_i}{m_i} \\ &= \frac{V_i}{m_n} \end{aligned}$$

Now if we add all of these up we obtain:

$$\sum\left(\frac{x_i}{\rho_i}\right) = \frac{\sum V_i}{m_n}$$

Now we have to make an assumption, and it's different from that in the first case. This time we assume that the **Volumes are additive**. This is true in two cases:

1. In an **ideal solution**. The idea of an ideal solution will be explained more later, but for now you need to know that ideal solutions:

- Tend to involve similar compounds in solution with each other, or when one component is so dilute that it doesn't effect the solution properties much.
- Include Ideal Gas mixtures at constant temperature and pressure.

2 In a **Completely immiscible nonreacting mixture**. In other words, if two substances don't mix at all (like oil and water, or if you throw a rock into a puddle), the total volume will not change when you mix them.

If the solution is ideal, then we can write:

$$\frac{\sum \dot{V}_i}{\dot{m}_n} = \frac{\dot{V}_n}{\dot{m}_n} = \frac{1}{\rho_i}$$

Hence, for an ideal solution,

$$\frac{1}{\rho_n} = \sum \left(\frac{x_i}{\rho_i} \right)_n$$

Note that this is significantly different from the previous equation! This equation is more accurate for most cases. In all cases, however, it is most accurate to look up the value in a handbook such as Perry's Chemical Engineers Handbook if data is available on the solution of interest.

[\[edit\]](#) General Strategies for Multiple-Component Operations

The most important thing to remember about doing mass balances with multiple components is that *for each component, you can write one independent mass balance*. What do I mean by independent? Well, remember we can write the general, overall mass balance for any steady-state system:

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

And we can write a similar mass balance for any *component* of a stream:

$$\sum \dot{m}_{a,in} - \sum \dot{m}_{a,out} + m_{a,gen} = 0$$

This looks like we have three equations here, but in reality only two of them are independent because:

1. The sum of the masses of the components equals the total mass
2. The total mass generation due to reaction is always zero (by the law of mass conservation)

Therefore, if we add up all of the mass balances for the *components* we obtain the *overall* mass balance. Therefore, **we can choose any set of n equations we want, where n is the number of components, but if we choose the overall mass balance as one of them we cannot use the mass balance on one of the components.**

The choice of which balances to use depends on two particular criteria:

1. Which component(s) you have the most information on; if you don't have enough information you won't be able to solve the equations you write.
2. Which component(s) you can make the most reasonable assumptions about. For example, if you have a process involving oxygen and water at low temperatures and pressures, you may say that there is no oxygen dissolved in a liquid flow stream, so it all leaves by another path. This will simplify the algebra a good deal if you write the mass balance on that component.

[[edit](#)] Multiple Components in a Single Operation: Separation of Ethanol and Water



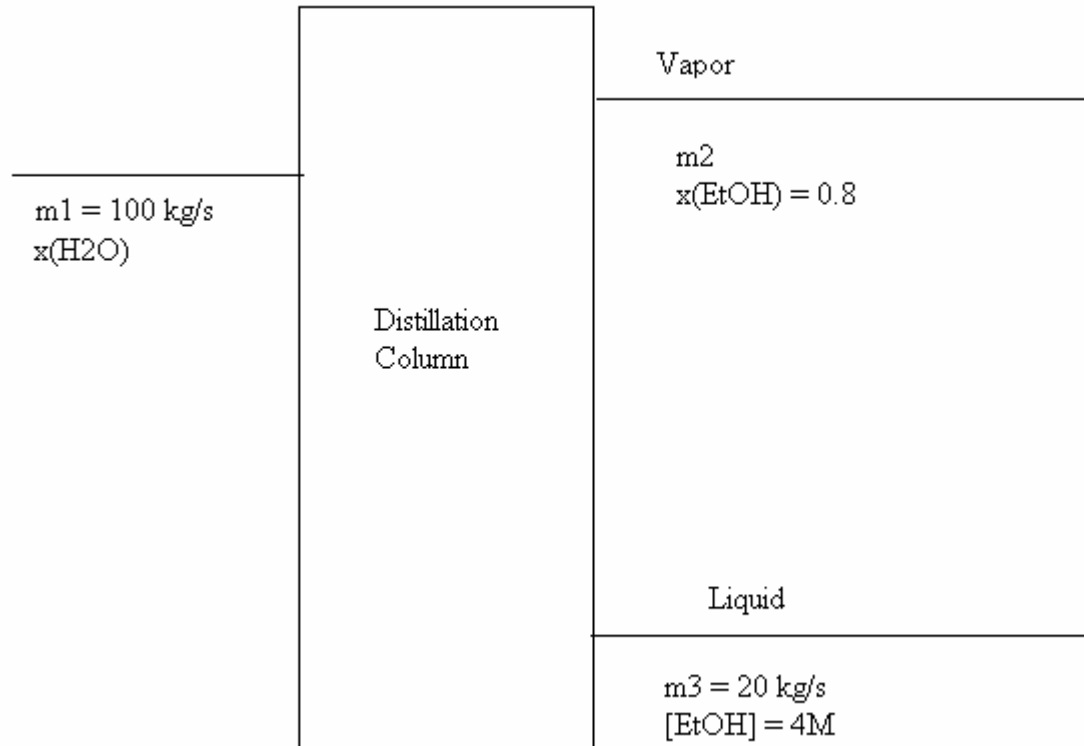
Example:

Suppose a stream containing ethanol and water (two fully miscible compounds) flows into a distillation column at 100 kg/s. Two streams leave the column: the vapor stream contains 80% ethanol by mass and the liquid bottoms has an ethanol concentration of 4M. The total liquid stream flowrate is 20 kg/s. Calculate the composition of the entrance stream.

Following the step-by-step method makes things easier.

[[edit](#)] Step 1: Draw a Flowchart

The first step as always is to draw the flowchart, as described previously. If you do that for this system, you may end up with something like this, where x signifies mass fraction, $[A]$ signifies molarity of A, and numbers signify stream numbers.



[\[edit\]](#) Step 2: Convert Units

Now, we need to turn to converting the concentrations into appropriate units. Since the total flowrates are given in terms of mass, a unit that expresses the concentration in terms of mass of the components would be most useful. The vapor stream compositions are given as mass percents, which works well with the units of flow. However, the liquid phase concentration given in terms of a molarity is not useful for finding a mass flow rate of ethanol (or of water). Hence we must convert the concentration to something more useful.

NOTE:

Converting between Concentration Measurements

The easiest way to convert between concentrations is to take a careful look at the *units* of both what you want and what you have, and ask what physical properties (i.e. molar mass, density) you could use to interchange them. In this example, we want to convert a molarity into a mass fraction. We have from the definitions that:

$$[A] = \frac{\text{mol}_A}{L_{\text{soln}}}$$

$$x_A = \frac{m_A}{m_{sln}}$$

To convert the numerators, we need to convert moles of A to mass of A, so we can use the molar mass for this purpose. Similarly, to convert the denominators we need to change Liters to Mass, which means we'll use a density. Hence, the conversion from molarity to mass fraction is:

$$x_A = [A] * \frac{(MW)_A}{\rho_{SLN}}$$

Since we have ways to estimate ρ_{SLN} (remember them?), we can inter-convert the conversions.

In order to convert the molarity into a mass fraction, then, we need the molecular weight of ethanol and the density of a 4M ethanol solution. The former is easy if you know the chemical formula of ethanol: CH_3CH_2OH . Calculating the molecular weight (as you did in chem class) you should come up with about $46 \frac{g}{mol}$.

Calculating the density involves plugging in mass fractions in and of itself, so you'll end up with an implicit equation. Recall that one method of estimating a solution density is to assume that the solution is ideal (which it probably is not in this case, but if no data are available or we just want an estimate, assumptions like these are all we have, as long as we realize the values will not be exact):

$$\frac{1}{\rho_{SLN}} = \sum \left(\frac{x_k}{\rho_k} \right)$$

In this case, then,

$$\frac{1}{\rho_{SLN}} = \frac{x_{EtOH}}{\rho_{EtOH}} + \frac{x_{H_2O}}{\rho_{H_2O}}$$

We can look up the densities of pure water and pure ethanol, they are as follows (from Wikipedia's articles [w:Ethanol](#) and [w:Water](#)):

$$\rho_{EtOH} = 0.789 \frac{g}{cm^3} = 789 \frac{g}{L}$$

$$\rho_{H_2O} = 1.00 \frac{g}{cm^3} = 1000 \frac{g}{L}$$

Therefore, since the mass fractions add to one, our equation for density becomes:

$$\frac{1}{\rho_{sln}} = \frac{x_{EtOH}}{789 \frac{g}{L}} + \frac{1 - x_{EtOH}}{1000 \frac{g}{L}}$$

From the NOTE above, we can now finally convert the molarity into a mass fraction as:

$$x_{EtOH} = [EtOH] * \frac{(MW)_{EtOH}}{\rho_{SLN}} = 4 \frac{mol}{L} * 46 \frac{g}{mol} * \left(\frac{x_{EtOH}}{789 \frac{g}{L}} + \frac{1 - x_{EtOH}}{1000 \frac{g}{L}} \right)$$

Solving this equation yields:

$$x_{EtOH} = 0.194_{(unitless)}$$

[edit] Step 3: Relate your Variables

Since we are seeking properties related to mass flow rates, we will need to relate our variables with mass balances.

Remember that we can do a mass balance on any of the N independent species and one on the overall mass, but since the sum of the individual masses equals the overall only $N - 1$ of these equations will be independent. It is often easiest mathematically to choose the overall mass balance and $N - 1$ individual species balances, since you don't need to deal with concentrations for the overall measurements.

Since our concentrations are now in appropriate units, we can do any two mass balances we want. Lets choose the overall first:

$$\dot{m}_1 - \dot{m}_2 - \dot{m}_3 = 0$$

Plugging in known values:

$$\dot{m}_2 = 100 \frac{kg}{s} - 20 \frac{kg}{s}$$

$$\dot{m}_2 = 80 \frac{kg}{s}$$

Now that we know \dot{m}_2 we can do a mass balance on either ethanol or water to find the composition of the input stream. Lets choose ethanol (A):

$$\dot{m}_{A1} = \dot{m}_{A2} + \dot{m}_{A3}$$

Written in terms of mass fractions this becomes:

$$x_{A1} * \dot{m}_1 = x_{A2} * \dot{m}_2 + x_{A3} * \dot{m}_3$$

Plugging in what we know:

$$x_{A1} * 100 \frac{kg}{s} = 0.8 * 20 \frac{kg}{s} + 0.194 * 80 \frac{kg}{s}$$

$$x_{A1} = 0.3152$$

Hence, **the feed is 32% Ethanol and 68% Water.**

[\[edit\]](#) Introduction to Problem Solving with Multiple Components and Processes

In the vast majority of chemical processes, in which some raw materials are processed to yield a desired end product or set of end products, there will be more than one raw material entering the system and more than one unit operation through which the product must pass in order to achieve the desired result. The calculations for such processes, as you can probably guess, are considerably more complicated than those either for only a single component, or for a single-operation process. Therefore, several techniques have been developed to aid engineers in their analyses. This section describes these techniques and how to apply them to an example problem.

[\[edit\]](#) Degree of Freedom Analysis

For more complex problems than the single-component or single-operation problems that have been explored, it is essential that you have a method of determining if a problem is even solvable given the information that you have. There are three ways to describe a problem in terms of its solvability:

1. If the problem has a finite (not necessarily unique!) set of solutions then it is called **well-defined**.
2. The problem can be **overdetermined** (also known as **overspecified**), which means that you have too much information and it is either redundant or inconsistent. This could possibly be fixed by consolidating multiple data into a single function or, in extreme cases, a single value (such as a slope of a linear correlation), or it could be fixed by removing an assumption about the system that one had made.
3. The problem can be **underdetermined** (or **underspecified**), which means that you don't have enough information to solve for all your unknowns. There are several ways of dealing with this. The most obvious is to gather additional information, such as measuring additional temperatures, flow rates, and so on until you have a well-defined problem. Another way is to use additional equations or information about what we want out of a process, such as how much conversion you obtain in a reaction, how efficient a separation process is, and so on. Finally, we can **make assumptions** in order to simplify the equations, and perhaps they will simplify enough that they become solvable.

The method of analyzing systems to see whether they are over or under-specified, or if they are well-defined, is called a **degree of freedom analysis**. It works as follows for mass balances on a **single process**:

1. From your flowchart, determine the number of **unknowns** in the process. What qualifies as an unknown depends on what you're looking for, but in a material balance calculation, masses and concentrations are the most common. In equilibrium and energy balance calculations, temperature and pressure also become important unknowns. In a reactor, you should include the conversion as an unknown unless it is given OR you are doing an atom balance.
2. Subtract the number of **Equations** you can write on the process. This can include mass balances, energy balances, equilibrium relationships, relations between concentrations, and any equations derived from additional information about the process.
3. The number you are left with is the degrees of freedom of the process.

If the degrees of freedom are **negative** that means the unit operation is **overspecified**. If it is **positive**, the operation is **underspecified**. If it is **zero** then the unit operation is **well-defined**, meaning that it is theoretically possible to solve for the unknowns with a finite set of solutions.

[\[edit\]](#) Degrees of Freedom in Multiple-Process Systems

Multiple-process systems are tougher but not undoable. Here is how to analyze them to *see if a problem is uniquely solvable*:

1. Label a flowchart completely with all the relevant unknowns.
2. Perform a degree of freedom analysis on each unit operation, as described above.
3. Add the degrees of freedom for each of the operations.
4. Subtract the number of variables in *intermediate streams*, i.e. streams between two unit operations. This is because each of these was counted twice, once for the operation it leaves and once for the one it enters.

The number you are left with is the **process degrees of freedom**, and this is what will tell you if the process as a *whole* is overspecified, underspecified, or well-defined.

NOTE:

If any single process is overspecified, and is found to be inconsistent, then the problem as a whole cannot be solved, regardless of whether the process as a whole is well-defined or not.

[\[edit\]](#) Using Degrees of Freedom to Make a Plan

Once you have determined that your problem is solvable, you still need to figure out how you'll solve for your variables. This is the suggested method.

1. Find a unit operation or combination of unit operations for which the degrees of freedom are zero.
2. Calculate all of the unknowns involved in this combination.
3. **Recalculate** the degrees of freedom for each process, treating the calculated values as known rather than as variables.
4. Repeat these steps until everything is calculated (or at least that which you seek)

NOTE:

You must be careful when recalculating the degrees of freedom in a process. You have to be aware of the **sandwich effect**, in which calculations from one unit operation can trivialize balances on another operation. For example, suppose you have three processes lined up like this:

-> A -> B -> C ->

Suppose also that through mass balances on operations A and C, you calculate the exit composition of A and the inlet composition of C. Once these are performed, *the mass balances on B are already completely defined*. The moral of the story is that **before you claim that you can write an equation to solve an unknown, write the equation and make sure that it contains an unknown**. Do not count equations that have no unknowns in your degree of freedom analysis.

[[edit](#)] Multiple Components and Multiple Processes: Orange Juice Production



Example:

Consider a process in which raw oranges are processed into orange juice. A possible process description follows:

1. The oranges enter a crusher, in which all of the water contained within the oranges is released.
2. The now-crushed oranges enter a strainer. The strainer is able to capture 90% of the solids, the remainder exit with the orange juice as pulp.

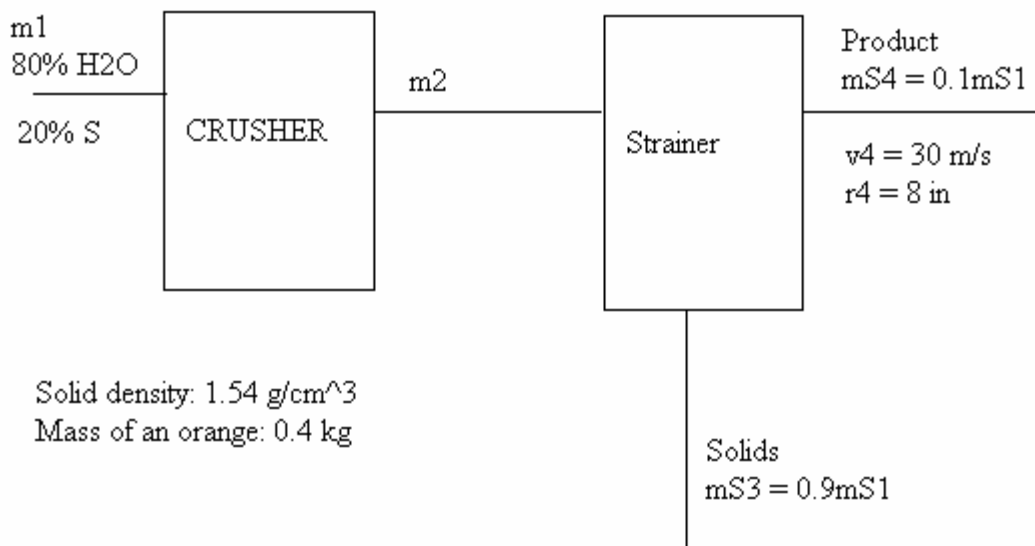
The velocity of the orange juice stream was measured to be $30 \frac{m}{s}$ and the radius of the piping was 8 inches. Calculate:

a) The mass flow rate of the orange juice product. b) The number of oranges per year that can be processed with this process if it is run 8 hours a day and 360 days a year. Ignore changes due to unsteady state at startup.

Use the following data: Mass of an orange: 0.4 kg Water content of an orange: 80% Density of the solids: Since its mostly sugars, its about the density of glucose, which is $1.540 \frac{g}{cm^3}$

[edit] Step 1: Draw a Flowchart

This time we have multiple processes so it's especially important to label each one as its given in the problem.



Notice how I changed the 90% capture of solids into an algebraic equation relating the mass of solids in the solid waste to the mass in the feed. This will be important later, because *it is an additional piece of information that is necessary to solve the problem.*

Also note that from here in, "solids" are referred to as S and "water" as W.

[edit] Step 2: Degree of Freedom analysis

Recall that for each stream there are C independent unknowns, where C is the number of components in the individual stream. These generally are **concentrations** of C-1 species and the **total mass flow rate**, since with C-1 concentrations we can find the last one, but we cannot obtain the total mass flow rate from only concentration.

Let us apply the previously described algorithm to determining if the problem is well-defined.

On the strainer:

- There are **6** unknowns: m_2 , x_{S3} , m_3 , x_{S3} , m_4 , and x_{S4}
- We can write **2** independent mass balances on the overall system (one for each component).
- We are given a conversion and enough information to write the mass flow rate in the product in terms of only concentration of one component (which eliminates one unknown). Thus we have **2** additional pieces of information.
- Thus the degrees of freedom of the strainer are $6 - 2 - 2 = \mathbf{2 \text{ DOF}}$

NOTE:

We are given the mass of an individual orange, but since we cannot use that information alone to find a total mass flow rate of oranges in the feed, and we already have used up our allotment of C-1 independent concentrations, we cannot count this as "given information". If, however, we were told the number of oranges produced per year, then we could use the two pieces of information in tandem to eliminate a single unknown (because then we can find the mass flow rate)

On the crusher:

- There are **3** unknowns (m_1 , m_2 , and x_{S2}).
- We can write **2** independent mass balances.
- Thus the crusher has $3 - 2 = \mathbf{1 \text{ DOF}}$

Therefore for the **system as a whole:**

- Sum of DOF for unit operations = $2 + 1 = 3 \text{ DOF}$
- Number of intermediate variables = 2 (m_2 and x_{S2})
- Total DOF = $3 - 2 = \mathbf{1 \text{ DOF}}$.

Hence the problem is **underspecified**.

[edit] So how to we solve it?

In order to solve an underspecified problem, one way we can obtain an additional specification is to **make an assumption**. What assumptions could we make that would reduce the number of unknowns (or equivalently, increase the number of variables we do know)?

The most common type of assumption is to assume that something that is relatively insignificant is zero.

In this case, one could ask: will the solid stream from the strainer contain any water? It might, of course, but this amount is probably very small compared to both the amount of solids that are

captured and how much is strained, provided that it is cleaned regularly and designed well. If we make this assumption, then *this specifies that the mass fraction of water in the waste stream is zero* (or equivalently, that the mass fraction of solids is one). Therefore, we know one additional piece of information and the degrees of freedom for the overall system become zero.

[\[edit\]](#) Step 3: Convert Units

This step should be done *after* the degree of freedom analysis, because that analysis is independent of your unit system, and if you don't have enough information to solve a problem (or worse, you have too much), you shouldn't waste time converting units and should instead spend your time defining the problem more precisely and/or seeking out appropriate assumptions to make.

Here, the most sensible choice is either to convert everything to the cgs system or to the m-kg-s system, since most values are already in metric. Here, the latter route is taken.

$$r_4 = 8 \text{ in} * \frac{2.54 \text{ cm}}{\text{in}} * \frac{1 \text{ m}}{100 \text{ cm}} = 0.2032 \text{ m}$$

$$\rho_S = 1.54 \frac{\text{g}}{\text{cm}^3} = 1540 \frac{\text{kg}}{\text{m}^3}$$

Now that everything is in the same system, we can move on to the next step.

[\[edit\]](#) Step 4: Relate your variables

First we have to relate the velocity and area given to us to the mass flowrate of stream 4, so that we can actually use that information in a mass balance. From chapter 2, we can start with the equation:

$$\rho_n * v_n * A_n = \dot{m}_n$$

Since the pipe is circular and the area of a circle is $\pi * r^2$, we have:

$$A_4 = \pi * 0.2032^2 = 0.1297 \text{ m}^2$$

So we have that:

$$\rho_4 * 30 * 0.1297 = 3.8915 * \rho_4 = \dot{m}_4$$

Now to find the density of stream 4 we assume that volumes are additive, since the solids and water are essentially immiscible (does an orange dissolve when you wash it?). Hence we can use the ideal-fluid model for density:

$$\frac{1}{\rho_4} = \frac{x_{S4}}{\rho_S} + \frac{x_{W4}}{\rho_W} = \frac{x_{S4}}{\rho_S} + \frac{1 - x_{S4}}{\rho_W}$$

$$= \frac{x_{S4}}{1540} + \frac{1 - x_{S4}}{1000}$$

Hence, we have the equation we need with only concentrations and mass flowrates:

EQUATION 1:
$$\frac{x_{S4}}{1540} + \frac{1 - x_{S4}}{1000} = \frac{3.8915}{\dot{m}_4}$$

Now we have an equation but we haven't used either of our two (why two?) independent mass balances yet. We of course have a choice on which two to use.

In this particular problem, since we are directly given information concerning the amount of *solid* in stream 4 (the product stream), it seems to make more sense to do the balance on this component. Since we don't have information on stream 2, and finding it would be pointless in this case (all parts of it are the same as those of stream 1), lets do an overall-system balance on the solids:

$$\Sigma \dot{m}_{S,in} - \Sigma \dot{m}_{S,out} = 0$$

NOTE:

Since there is no reaction, the generation term is 0 even for individual-species balances.

Expanding the mass balance in terms of mass fractions gives:

$$\dot{m}_1 * x_{S1} = \dot{m}_3 * x_{S3} + \dot{m}_4 * x_{S4}$$

Plugging in the known values, **with the assumption that stream 3 is pure solids (no water)** and hence $x_{S3} = 1$:

EQUATION 2:
$$0.2 * \dot{m}_1 = (0.9 * 0.2 * \dot{m}_1) * 1 + x_{S4} * \dot{m}_4$$

Finally, we can utilize one further mass balance, so let's use the easiest one: the overall mass balance. This one again assumes that the total flowrate of stream 3 is equal to the solids flowrate.

$$\text{EQUATION 3: } \dot{m}_1 = 0.9 * 0.2 * \dot{m}_1 + \dot{m}_4$$

We now have three equations in three unknowns ($\dot{m}_1, \dot{m}_4, x_{S4}$) so the problem is solvable. This is where all those system-solving skills will come in handy.

If you don't like solving by hand, there are numerous computer programs out there to help you solve equations like this, such as [MATLAB](#), POLYMATH, and many others. You'll probably want to learn how to use the one your school prefers eventually so why not now?

Using either method, the results are:

$$\dot{m}_1 = 4786 \frac{kg}{s}$$

$$\dot{m}_4 = 3925.07$$

$$x_{S4} = 0.0244$$

We're almost done here, now we just have to calculate the number of oranges per year.

$$4786 \frac{kg}{s} * 1 \frac{orange}{0.4 kg} * 3600 \frac{s}{hr} * 8 \frac{wk hr}{day} * 360 \frac{wk day}{year}$$

$$\text{Yearly Production: } 1.24 * 10^{11} \frac{oranges}{year}$$

[[edit](#)] Chapter 3 Practice Problems



Problem:

1. a) Look up the composition of air. Estimate its average molecular weight.
- b) Qualitatively describe whether the density of air should be large or small compared to the density of water.
- c) Qualitatively describe whether the mass density of air should be large or small compared to that of oxygen if the same number of *moles* of the two gasses are contained in identical containers.
- d) If the density of air under certain conditions is 1.06 g/m^3 , how much does a gallon of air weigh?



Problem:

2. a) Using both of the formulas for average density, calculate estimates for the density of a 50% by mass solution of toluene and benzene. Comment on the results.
- b) Repeat this calculation for varying concentrations of toluene. When does it make the most difference which formula you use? When does it make the least? Show the results graphically. Would the trend be the same for any binary solution?
- c) Suppose that a 50% mixture of toluene and benzene is to be separated by crystallization. The solution is cooled until one of the components completely freezes and only the other is left as a liquid. The liquid is then removed. What will the majority of the solid be? What will the liquid be? What temperature should be used to achieve this? (give an estimate)
- d) In the crystallization process in part c, suppose that the after separation, the solid crystals contained all of the benzene and 1% of the toluene from the original mixture. Suppose also that after melting the solid, the resulting liquid weighed 1435 g. Calculate the mass of the original solution.



Problem:

3. Consider a publishing company in which books are to be bound, printed, and shipped. At 5 a.m. every morning, a shipment of 10,000 reams of paper comes in, as well as enough materials to make 150,000 books, and 30000 pounds of ink. In this particular plant, the average size of a book is 250 pages and each uses about 0.2 pounds of ink.

a) How many books can be printed for each shipment? (Hint: What is the limiting factor?)

b) Suppose that, on average, 4% of all books printed are misprints and must be destroyed. The remaining books are to be distributed to each of 6 continents in the following proportions:

North America	15%
South America	10%
Europe	20%
Africa	20%
Asia	25%
Australia	10%

Each book that is printed (including those that are destroyed) costs the company US\$0.50 to print. Those that are shipped cost the following prices to ship from the US:

North America	\$0.05
South America	\$0.08
Europe	\$0.10
Africa	\$0.20
Asia	\$0.12
Australia	\$0.15

If each book sells for an equivalent of US\$1.00, what is the maximum profit that the company can make per day?

c) **Challenge** What is the *minimum* number of books that the company can sell (from any continent) in order to return a profit? (Hint: what is the total cost of this scheme? Does it matter where the books are sold once they are distributed?)

d) How many pounds of ink per day end up in each continent under the scheme in part b? How many pages of paper?

e) Can you think of any ways you can improve this process? What may be some ways to improve the profit margin? How can inventory be reduced? What are some possible problems with your proposed solutions?

[[edit](#)] Chapter 4: Mass balances with recycle

[[edit](#)] What Is Recycle?

Recycling is the act of taking one stream in a process and reusing it in an earlier part of the process rather than discarding it. It is used in a wide variety of processes.

[[edit](#)] Uses and Benefit of Recycle

The use of recycle makes a great deal of environmental *and* economic sense, for the following reasons among others:

- Using recycle lets a company achieve a wider range of separations

This will be demonstrated in the next section. However, there is a tradeoff: the more dilute or concentrated you want your product to be, the lower the flowrate you can achieve in the concentrated or dilute stream.

- By using recycle, in combination with some sort of separation process, a company can increase the overall conversion of an **equilibrium reaction**.

You may recall from general chemistry that many reactions do not go to completion but only up to a certain point, because they are *reversible*. How far the reaction goes depends on the concentrations (or partial pressures for a gas) of the products and the reactants, which are related by the reaction stoichiometry and the equilibrium constant K . If we want to increase the amount of conversion, one way we can do this is to separate out the products from the product mixture and re-feed the purified reactants in to the reactor. By Le Chatlier's Principle, this will cause the reaction to continue moving towards the products.

- By using recycle, it is possible to recover expensive **catalysts and reagents**.

Catalysts aren't cheap, and if we don't try to recycle them into the reactor, they may be lost in the product stream. This not only gives us a contaminated product but also wastes a lot of catalyst.

- Because of the previous three uses, recycle can decrease the amount of equipment needed to get a process meet specifications and consumer demand.

For example, it may improve reaction conversion enough to eliminate the need for a second reactor to achieve an economical conversion.

- Recycle reduces the amount of waste that a company generates.

Not only is this the most environmentally sounds way to go about it, it also saves the company money in disposal costs.

- Most importantly, all of these things can save a company money.

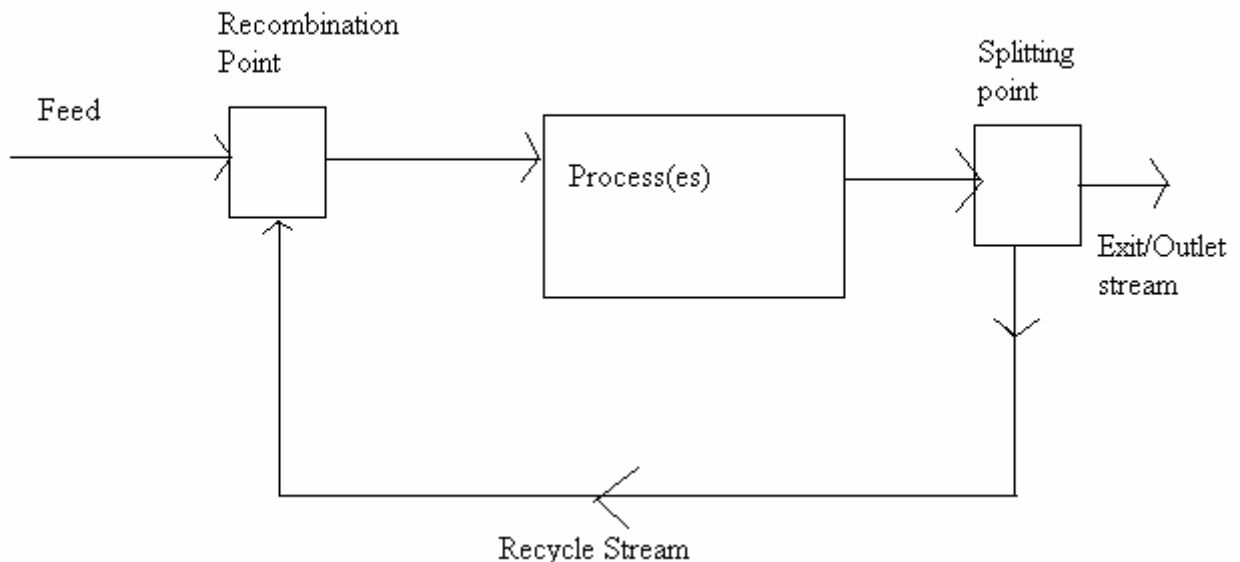
By using less equipment, the company saves maintenance as well as capital costs, and probably gets the product faster too, if the proper analysis is made.

[edit] Differences between Recycle and non-Recycle systems

The biggest difference between recycle and non-recycle systems is that *the extra splitting and recombination points must be taken into account, and the properties of the streams change from before to after these points*. To see what is meant by this, consider any arbitrary process in which a change occurs between two streams:

Feed -> Process -> Outlet

If we wish to implement a recycle system on this process, we often will do something like this:



The "extra" stream between the splitting and recombination point must be taken into account, but the way to do this is *not* to do a mass balance on the process, since *the recycle stream itself does not go into the process, only the recombined stream does*.

Instead, we take it into account by performing a mass balance on the *recombination point* and one on the *splitting point*.

[\[edit\]](#) Assumptions at the Splitting Point

The recombination point is relatively unpredictable because the composition of the stream leaving depends on both the composition of the feed and the composition of the recycle stream. However, the *splitting point* is special because **when a stream is split, it generally is split into two streams with equal composition**. This is a piece of information that counts towards "additional information" when performing a degree of freedom analysis.

As an additional specification, it is common to know the *ratio* of splitting, i.e. how much of the exit stream from the process will be put into the outlet and how much will be recycled. This also counts as "additional information".

[\[edit\]](#) Assumptions at the Recombination Point

The recombination point is generally not specified like the splitting point, and also the recycle stream and feed stream are very likely to have different compositions. The important thing to remember is that you can generally use the properties of the stream coming from the splitting point for the stream entering the recombination point, unless it goes through another process in between (which is entirely possible).

[\[edit\]](#) Degree of Freedom Analysis of Recycle Systems

Degree of freedom analyses are similar for recycle systems to those for other systems, but with a couple important points that the engineer must keep in mind:

1. The recombination point and the splitting point must be counted in the degree of freedom analysis as "processes", since they can have unknowns that aren't counted anywhere else.
2. When doing the degree of freedom analysis on the splitting point, *you should not label the concentrations as the same but leave them as separate unknowns until after you complete the DOF analysis* in order to avoid confusion, since labeling the concentrations as identical "uses up" one of your pieces of information and then you can't count it.

As an example, let's do a degree of freedom analysis on the hypothetical system above, assuming that all streams have two components.

- **Recombination Point:** 6 variables (3 concentrations and 3 total flow rates) - 2 mass balances = 4 DOF
- **Process:** Assuming it's not a reactor and there's only 2 streams, there's 4 variables and 2 mass balances = 2 DOF
- **Splitting Point:** 6 variables - 2 mass balances - **1 knowing compositions are the same - 1 splitting ratio = 2 DOF**

So the total is $4 + 2 + 2 - 6$ (in-between variables) = **2 DOF**. Therefore, if the feed is specified then this entire system can be solved! Of course the results will be different if the process has more than 2 streams, if the splitting is 3-way, if there are more than two components, and so on.

[[edit](#)] Suggested Solving Method

The solving method for recycle systems is similar to those of other systems we have seen so far but as you've likely noticed, they are increasingly complicated. Therefore, the importance of **making a plan** becomes of the utmost importance. The way to make a plan is generally as follows:

1. Draw a completely labeled flow chart for the process.
2. Do a DOF analysis to make sure the problem is solvable.
3. If it is solvable, **a lot of the time, the best place to start with a recycle system is with a set of overall system balances, sometimes in combination with balances on processes on the border.** The reason for this is that the overall system balance cuts out the recycle stream entirely, since the recycle stream does not enter or leave the system as a whole but merely travels between two processes, like any other intermediate stream. Often, the composition of the recycle stream is unknown, so this simplifies the calculations a good deal.
4. Find a set of independent equations that will yield values for a certain set of unknowns (this is often most difficult the first time; sometimes, one of the unit operations in the system will have 0 DOF so start with that one. Otherwise it'll take some searching.)
5. Considering those variables as known, do a new DOF balance until something has 0 DOF. Calculate the variables on that process.
6. Repeat until all processes are specified completely.

[[edit](#)] Example problem: Improving a Separation Process

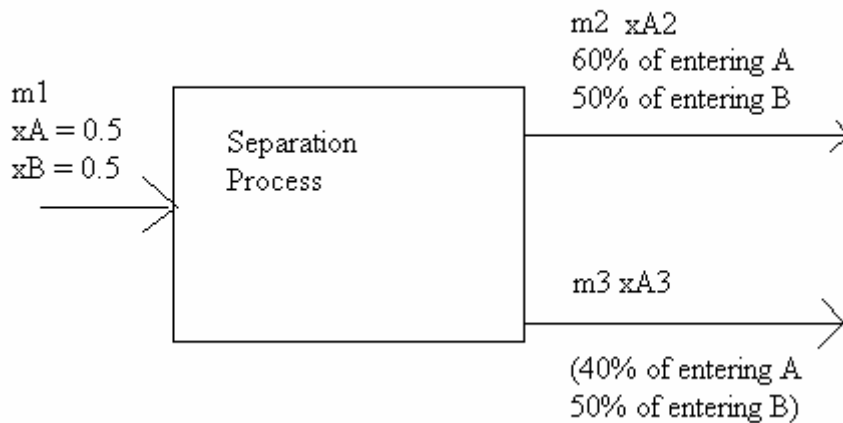
It has been stated that recycle can help to This example helps to show that this is true and also show some limitations of the use of recycle on real processes.

Consider the following proposed system without recycle.



Example:

A mixture of 50% A and 50% B enters a separation process that is capable of splitting the two components into two streams: one containing 60% of the entering A and half the B, and one with 40% of the A and half the B (all by mass):



If 100 kg/hr of feed containing 50% A by mass enters the separator, what are the concentrations of A in the exit streams?

A degree of freedom analysis on this process:

4 unknowns (\dot{m}_2 , x_{A2} , \dot{m}_3 , and x_{A3}), 2 mass balances, and 2 pieces of information (knowing that 40% of A and half of B leaves in stream 3 is not independent from knowing that 60% of A and half of B leaves in stream 2) = 0 DOF.

Methods of previous chapters can be used to determine that $\dot{m}_2 = 55 \frac{kg}{hr}$, $x_{A2} = 0.545$, $\dot{m}_3 = 45 \frac{kg}{hr}$ and $x_{A3} = 0.444$. This is good practice for the interested reader.

If we want to obtain a greater separation than this, one thing that we can do is use a *recycle system*, in which a portion of one of the streams is siphoned off and remixed with the feed stream in order for it to be re-separated. The choice of which stream should be re-siphoned depends on the desired properties of the exit streams. The effects of each choice will now be assessed.

[\[edit\]](#) Implementing Recycle on the Separation Process



Example:

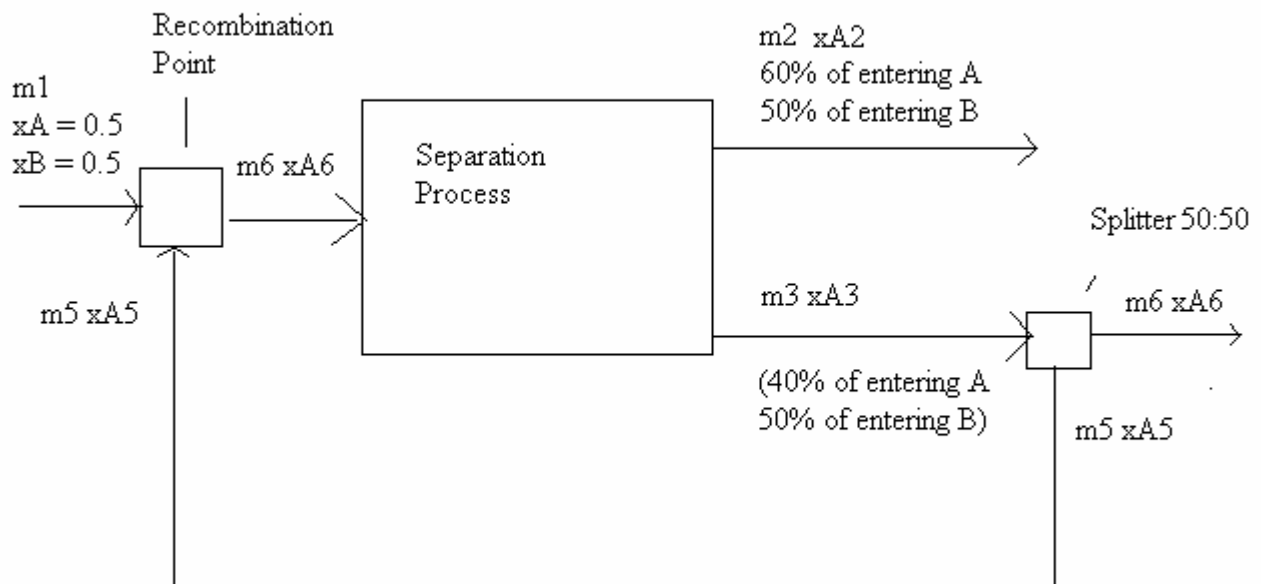
Suppose that in the previous example, a recycle system is set up in which half of stream 3 is siphoned off and recombined with the feed (which is still the same composition as before). Recalculate the concentrations of A in streams 2 and 3. Is the separation more or less effective

than that without recycle? Can you see a major limitation of this method? How might this be overcome?

This is a rather involved problem, and must be taken one step at a time. The analyses of the cases for recycling each stream are similar, so the first case will be considered in detail and the second will be left for the reader.

[edit] Step 1: Draw a Flowchart

You must be careful when drawing the flowchart because the separator separates 60% of all the A that enters it into stream 2, **not 60% of the fresh feed stream.**



[edit] Step 2: Do a Degree of Freedom Analysis

Recall that you must include the recombination and splitting points in your analysis.

- **Recombination point:** 4 unknowns - 2 mass balances = **2** degrees of freedom
- **Separator:** 6 unknowns (nothing is specified) - 2 independent pieces of information - 2 mass balances = **2** DOF
- **Splitting point:** 6 unknowns (again, nothing is specified) - 2 mass balances - 1 assumption that concentration remains constant - 1 splitting ratio = **2** DOF

- **Total** = 2 + 2 + 2 - 6 = 0. Thus the problem is completely specified.

[edit] Step 3: Devise a Plan and Carry it Out

First, look at the entire system, since none of the original processes individually had 0 DOF.

- **Overall mass balance on A:** $0.5 * 100 \frac{kg}{h} = \dot{m}_2 * x_{A2} + \dot{m}_6 * x_{A6}$
- **Overall mass balance on B:** $50 \frac{kg}{h} = \dot{m}_2 * (1 - x_{A2}) + \dot{m}_6 * (1 - x_{A6})$

We have 4 equations and 2 unknowns at this point. This is where the problem solving requires some ingenuity. First, let's see what happens when we combine this information with the splitting ratio and constant concentration at the splitter:

- **Splitting Ratio:** $\dot{m}_6 = \frac{\dot{m}_3}{2}$
- **Constant concentration:** $x_{A6} = x_{A3}$

Plugging these into the overall balances we have:

- **On A:** $50 = \dot{m}_2 * x_{A2} + \frac{\dot{m}_3}{2} * x_{A3}$
- **Total:** $50 = \dot{m}_2 * (1 - x_{A2}) + \frac{\dot{m}_3}{2} * (1 - x_{A3})$

Again we have more equations than unknowns *but we know how to relate everything in these two equations to the inlet concentrations in the separator*. This is due to the conversions we are given:

- **60% of entering A goes into stream 2** means $\dot{m}_2 * x_{A2} = 0.6 * x_{A4} * \dot{m}_4$
- **40% of entering A goes into stream 3** means $\dot{m}_3 * x_{A3} = 0.4 * x_{A4} * \dot{m}_4$
- **50% of entering B goes into stream 2** means $\dot{m}_2 * (1 - x_{A2}) = 0.5 * (1 - x_{A4}) * \dot{m}_4$
- **50% of entering B goes into stream 3** means $\dot{m}_3 * x_{A3} = 0.5 * (1 - x_{A4}) * \dot{m}_4$

Spend some time trying to figure out where these equations come from, it's all definition of mass fraction and translating words into algebraic equations.

Plugging in all of these into the existing balances, we finally obtain 2 equations in 2 unknowns:

$$\text{On A: } 50 = 0.6\dot{m}_4 * x_{A4} + \frac{0.4}{2}\dot{m}_4 * x_{A4}$$

$$\text{On B: } 50 = 0.5\dot{m}_4 * (1 - x_{A4}) + \frac{0.5}{2}\dot{m}_4 * (1 - x_{A4})$$

Solving these equations gives:

$$\dot{m}_4 = 129.17 \frac{kg}{h}, x_{A4} = 0.484$$

NOTE:

Notice that two things happened as expected: the concentration of the stream entering the evaporator went down (because the feed is mixing with a more dilute recycle stream), and the total flowrate went up (again due to contribution from the recycle stream). This is always a good rough check to see if your answer makes sense, for example if the flowrate was lower than the feed rate you'd know something went wrong

Once these values are known, you can choose to do a balance either on the separator or on the recombination point, since both now have 0 degrees of freedom. We choose the separator because that leads directly to what we're looking for.

The mass balances on the separator can be solved using the same method as that without a recycle system, the results are:

$$\dot{m}_2 = 70.83 \frac{kg}{hr}, x_{A2} = 0.530, \dot{m}_3 = 58.33 \frac{kg}{hr}, x_{A3} = 0.429$$

Now since we know the flowrate of stream 3 and the splitting ratio we can find the rate of stream 6:

$$\dot{m}_6 = \frac{\dot{m}_3}{2} = 29.165 \frac{kg}{hr}, x_{A6} = x_{A3} = 0.429$$

NOTE:

You should check to make sure that m_2 and m_6 add up to the total feed rate, otherwise you made a mistake.

Now we can assess how effective the recycle is. The concentration of A in the liquid stream *was* reduced, by a small margin of 0.015 mole fraction. However, this extra reduction came at a pair of costs: the flow rate of dilute stream was significantly reduced: from 45 to 29.165 kg/hr! **This limitation is important to keep in mind and also explains why we bother trying to make very efficient separation processes.**

[\[edit\]](#) Systems with Recycle: a Cleaning Process

[\[edit\]](#) Problem Statement



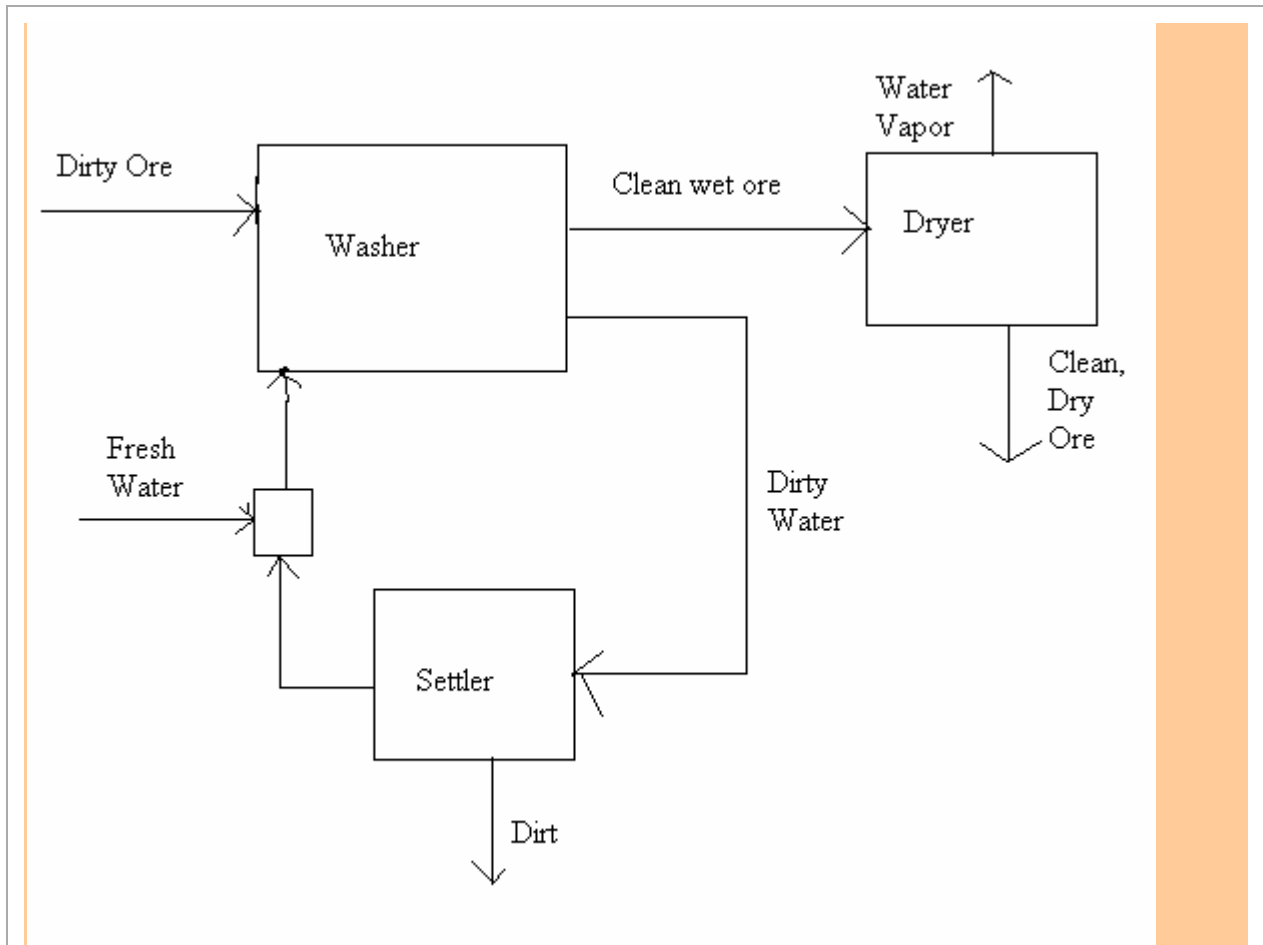
Example:

Consider a process in which freshly-mined ore is to be cleaned so that later processing units do not get contaminated with dirt. 3000 kg/hr of dirty ore is dumped into a large washer, in which water is allowed to soak the ore on its way to a drain on the bottom of the unit. The amount of dirt remaining on the ore after this process is negligible, but water remains absorbed on the ore surface such that the net mass flow rate of the cleaned ore is 3100 kg/hr.

The dirty water is cleaned in a settler, which is able to remove 90% of the dirt in the stream without removing a significant amount of water. The cleaned stream then is combined with a fresh water stream before re-entering the washer.

The wet, clean ore enters a dryer, in which all of the water is removed. Dry ore is removed from the dryer at 2900 kg/hr.

The design schematic for this process was as follows:

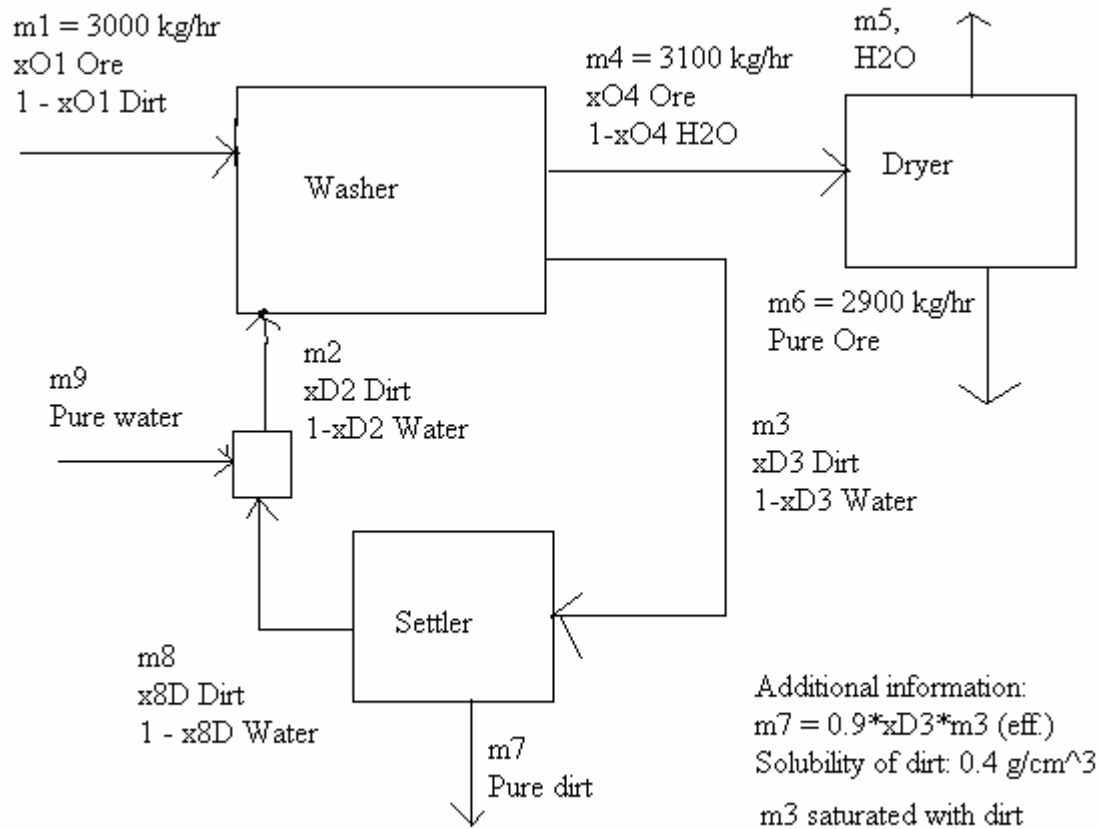


a) Calculate the necessary mass flow rate of fresh water to achieve this removal at steady state.

b) Suppose that the solubility of dirt in water is $0.4 \frac{g \text{ dirt}}{cm^3 \text{ H}_2\text{O}}$. Assuming that the water leaving the washer is saturated with dirt, calculate the mass fraction of dirt in the stream that enters the washer (after it has been mixed with the fresh-water stream).

[edit] First Step: Draw a Flowchart

A schematic is given in the problem statement but it is very incomplete, since it does not contain any of the design specifications (the efficiency of the settler, the solubility of soil in water, and the mass flow rates). Therefore, *it is highly recommended that you draw your own picture even when one is provided for you.* Make sure you label all of the streams, and the unknown concentrations.



[edit] Second Step: Degree of Freedom Analysis

- **Around the washer:** 6 independent unknowns ($x_{O1}, \dot{m}_2, x_{D2}, \dot{m}_3, x_{D3}, x_{O4}$), three independent mass balances (ore, dirt, and water), and one solubility. The washer has **2 DOF**.
- **Around the dryer:** 2 independent unknowns (x_{O4}, \dot{m}_5) and two independent equations = **0 DOF**.

NOTE:

Since the dryer has no degrees of freedom already, we can say that *the system variables behave as if the stream going into the dryer was not going anywhere*, and therefore this stream should not be included in the "in-between variables" calculation.

- **Around the Settler:** 5 independent unknowns ($\dot{m}_3, x_{D3}, \dot{m}_7, \dot{m}_8, x_{D8}$), two mass balances (dirt and water), the solubility of saturated dirt, and one additional information (90% removal of dirt), leaving us with **1 DOF**.

- **At the mixing point:** We need to include this in order to calculate the total degrees of freedom for the process, since otherwise we're not counting m_9 anywhere. 5 unknowns ($\dot{m}_2, x_{D2}, \dot{m}_8, x_{D8}, \dot{m}_9$) and 2 mass balances leaves us with **3 DOF**.

Therefore, Overall = $3+2+1 - 6$ intermediate variables (not including x_{O4} since that's going to the dryer) = 0

The problem is well-defined.

[edit] Devising a Plan

Recall that the idea is to look for a unit operation or some combination of them with 0 Degrees of Freedom, calculate those variables, and then recalculate the degrees of freedom until everything is accounted for.

From our initial analysis, the dryer had 0 DOF so we can calculate the two unknowns x_{O4} and m_5 . Now we can consider x_{O4} and m_5 known and redo the degree of freedom analysis on the unit operations.

- **Around the washer:** We only have 5 unknowns now ($x_{O1}, \dot{m}_2, x_{D2}, \dot{m}_3, x_{D3}$), but still only three equations and the solubility. **1 DOF**.
- **Around the settler:** Nothing has changed here since x_{O4} and m_5 aren't connected to this operation.
- **Overall System:** We have three unknowns ($x_{O1}, \dot{m}_7, \dot{m}_9$) since \dot{m}_5 is already determined, and we have three mass balances (ore, dirt, and water). Hence we have **0 DOF** for the overall system.

Now we can say we know x_{O1}, \dot{m}_7 and \dot{m}_9 .

- **Around the settler again:** since we know m_7 the settler now has **0 DOF** and we can solve for $\dot{m}_3, x_{D3}, \dot{m}_8$ and x_{D8} .
- **Around the washer again:** Now we know m_8 and x_{D8} . How many balances can we write?

NOTE:

If we try to write a balance on the ore, we will find that *the ore is already balanced because of the other balances we've done*. If you try to write an ore balance, you'll see you already know the values of all the unknowns in the equations. Hence we can't count that balance as an equation we can use (I'll show you this when we work out the actual calculation).

The washer therefore has 2 unknowns (m_2, x_{D2}) and 2 equations (the dirt and water balances) = **0 DOF**

This final step can also be done by balances on the recombination point (as shown below). Once we have m_2 and x_{D2} the system is completely determined.

[\[edit\]](#) Converting Units

The only given information in inconsistent units is the solubility, which is given as $0.4 \frac{g \text{ dirt}}{cm^3 H_2O}$. However, since we know the density of water (or can look it up), we can convert this to $\frac{kg \text{ dirt}}{kg H_2O}$ as follows:

$$0.4 \frac{g \text{ dirt}}{cm^3 H_2O} * 1 \frac{cm^3 H_2O}{g H_2O} = 0.4 \frac{g \text{ dirt}}{g H_2O} = 0.4 \frac{kg \text{ dirt}}{kg H_2O}$$

Now that this information is in the same units as the mass flow rates we can proceed to the next step.

[\[edit\]](#) Carrying Out the Plan

First, do any two mass balances on the dryer. I choose total and ore balances. Remember that the third balance is not independent of the first two!

- **Overall Balance:** $\dot{m}_4 = \dot{m}_5 + \dot{m}_6$
- **Ore Balance:** $\dot{m}_4 * x_{O4} = \dot{m}_5 * x_{O5} + \dot{m}_6 * x_{O6}$

Substituting the known values:

- Overall: $3100 = \dot{m}_5 + 2900$
- Ore: $x_{O4} * 3100 = 1 * 2900$

Solving gives:

$$\dot{m}_5 = 200 \frac{kg}{hr}$$
$$x_{O4} = 0.935 \frac{kg}{hr}$$

Now that we have finished the dryer we do the next step in our plan, which was the overall system balance:

- **Water Balance:** $\dot{m}_9 = \dot{m}_5$
- **Ore Balance:** $x_{O1} * \dot{m}_1 = \dot{m}_6$
- **Dirt Balance:** $(1 - x_{O1}) * \dot{m}_1 = \dot{m}_7$

$$\dot{m}_9 = 200 \frac{kg}{hr}, x_{O1} = 0.967,$$

$$\dot{m}_7 = 100 \frac{kg}{hr}$$

Next we move to the settler as planned, this one's a bit trickier since the solutions aren't immediately obvious but a system must be solved.

- **Overall Balance:** $\dot{m}_3 = \dot{m}_7 + \dot{m}_8$
- **Dirt Balance:** $\dot{m}_3 * x_{D3} = \dot{m}_7 * x_{D7} + \dot{m}_8 * x_{D8}$
- **Efficiency of Removal:** $\dot{m}_7 = 0.9 * \dot{m}_3 * x_{D3}$

Using the solubility is slightly tricky. You use it by noticing that *the mass of dirt in stream 3 is proportional to the mass of water*, and hence you can write that:

- mass dirt in stream 3 = 0.4 * mass water in stream 3
- **Solubility:** $\dot{m}_3 * x_{D3} = 0.4 * \dot{m}_3 * (1 - x_{D3})$

Plugging in known values, the following system of equations is obtained:

- $\dot{m}_3 = 100 + \dot{m}_8$
- $\dot{m}_3 * x_{D3} = 100 + \dot{m}_8 * x_{D8}$
- $\dot{m}_3 * x_{D3} = 111.11$
- $\dot{m}_3 * x_{D3} = 0.4 * \dot{m}_3 * (1 - x_{D3})$

Solving these equations for the 4 unknowns, the solutions are:

$$\dot{m}_3 = 388.89 \frac{kg}{hr}, \dot{m}_8 = 288.89 \frac{kg}{hr},$$

$$x_{D3} = 0.286, x_{D8} = 0.0385$$

Finally, we can go to the mixing point, and say:

- **Overall:** $\dot{m}_8 + \dot{m}_9 = \dot{m}_2$
- **Dirt:** $\dot{m}_8 * x_{D8} = \dot{m}_2 * x_{D2}$

From which the final unknowns are obtained:

$$\dot{m}_2 = 488.89 \frac{kg}{hr}$$

$$x_{D2} = 0.0229$$

Since the problem was asking for \dot{m}_2 , we are now finished.

[\[edit\]](#) Check your work

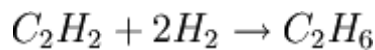
These values should be checked by making a new flowchart with the numerical values, and ensuring that the balances on the washer are satisfied. This is left as an exercise for the reader.

[\[edit\]](#) Chapter 5: Mass/mole balances in reacting systems

[\[edit\]](#) Review of Reaction Stoichiometry

Up until now, all of the balances we have done on systems have been in terms of **mass**. However, mass is inconvenient for a reacting system because it does not allow us to take advantage of the *stoichiometry* of the reaction in relating the relative amounts of reactants and of products.

Stoichiometry is the relationship between reactants and products in a balanced reaction as given by the ratio of their coefficients. For example, in the reaction:



the reaction stoichiometry would dictate that for every **one** molecule of C_2H_2 (acetylene) that reacts, two molecules of H_2 (hydrogen) are consumed and one molecule of C_2H_6 are formed. However, **this does not hold for grams of products and reactants**.

Even though the number of molecules in *single substance* is proportional to the mass of that substance, the constant of proportionality (the molecular mass) is not the same for every molecule. Hence, it is necessary to use the molecular weight of each molecule to convert from grams to *moles* in order to use the reaction's coefficients.

[\[edit\]](#) Molecular Mole Balances

We can write balances on moles like we can on anything else. We'll start with our ubiquitous general balance equation:

$$Input - Output = Accumulation - Generation$$

As usual we assume that accumulation = 0 in this book so that:

$$Input - Output + Generation = 0$$

Let us denote molar flow rates by \dot{n} to distinguish them from mass flow rates. We then have a similar equation to the mass balance equation:

$$\Sigma \dot{n}_{in} - \Sigma \dot{n}_{out} + n_{gen} = 0$$

The same equation can be written in terms of each individual species.

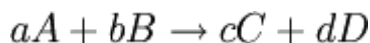
There are a couple of important things to note about this type of balance as opposed to a mass balance:

1. Just like with the mass balance, in a mole balance, a non-reactive system has $n_{gen} = 0$ for all species.
2. **Unlike the mass balance**, the TOTAL generation of moles isn't necessarily 0 even for the overall mole balance! To see this, consider how the total number of moles changes in the above reaction; the final number of moles will not equal the initial number because 3 total moles of molecules are reacting to form 1 mole of products.

Why would we use it if the generation isn't necessarily 0? We use the molecular mole balance because **if we know how much of any one substance is consumed or created in the reaction, we can find all of the others from the reaction stoichiometry**. This is a very powerful tool because *each reaction only creates one new unknown* if you use this method! The following section is merely a formalization of this concept, which can be used to solve problems involving reactors.

[edit] Extent of Reaction

In order to formalize the previous analysis of reactions in terms of a single variable, let us consider the generic reaction:



The **Molar Extent of Reaction X** is defined as:

$$X = -\frac{\Delta n_A}{a} = -\frac{\Delta n_B}{b} = \frac{\Delta n_C}{c} = \frac{\Delta n_D}{d}$$

Since all of these are equivalent, it is possible to find the change in moles of any species in a given reaction if the extent of reaction X is known.

NOTE:

Though they won't be discussed here, there are other ways in which the extent of reaction can be defined. Some other definitions are dependent on the **percent** change of a particular substrate, and the stoichiometry is used in a different way to determine the change in the others. This definition makes X independent of the substrate you choose.

The following example illustrates the use of the extent of reaction.



Example:

Consider the reaction $H_2O_2 + O_3 \rightarrow H_2O + 2O_2$. If you start with 50 g of H_2O_2 and 25 grams of O_3 , and 25% of the moles of O_3 are consumed, find the molar extent of reaction and the changes in the other components.

Solution: First we need to convert to moles, since stoichiometry is **not** valid when units are in terms of mass.

$$50 \text{ g } H_2O_2 * \frac{1 \text{ mol}}{34 \text{ g}} = 1.471 \text{ moles } H_2O_2$$

$$25 \text{ g } O_3 * \frac{1 \text{ mol}}{48 \text{ g}} = 0.5208 \text{ moles } O_3$$

Clearly ozone is the limiting reactant here. Since 25% is consumed, we have that:

$$\Delta n(O_3) = -0.25 * 0.5208 = -0.1302 \text{ moles } O_3$$

Hence, by definition,
$$X = \frac{-0.1302}{1} = 0.1302$$

And then we have $\Delta n(H_2O_2) = -0.1302$, $\Delta n(H_2O) = 0.1302$, $\Delta n(O_2) = 2 * 0.1302 = 0.2604$, all in moles of the appropriate substrate.

[[edit](#)] Mole Balances and Extents of Reaction

The mole balance written above can be written in terms of extent of reaction *if we notice that the $\Delta n(A)$ term defined above is exactly the number of moles of a generated or consumed by the reaction.*

NOTE:

This is only useful for *individual species* balances, not the overall mole balance. When doing balances on reactive systems, unlike with non-reactive systems, it is generally easier to use all individual species balances possible, rather than the total mole balance and then all but one of the individual species. This is because the total generation of moles in a reaction is generally not 0, so no algebraic advantage is gained by using the total material balance on the system.

Therefore we can write that:

$$n_{A,gen} = \Delta n(A) = -X * a$$

where X is the molar extent of reaction and a is the stoichiometric coefficient of A. Plugging this into the mole balance derived earlier, we arrive at the **molecular mole balance** equation:

$$\Sigma \dot{n}_{A,out} - \Sigma n_{A,in} - X * a = 0; \text{if A is consumed, or } +Xa \text{ if it is generated in the reaction}$$

[[edit](#)] Degree of Freedom Analysis on Reacting Systems

If we have N different molecules in a system, we can write N mass balances *or* N mole balances, whether a reaction occurs in the system or not. The only difference is that in a reacting system, we have one additional unknown, the molar extent of reaction, for each reaction taking place in the system. Therefore **each reaction taking place in a process will add one degree of freedom to the process.**

NOTE:

This will be different from the *atom* balance which is discussed later.

[[edit](#)] Complications

Unfortunately, life is not ideal, and even if we want a single reaction to occur to give us only the desired product, this is either impossible or uneconomical compared to dealing with byproducts, side reactions, equilibrium limitations, and other non-idealities.

[[edit](#)] Independent and Dependent Reactions

When you have more than one reaction in a system, you need to make sure that they are **independent**. The idea of independent reactions is similar to the idea of [linear independence](#) in mathematics.

Lets consider the following two general parallel competing reactions:

- $aA + bB \rightarrow cC + dD$
- $a_2A + b_2B \rightarrow e_2E$

We can represent each of the reactions by a *vector* of the coefficients:

- $V = [A \text{ coeff}, B \text{ coeff}, C \text{ coeff}, D \text{ coeff}, E \text{ coeff}]$
- $v_1 = [-a, -b, c, d, 0]$

- $v_2 = [-a_2, -b_2, 0, 0, e_2]$

[This site](#)

NOTE:

The site above gives a nice tool to tell whether any number of vectors are linearly dependent or not. Lacking such a tool, it is necessary to assess by hand whether the equations are independent. **Only independent equations should be used in your analysis of multiple reactions**, so if you have dependent equations, you can eliminate reactions from consideration until you've obtained an independent set.

By definition a set of vectors is only linearly independent if the equation:

$$K_1 * v_1 + K_2 * v_2 = 0$$

where K_1 and K_2 are constants only has one solution: $K_1 = K_2 = 0$.

Lets plug in our vectors:

$$K_1 * [-a, -b, c, d, 0] + K_2 * [-a_2, -b_2, 0, 0, e_2] = 0$$

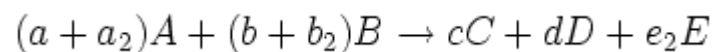
Since *all components* must add up to 0, the following system follows:

- $-K_1 * a - K_2 * a_2 = 0$
- $-K_1 * b - K_2 * b_2 = 0$
- $K_1 * c + 0 = 0$
- $K_1 * d + 0 = 0$
- $0 + K_2 * e_2 = 0$

Obviously, the last three equations imply that unless $c = d = 0$ and $e_2 = 0$, $K_1 = K_2 = 0$ and thus the reactions are independent.

[\[edit\]](#) Linearly Dependent Reactions

Now let's observe what happens if we add the reactions together:



We could solve the linear independence relation as we did in the previous case but let's save ourselves the time (it's difficult to solve because there's an infinite number of solutions!) and notice that a nontrivial solution to this equation is:

$$K_1 = -1, K_2 = -1, K_3 = 1$$

We can tell this *because* we notice that the second vector is simply the sum of the first two. Therefore, the vectors are not independent. This important result can be generalized as follows:

If any non-zero multiple of one reaction can be added to a multiple of a second reaction to yield a third reaction, then the three reactions are not independent.

All degree of freedom analyses in this book assume that the reactions are independent. You should check this by inspection or, for a large number of reactions, with numerical methods.

[\[edit\]](#) Extent of Reaction for Multiple Independent Reactions

When you are setting up extents of reaction in a molecular species balance, you *must* make sure that you set up one for *each* reaction, and include both in your mole balance. So really, your mole balance will look like this:

$$\sum n_{A,in} - \sum n_{A,out} + \sum a_k X_k = 0$$

for all k reactions. In such cases it is generally easier, if possible, to use an atom balance instead due to the difficulty of solving such equations.

[\[edit\]](#) Equilibrium Reactions

In many cases (actually, the majority of them), a given reaction will be **reversible**, meaning that instead of reacting to completion, it will stop at a certain point and not go any farther. How far the reaction goes is dictated by the value of the *equilibrium coefficient*. Recall from general chemistry that the equilibrium coefficient for the reaction $aA + bB \rightarrow cC + dD$ is defined as follows:

$$K = \frac{C_{C,eq}^c * C_{D,eq}^d}{C_{A,eq}^a * C_{B,eq}^b}$$

with concentration C_i expressed as molarity for liquid solutes or partial pressure for gasses

Here [A] is the equilibrium concentration of A, usually expressed in molarity for an aqueous solution or partial pressure for a gas. *This equation can be remembered as "products over reactants"*.

Usually **solids and solvents are omitted** by convention, since their concentrations stay approximately constant throughout a reaction. For example, in an aqueous solution, if water reacts, it is left out of the equilibrium expression.

Often, we are interested in obtaining the extent of reaction of an equilibrium reaction when it is in equilibrium. In order to do this, first recall that:

$$X = \frac{-\Delta n_A}{a}$$

and similar for the other species.

[\[edit\]](#) Liquid-phase Analysis

Rewriting this in terms of molarity (moles per volume) by dividing by volume, we have:

$$\frac{X}{V} = \frac{[A]_0 - [A]_f}{a}$$

Or, since the final state we're interested in is the equilibrium state,

$$\frac{X}{V} = \frac{[A]_0 - [A]_{eq}}{a}$$

Solving for the desired equilibrium concentration, we obtain the equation for equilibrium concentration of A in terms of conversion:

$$[A]_{eq} = [A]_0 - \frac{aX}{V}$$

Similar equations can be written for B, C, and D using the definition of extent of reaction. Plugging in all the equations into the expression for K, we obtain:

$$K = \frac{([C]_0 + \frac{cX}{V})^c ([D]_0 + \frac{dX}{V})^d}{([A]_0 - \frac{aX}{V})^a ([B]_0 - \frac{bX}{V})^b}$$

At equilibrium for liquid-phase reactions **only**

Using this equation, knowing the value of K, the reaction stoichiometry, the initial concentrations, and the volume of the system, the equilibrium extent of reaction can be determined.

NOTE:

If you know the reaction reaches equilibrium in the reactor, this counts as an additional piece of information in the DOF analysis because it allows you to find X. This is the same idea as the idea that, if you have an irreversible reaction and know it goes to completion, you can calculate the extent of reaction from that.

[edit] Gas-phase Analysis

By convention, gas-phase equilibrium constants are given in terms of **partial pressures** which, for ideal gasses, are related to the mole fraction by the equation:

$$P_A = y_A P \text{ for ideal gasses only}$$

If A, B, C, and D were all gases, then, the equilibrium constant would look like this:

$$\frac{P_C^c P_D^d}{P_A^a P_B^b} \text{ Gas-Phase Equilibrium Constant}$$

In order to write the gas equilibrium constant in terms of extent of reaction, let us assume for the moment that we are dealing with ideal gases. You may recall from general chemistry that for an ideal gas, we can write the ideal gas law for *each species* just as validly as we can on the *whole gas* (for a non-ideal gas, this is in general not true). Since this is true, we can say that:

$$\frac{n_A}{V} = [A] = \frac{P_A}{RT}$$

Plugging this into the equation for $\frac{X}{V}$ above, we obtain:

$$\frac{aX}{V} = [A] - [A]_{eq} = \frac{P_{A0}}{RT} - \frac{P_{A,eq}}{RT}$$

Therefore,

$$P_{a,eq} = P_{A0} - \frac{aXRT}{V}$$

Similar equations can be written for the other components. Plugging these into the equilibrium constant expression:

$$K = \frac{(P_{C0} + \frac{cXRT}{V})^c (P_{D0} + \frac{dXRT}{V})^d}{(P_{A0} - \frac{aXRT}{V})^a (P_{B0} - \frac{bXRT}{V})^b}$$

Gas Phase Ideal-Gas Equilibrium Reaction at Equilibrium

Again, if we know we are at equilibrium and we know the equilibrium coefficient (which can often be found in standard tables) we can calculate the extent of reaction.

[\[edit\]](#) Special Notes about Gas Reactions

You need to remember that *In a constant-volume, isothermal gas reaction, the total pressure will change as the reaction goes on*, unless the same number of moles are created as produced. In order to show that this is true, you only need to write the ideal gas law for the total amount of gas, and realize that the total number of moles in the system changes.

This is why we don't want to use *total* pressure in the above equations for K, we want to use *partial* pressures, which we can conveniently write in terms of extent of reaction.

[\[edit\]](#) Inert Species

Notice that all of the above equilibrium equations depend on *concentration* of the substance, in one form or another. Therefore, if there are species present that don't react, they may still have an effect on the equilibrium because they will decrease the concentrations of the reactants and products. Just make sure you take them into account when you're calculating the concentrations or partial pressures of each species in preparation for plugging into the equilibrium constant.

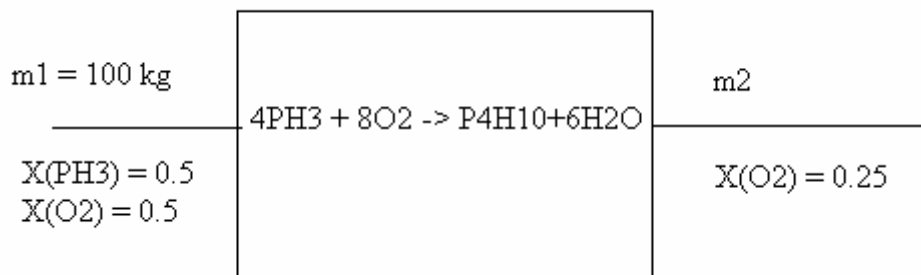
[\[edit\]](#) Example Reactor Solution using Extent of Reaction and the DOF

**Example:**

Consider the reaction of Phosphene with oxygen: $4PH_3 + 8O_2 \rightarrow P_4O_{10} + 6H_2O$

Suppose a 100-kg mixture of 50% PH_3 and 50% O_2 by mass enters a reactor in a single stream, and the single exit stream contains 25% O_2 by mass. Assume that all the reduction in oxygen occurs due to the reaction. How many degrees of freedom does this problem have? If possible, determine mass composition of all the products.

It always helps to draw a flowchart:



There are **four** independent unknowns: the total mass (mole) flowrate out of the reactor, the concentrations of two of the exiting species (once they are known, the fourth can be calculated), and the extent of reaction.

Additionally, we can write four independent equations, one on each reacting substance. Hence, there are **0** DOF and this problem can be solved.

Let's illustrate how to do it for this relatively simple system, which illustrates some very important things to keep in mind.

First, recall that **total mass is conserved even in a reacting system**. Therefore, we can write that:

$$\dot{m}_{out} = \dot{m}_{in} = 100 \text{ kg}$$

Now, since component masses aren't conserved, we need to convert as much as we can into moles so we can apply the extent of reaction.

$$\dot{n}_{PH_3,in} = 0.5 * (100 \text{ kg}) * \frac{1 \text{ mol}}{0.034 \text{ kg}} = 1470.6 \text{ moles } PH_3 \text{ in}$$

$$\dot{n}_{O_2,in} = 0.5 * (100 \text{ kg}) * \frac{1 \text{ mol}}{0.032 \text{ kg}} = 1562.5 \text{ moles } O_2 \text{ in}$$

$$\dot{n}_{O_2,out} = 0.25 * (100 \text{ kg}) * \frac{1 \text{ mol}}{0.032 \text{ kg}} = 781.25 \text{ moles } O_2 \text{ out}$$

Let's use the **mole balance on oxygen** to find the extent of reaction, since we know how much enters and how much leaves. Recall that:

$$\sum \dot{n}_{A,in} - \sum \dot{n}_{A,out} - a * X = 0$$

where a is the stoichiometric coefficient for A. Plugging in known values, including a = 8 (from the reaction written above), we have:

$$1562.5 - 781.25 - 8X = 0$$

Solving gives:

$$X = 97.66 \text{ moles}$$

Now let's apply the mole balances to the other species to find how much of them is present:

- PH_3 : $1470.6 - \dot{n}_{PH_3,out} - 4(97.66) = 0 \rightarrow \dot{n}_{PH_3,out} = 1080.0 \text{ moles } PH_3$
- P_4H_{10} : $0 - \dot{n}_{P_4H_{10},out} + 1(97.66) = 0 \rightarrow \dot{n}_{P_4H_{10},out} = 97.66 \text{ moles } P_4H_{10}$
(note it's + instead of - because it's being generated rather than consumed by the reaction)
- H_2O : $0 - \dot{n}_{H_2O,out} + 6(97.66) = 0 \rightarrow \dot{n}_{H_2O,out} = 586.0 \text{ moles } H_2O$

Finally, the last step we need to do is find the mass of all of these, and divide by the total mass to obtain the mass percents. As a sanity check, all of these plus 25 kg of oxygen should yield 100 kg total.

- Mass PH_3 out = 1080 moles * 0.034 kg/mole = 36.72 kg
- Mass P_4H_{10} out = 97.66 moles * .284 kg/mole = 27.74 kg
- Mass H_2O out = 586 moles * 0.018 kg/mole = 10.55 kg

Sanity check: 36.72 + 27.74 + 10.55 + 25 (oxygen) = 100 kg (total), so we're still sane.

Hence, we get:

36.72% PH_3 , 27.74% P_4H_{10} , 10.55% H_2O , 25% O_2 by mass

[edit] Example Reactor with Equilibrium



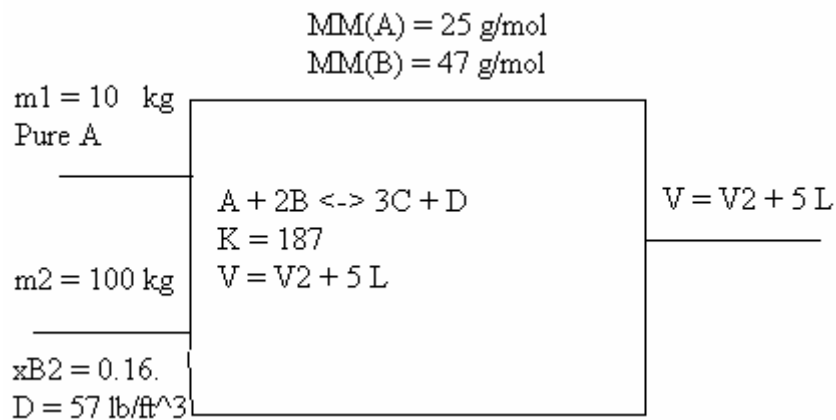
Example:

Suppose that you are working in an organic chemistry lab in which 10 kg of compound A is added to 100 kg of a 16% aqueous solution of B (which has a density of 57 lb/ft³) The following reaction occurs:



A has a molar mass of 25 g/mol and B has a molar mass of 47 g/mol. If the equilibrium constant for this reaction is 187 at 298K, how much of compound C could you obtain from this reaction? Assume that all products and reactants are soluble in water at the design conditions. Adding 10 kg of A to the solution causes the volume to increase by 5 L. Assume that the volume does not change over the course of the reaction.

Solution: First, draw a flowchart of what we're given.



Since all of the species are dissolved in water, we should write the equilibrium constant in terms of molarity:

$$K = 187 = \frac{[C]^3[D]}{[A][B]^2}$$

We use initial *molarities* of A and B, while we are given mass percents, so we need to convert.

Let's first find the number of *moles* of A and B we have initially:

$$n_{A0} = 10 \text{ kg A} * \frac{1 \text{ mol A}}{0.025 \text{ kg A}} = 400 \text{ mol A}$$

$$n_{B0} = 100 \text{ kg solution} * \frac{0.16 \text{ kg B}}{\text{kg sln}} = 16 \text{ kg B} * \frac{1 \text{ mol B}}{0.047 \text{ kg B}} = 340.43 \text{ mol B}$$

Now, the volume contributed by the 100kg of 16% B solution is:

$$V = \frac{m}{\rho} = \frac{100 \text{ kg}}{57 \frac{\text{lb}}{\text{ft}^3} * \frac{1 \text{ kg}}{2.2 \text{ lb}} * \frac{1 \text{ ft}^3}{28.317 \text{ L}}} = 109.3 \text{ L}$$

Since adding the A contributes 5L to the volume, the volume after the two are mixed is $109.3 \text{ L} + 5 \text{ L} = 114.3 \text{ L}$.

By definition then, the molarities of A and B before the reaction occurs are:

- $[A]_0 = \frac{400 \text{ moles A}}{114.3 \text{ L}} = 3.500M$
- $[B]_0 = \frac{340.42 \text{ moles B}}{114.3 \text{ L}} = 2.978M$

In addition, there is no C or D in the solution initially:

- $[C]_0 = [D]_0 = 0$

According to the stoichiometry of the reaction, $a = 1, b = 2, c = 3, d = 1$. Therefore we now have enough information to solve for the conversion. Plugging all the known values into the equilibrium equation for liquids, the following equation is obtained:

$$187 = \frac{\left(\frac{3X}{114.3}\right)^3 \left(\frac{X}{114.3}\right)}{\left(3.5 - \frac{X}{114.3}\right) \left(2.978 - \frac{2X}{114.3}\right)^2}$$

This equation can be solved using Goalseek or one of the numerical methods in appendix 1 to give:

$X = 146.31 \text{ moles}$

Since we seek the amount of compound C that is produced, we have:

$$X = \frac{\Delta n_C}{c}$$

- Since $c = 3, n_{C0} = 0$, and $X = 146.31$, this yields
- $n_C = 3 * 146.31 = 438.93$ moles C

438.93 moles of C can be produced by this reaction.

[[edit](#)] Introduction to Reactions with Recycle

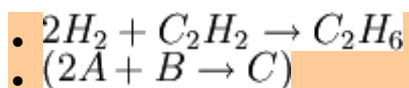
Reactions with recycle are very useful for a number of reasons, most notably because they can be used to improve the selectivity of multiple reactions, push a reaction beyond its equilibrium conversion, or speed up a catalytic reaction by removing products. A recycle loop coupled with a reactor will generally contain a separation process in which unused reactants are (partially) separated from products. These reactants are then fed back into the reactor along with the fresh feed.

[[edit](#)] Example Reactor with Recycle



Example:

Consider a system designed for the hydrogenation of ethylene into ethane:



The reaction takes too long to go to completion (and releases too much heat) so the designers decided to implement a recycle system in which, after only part of the reaction had finished, the mixture was sent into a membrane separator. There, most of the ethylene was separated out, with little hydrogen or ethylene contamination. After this separation, the cleaned stream entered a splitter, where some of the remaining mixture was returned to the reactor and the remainder discarded.

The system specifications for this process were as follows:

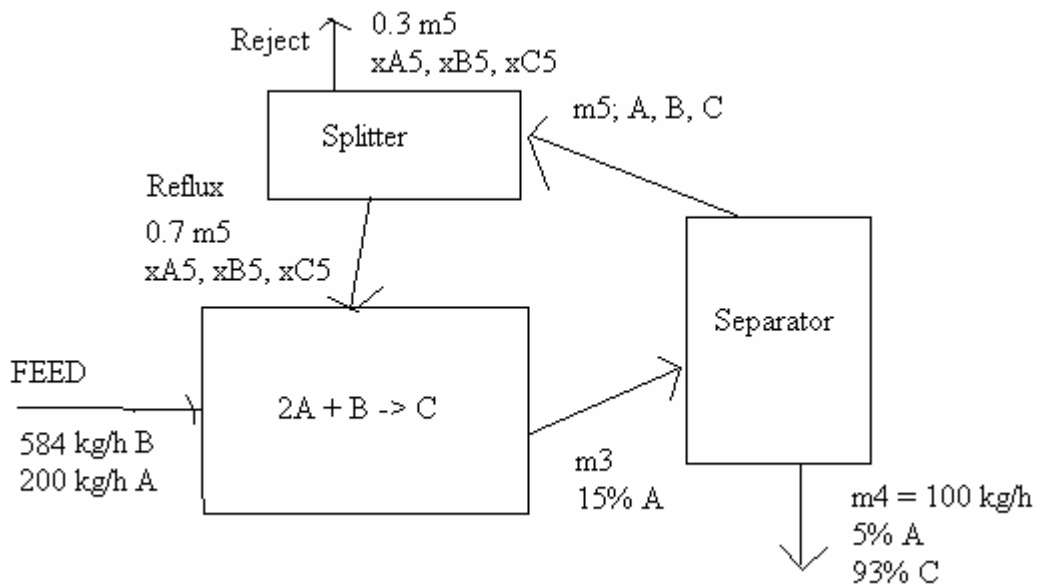
- Feed: 584 kg/h ethylene, 200 kg/h hydrogen gas
- Outlet stream from reactor contains 15% hydrogen by mass
- Mass flows from membrane separator: 100 kg/h, 5% Hydrogen and 93% ethane

- Splitter: 30% reject and 70% reflux

What was the extent of reaction for this system? What would the extent of reaction be if there was no separation/recycle process after (assume that the mass percent of hydrogen leaving the reactor is the same)? What limits how effective this process can be?

Solution:

Let's first draw our flowchart as usual:



[edit] DOF Analysis

- On reactor: 6 unknowns ($\dot{m}_5, x_{A5}, x_{B5}, \dot{m}_3, x_{B3}, X$) - 3 equations = 3 DOF
- On separator: 5 unknowns ($\dot{m}_3, x_{B3}, \dot{m}_5, x_{A5}, x_{B5}$) - 3 equations = 2 DOF
- On splitter: 3 unknowns - 0 equations (we used all of them in labeling the chart) -> 3 DOF
- Duplicate variables: 8 ($\dot{m}_5, x_{A5}, x_{B5}$ twice each and \dot{m}_3, x_{B3} once)
- Total DOF = 8 - 8 = 0 DOF

[edit] Plan and Solution

Generally, though not always, it is easiest to deal with the reactor itself *last* because it usually has the most unknowns. Let's begin by looking at the overall system because we can often get some valuable information from that.

Overall System DOF(overall system) = 4 unknowns ($\dot{m}_5, x_{A5}, X, x_{B5}$) - 3 equations = 1 DOF.

NOTE:

We CANNOT say that total mass of A and B is conserved because we have a reaction here! Therefore we must include the conversion X in our list of unknowns for both the reactor *and* the overall system. However, the *total* mass in the system is conserved so we can solve for \dot{m}_5 .

Let's go ahead and solve for \dot{m}_5 though because that'll be useful later.

$$784 = 100 + 0.3(\dot{m}_5)$$

$$\dot{m}_5 = 2280 \text{ kg/h}$$

We can't do anything else with the overall system without knowing the conversion so let's look elsewhere.

DOF(separator) = 4 unknowns ($\dot{m}_3, x_{B3}, x_{A5}, x_{B5}$) - 3 equations = 1 DOF. Let's solve for those variables we can though.

We can solve for \dot{m}_3 because from the overall material balance on the separator:

- $\dot{m}_3 = \dot{m}_4 + \dot{m}_5$
- $\dot{m}_3 = 100 + 2280$

$$\dot{m}_3 = 2380 \text{ kg/h}$$

Then we can do a mass balance on A to solve for x_{A5} :

- $\dot{m}_3 x_{A3} = \dot{m}_4 x_{A4} + \dot{m}_5 x_{A5}$
- $2380(0.15) = 100(0.05) + 2380(x_{A5})$

$$x_{A5} = .1544$$

Since we don't know x_{B5} or x_{B3} , we cannot use the mass balance on B or C for the separator, so let's move on. Let's now turn to the reactor:

[edit] Reactor Analysis

DOF: 3 unknowns remaining (x_{B3} , x_{B5} , and X) - 2 equations (because the overall balance is already solved!) = **1 DOF**. Therefore we still cannot solve the reactor completely. However, we can solve for the conversion and generation terms given what we know at this point. Lets start by writing a *mole* balance on A in the reactor.

$$\dot{n}_{A1} + \dot{n}_{A,recycle} - X * a = \dot{n}_{A3}$$

To find the three n_A terms we need to convert from mass to moles (since A is hydrogen, H₂, the molecular weight is $\frac{1 \text{ mol}}{0.002016 \text{ g}}$):

- $\dot{n}_{A1} = 200 \frac{\text{kg}}{\text{h}} * \frac{1 \text{ mol}}{0.002016 \text{ kg}} = 99206 \frac{\text{mol A}}{\text{h}}$
- $\dot{n}_{A,recycle} = 0.7 * \frac{m_5 * x_{A5}}{MW_A} = \frac{0.7(2280)(0.1544)}{0.002016} = 122000 \frac{\text{mol A}}{\text{h}}$

Thus the *total* amount of A entering the reactor is:

- $\dot{n}_{A,in} = 99206 + 122000 = 221428 \frac{\text{mol A}}{\text{h}}$

The amount exiting is:

- $\dot{n}_{A,out} = \frac{\dot{m}_3 * x_{A3}}{MM_A} = \frac{2380 * 0.15}{0.002016} = 177083 \frac{\text{mol A}}{\text{h}}$

Therefore we have the following from the mole balance:

- $221428 - 2X = 177083$

$$X = 22173 \frac{\text{moles}}{\text{h}}$$

Now that we have this we can calculate the mass of B and C generated:

- $m_{B,gen} = -Xb * MW_B = 22173 \frac{\text{mol B}}{\text{h}} * 0.026 \frac{\text{kg}}{\text{mol B}} = -576.5 \frac{\text{kg B}}{\text{h}}$

- $m_{C,gen} = +X_C * MW_C = 22173 \frac{\text{mol C}}{h} * 0.030 \frac{\text{kg}}{\text{mol C}} = +665.2 \frac{\text{kg C}}{h}$

At this point you may want to calculate the amount of B and C leaving the reactor with the mass balances on B and C:

- $584 + 0.7 * x_{B5} * 2280 - 576.5 = x_{B3} * 2380$
- (1) $0.7 * (1 - 0.1544 - x_{B5}) * 2280 + 665.2 = (1 - 0.15 - x_{B3}) * 2380$

However, *these equations are exactly the same!* Therefore, we have proven our assertion that there is still 1 DOF in the reactor. So we need to look elsewhere for something to calculate x_{B5} . That place is the separator balance on B:

- $\dot{m}_3 * x_{B3} = \dot{m}_4 * x_{B4} + \dot{m}_5 * x_{B5}$
- (2) $2380x_{B3} = 0.02(100) + 2280x_{B5}$

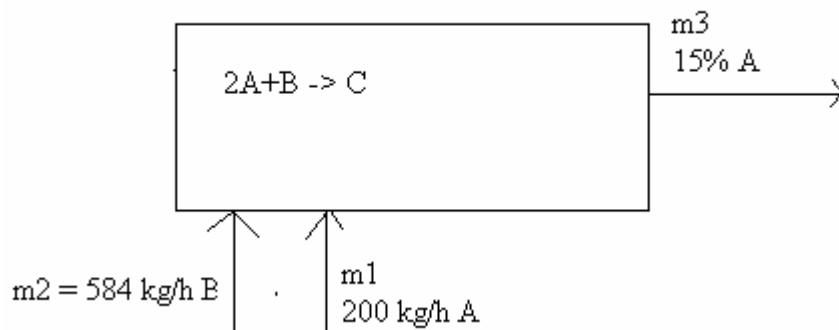
Solving these two equations (1) and (2) yields the final two variables in the system:

$x_{B3} = 0.00856, x_{B5} = 0.008058$

Note that this means the predominant species in stream 5 is also C ($x_{C5} = 0.838$). However, the separator/recycle setup **does** make a big difference, as we'll see next.

[\[edit\]](#) Comparison to the situation without the separator/recycle system

Now that we know how much ethane we can obtain from the reactor after separating, let's compare to what would happen without any of the recycle systems in place. With the same data as in the first part of this problem, the new flowchart looks like this:



There are three unknowns (\dot{m}_3, x_{B3}, X) and three independent material balances, so the problem can be solved. Starting with an overall mass balance because total mass is conserved:

- $\dot{m}_1 + \dot{m}_2 = \dot{m}_3$
- $\dot{m}_3 = 789 \frac{kg}{h}$

We can carry out the same sort of analysis on the reactor as we did in the previous section to find the conversion and mass percent of C in the exit stream, which is left as an exercise to the reader. The result is that:

- $X = 20250 \text{ moles}, x_{C3} = 0.77$

Compare this to the two exit streams in the recycle setup. **Both of the streams were richer in C than 77%, even the reject stream.** This occurred because the unreacted A and B was allowed to re-enter the reactor and form more C, and the separator was able to separate almost all the C that formed from the unreacted A and B.

[\[edit\]](#) Appendix 1: Useful Mathematical Methods

[\[edit\]](#) Mean and Standard Deviation

A lot of the time, when you're conducting an experiment, you will run it more than once, especially if it is inexpensive. Scientists run experiments more than once so that the *random errors* that result from taking measurements, such as having to guess a length between two hash marks on a ruler, cancel themselves out and leave them with a more precise measurement. However, the question remains: how should you consolidate all of the data into something that's more manageable to use?

[\[edit\]](#) Mean

Suppose you have n data points taken **under the same conditions** and you wish to consolidate them to as few as feasibly possible. One thing which could help is to use some centralized value, which is in some way "between" all of the original data points. This, in fact, is called the **mean** of the data set.

There are many ways of computing the mean of a data set depending on how it is believed to be distributed. One of the most common methods is to use the *arithmetic mean*, which is defined as:

$$\bar{x} = \frac{\sum \hat{x}_k}{n}$$

Other types of mean include the [w:Geometric mean](#), which should be used when the data are very widely distributed (ex. an exponential distribution) and the "log-mean" which occurs often in transport phenomena.

[\[edit\]](#) Standard Deviation

Having a value for the mean tells you what value the data points "cluster" around but it does not tell you how spread out they are from the center. A second statistical variable called the **standard deviation** is used for that. The standard deviation is essentially *the average distance between the data points and their mean*. The distance is expressed as a squared distance in order to prevent negative deviations from lessening the effect of positive deviations.

The mathematical formulation for the standard deviation σ is:

$$\sigma^2 = \frac{\sum(\hat{x}_k - \bar{x})^2}{n - 1}$$

The denominator is n-1 instead of n because statisticians found that it gives better results for small numbers of experiments; see [w:Standard deviation](#) for a more thorough explanation of this.

[\[edit\]](#) Putting it together

The standard deviation of a data set measured under constant conditions is a measure of how precise the data set is. Because this is true, the standard deviation of a data set is often used in conjunction with the mean in order to report experimental results. Typically, results are reported as:

$$\bar{x} \pm \sigma$$

If a distribution is assumed, knowing both the mean and standard deviation can help us to estimate the probability that the actual value of the variable is within a certain range, *if there is no systematic bias in the data*. If there is (such as use of broken equipment, negligence, and so on) then no statistics could predict the effects of that.

[\[edit\]](#) Linear Regression

Suppose you have a set of data points (\hat{x}_k, \hat{y}_k) taken **under differing conditions** which you suspect, from a graph, can be reasonably estimated by drawing a line through the points. Any line that you could draw will have (or can be written in) the following form:

$$y = mx + b \text{ where } m \text{ is the slope of the line and } b \text{ is the y-intercept.}$$

We seek the *best* line that we could possibly use to estimate the pattern of the data. This line will be most useful for both interpolating between points that we know, and extrapolating to unknown values (as long as they're close to measured values). In the most usual measure, how "good" the fit is is determined by the vertical distance between the line and the data points (R_k), which is called the **residual**:

$$R_k = (m\hat{x}_k + b) - \hat{y}_k$$

In order to normalize the residuals so that they don't cancel when one's positive and one's negative (and thus helping to avoid statistical bias), we are usually concerned with the *square* of R_k when doing least-squares regression. We use squared terms and not absolute values so that the function is [differentiable](#), don't worry about this if you haven't taken calculus yet.

In order to take into account *all* of the data points, we simply seek to minimize the sum of the squared residuals:

$$\text{minimize } \sum R_k^2$$

Using calculus, we can take the derivative of this with respect to m and with respect to b and solve the equations to come up with the values of m and b that minimize the sum of squares (hence the alternate name of this technique: **least-squares regression**). The formulas are as follows, where n is the total number of data points you are regressing[1]:

$$m^* = \frac{n * \sum(\hat{x}_k * \hat{y}_k) - \sum(\hat{x}_k) * \sum(\hat{y}_k)}{n * \sum(\hat{x}_k^2) - (\sum(\hat{x}_k))^2}$$

$$b^* = \frac{\sum(\hat{y}_k) - m^* * \sum(\hat{x}_k)}{n}$$

[\[edit\]](#) Example of linear regression



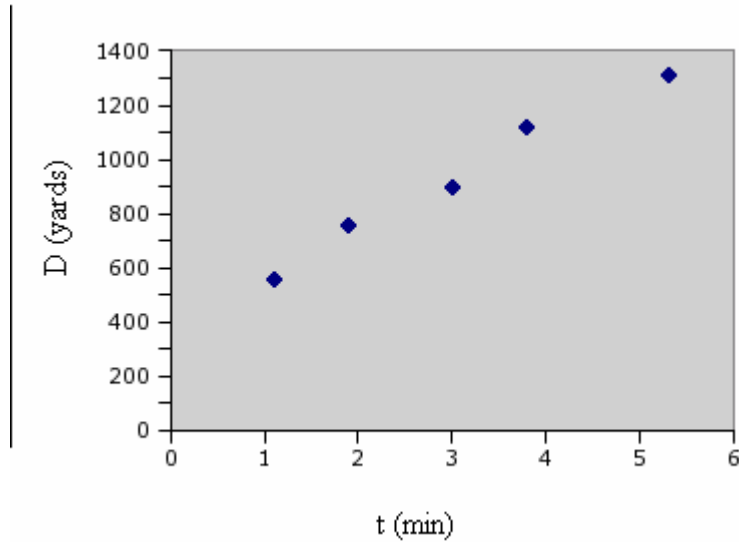
Example:

Suppose you wanted to measure how fast you got to school by a less direct route than looking at the speedometer of your car. Instead, you look at a map and read the distances between each intersection, and then you measure how long it takes to go each distance. Suppose the results were as follows (D is total distance from home):

t (min)	D (yards)
1.1	559.5
1.9	759.5
3.0	898.2
3.8	1116.3
5.3	1308.7

How far from home did you start, and what is the best estimate for your average speed?

The first thing we should do with any data like this is to graph it and see if a linear fit would be reasonable. Plotting this data, we can see by inspection that a linear fit appears to be reasonable.



Now we need to compute all of the values in our regression formulas, and to do this (by hand) we set up a table:

Trial	t	t ²	D	D ²	t*D
1	1.1	1.21	559.5	313040	615.45
2	1.9	3.61	759.5	576840	1443.05
3	3.0	9.00	898.2	806763	2694.6
4	3.8	14.44	1116.3	1246126	4241.94
5	5.3	28.09	1308.7	1712695	6936.11
TOTAL	15.1	56.35	4642.2	4655464	15931.15

Now that we have this data we can plug it into our linear regression equation:

$$m^* = \frac{n * \Sigma(\hat{x}_k * \hat{y}_k) - \Sigma(\hat{x}_k) * \Sigma(\hat{y}_k)}{n * \Sigma(\hat{x}_k^2) - (\Sigma(\hat{x}_k))^2}$$

$$= \frac{5 * 15931.13 - 15.1 * 4642.2}{5 * 56.35 - (15.1)^2}$$

$$= 177.9 \frac{\text{yard}}{\text{min}}$$

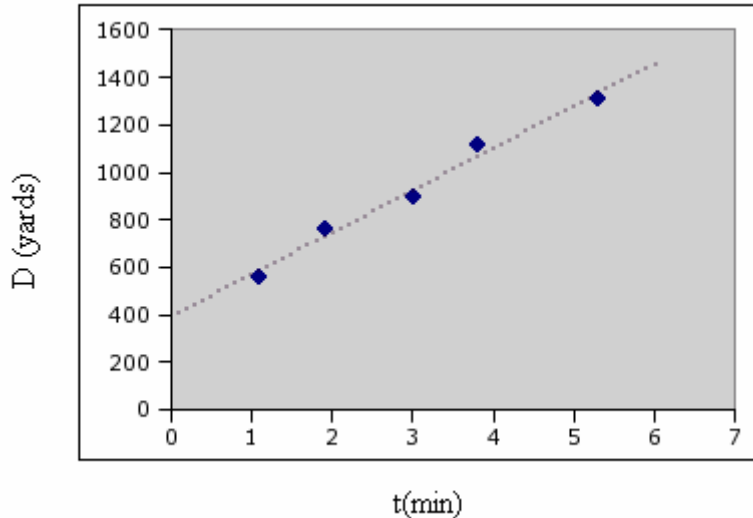
$$\text{So } b = \frac{\Sigma(\hat{y}_k) - m^* * \Sigma(\hat{x}_k)}{n}$$

$$= \frac{4642.2 - 177.9 * 15.1}{5} = 391.2 \text{ yards}$$

Hence the equation for the line of best fit is:

$$D = 177.9 * t + 391.2$$

The graph of this plotted against the data looks like this:



[\[edit\]](#) How to tell how good your regression is

In the previous example, we visually determined if it would be reasonable to perform a linear fit, but it is certainly possible to have a less clear-cut case! If there is some slight curve to the data, is it still "close enough" to be useful? Though it will always come down to your own judgment after seeing the fit line graph against the data, there is a mathematical tool to help you called a **correlation coefficient**, r , which can be defined in several different ways. One of them is as follows [1]:

$$r = \frac{n * \sum(\hat{x}_k * \hat{y}_k) - \sum(\hat{x}_k) * \sum(\hat{y}_k)}{\sqrt{n * \sum(\hat{x}_k^2) - (\sum\hat{x}_k)^2} * \sqrt{n * \sum(\hat{y}_k^2) - (\sum\hat{y}_k)^2}}$$

It can be shown that this value always lies between -1 and 1. The closer it is to 1 (or -1), the more reasonable the linear fit. In general, the more data points you have, the smaller r needs to be before it's a good fit, but a good rule of thumb is to look for high (higher than 0.85 or 0.9) values and then graph to see if the graph makes sense. Sometimes it will, sometimes it won't, the method is not foolproof.

In the above example we have:

$$r = \frac{5 * 15931.13 - 15.1 * 4642.2}{\sqrt{5 * 56.35 - (15.1)^2} * \sqrt{5 * 4655464 - (4642.2)^2}}$$

$$r = 0.992$$

Hence the data correlates very well with a linear model.

[\[edit\]](#) Linearization

[\[edit\]](#) In general

Whenever you have to fit a parameter or multiple parameters to data, it is a good idea to try to **linearize** the function first, because linear regression is much less intensive and more accurate than nonlinear regression. The goal with any linearization is to reduce the function to the form:

$$\text{Variable 1} = \text{constant} + \text{constant} * \text{Variable 2}$$

The difference between this and "standard" linear regression is that Variable 1 and Variable 2 can be *any functions* of x and y, as long as they are not combined in any way (i.e. you can't have $\ln(x + y)$ as one variable). The technique can be extended to more than two variables using a method called [w:multiple linear regression](#) but as that's more difficult to perform, this section will focus on two-dimensional regression.

[\[edit\]](#) Power Law

To see some of the power of linearization, let's suppose that we have two variables, x and y, related by a power law:

$$y = A * x^b$$

where A and b are constants. If we have data connecting changes in y to changes in x, we would like to know the values of a and b. This is difficult to do if the equation is in its current form but we can change it into a linear-type function!

The trick here is we need to get rid of the exponent b, so in order to do that we take the natural log of both sides:

$$\ln y = \ln (A * x^b)$$

Using laws of logarithms we can simplify the right-hand side to obtain the following:

$$y = A * x^b \iff \ln y = \ln A + b * \ln x$$

The beauty of this equation is that it is, in a sense, linear. **If we graph $\ln(y)$ vs. $\ln(x)$ obtain a straight line with slope b and y-intercept $\ln(A)$.**

[\[edit\]](#) Exponentials

Another common use of linearization is with exponentials, where x and y are related by an expression of the form:

$$y = A * b^x$$

This works for any base but the most common base encountered in practice is Euler's constant, e . Again, we take the natural log of both sides, in order to get rid of the exponent:

$$y = A * b^x \iff \ln y = \ln A + x * \ln b$$

This time, **Graph $\ln y$ vs. x to obtain a line with slope $\ln(b)$ and y-intercept $\ln(A)$.**

[\[edit\]](#) Linear Interpolation

Often, when you look up properties on a chart, you will be looking them up at conditions in *between* two charted conditions. For example, if you were looking up the specific enthalpy of steam at 10 MPa and 430oC you would look in the steam tables and see something like this: [2]

P = 10 MPa	
T (oC)	H (kJ/kg)
400	2832.4
450	2943.4

How can you figure out the intermediate value for this? We can't exactly but we can **assume that $H(T)$ is a linear function**. If we assume that it is linear, then we can easily find the intermediate value. First, we set up a table, including the unknown value like this:

	T (oC)	H (kJ/kg)
1	400	2832.4
2	430	x
3	450	2943.4

Then since we're assuming the relationship between T and H is linear, and the slope of a line is a constant *the slope between points 3 and 2 has to equal the slope between points 3 and 1*.

Therefore, we can write that:

$$\frac{2943.4 - x}{450 - 430} = \frac{2943.4 - 2832.4}{450 - 400}$$

Solving gives $x = 2899 \text{ kJ/kg}$

The same method can be used to find an unknown T for a given H between two tabulated values.

[\[edit\]](#) General formula

To derive a more general formula (though I always derive it from scratch anyways, it's nice to have a formula), lets replace the numbers by variables and give them more generic symbols:

	x	y
1	x1	y1
2	x*	y*
3	x2	y2

Setting the slope between points 3 and 2 equal to that between 3 and 1 yields:

$$\frac{y2 - y1}{x2 - x1} = \frac{y2 - y^*}{x2 - x^*}$$

This equation can then be solved for x^* or y^* as appropriate.

[\[edit\]](#) Limitations of Linear Interpolation

It is important to remember that *linear interpolation is not exact*. How inexact it is depends on two major factors:

1. What the real relationship between x and y is (the more curved it is, the worse the linear approximation)
2. The difference between consecutive x values on the table (the smaller the distance, the closer almost any function will resemble a line)

Therefore, it is not recommended to use linear interpolation if the spaces are very widely separated. However, if no other method of approximation is available, linear interpolation is often the only option, or other forms of interpolation (which may be just as inaccurate, depending on what the actual function is).

See also [w:interpolation](#).

[[edit](#)] References

[1]: Smith, Karl J. The Nature of Mathematics. Pacific Grove, California: Brooks/Cole Publishing company, 6e, p. 683

[2]: Sandler, Stanley I. Chemical, Biochemical, and Engineering Thermodynamics. University of Delaware: John Wiley and Sons inc., 4e, p. 923

[[edit](#)] Basics of Rootfinding

Rootfinding is the determination of solutions to single-variable equations or to systems of n equations in n unknowns (provided that such solutions exist). The basics of the method revolve around the determination of *roots*

A **root** of a function $F(x_1, x_2, \dots)$ in any number of variables is defined as the solution to the equation $F(x_1, x_2, \dots) = 0$. **In order to use any of the numerical methods in this section, the equation should be put in a specific form**, and this is one of the more common ones, used for all methods except the iterative method.

However, it is easy to put a function into this form. If you start with an equation of the form:

$$F_1(x_1, x_2, \dots) = F_2(x_1, x_2, \dots)$$

then subtracting F_2 will yield the required form. *Do not forget to do this, even if there is only a constant on one side!*



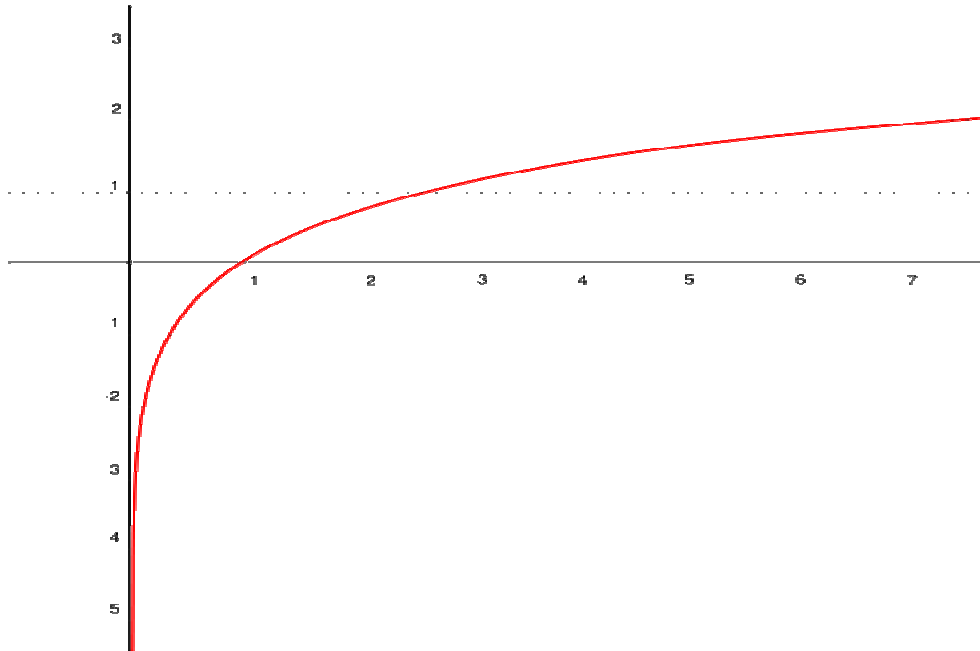
Example:

If you want to use the bisection method later in this section to find one of the solutions of the equation $1 = x^2$, you should rewrite the equation as $0 = x^2 - 1$ so as to put it in the correct form.

Since any equation can be put into this form, the methods can potentially be applied to any function, though they work better for some functions than others.

[[edit](#)] Analytical vs. Numerical Solutions

An **analytical** solution to an equation or system is a solution which can be arrived at exactly using some mathematical tools. For example, consider the function $y = \ln(x)$, graphed below.



The root of this function is, by convention, when $y = 0$, or when this function crosses the x-axis. Hence, the root will occur when $\ln(x) = 0 \rightarrow x = e^0 = 1$

The answer $x=1$ is an analytical solution because through the use of algebra, we were able to come up with an exact answer.

On the other hand, attempting to solve an equation like:

$$-x = \ln(x)$$

analytically is sure to lead to frustration because it is not possible with elementary methods. In such a case it is necessary to seek a **numerical** solution, in which guesses are made until the answer is "close enough", but you'll never know what the *exact* answer is.

All that the numerical methods discussed below do is give you a systematic method of guessing solutions so that you'll be likely (and in some cases guaranteed) to get closer and closer to the true answer. The problem with numerical methods is that most are not guaranteed to work without a good enough *initial guess*. Therefore it is valuable to try a few points until you get somewhere close and *then* start with the numerical algorithm to get a more accurate answer. They are roughly in order from the easiest to use to the more difficult but faster-converging algorithms.

[[edit](#)] Rootfinding Algorithms

[[edit](#)] Iterative solution

Iterative solutions in their purest form will solve the desired function so that it is in the form:

$$x = f(x)$$

Then, a value for x is guessed, and $f(x)$ is calculated. The new value of x is then re-inserted into $f(x)$, and the process is repeated until the value of x changes very little.

The following example illustrates this procedure.



Example:

Use an iterative solution to calculate the root of $x + \ln(x) = 0$

Solution: Solve the equation for x :

$$e^{-x} = x$$

First we need to guess an x to get it started. Let's try $x = 0.5$

Then we have:

$$x = e^{-0.5} = 0.6065$$

$$x_2 = e^{-0.6065} = 0.5453$$

$$x_3 = e^{-0.5453} = 0.5796$$

$$x_4 = e^{-0.5796} = 0.5601$$

$$x_5 = e^{-0.5601} = 0.5711$$

$$x_6 = e^{-0.5711} = 0.5649$$

$$x_7 = e^{-0.5649} = 0.5684$$

Thus to two decimal places the root is $x = 0.56$. More iterations could be performed to get a more accurate answer if desired.

This method has some rather severe limitations as we'll see in this example:



Example:

Repeat the above but this time solve for x a different way. What do you find?

Solution: To illustrate the point, let's start with a guess of $x = 0.56$

The other way to solve for x is the more obvious way: $x = -\ln(x)$

$$x = -\ln(0.56) = 0.5798$$

$$x_2 = -\ln(0.5798) = 0.5451$$

$$x_3 = -\ln(0.5451) = 0.6068$$

Clearly, even though we started with a very good guess, the solution is diverging!

This example shows that **the success of the iteration method strongly depends on the properties of the function on the right-hand side**. In particular, it has to do with how large the slope of the function is at the root. If the slope is too large, the method will not converge, and even if it is small the method converges slowly. Therefore it is generally undesirable to use this method, though some more useful algorithms are based on it (which is why it is presented here).

[edit] Iterative Solution with Weights

Although the iterative solution method has its downfalls, it can be drastically improved through the use of **averaging**. In this method, the function is still solved for x in the form:

$$x = f(x)$$

From the initial guess x_0 , the function $f(x)$ is used to generate the second guess x_1 . However, rather than simply putting x_1 into $f(x)$, a *weighted average* of x_0 and x_1 is made:

$$x_1(\text{New}) = \alpha * x_0 + (1 - \alpha) * x_1(\text{old}), 0 \leq \alpha \leq 1$$

The term α is called the **weight**. The most common value of the weight is one-half, in which case the next value to plug into $f(x)$ is simply the average of x_0 and $x_1(\text{old})$:

$$x_1(\text{New}) = \frac{x_0 + x_1(\text{Old})}{2}$$

This new value is then plugged into $f(x)$, averaged with the result, and this is repeated until convergence.

The following examples show that this method converges faster and with more reliability than normal iterative solution.



Example:

Find the root of $x + \ln(x) = 0$ using the iterative method with a weight of $\alpha = \frac{1}{2}$

Solution: Let's start with a guess of 0.5 like last time, and compare what happens this time from what happened with normal iteration.

$$x_1 = e^{-0.5} = 0.6065$$

$$x_1(\text{new}) = \frac{0.5 + 0.6065}{2} = 0.5533$$

$$x_2 = e^{-0.5533} = 0.5751$$

$$x_2(\text{new}) = \frac{0.5533 + 0.5751}{2} = 0.5642$$

$$x_3 = e^{-0.5642} = 0.5688$$

Here, after only three evaluations of the function (which usually takes the longest time of all the steps), we have the root to the same accuracy as **seven** evaluations with the other method!

The method is not only faster-converging but also more stable, so that it can actually be used solving the equation the other way too.

**Example:**

Starting with an initial guess of $x = 0.5$ and using $x = -\ln(x)$ and the weighted iteration method with $\alpha = \frac{1}{2}$, find the root of the equation.

Solution: Starting with $x_0 = 0.5$ we have:

$$x_1 = -\ln(0.5) = 0.693$$

$$x_1(\text{new}) = \frac{0.693 + 0.5}{2} = 0.597$$

$$x_2 = -\ln(0.597) = 0.517$$

$$x_2(\text{new}) = \frac{0.517 + 0.597}{2} = 0.557$$

$$x_3 = -\ln(0.557) = 0.5856$$

$$x_3(\text{new}) = \frac{0.5856 + 0.557}{2} = 0.571$$

$$x_4 = -\ln(0.571) = 0.560$$

$$x_4(\text{new}) = \frac{0.560 + 0.571}{2} = 0.565$$

$$x_5 = -\ln(0.565) = 0.570$$

Therefore we can (slowly) converge in this case using the weighted iteration method to the solution.

Notice that in this case, if we use regular iteration the result only converged if the equation was solved in a certain way. Using weighted iteration, it is possible to solve it either way and obtain a solution, but one way is clearly faster than the other. However, weighting will accelerate the algorithm in most cases and is relatively easy to implement, so it is a worthwhile method to use.

[edit] Bisection Method

Let us consider an alternative approach to rootfinding. Consider a function $f(x) = 0$ which we desire to find the roots of. If we let a second variable $y = f(x)$, then y will (almost always) change sign between the left-hand side of the root and the right-hand side. This can be seen in the above picture of $y = \ln(x)$, which changes from negative to the left of the root $x = 1$ to positive to its right.

The bisection method works by taking the observation that a function changes sign between two points, and narrowing the interval in which the sign change occurs until the root contained within is tightly enclosed. This only works for a [continuous](#) function, in which there are no jumps or holes in the graph, but a large number of commonly-used functions are like this including logarithms (for positive numbers), sine and cosine, and polynomials.

As a more formalized explanation, consider a function $y = f(x)$ that changes sign between $x = a$ and $x = b$. We can narrow the interval by:

1. Evaluating the function at the midpoint
2. Determining whether the function changes signs or not in each sub-interval
3. If the continuous function changes sign in a sub-interval, that means it contains a root, so we keep the interval.
4. If the function does not change sign, we discard it. This can potentially cause problems if there are two roots in the interval, so the bisection method is not guaranteed to find ALL of the roots.

Though the bisection method is not guaranteed to find *all* roots, it **is** guaranteed to find at least one if the original endpoints had opposite signs.

The process above is repeated until you're as close as you like to the root.



Example:

Find the root of $y = x + \ln(x)$ using the bisection method

By plugging in some numbers, we can find that the function changes sign between $x = 0.5$ ($y = -0.193$) and $x = 1$ ($y = 1$). Therefore, since the function is continuous, there must be at least one root in this interval.

- First Interval: $0.5(-) < x < 1(+)$
- Midpoint: $x = 0.75$
- y at midpoint: $y = 0.75 + \ln(0.75) = 0.462$ Therefore, the sign changes between 0.5 and 0.75 and does not between 0.75 and 1.

- New Interval: $0.5(-) < x < 0.75(+)$
- Midpoint: $x = 0.625$

- y at midpoint: $y = 0.155$
- New Interval: $0.5(-) < x < 0.625(+)$
- Midpoint: $x = 0.5625$
- y at midpoint: $y = -0.0129$

We could keep doing this, but since this result is very close to the root, let's see if there's a number smaller than 0.625 which gives a positive function value and save ourselves some time.

- x Value: $x = 0.57$
- y value: $y = 0.00788$

Hence x lies between 0.5625 and 0.57 (since the function changes sign on this interval).

Note that convergence is slow but steady with this method. It is useful for refining crude approximations to something close enough to use a faster but non-guaranteed method such as weighted iteration.

[\[edit\]](#) Regula Falsi

The Regula Falsi method is similar to the bisection method. You must again start with two x values between which the function $f(x)$ you want to find the root of changes. However, this method attempts to find a better place than the midpoint of the interval to split it. It is based on the hypothesis that instead of arbitrarily using the midpoint of the interval as a guide, we should do one extra calculation to try and take into account the *shape* of the curve. This is done by finding the secant line *between two endpoints* and using the root of that line as the splitting point.

More formally:

- Draw or calculate the equation for the line between the two endpoints $(a, f(a))$ and $(b, f(b))$.
- Find where this line intersects the x-axis (or when $y = 0$), giving you $x = c$
- Use this x value to evaluate the function, giving you $f(c)$
- The sub-intervals are then treated as in the bisection method. If the sign changes between $f(a)$ and $f(c)$, keep the interval; otherwise, throw it away. Do the same between $f(c)$ and $f(b)$.
- Repeat until you're at a desired accuracy.

Use these two formulas to solve for the secant line $y = mx + B$:

$$m = \frac{f(b) - f(a)}{b - a}$$

$$B = f(b) - m * b = f(a) - m * a \text{ (you can use either)}$$

The regula falsi method is guaranteed to converge to a root, but it may or may not be faster than the bisection method, depending on how long it takes to calculate the slope of the line and the shape of the function.



Example:

Find the root of $x + \ln(x) = 0$ but this time use the regula falsi method.

Solution: Be careful with your bookkeeping with this one! It's more important to keep track of y values than it was with bisection, where all we cared about was the sign of the function, not it's actual value.

For comparison with bisection, let's choose the same initial guesses: $a = 0.5$ and $b = 1$, for which $f(a) = -0.693$ and $f(b) = 1$.

- First interval: $0.5 < x < 1, -0.193(-) < f(x) < 1(+)$
- Secant line: $y = 2.386x - 1.386$
- Root of secant line: $x = 0.581$
- Function value at root: $f(x) = 0.581 + \ln(0.581) = 0.038(+)$

Notice that in this case, we can discard a MUCH larger interval than with the bisection method (which would use $x = 0.75$ as the splitting point)

- Second interval: $0.5 < x < 0.581, -0.193(-) < f(x) < 0.038(+)$
- Secant line: $y = 2.852x - 1.619$
- Root of secant line: $x = 0.5676$
- Function value at root: $f(x) = 0.0013$

We come up with practically the exact root after only two iterations!

In some cases, the regula falsi method will take longer than the bisection method, depending on the shape of the curve. However, it generally worth trying for a couple of iterations due to the drastic speed increases possible.

[\[edit\]](#) Secant Method

[\[edit\]](#) Tangent Method (Newton's Method)

In this method, we attempt to find the root of a function $y = f(x)$ using the *tangent* lines to functions. This is similar to the secant method, except it "cuts loose" from the old point and only concentrates on the new one, thus hoping to avoid hang-ups such as the one experienced in the example.

Since this class assumes students have not taken calculus, the tangent will be approximated by finding the equation of a line between two very close points, which are denoted (x) and $(x + \delta x)$. The method works as follows:

1. Choose **one** initial guess, x_1
2. Evaluate the function $f(x)$ at $x = x_1$ and at $x = x_1 + \delta x$ where δx is a small number. These yield two points on your (approximate) tangent line.
3. Find the equation for the tangent line using the formulas given above.
4. Find the root of this line. This is x_2
5. Repeat steps 2-4 until you're as close as you like to the root.

This method is **not guaranteed to converge** unless you start off with a good enough first guess, which is why the guaranteed methods are useful for generating one. However, since this method, when it converges, is much faster than any of the others, it is preferable to use if a suitable guess is available.



Example:

Find the root of $x + \ln(x) = y$ using the tangent method.

Solution: Let's guess $x_1 = 0.5$ for comparison with iteration. Choose $\delta(x) = 0.001$

- $f(x_1) = f(0.5) = -0.193$
- $f(x_1 + \delta x) = f(0.501) = -0.190$
- Tangent line: $y = 2.85x - 1.618$
- Root of tangent line: $x = 0.5677$

Already we're as accurate as any other method we've used so far after only **one** calculation!

[\[edit\]](#) What is a System of Equations?

A **system** of equations is any number of equations with more than one total unknown, such that the same unknown must have the same value in every equation. You have probably dealt a great deal, in the past, with *linear systems of equations*, for which many solution methods exist. A linear system is a system of the form:

Linear Systems

$$C_1 = a_1x_1 + a_2x_2 + \dots$$

$$C_2 = b_1x_1 + b_2x_2 + \dots$$

And so on, where the a's and b's are constant.

Any system that is not linear is **nonlinear**. Nonlinear equations are, generally, far more difficult to solve than linear equations but there are techniques by which some special cases can be solved for an exact answer. For other cases, there may not be any solutions (which is even true about linear systems!), or those solutions may only be obtainable using a *numerical method* similar to those for single-variable equations. As you might imagine, these will be considerably more complicated on a multiple-variable system than on a single equation, so it is recommended that you use a computer program if the equations get too nasty.

[\[edit\]](#) Solvability

A system is **solvable** if and only if there are only a finite number of solutions. This is, of course, what you usually want, since you want the results to be somewhat predictable of whatever you're designing.

Here is how you can tell if it will *definitely* be impossible to solve a set of equations, or if it merely *may* be impossible.

Solvability of systems:

1. If a set of n **independent** equations has n unknowns, then the system has a finite (possibly 0) number of solutions.
2. If a set of n **independent** equations has *less than* n unknowns then the system has an infinite number of solutions.
3. If a set of n **independent or dependent** equations has *more than* n unknowns then the system has no solutions.
4. Any dependent equations in a system do not count towards n.

Note that even if a system is solvable it doesn't mean it has solutions, it just means that there's not an infinite number.

[[edit](#)] Methods to Solve Systems

As you may recall there are many ways to solve systems of *linear* equations. These include:

- **Linear Combination:** Add multiples of one equation to the others in order to get rid of one variable. This is the basis for [Gaussian elimination](#) which is one of the faster techniques to use with a computer.
- **Cramer's rule** which involves determinants of coefficient matrices.
- **Substitution:** Solve one equation for one variable and then substitute the resulting expression into all other equations, thus eliminating the variable you solved for.

The last one, substitution, is most useful when you have to solve a set of **nonlinear** equations. Linear combination can only be employed if the same type of term appears in all equations (which is unlikely except for a linear system), and no general analogue for Cramer's rule exists for nonlinear systems. However, substitution is still equally valid. Let's look at a simple example.

[[edit](#)] Example of the Substitution Method for Nonlinear Systems



Example:

Solve the following system of equations for X and Y

1. $X + Y^2 = 4$
2. $X^2 - Y^2 = 22$

Solution: We want to employ substitution, so we should ask: **which variable is easier to solve for?** In this case, X (in the top equation) is easiest to solve for so we do that to obtain:

$$X = 4 - Y^2$$

Substituting into the bottom equation gives:

$$(4 - Y^2)^2 - Y^2 = 22$$

$$4 - 8Y^2 + Y^4 - Y^2 = 22$$

$$Y^4 - 9Y^2 - 18 = 0$$

This can be solved by the **method of substitution:**

Let $U = Y^2$. Plugging this in:

$$U^2 - 9U - 18 = 0$$

NOTE:

All Ys must be eliminated for this method to be valid. Do something like this when the same variable (or set of variables) appears *in the same for every time*. If it's not in the same form **every time**, i.e. if the equation was something like $Y^4 - 9Y^2 - 18 + e^Y$, then the method would not simplify your calculations enough to make it worth doing.

Solving by factoring:

$$(U - 6)(U - 3) = 0$$

$$U = 3, 6$$

Thus since $U = Y^2$ we obtain **four** solutions for Y!

$$Y = \pm\sqrt{3}, Y = \pm\sqrt{6}$$

Notice, however, that depending on where this system *came* from, the negative solutions may not make sense, so think before you continue!

Let's take into account all of them for now. Since we have Y we can now solve for X:

$$X = 4 - Y^2 = 4 - U$$

$$X = 1, -2$$

NOTE:

Again, it may be true that only positive values of X make sense. If only positive values of X and Y make sense then the **ONLY** solution that is of any worth to us is the solution $(X, Y) = (1, \sqrt{3})$ since $Y = \sqrt{6}$ results in a negative value for X.

Notice that even a small system like this has a large number of solutions and, indeed, some systems will have an infinite number, such as:

1. $y = \sin(x)$
2. $y = \cos(x)$

[edit] Numerical Methods to Solve Systems

There are numerical equivalents in multiple variables to *some* of the methods demonstrated in the previous section. Many of them in their purest forms involve the use of calculus (in fact, the Taylor method does as well), but as before, they can be reduced to approximate algebraic forms at the expense of some accuracy.

[\[edit\]](#) **Shots in the Dark**

If you can solve all of the equations explicitly for the same variable (say, y) you can guess all but one and then compare how different the resulting values of y are in each equation. This method is entirely brute-force, because **if there are more than two equations, it is necessary to guess all of the variables but one using this method**, and there is no way to tell what the next guess should be. Trying to guess multiple variables at once from thin air gets to be a hassle even with a computer.

Since there are so many problems with this method, it will not be discussed further

[\[edit\]](#) **Fixed-point iteration**

Again, the multivariate form of fixed-point iteration is so unstable that it generally can be assumed that it will not work. Weighted iteration is also significantly more difficult.

[\[edit\]](#) **Looping method**

This is one method that *does* work, and that is somewhat different from any single-variable method. In the looping method technique, it is necessary to be able to solve *each equation for a unique variable*, and then you'll go around in a loop essentially, starting with an initial guess on (ideally) a *single* variable, say y , and then evaluating all equations until you return to your original variable with a new value y' . If the result is not the same as the guess(es) you started with, you need to make a new guess based on the *trends in the results*.

NOTE:

What kind of trends am I talking about? If you have a well-behaved system, an increase in y will consistently lead to either an increase or a decrease in y' , so you can take advantage of this to see which way you need to adjust your original guess. **DO NOT** attempt to use the value for y' as a new guess!

More specifically, here is an algorithm you can use:

1. Solve all equations for a **different variable**.
2. Make a guess on one variable (or as many as necessary to evaluate a second one, if it's more than one it gets harder though, so it is recommended to use another method)
3. Go through all of the equations until you end up recalculating the variable (or all of the variables) which you had originally guessed. Note whether the result is higher or lower than your guess.
4. Make another guess on the variable(s). Go through the loop again.

5. After these two guesses, we know whether increasing or guess will increase or decrease the recalculated value. Therefore, we can deduce whether we need to increase or decrease our guess to get a recalculated value equal to the guess.
6. Keep guessing appropriately until the recalculated value equals the guess.

This technique is often necessary in engineering calculations because they are based on data, not on explicit equations for quantities. As we'll see, however, it can be difficult to get it to converge, and this method isn't that convenient to do by hand (though it is the most reliable one to do realistically). It is great, however, for inputting guesses into a computer or spreadsheet until it works.



Example:

Solve this system:

1. $y = e^{-x}$
2. $y = \ln(x)$

First we need to solve one of them for x, let's choose the first one:

$$x = -\ln(y)$$

- To start off, we make a guess: $y = 0.1$ Then from the first equation, $x = 2.303$
- Plug this back into the second equation and you'll come out with $y' = 0.834$. The recalculated value is **too high**.
- Now make a new guess on y: say, $y = 0.5$. This results in $x = 0.6931$
- Plugging back into the second equation gives $y' = -0.3665$. The recalculated value is **too low**.

NOTE:

Now we know that increasing the guess decreases the recalculated value y' and vice versa. Since the second value of y' is too low this means that we need the guess to be smaller than 0.5; likewise, since the first y' was too high we need it to be greater than 0.1.

- Lets now try $y = 0.25$.
- This results in $x = 1.386$ from the first equation and $y' = 0.326$ from the second. **Too high** so we need to increase our guess.
- Let's guess $y = 0.3$

- This yields $x = 1.204$ and thus $y' = 0.185$, which is **too low** indicating the guessed value was too high.
- Guess $y = 0.28$, hence $x = 1.273$ and $y' = 0.241$. The guess is therefore still too high.
- Guess $y = 0.27$, hence $x = 1.309$ and $y' = 0.269$. Therefore we have now converged:

$$x = 1.309, y = 0.27$$


[edit] Looping Method with Spreadsheets

We can do the guessing procedure more easily by programming it into a spreadsheet. First set up three rows like so:

	A	B	C
1	y guess	x	y'
2		$= -\ln(A2)$	$= \ln(B2)$

In B2 we put the first function solved for x, and in C2 we have the second function solved for y. Now all we need to do is type in guesses in A2 until the value in C2 is the same as our guess (the spreadsheet will automatically calculate B2 and C2 for you). To make things even easier, put the line $= A2 - C2$ into cell D2. Since we want y' to equal y, just keep guessing until the value in D2 is as close to zero as you like.

As a more in-depth example (which would be significantly more difficult to do by hand), consider the system:



Example:

Solve:

- $T = \frac{2P^2 X^2 - 3e^{-X/T}}{T - 2}$
- $X^2 = T^3 - P$
- $10P = T$

In order for this to work, we only need to solve each equation for a unique variable, the expression need not be explicit! The following will work (assuming that X is a positive quantity), and this will be evident shortly:

- $$T = \frac{2 * P^2 * X^2 - 3 * e^{-X/T}}{T - 2}$$
- $$X = \sqrt{T^3 - P}$$
- $$P = 0.1T$$

Now we need to ask: which variable would be the best to guess to start the iteration procedure? In this case the best answer is T because from this guess, we can calculate P from equation 3, then X from equation 2, and finally a new guess on T from equation 1, and use this new value as a gauge of our old guess.

NOTE:

Generally you want to start the loop with a variable that allows you to calculate a second value with only that one guess. Try to algebraically manipulate your equations so that this is the case before solving, because we want to avoid guessing on multiple variables if at all possible.

Lets program this into the spreadsheet:

	A	B	C	D
E				
1	T guess	P	X	T'
	T' - T guess			
2		=0.1*A2	=sqrt(A2^3 - B2)	
	C2/A2)) / (A2 - 2)	=D2 - A2		

Once all this is programmed in, you can just input guesses as before, with the eventual result that:

$$P = 0.2453, X = 3.8098, T = 2.453$$

[edit] Multivariable Newton Method

NOTE:

You may want to skip this section if you don't know how to invert matrices, add them, or multiply them.

There is a multivariate extension to [Newton's method](#) which is highly useful. It converges quickly, like the single-variable version, with the downside that, at least by hand, it is tedious. However, a computer can be programmed to do this with little difficulty, and the method is not limited only to systems which can be explicitly solved like the looping method is. In addition, unlike the looping method, the Newton method will actually give you the next set of values to use as a guess.

The method works as follows:

1. Solve all of the equations for 0, i.e. let $0 = F(x_1, x_2, \dots)$ for all functions F in the system.
2. Guess a value for all variables, and put them into a matrix (X). Calculate the value of all functions F at this guess, and put them into a *column* matrix (F*).
3. We need to find estimates for all the **partial derivatives** of the function at the guessed values, which is described later.
4. Construct a matrix (to become the Jacobian) as follows: make an empty matrix with n rows and n columns, where n is the number of equations or the number of variables (remember, a solvable system generally has the same number of equations as variables. Then label the columns with the names of variables and the rows with the names of your functions. It should look something like this:

$$\begin{bmatrix} \text{---} & x_1 & y_2 & \dots \\ F_1 & & & \\ F_2 & & & \\ \dots & & & \end{bmatrix}.$$

5. Put the appropriate partial derivative in the labeled spot. For example, put the partial derivative with respect to x1 from function 1 in the first spot.
6. Once the Jacobian matrix is completely constructed, find the [inverse](#) of the matrix. There are multiple computer programs that can do this including [this one](#) (WARNING:Not tested software, use at your own risk!). Or you can do it by hand if you know how.
7. Matrix-multiply the inverse Jacobian with the **transposition** of F* (F^T), then add the **transposition** of X (again, make it a column matrix):

$$X_{n+1}^T = X_n^T - J^{-1} * F_n(X_n)^T$$

Multivariable Newton Method Formula

8. The result is your next guess. Repeat until convergence.

[\[edit\]](#) **Estimating Partial Derivatives**



You **MUST** make sure you carry out quite a few decimal places when doing this, because changing the variables by a very small amount may not change the function values too much, but even small changes are important!

A **Partial derivative** is, in its most basic sense, the slope of the tangent line of a function with more than one variable when all variables except one are held constant. The way to calculate it is:

1. Calculate one function F at your guess.
2. Increase *one* variable, x , by a very small amount δ . **Leave all other variables constant.**
3. Recalculate F at the modified guess to give you F' .

The partial derivative of the function F with respect to x is then $\frac{F' - F}{\delta}$.

[\[edit\]](#) Example of Use of Newton Method

Let's go back to our archetypal example:

- $y = e^{-x}$
- $y = \ln(x)$

Step 1: We need to solve each for zero:

- $F_1 = 0 = e^{-x} - y$
- $F_2 = 0 = \ln(x) - y$

Step 2: Lets guess that $x = 2.303$ and $y = 0.1$ (it's a good idea to choose guesses that satisfy one of the equations). Then:

$$X = [2.303, 0.1]$$

The values of F at this guess are $F_1 = 0$, $F_2 = 0.734213$, and hence by definition:

$$F = [0, 0.724213]$$

Step 3-5: Now we need to stay organized, so let's introduce some notation:



$$\frac{\delta F_i}{\delta x_j}$$

is the partial derivative of function i with respect to variable j.

Lets choose $\delta = 0.01$. Then:

$$\begin{aligned} \frac{\delta F_1}{\delta x} &= \frac{F_1(x + \delta, y) - F_1(x, y)}{\delta} \\ &= \frac{(e^{-2.303+0.01} - 0.1) - (e^{-2.303} - 0.1)}{0.01} = -0.1036 \end{aligned}$$

$$\begin{aligned} \frac{\delta F_1}{\delta y} &= \frac{F_1(x, y + \delta) - F_1(x, y)}{\delta} \\ &= \frac{(e^{-2.303} - (0.1 + 0.01)) - (e^{-2.303} - 0.1)}{0.01} = -1 \end{aligned}$$

The partial derivatives of F2 can be similarly calculated to be $\delta F_2 \delta x = 0.433$ and $\delta F_2 \delta y = -1$

Therefore, the Jacobian of the system is:

$$\begin{bmatrix} \frac{\delta F_1}{\delta x} & \frac{\delta F_1}{\delta y} \\ \frac{\delta F_2}{\delta x} & \frac{\delta F_2}{\delta y} \end{bmatrix} = \begin{bmatrix} -0.1036 & -1 \\ 0.433 & -1 \end{bmatrix}$$

Step 6: Using any method you know how to do, you can come up with the inverse of the matrix:

$$J^{-1} = \begin{bmatrix} \frac{\delta F_1}{\delta x} & \frac{\delta F_1}{\delta y} \\ \frac{\delta F_2}{\delta x} & \frac{\delta F_2}{\delta y} \end{bmatrix}^{-1} = \begin{bmatrix} -1.3636 & 1.8636 \\ -0.8069 & -0.1931 \end{bmatrix}$$

Step 7: The transposition of F is simply:

$$F^T = \begin{bmatrix} F \\ 0 \\ 0.734213 \end{bmatrix}$$

Therefore by doing matrix multiplication you can come up with the following *modifying matrix*:

$$J^{-1} * F^T = \begin{bmatrix} \Delta \\ 1.3682 \\ 0.1418 \end{bmatrix}.$$

Therefore, we should subtract 1.3682 from x and 0.1418 from y to get the next guess:

$$x = 0.9373, y = 0.2418$$

Notice how much closer this is to the true answer than what we started with. However, this method is generally better suited to a computer due to all of the tedious matrix algebra.



Problem:

1. In enzyme kinetics, one common form of a rate law is [Michaelis-Menten kinetics](#), which is of the form:

$$-r_S = \frac{V_{max} * [S]}{K_m + [S]}$$

where V_{max} and K_m are constants.

a. Write this equation in a linearized form. What should you plot to get a line? What will the slope be? How about the y-intercept?

b. Given the following data and the linearized form of the equation, predict the values of V_{max} and K_m

[S], M	r _S , M/s
0.02	0.0006
0.05	0.0010
0.08	0.0014
0.20	0.0026
0.30	0.0028
0.50	0.0030
0.80	0.0036
1.40	0.0037
2.00	0.0038

Also, calculate the R value and comment on how good the fit is.

c. Plot the rate expression in its nonlinear form with the parameters from part b. What might V_{max} represent?

d. Find the value of $-rS$ when $[S]$ is 1.0 M in three ways:

1. Plug 1.0 into your expression for $-rS$ with the best-fit parameters.
2. Perform a linear interpolation between the appropriate points nearby.
3. Perform a linear extrapolation from the line between points (0.5, 0.0030) and (0.8, 0.0036).

Which is probably the most accurate? Why?



Problem:

2. Find the standard deviation of the following set of arbitrary data. Write the data in $\mu \pm \sigma$ form. Are the data very precise?

1.01	1.00	0.86	0.93	0.95
1.1	1.04	1.02	1.08	1.12
0.97	0.93	0.92	0.89	1.15

Which data points are most likely to be erroneous? How can you tell?



Problem:

3. Solve the following equations for x using one of the rootfinding methods discussed earlier. Note that some equations have multiple real solutions (the number of solutions is written next to the equation)

a. $x^2 - 14x + 15 = 0$ (2 solutions). Use the quadratic formula to check your technique before moving on to the next problems.

b. $x^2 - 14x + 15 - \ln(x) = 0$ (1 solution)

c. $e^{3x} = -x$ (1 solution)

d. $\frac{x}{2x^2 - 3} - \frac{2x^3 - x^2}{2x - x^2} = 10$ (2 solutions)

[[edit](#)] Appendix 2: Problem Solving using Computers

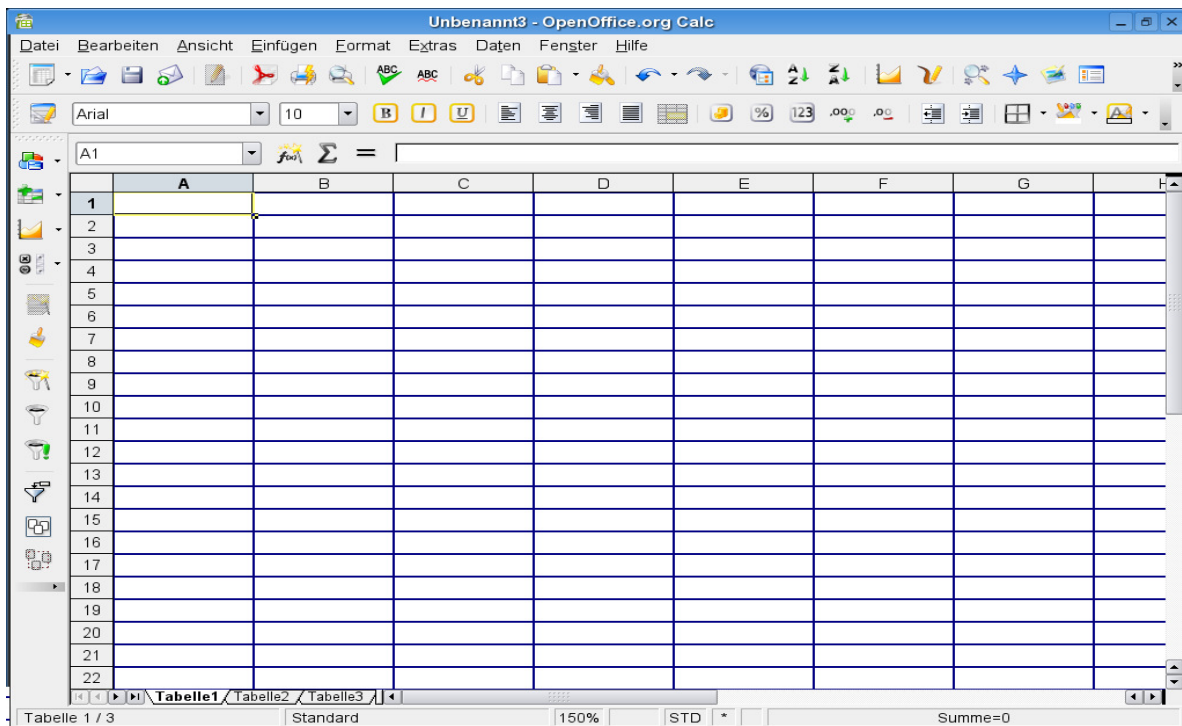
[[edit](#)] Introduction to Spreadsheets

This tutorial probably works with other spreadsheets (such as [w:open_office](#)) with minor modifications.

A **spreadsheet** such as Excel is a program that lets you analyze moderately large amounts of data by placing each data point in a **cell** and then performing the same operation on groups of cells at once. One of the nice things about spreadsheets is that data input and manipulation is relatively intuitive and hence easier than doing the same tasks in a programming language like MATLAB (discussed next). This section shows how to do some of these manipulations so that you don't have to by hand.

[[edit](#)] Anatomy of a spreadsheet

A spreadsheet has a number of parts that you should be familiar with. When you first open up the spreadsheet program, you will see something that looks like this (the image is from the German version of open office)



First off, notice that the entire page is split up into boxes, and each one is labeled. *Rows are labeled with numbers and columns with letters.* Also, try typing something in, and notice that the

box above the spreadsheet (to the right of $\Sigma \Rightarrow$) will change automatically as you type. When you're just putting in numbers, this **info box** will just have the same number in there. But when you're putting in formulas, the cell will display the value calculated from the formula, while the info box will display what the formula was.

[\[edit\]](#) Inputting and Manipulating Data in Excel

The first step in any spreadsheet analysis is to input the raw data you want to analyze. It is most effective if you put it in columns, with one column for each variable. It lets you see more data at once, and it also is less limited because the maximum number of rows is much larger than the maximum number of columns.

It is good practice to use the first row for the names of the variables, and the remaining for the data points. Make sure you include units. In this section, the following data will be used as illustration:

	A	B
1	t (min)	D (yards)
2	1.1	559.5
3	1.9	759.5
4	3.0	898.2
5	3.8	1116.3
6	5.3	1308.7

[\[edit\]](#) Using formulas

In order to tell the spreadsheet that you want to use a formula rather than just enter a number, you have to start the entry with an equal sign (=). You can then use combinations of decimal values and **cell designations**. A cell designation is simply the column letter followed by the row number containing the value you wish to manipulate. For example, if you wanted to find the product of the distance traveled and the time spent traveling, you could put in the formula:

= A2*B2

into any empty cell and it would give you the answer. From here out it will be assumed that this value is in cell C2. You should label the column with the type of calculation you're performing.

[\[edit\]](#) Performing Operations on Groups of Cells

The question may arise: why not just put in the numbers themselves instead of referencing the cell? There are two major reasons for this:

1. If you change the value in the referenced cell, the value calculated in the formula will automatically change.
2. The built-in **dragging** capability of most spreadsheets.

The dragging capability is a simple concept. If you have put a formula into a spreadsheet, you can have it *copied* to any number of cells you want. To do this, select the cell with the formula and bring the mouse pointer to its lower-right hand corner. You should see a dark + icon:

	A	Info Bar B	= A2*B2 C
1	t (min)	D (yards)	
2	1.1	559.5	625.45
3	1.9	759.5	-----+
4	3.0	898.2	
5	3.8	1116.3	
6	5.3	1308.7	

Click on the + and drag it down. **This will cause the formulas to change according to how you drag the box.** In this case, if you drag it down to row 6, the spreadsheet will produce the following:

	A	B	C
1	t (min)	D (yards)	t*D
2	1.1	559.5	615.45
3	1.9	759.5	1443.05
4	3.0	898.2	2694.6
5	3.8	1116.3	4241.94
6	5.3	1308.7	6936.11

If you click on the last value in column C (6936.11) the info bar will display:

=A6*B6

This is very useful for performing the same operations on multiple sets of data at once; rather than having to do the multiplication 5 separate times here, we just do it once and drag down the box.

[\[edit\]](#) Special Functions in Excel

In order to do many mathematical operations in Excel (or at least the easiest way), it is necessary to use *functions* (not to be confused with formulas). A function is simply an implementation someone already wrote for the mathematical operation, so all you have to do is know how to tell it to do the operation and where to put it when it's done. In excel, you can call a function named "function" by typing the following into a cell:

=function(inputs)

The function will then execute, and the cell containing the call will display the answer. The necessary inputs are sometimes numbers but are more often the cell addresses. For example, in the data above, say you wanted to take the exponential (e^x) of all the time points in column A, and place the result in column D. The function for exponential is **exp**, and it can only accept one input at a time, but due to the dragging capability of Excel this will not matter much, you can just

call it once and then drag the cell *as you would with any formula containing cell addresses*. So to do this you would type into cell D2:

```
=exp(A2)
```

Hit enter, then click the + in the bottom right and drag the cell down. You should end up with something like this after labeling the D column appropriately:

	A	B	C	D
1	t (min)	D(yards)	t*D	e^t
2	1.1	559.5	615.45	3.004166024
3	1.9	759.5	1443.05	6.685894442
4	3	898.2	2694.6	20.08553692
5	3.8	1116.3	4241.94	44.70118449
6	5.3	1308.7	6936.11	200.33681

All excel functions output only one value at a time, though some can accept multiple cells at a time as input (mostly statistical functions).

Following is a brief synopsis of the functions available. For a complete list, see the help files for your spreadsheet, as the availability of each function may vary depending on which one you are using. CELL signifies either the row/column designation of the cell you want to pass to the function as input, or some numerical value you enter manually.

[\[edit\]](#) Mathematics Functions

Generally these only take one input at a time.

abs(CELL): [Absolute value](#) of CELL
sqrt(CELL): [Square root](#) of CELL [to do nth roots, use CELL^(1/n)]
ln(CELL): [Natural log](#) of CELL
log10(CELL): Log of CELL to base 10
log(CELL, NUM): Log of CELL to the base NUM (use for all bases except e and 10)
exp(CELL): [Exponential](#) (e^x) of CELL. Use since Excel doesn't have a built-in constant "e".
sin(CELL), cos(CELL), tan(CELL): [Trigonometric functions](#) sine, cosine, and tangent of CELL. CELL must be in **radians**
asin(CELL), acos(CELL), atan(CELL): [Inverse trigonometric functions](#) (returns values in **radians**)
sinh(CELL), cosh(CELL), tanh(CELL): [Hyperbolic functions](#)
asinh(CELL), acosh(CELL), atanh(CELL): Inverse hyperbolic functions

[\[edit\]](#) Solving Equations in Spreadsheets: Goal Seek

Excel and possibly other spreadsheets have a very useful tool called *goalseek* which allows the user to solve single-variable equations (and can be used as an aid in guess-and-check for systems of algebraic equations). Let's suppose for the purposes of this tutorial that you wish to find a solution to the equation:

$$0 = X^3 + 2X^2 - X + 1$$

In order to set up the problem in Goalseek, it is necessary to define a cell for the variable you want to change (X) and a cell for the function you want to evaluate.

NOTE:

Goalseek will **only work** if you tell it to evaluate some function until it reaches a *constant value*. You cannot tell it to equal something that can change, so for example you cannot do something like this:

$$X - X^3 = 2X^2 + 1$$

because neither side is a constant. The easiest way around this is generally to solve the function for zero and then use that as the evaluating function.

Here, we could set up the cells as follows:

	A	B
1	X	f(X)
2	-1	=A2^3 + 2*A2^2 - A2 + 1

To solve this one, go to

Tools > Goalseek...

It'll give you three boxes: "Set Cell", "To Value", and "By Changing Cell". Since we want the value in cell B2 to equal 0, enter B2 into the "Set Cell" box and 0 into the "To Value" box. Since cell B2 depends on cell A2, we want to change A2 so that B2 equals 0. Hence, the "By Changing Cell" box should contain A2. Put that in and click "OK", and Goalseek will converge to an answer:

	A	B
1	X	f(X)
2	-2.54683	-0.00013

Notice that *the success of the goalseek depends on what your initial guess was*. If you try to put in an initial guess of 0 in this example (instead of -1), goalseek will diverge. It will tell you so, saying "Goal Seeking with Cell B2 May Not have Found a Solution". However, the algorithm is generally fairly robust so it shouldn't take too many guesses to obtain convergence.

NOTE:

You can only enter *one cell* into each of the "Set Cell" and "By Changing Cell" boxes, and the value in "To Value" must be a constant

[\[edit\]](#) Graphing Data in Excel

In Excel, there are a variety of ways to graph the data you have inserted, such as bar graphs, pie charts, and many others. The most commonly-used in my experience is the **scatterplot**, which is the name Excel uses for the typical x-y "line graph" plot that you probably think of first when you think of a graph.

[\[edit\]](#) Scatterplots

Scatterplots can be made relating any one independent variable to any number of dependent variables, though if you try to graph too many it will get crowded and hard to read. Excel will automatically give each different dependent variable a different color and a different shape, so that you can distinguish between them. You can also name each "series" of data differently and Excel will automatically set up a legend for you.

This is how to make a scatterplot:

1. Put the data into columns just like it was given in the problem statement.
2. Now we need to set up the graph. Go to: *Insert* → *Chart*.
3. Select "XY (scatter)" and click "next".
4. Click the "series" tab (on top). If there are any series present, remove them with the remove button (since it usually guesses wrong what you want to graph).

Now we can add a series for each dependent variable we want to graph as follows:

1. Click "add".
2. Next to "X values" click the funky arrow symbol to the right of the text box. A small box will pop up.
3. Click on the first value for the *independent variable* and drag the mouse down to the last value. Click the funky symbol again to bring you back to the main window.
4. Do the same thing with the "Y values" but this time you want to select the values of the *dependent variable*.
5. Click next, and give the graph a title and labels if you want. Then click next and "finish" to generate your graph.

[\[edit\]](#) Performing Regressions of the Data from a Scatterplot

Once you have a scatterplot of your data, you can do one of several types of regression: logarithmic, exponential, polynomial (up to 6th degree), linear, or moving-average. Excel will plot the regression curve against your data automatically, and (except for moving average) you can tell it to give you an equation for the curve. To do this:

1. Right click on one of the data points (it doesn't matter which). Click "add trendline..."
2. A new window will come up, asking you for the type of regression. Choose the type of regression you want to use.

3. Click on the "options" tab, and check the "Display Equation on Chart" box (and, if you want, the "Display R-squared value on Chart" box). Click OK.

If you chose a "linear" regression with the sample data above, the equation and R^2 value appear on the graph as $y = 177.87x + 391.28, R^2 = 0.9843$. Note Excel displays R^2 rather than R (so that we don't need to worry about negative vs. positive values); if you want R just take the square root, which is 0.9921 as we calculated in the section on linear regressions.

[\[edit\]](#) Further resources for Spreadsheets

Excel and other spreadsheets can do far more than what is described here. For additional information, see [Excel](#), [w:Excel](#), or the help files for the program you are using.

[\[edit\]](#) Graphing Data in MATLAB

[\[edit\]](#) Polynomial Regressions

[MATLAB](#) is able to do regressions up to very large polynomial orders, using the "polyfit" function. The syntax for this function is:

```
polyfit(XDATA, YDATA, Order)
```

The x data and y data must be in the form of *arrays*, which for the purposes of this application are simply comma-separated lists separated by brackets. For example, suppose you want to perform the same linear regression that had been performed in the "linear regression" section. The first step is to define the two variables:

```
>> XDATA = [1.1, 1.9, 3.0, 3.8, 5.3];  
>> YDATA = [559.5, 759.4, 898.2, 1116.3, 1308.7];
```

Then just call polyfit with order '1' since we want a linear regression.

```
>> polyfit(XDATA, YDATA, 1)  
ans = 1.0e+002 *  
    1.77876628209900    3.91232582806103
```

The way to interpret this answer is that the first number is the slope of the line (1.778×10^2) and the second is the y-intercept (3.912×10^2).

[\[edit\]](#) Appendix 3: Miscellaneous Useful Information

[\[edit\]](#) What is a "Unit Operation"?

A **unit operation** is any part of potentially multiple-step process which can be considered to have a single function. Examples of unit operations include:

- Separation Processes
- Purification Processes
- Mixing Processes
- Reaction Processes
- Power Generation Processes
- Heat Exchangers

In general the ductwork between the processes is not explicitly included, though a single pipe can be analyzed for purposes of determining friction loss, heat losses, pressure drop, and so on.

Large processes are broken into unit operations in order to make them easier to analyze. The key thing to remember about them is that *the conservation laws apply not only to the process as a whole but also to each individual unit operation.*

The purpose of this section is not to show how to design these operations (that's a whole other course) but to give a general idea of how they work.

[\[edit\]](#) Separation Processes

There are a large number of types of separation processes, including distillation, extraction, absorption, membrane filtration, and so on. Each of these can also be used for purification, to varying degrees.

[\[edit\]](#) Distillation

Distillation is a process which is generally used to separate a mixture of two or more liquids based on their boiling points. The idea is that the mixture is fed into a column and is heated up until it starts to boil. When a solution boils, the resulting gas is **still a mixture**, but the gaseous mixture will in general have more of the lower-boiling compound than the higher-boiling compound. Therefore, the higher-boiling compound can be separated from the lower-boiling compound.

Two examples of distillation processes are petroleum distillation and the production of alcoholic beverages. In the first case, oil is separated into its many components, with the lightest on the

bottom and the heaviest on top. In the latter, the gas is enriched in ethanol, which is later recondensed.

Distillation has a limit, however: nonideal mixtures can form **azeotropes**. An azeotrope is a point at which when the solution boils, the vapor has the same composition as the liquid. Therefore no further separation can be done without another method or without using some special tricks.

[\[edit\]](#) Gravitational Separation

Gravitational separation takes advantage of the well-known effect of **density differences**: something that is less dense will float on something that is more dense. Therefore, if two immiscible liquids have significantly different densities, they can be separated by simply letting them settle, then draining the denser liquid out the bottom. Note that the key word here is *immiscible*; if the liquids are soluble in each other, then it is impossible to separate them by this method.

This method can also be used to separate out solids from a liquid mixture, but again the solids must not be soluble in the liquid (or must be less soluble than they are as present in the solution).

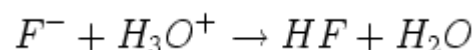
[\[edit\]](#) Extraction

Extraction is the general practice of taking something dissolved in one liquid and forcing it to become dissolved in another liquid. This is done by taking advantage of the **relative solubility** of a compound between two liquids. For example, caffeine must be extracted from coffee beans or tea leaves in order to be used in beverages such as coffee or soda. The common method for doing this is to use *supercritical carbon dioxide*, which is able to dissolve caffeine as if it were a liquid. Then, in order to take the caffeine out, the temperature is lowered (lowering the "solubility" in carbon dioxide) and water is injected. The system is then allowed to reach equilibrium. Since caffeine is more soluble in water than it is in carbon dioxide, the majority of it goes into the water.

Extraction is also used for purification, if some solution is contaminated with a pollutant, the pollutant can be extracted with another, clean stream. Even if it is not very soluble, it will still extract *some* of the pollutant.

Another type of extraction is *acid-base extraction*, which is useful for moving a basic or acidic compound from a polar solvent (such as water) to a nonpolar one. Often, the ionized form of the acid or base is soluble in a polar solvent, but the non-ionized form is not as soluble. The reverse is true for the non-ionized form. Therefore, in order to manipulate where the majority of the compound will end up, we alter the pH of the solution by adding acid or base.

For example, suppose you wanted to extract Fluoride (F⁻) from water into benzene. First, you would add *acid*, because when a strong acid is added to the solution it undergoes the following reaction with fluoride, which is practically irreversible:



The hydrogen fluoride is more soluble in benzene than fluoride itself, so it would move into the benzene. The benzene and water fluoride solutions could then be separated by density since they're immiscible.

The term **absorption** is a generalization of extraction that can involve different phases (gas-liquid instead of liquid-liquid). However, the ideas are still the same.

[\[edit\]](#) Membrane Filtration

A membrane is any barrier which allows one substance to pass through it more than another. There are two general types of membrane separators: those which separate based on the **size of the molecules** and those which separate based on **diffusivity**.

An example of the first type of membrane separator is your everyday vacuum cleaner. Vacuum cleaners work by taking in air laden with dust from your carpet. A filter inside the vacuum then traps the dust particles (which are relatively large) and allows the air to pass through it (since air particles are relatively small). A larger-scale operation that works on the same principle is called a **fabric filter** or "Baghouse", which is used in air pollution control or other applications where a solid must be removed from a gas.

Some fancy membranes exist which are able to separate hydrogen from a gaseous mixture by size. These membranes have very small pores which allow hydrogen (the smallest possible molecule, by molecular weight) to pass through by convection, but other molecules cannot pass through the pores and must resort to diffusion (which is comparatively slow). Hence a purified hydrogen mixture results on the other side.

Membranes can separate substances by their diffusivity as well, for example water may diffuse through a certain type of filter faster than ethanol, so if such a filter existed it could be used to enrich the original solution with ethanol.

[\[edit\]](#) Reaction Processes

[\[edit\]](#) Plug flow reactors (PFRs) and Packed Bed Reactors (PBRs)

A **plug flow reactor** is a (idealized) reactor in which the reacting fluid flows through a tube at a rapid pace, but without the formation of eddies characteristic of rapid flow. Plug flow reactors tend to be relatively easy to construct (they're essentially pipes) but are problematic in reactions which work better when reactants (or products!) are dilute.

Plug flow reactors can be combined with membrane separators in order to increase the yield of a reactor. The products are selectively pulled out of the reactor as they are made so that the equilibrium in the reactor itself continues to shift towards making more product.

A packed bed reactor is essentially a plug flow reactor packed with catalyst beads. They are used if, like the majority of reactions in industry, the reaction requires a catalyst to significantly progress at a reasonable temperature.

[\[edit\]](#) Continuous Stirred-Tank Reactors (CSTRs) and Fluidized Bed Reactors (FBs)

A **continuous stirred-tank reactor** is an idealized reactor in which the reactants are dumped in one large tank, allowed to react, and then the products (and unused reactants) are released out of the bottom. In this way the reactants are kept relatively dilute, so the temperatures in the reactor are generally lower. This also can have advantages or disadvantages for the selectivity of the reaction, depending on whether the desired reaction is faster or slower than the undesired one.

CSTRs are generally more useful for liquid-phase reactions than PFRs since less transport power is required. However, gas-phase reactions are harder to control in a CSTR.

A **fluidized bed reactor** is, in essence, a CSTR which has been filled with catalyst. The same analogy holds between an FB and CSTR as does between a PFR and a PBR.

[\[edit\]](#) Bioreactors

A **bioreactor** is a reactor that utilizes either a living organism or one or more enzymes from a living organism to accomplish a certain chemical transformation. Bioreactors can be either CSTRs (in which case they are known as **chemostats**) or PFRs.

Certain characteristics of a bioreactor must be more tightly controlled than they must be in a normal CSTR or PFR because cellular enzymes are very complex and have relatively narrow ranges of optimum activity. These include, but are not limited to:

1. Choice of organism. This is similar to the choice of catalyst for an inorganic reaction.
2. *Strain* of the organism. Unlike normal catalysts, organisms are very highly manipulable to produce more of what you're after and less of other products. However, also unlike normal catalysts, they generally require a lot of work to get any significant production at all.
3. Choice of substrate. Many organisms can utilize many different carbon sources, for example, but may only produce what you want from one of them.
4. Concentration of substrate and aeration. Two inhibitory effects exist which could prevent you from getting the product you're after. Too much substrate leads to the **glucose effect** in which an organism will ferment regardless of the air supply, while too much air will lead to the **pasteur effect** and a lack of fermentation.
5. pH and temperature: Bacterial enzymes tend to have a narrow range of optimal pH and temperatures, so these must be carefully controlled.

However, bioreactors have several distinct advantages. One of them is that enzymes tend to be stereospecific, so for example you don't get useless D-sorbose in the production of vitamin C, but you get L-sorbose, which is the active form. In addition, very high production capacities are possible after enough mutations have been induced. Finally, substances which have not been made artificially or which would be very difficult to make artificially (like most antibiotics) can be made relatively easily by a living organism.

[\[edit\]](#) Heat Exchangers

In general, a **heat exchanger** is a device which is used to facilitate the exchange of heat between two mixtures, from the hotter one to the cooler one. Heat exchangers very often involve steam because steam is very good at carrying heat by convection, and it also has a high heat capacity so it won't change temperature as much as another working fluid would. In addition, though steam can be expensive to produce, it is likely to be less expensive than other working fluids since it comes from water.

[\[edit\]](#) Tubular Heat Exchangers

A **tubular heat exchanger** is essentially a jacket around a pipe. The working fluid (often steam) enters the jacket on one side of the heat exchanger and leaves on the other side. Inside the pipe is the mixture which you want to heat or cool. Heat is exchanged through the walls of the device in accordance to the second law of thermodynamics, which requires that heat flow from higher to lower temperatures. Therefore, if it is desired to cool off the fluid in the pipe, the working fluid must be cooler than the fluid in the pipe.

Tubular heat exchangers can be set up in two ways: **co-current** or **counter-current**. In a co-current setup, the working fluid and the fluid in the pipe enter on the same side of the heat exchanger. This setup is somewhat inefficient because as heat is exchanged, the temperature of the working fluid will approach that of the fluid in the pipe. The closer the two temperatures become, the less heat can be exchanged. Worse, if the temperatures become equal somewhere in the middle of the heat exchanger, the remaining length is wasted because the two fluids are at thermal equilibrium (no heat is released).

To help counteract these effects, one can use a counter-current setup, in which the working fluid enters the heat exchanger on one end and the fluid in the pipe enters at the *other end*. As an explanation for why this is more efficient, suppose that the working fluid is hotter than the fluid in the pipe, so that the fluid in the pipe is heated up. The fluid in the pipe will be at its highest temperature when it exits the heat exchanger, and at its coolest when it enters. *The working fluid will follow the same trend* because it cools off as it travels the length of the exchanger. Because it's counter-current, though, the fact that the working fluid cools off has less of an effect because it's exchanging heat with cooler, rather than warmer, fluids in the pipe.

[\[edit\]](#) Appendix 4: Notation

[\[edit\]](#) A Note on Notation

[\[edit\]](#) Base Notation (in alphabetical order)

$[i]_n$: Molarity of species i in stream n

A: Area

m: mass

MW: Molecular Weight (Molar Mass)

n: moles

N: Number of components

x: Mass fraction

y: Mole fraction

v: velocity

V: Volume

[\[edit\]](#) Greek

ρ : Density

Σ : Sum

[\[edit\]](#) Subscripts

If a particular component (rather than an arbitrary one) is considered, a specific letter is assigned to it:

- $[A]$ is the molarity of A
- x_{Ais} is the mass fraction of A

Similarly, referring to a specific stream (rather than any old stream you want), each is given a different number.

- \dot{n}_{1is} is the molar flowrate in stream 1.
- \dot{n}_{A1is} is the molar flow rate of component A in stream 1.

Special subscripts:

If A is some value denoting a property of an *arbitrary* component stream, the letter i signifies the arbitrary *component* and the letter n signifies an arbitrary *stream*, i.e.

- A_{nis} is a property of *stream* n . Note \dot{n}_{nis} is the molar flow rate of stream n .
- A_{iis} is a property of *component* i .

The subscript "gen" signifies generation of something inside the system.

The subscripts "in" and "out" signify flows into and out of the system.

[\[edit\]](#) Embellishments

If A is some value denoting a property then:

\bar{A}_n denotes the *average* property in stream n

\dot{A}_n denotes a *total flow rate* in stream n

\dot{A}_{in} denotes the flow rate of component i in stream n.

\hat{A} indicates a data point in a set.

[\[edit\]](#) Units Section/Dimensional Analysis

In the units section, the generic variables L, t, m, s, and A are used to demonstrate dimensional analysis. In order to avoid confusing dimensions with units (for example the unit m, meters, is a unit of length, not mass), if this notation is to be used, use the *unit equivalence* character $\stackrel{\sim}{=}$ rather than a standard equal sign.

[\[edit\]](#) Appendix 5: Further Reading

Chapra, S. and Canale, R. 2002. *Numerical Methods for Engineers*, 4th ed. New York: McGraw-Hill.

Felder, R.M. and Rousseau, R.W. 2000. *Elementary Principles of Chemical Processes*, 3rd ed. New York: John Wiley & Sons.

Masterton, W. and Hurley, C. 2001. *Chemistry Principles and Reactions*, 4th ed. New York: Harcourt.

Perry, R.H. and Green, D. 1984. *Perry's Chemical Engineers Handbook*, 6th ed. New York: McGraw-Hill.

Windholz *et al.* 1976. *The Merck Index*, 9th ed. New Jersey: Merck.

[General Chemistry](#): For a more in-depth analysis of general chemistry

[Matlab](#): For more information on how to use MATLAB to solve problems.

[Numerical Methods](#): For more details on the rootfinding module and other fun math (warning: it's written at a fairly advanced level)

[\[edit\]](#) Appendix 6: External Links

Data Tables

[Unit conversion table \(Wikipedia\)](#)

[Enthalpies of Formation \(Wikipedia\)](#)

[Periodic Table \(Los Alamos National Laboratory\)](#)

[Chemical Sciences Data Tables](#): Has a fair amount of useful data, including a fairly comprehensive List of Standard Entropies, and Gibbs Energies at 25oC (also a list for ions), a chart with molar masses of the elements, acid equilibrium constants, solubility products, and electric potentials. Definitely one to check out.

[NIST properties](#): You can look up properties of many common substances, including water, many light hydrocarbons, and many gases. Data available can include density, enthalpy, entropy, Pitzer accentric factor, surface tension, Joule-Thompson coefficients, and several other variables depending on the substance and conditions selected. To see the data in tabular form, once you enter the temperature and pressure ranges you want, click "view table" and then select the property you want from the pull-down menu. It'll tell you acceptable ranges.

[\[edit\]](#) Appendix 7: License

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