## Chapter 4 - Material Balances

Note: Be sure to read carefully through all the examples in this chapter. The key concepts are best learned by problem solving.

Material balances: material balances express the constraint of conservation of mass, as applied to a process.

Batch process: In a batch process, raw materials are fed into the process at the outset. The process then runs for some length of time, producing product, but no product is removed, and no additional raw materials are input (but energy may be input or withdrawn), while the process runs. At the end, the product is removed. The bottom line is that no mass enters or leaves while the process is running.

Continuous process: In this type of process, raw materials continuously enter and product continuously leaves the process.

Semibatch process: A semibatch process does not fall fully under either "batch" or "continuous" classification.

Steady-state operation: Under steady-state, the values of all variables associated with the process do not change with time. That is, at any given location in the process, the values of temperature, pressure, composition, flow rates, etc. are independent of time. Even though a process may be steady state, it is important to realize that temperature, flow rates, or other variables may, and typically do, change from one location to another (e.g. from one process stream to another).

Transient or unsteady-state operation: If some process variables change with time, then the process is transient. A process must be either steady-state or transient.

Batch and semibatch processes must be transient. Continuous processes may be transient or steady-state.

Example: How would you classify the following processes?
i). a soda can is opened and goes flat with time.
ii). hot and cold water flows come together and mix to deliver a continuous, constant temperature output water flow
iii). A car engine burns fuel at a constant rate. What else must be true for the engine to be operating at steady-state?
iv). In example (iii) above, how would you classify the changes in the gas tank? Are these changes indicative of a batch, continuous, or semibatch type operation? Transient or steady-state?
v). Water freezes in a sealed bottle.

## General Material Balance Equation

$$
\begin{equation*}
\text { input }+ \text { generation }- \text { output }- \text { consumption }=\text { accumulation } \tag{0}
\end{equation*}
$$

Input: enters through system boundaries
Generation: is produced within the system
Output: exits through system boundaries
Consumption: is used up within the system
Accumulation: is built up within the system
Example: How would the material balance look for mass of species A, mass of species B, and mass of species C, for the below process?


What would the $\mathrm{A}, \mathrm{B}$, and C balances be if the operation were steady state?

What would the balance be for total mass, $\mathrm{A}+\mathrm{B}+\mathrm{C}$, at steady state?

Differential balances: The terms in a differential material balance are expressed as rates; that is, rate of input (e.g. moles/s, kg/s), rate of generation, rate of output, and rate of accumulation. Differential balances are applied to continuous processes.

Integral balances: These usually apply to batch processes. The terms in a batch material balance are expressed as amounts (molar or mass). Input is the amount placed into the system initially at the start of the process. The process is then sealed while the reaction/transformation of the input materials takes place. At the end, the process is opened and the contents are removed: output is the amount removed at this stage, including products and any unconverted reactants. Generation/consumption are the amounts produced/consumed during the time between the start and the end of the process. Accumulation is the amount left behind in the process (this is zero if all materials are removed).

One thousand kilograms per hour of a mixture of benzene (B) and toluene (T) containing $50 \%$ benzene by mass is separated by distillation into two fractions. The mass flow rate of benzene in the top stream is $450 \mathrm{~kg} \mathrm{~B} / \mathrm{h}$ and that of toluene in the bottom stream is 475 $\mathrm{kg} \mathrm{T} / \mathrm{h}$. The operation is at steady state. What are the unknown benzene and toluene flow rates in the output streams?

Example 4.2-3 (Material balances on a batch mixing process)
Two methanol-water mixtures are contained in separate flasks. The first mixture is 40.0 wt $\%$ methanol, and the second is $70.0 \mathrm{wt} \%$ methanol. If 200 g of the first mixture is combined with 150 g of the second, what will be the mass and composition of the resulting mixture?

Example 4.2-4 (Material balances on a semibatch process)
Air is bubbled through a container of liquid hexane at a rate of $0.100 \mathrm{kmol} / \mathrm{min}$. It then leaves the container, such that the output gas contains 10.0 mole $\%$ hexane vapor. Assume that air is insoluble in liquid hexane. What is the time required to vaporize 10.0 $\mathrm{m}^{3}$ of the hexane?

## Flowcharts

Flowcharts are used to summarize the layout of a process as well as to indicate known information about the state of the process streams. Such information may include flow rates, compositions, pressures, temperatures, and energy inputs. Flowcharts are also used to indicate all unknown variables of interest. Being able to draw and label a flowchart, based on a textual description of a problem, is EXTREMELY important in learning to properly set up material and energy balance problems.

## Example 4.3-1 (Flowchart of an air humidification and oxygenation process)

Three streams are fed into an evaporation chamber to produce a single gas output stream containing 1.5 mole $\%$ water. The three input streams are:
1). water at $20.0 \mathrm{~cm}^{3} / \mathrm{min}$
2). Air ( 21 mole $\% \mathrm{O}_{2}, 79$ mole $\% \mathrm{~N}_{2}$ )
3). Pure oxygen, at a molar flow rate that is $1 / 5$ that of the air stream.

Draw and label a flowchart for this process.

CBE2124, Levicky

Flowchart scaling: the flowrates or material amounts on a flowchart can be scaled up or down without violating material balance constraints, as long as all flowrates or material amounts are scaled by the same factor.

Example: Given the following, steady-state, balanced mixing process,


How would the above diagram change if we scale it to a $10 \mathrm{~kg} / \mathrm{min}$ flowrate of the pure A stream? $\left(1 \mathrm{~kg}=2.204 \mathrm{lb}_{\mathrm{m}}\right)$


## Degree of Freedom Analysis

Recall: If you have $N$ unknown variables (such as flowrates, compositions) whose value you need to solve for, you will need exactly $N$ independent equations relating these variables ("number of independent equations = number of unknowns").

Independent equations: equations are independent if none of them can be derived from the others. For example, not one of the set of equations can be obtained by adding or subtracting multiples of the others.

Example: Try to obtain the numerical vale of $x$ and $y$ in the following examples. If it is not possible, why not?
(i) $x+y=1$
(ii) $x+y=1 ; x-y=2$
(iii) $x+y=1 ; x-y=2 ; y=3$
(iv) $x+y=1 ; 2 x+2 y=2$

Degrees of freedom $\left(\operatorname{symbol} n_{\mathrm{df}}\right): \quad n_{\mathrm{df}}=n_{\text {unknowns }}-n_{\text {indep eqns }}$

If, for a given problem,
$\boldsymbol{n}_{\mathbf{d f}}=\mathbf{0}$ : A numerical value for each unknown can be obtained. The problem is solvable. $\boldsymbol{n}_{\mathbf{d f}}>\mathbf{0}$ : The problem is underspecified (underdetermined). There is not enough information (i.e. not enough independent equations) to provide a solution.
$\boldsymbol{n}_{\mathbf{d f}}<\mathbf{0}$ : The problem is overspecified (overdetermined). The problem is mathematically and possibly physically inconsistent.

## General Procedure for Solving Material Balance Calculations

1). Choose a basis of calculation.
2). Draw and completely label the flowchart. The flowchart is fully labeled if the composition and flowrate (or amount) of each process stream can be expressed in terms of the labeled quantities. For each stream, usually you will either label (1) the total mass flow together with the mass fractions of all the stream components, (2) the total molar flow and mole fractions of all stream components, or (3) the mass or molar flows for each of the stream components. If you are starting from mixed mass and mole units for a stream, convert all quantities to either the mass or the molar basis first.

Example: these are three possible representations of the same stream:


$$
\xrightarrow[\substack{\mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}=0.53 \\ \mathrm{X}_{2} \mathrm{OH} / \mathrm{OH}=0.47}]{\text { 34 }}
$$

$$
\xrightarrow[\substack{\mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}=0.67 \\ \mathrm{X}_{\mathrm{CH}_{3} \mathrm{OH}}=0.33}]{1.5 \mathrm{gmol} / \mathrm{min}}
$$

3). Express the result (unknown) of interest in terms of the quantities on the flowchart.
4). Perform a degree of freedom analysis. Add up the number of unknown variables you'll need to determine. Then add up the number of independent equations relating the unknown variables. Independent equations can come in different flavors - you need to account for all of them to do the degree of freedom analysis properly. The equations may include material balances, an energy balance (to be discussed in later chapters), information from the problem statement not already listed on the flowchart, physical properties and laws (e.g. ideal gas equation to relate $P, V$ and $T$; tables of density to interconvert mass and volume), physical constraints (such as the sum of all mass or all molar fractions must add up to 1) and, for a reactive process, stoichiometric constraints derived from the chemical reactions taking place (to be discussed later). If the number of degrees of freedom $=0$, the problem is solvable.

Note: For a nonreactive process, the number of independent material balances cannot exceed the number of chemical species in the process.
5). Write down the equations you will solve. Try to write them in an order that will simplify the calculations. For example, write equations with only one unknown first, as these can be solved right away and, once solved, will eliminate an unknown from subsequent calculations.
6). Solve the equations. Scale the process if the scale used for the calculations was different from that needed.

Example 4.3-5 (Material balances on a distillation column) A liquid mixture containing $45.0 \%$ benzene $(\mathrm{B})$ and $55.0 \%$ toluene $(\mathrm{T})$ by mass is fed to a distillation column. The overhead product stream contains 95.0 mole $\% \mathrm{~B}$. The bottom product stream contains $8.0 \%$ of the benzene fed to the column. The feed stream flowrate is $2000 \mathrm{~L} / \mathrm{h}$ and the specific gravity of the feed mixture is 0.872 .

What is the mass flowrate of the overhead product stream, and what are the mass flowrate and composition, in mass fractions, of the bottom product stream? Follow the aboveoutlined methodology to arrive at the solution. Note that the column operates at steady state.

CBE2124, Levicky

## Multiple Unit Processes

When an interconnected network of process units is involved in a material balance calculation, one typically has to make balances on individual process units, combinations of several units, as well as the overall, multiple unit system in order to arrive at the solution. Balances that are taken on the overall system, which do not involve any internal process streams, are referred to as overall balances. For each subsystem (e.g. a single unit, a combination of units), as well as the total process, a degree of freedom analysis will apply. You may need to solve the balances on one subsystem first in order to determine values of variables needed to solve balances on another.

Recycle: When a part of a process stream is fed back into an earlier stage of the process, the stream is said to be "recycled." Recycle is often used to increase the rates of conversion of a reactant. By passing a reactant molecule through the process several times, its chances to react and convert to product are increased. Other reasons to recycle part of a stream include recovery of valuable materials, such as catalysts, improved temperature control over a process, and decreased waste of working (carrier) fluid.

Bypass: When a part of a process stream is fed forward into a later stage of the process, the stream is being "bypassed." Bypass is useful, for example, for decreasing the extent of conversion of input materials or for providing improved control over stream temperatures.

## Example 4.5-2 (An evaporative crystallization process)



The process is steady-state. $4500 \mathrm{~kg} / \mathrm{h}$ of a solution that is $1 / 3 \mathrm{~K}_{2} \mathrm{CrO}_{4}$ by mass is joined by a recycle stream containing $36.4 \% \mathrm{~K}_{2} \mathrm{CrO}_{4}$, and the combined stream is fed into an evaporator. The concentrated stream leaving the evaporator contains $49.4 \% \mathrm{~K}_{2} \mathrm{CrO}_{4}$, and is in turn fed into a crystallizer in which it is cooled. The cooling causes crystals of $\mathrm{K}_{2} \mathrm{CrO}_{4}$ to precipitate. The crystals are then filtered out of the solution. The "filter cake" consists of $\mathrm{K}_{2} \mathrm{CrO}_{4}$ crystals and a solution that contains $36.4 \% \mathrm{~K}_{2} \mathrm{CrO}_{4}$ by mass, such
that the crystals account for $95 \%$ of the total mass of the filter cake. The "filtrate" solution that passes through the filter also contains $36.4 \% \mathrm{~K}_{2} \mathrm{CrO}_{4}$, and is recycled.

Use (K) to denote $\mathrm{K}_{2} \mathrm{CrO}_{4}$, and (W) to denote water.

What are the (i) mass rate of evaporation, (ii) the mass rate of production of $\mathrm{K}_{2} \mathrm{CrO}_{4}$ crystals, (iii) the mass feed rates that the evaporator and the crystallizer must handle, and (iv) the recycle ratio? The recycle ratio $=($ mass of recycle $) /($ mass of fresh feed $)$.

What would be the mass production rate of the crystals if the filtrate was discarded instead of recycled?

CBE2124, Levicky

## Material Balances on Processes with Chemical Reactions

## Definitions and Terminology.

Chemical reaction equations. Chemical reactions do not create, destroy, or convert atoms. Therefore, the quantities of each type of atom on the two sides of a chemical reaction equation MUST be the same. In other words, chemical reaction equations must be stoichiometrically balanced.

## Example:

Is $\mathrm{CH}_{4}+2 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$ stoichiometrically balanced?
Is $6 \mathrm{HF}+2 \mathrm{SiO}_{2} \rightarrow \mathrm{H}_{2} \mathrm{SiF}_{6}+2 \mathrm{H}_{2} \mathrm{O}$ stoichiometrically balanced?
Stoichiometric coefficient of a reacting species is the numeric prefactor of the species in the chemical reaction equation. What are the stoichiometric coefficients in the above (correctly balanced) equation involving combustion of methane?

Stoichiometric ratio is the ratio of the stoichiometric coefficients of two species involved in a chemical reaction. This ratio is useful for calculating how much of a reactant (or product) is consumed (or produced) relative to the consumption or production of the other species.

What is stoichiometric ratio of $\mathrm{CO}_{2}$ to $\mathrm{CH}_{4}$ in the reaction $\mathrm{CH}_{4}+2 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$ ? How many molecules of $\mathrm{CO}_{2}$ are produced per one molecule of $\mathrm{CH}_{4}$ ?

Stoichiometric proportion: Two chemical species participating in the same chemical reaction are in stoichiometric proportion if their actual amounts present are in the same proportion as their stoichiometric coefficients. In the case that all reactants are present in stoichiometric proportion, if the reaction proceeds to full conversion there will be no reactant molecules (of any type) left.

If there are $0.5 \mathrm{gmol} \mathrm{CH}_{4}$ available to react, what quantity of $\mathrm{O}_{2}$ would be in stoichiometric proportion, in the reaction $\mathrm{CH}_{4}+2 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$ ?

Limiting reactant: Usually reactants are not present in stoichiometric proportion. In that case, if the reaction proceeds sufficiently far, one of the reactants will be the first to be used up. That reactant is the limiting reactant. The other reactants are excess reactants.

Stoichiometric requirement: The amount of an excess reactant that would be needed to completely react with the limiting reactant.

If there are $11 \mathrm{gmol} \mathrm{CH}_{4}$ available to react in the reaction $\mathrm{CH}_{4}+2 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$, what is the stoichiometric requirement of $\mathrm{O}_{2}$ ?

Fractional excess: the fractional excess of a reactant A is defined by
Fractional excess of $\mathrm{A}=\frac{\text { amount } A \text { present }- \text { stoichiometric requirement of } A}{\text { stoichiometric requirement of } A}$
For the reaction $\mathrm{CH}_{4}+2 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$, if there are $2 \mathrm{gmol} \mathrm{CH}_{4}$ available to react, and the amount of $\mathrm{O}_{2}$ available is 6 gmol , what is the fractional excess of $\mathrm{O}_{2}$ ?

Percentage excess $=($ fractional excess $) \times 100 \%$
Fractional conversion: the fraction of reactant that has reacted.
Fractional conversion $=($ moles reactant reacted $) /($ moles reactant fed in $)$
If 10 kg -moles of $\mathrm{CH}_{4}$ are fed into the reaction $\mathrm{CH}_{4}+2 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$, and 6 kg moles react, what is the fractional conversion?

Percentage conversion: (fractional conversion) $\times 100 \%$
Yield: Reactions, in general, do not go to $100 \%$ conversion of the reactant into the desired product. This is because of side reactions taking place as well as thermodynamic limitations (see below). "Yield" is used to measure how effective a reaction is in converting reactant to the desired product. It has several possible definitions, so it is important to always note which one is being used. Often, yield is defined as

Yield $=$
moles of desired product formed
$\overline{\text { moles of desired product that would have been formed if there were no side reactions and if complete conversion }}$ of the limiting reactant had taken place

Selectivity: Selectivity measures how effective a reaction is in producing the desired product relative to undesired products that result from side reactions.

Selectivity $=\frac{\text { moles of desired product formed }}{\text { moles of undesired product formed }}$

Extent of reaction: Let's take a chemical reaction in which $n$ reactants are converted to $m$ products:

$$
\begin{equation*}
v_{\mathrm{R} 1} \mathrm{R}_{1}+v_{\mathrm{R} 2} \mathrm{R}_{2}+\ldots+v_{\mathrm{Rn}} \mathrm{R}_{\mathrm{n}} \leftrightarrow v_{\mathrm{P} 1} \mathrm{P}_{1}+v_{\mathrm{P} 2} \mathrm{P}_{2}+\ldots+v_{\mathrm{Pm}} \mathrm{P}_{\mathrm{m}} \tag{4}
\end{equation*}
$$

$R_{1}$ is reactant \#1, $R_{2}$ reactant \#2, $P_{1}$ is product \#1, etc., and the $v_{i}$ are the stoichiometric coefficients. The "distance" the reaction has gone in converting reactants to products can be represented by a "reaction coordinate" or "extent of reaction" $\xi$. As the reaction progresses, $\xi$ increases. $\xi$ is defined such that multiplication of $\xi$ by the stoichiometric coefficient of a reactant equals the amount of that reactant consumed so far. For example: $\nu_{\mathrm{R} 1} \xi$ is the amount, in mass or molar units, of $R_{1}$ consumed by the reaction. Note that $\xi$ has units of an "amount"; for instance $\mathrm{g}, \mathrm{kg}$, mol, or $\mathrm{lb}_{\mathrm{m}}$-mol. Similarly, multiplying $\xi$ by the stoichiometric coefficient of a product is the amount of that product produced so far. At any time during the progress of the reaction, the amount of species $i$ is

$$
\begin{equation*}
n_{\mathrm{i}}=n_{\mathrm{i}}^{0}+v_{\mathrm{i}} \xi \tag{5}
\end{equation*}
$$

where $n_{\mathrm{i}}{ }^{0}$ is the initial (at time $=0$ ) amount of species $i$, and $\xi$ is the extent of reaction at the time of interest. Note that in equation 5 , and equation 6 below, $v_{i}$ has a negative value for reactants - that is, as $\xi$ increases the reactant amounts decrease.

In equation 5, the amounts $n$ and extent of reaction $\xi$ are in mass or molar amounts, such as kg or $\mathrm{kg}-\mathrm{mol}$, appropriate to batch processes. If we are dealing with continuous processes, it is customary to instead use molar ( $\dot{n}$ ) or mass ( $\dot{m}$ ) flowrates; under these conditions, expression 5 becomes

$$
\begin{equation*}
\dot{n}_{\mathrm{i}}=\dot{n}_{\mathrm{i}}^{0}+v_{\mathrm{i}} \dot{\xi} \tag{6}
\end{equation*}
$$

where the outlet flowrate $\dot{n}_{i}$ of species $i$ from a process unit equals its inflow rate $\dot{n}_{\mathrm{i}}{ }^{0}$ into the unit, plus the rate at which that species is produced (product) or minus the rate at which it is consumed (reactant) inside the unit.

When a chemical species is simultaneously involved in multiple reactions, equations (5) and (6) are modified as follows

$$
\begin{align*}
n_{\mathrm{i}} & =n_{\mathrm{i}}^{0}+\sum_{j} v_{i j} \xi_{j}  \tag{5b}\\
\dot{n}_{\mathrm{i}} & =\dot{n}_{\mathrm{i}}^{0}+\sum_{j} v_{i j} \dot{\xi}_{j} \tag{6b}
\end{align*}
$$

In the above equations, $v_{\mathrm{ij}}$ is the stoichiometric coefficient of species $i$ in the $j$ th reaction, and $\xi_{j}$ is the extent of the $j$ th reaction.

Example 4.6-3 (Yield and selectivity in a dehydrogenation reactor)
Two reactions take place in a continuous reactor operating at steady state,
\#1 $\quad \mathrm{C}_{2} \mathrm{H}_{6} \rightarrow \mathrm{C}_{2} \mathrm{H}_{4}+\mathrm{H}_{2}$
\#2 $\quad \mathrm{C}_{2} \mathrm{H}_{6}+\mathrm{H}_{2} \rightarrow 2 \mathrm{CH}_{4}$
The feed stream contains 85.0 mole $\%$ ethane $\left(\mathrm{C}_{2} \mathrm{H}_{6}\right)$ and 15 mole $\%$ inert (i.e. unreactive) components. The fractional conversion of ethane is 0.501 , and the fractional yield of ethylene $\left(\mathrm{C}_{2} \mathrm{H}_{4}\right)$ is 0.471 . What is the molar composition of the product gas, and what is the selectivity of ethylene to methane $\left(\mathrm{CH}_{4}\right)$ production?

CBE2124, Levicky

## Chemical equilibrium

You will study chemical thermodynamics in future courses. For the present discussion, let us define equilibrium as the "preferred" state of a system from which the system would not, spontaneously and of its own accord, move. If the "system" is a solution containing reactive molecules then, at a given $T$, there exists an equilibrium state in which the composition is such that the rates of forward and reverse reactions are equal. That is, for a general reaction such as

$$
v_{\mathrm{R} 1} \mathrm{R}_{1}+v_{\mathrm{R} 2} \mathrm{R}_{2}+\ldots+v_{\mathrm{Rn}} \mathrm{R}_{\mathrm{n}} \leftrightarrow v_{\mathrm{P} 1} \mathrm{P}_{1}+v_{\mathrm{P} 2} \mathrm{P}_{2}+\ldots+v_{\mathrm{Pm}} \mathrm{P}_{\mathrm{m}}
$$

the forward rate at which reactant molecules rearrange their bonds to form product species is equal to, at equilibrium, the reverse rate at which product species decompose back into the reactants. Complete ( $100.00000 \ldots \%$ ) conversion of reactant is generally not achieved, but in certain situations conversions can come extremely close to being complete. Such reactions are called irreversible; that is, for practical purposes the reverse rate at which products convert back to reactants can be taken as zero. A reaction modeled as irreversible only runs in the forward direction.

For reversible reactions, at equilibrium, the compositions of reactants and products in the reaction mixture are related by the so-called equilibrium constant, which is usually given the symbol $K$ and is a function of temperature only, $K(T)$. For the purposes of this course, $K(T)$ will be related to mole fractions as follows

$$
\begin{equation*}
K(T)=\frac{\prod_{i}^{\text {products }} y_{i}^{v_{i}}}{\prod_{i}^{\text {reactunss }} y_{i}^{v_{i}}} \tag{7}
\end{equation*}
$$

In (7), the product in the numerator is taken over all reaction products, while the product in the denominator is taken over all the reactants. Given the mole fractions $y_{i}$ of all species but one, all of the stoichiometric coefficients $\left\{v_{\mathrm{i}}\right\}$, and the value of $K$, the mole fraction of the remaining single species can be determined $\operatorname{IF}(!)$ the reaction mixture is at equilibrium.

Independent Reactions: Chemical reactions are independent if the stoichiometric equation of any one reaction cannot be obtained by adding and/or subtracting multiples of the stoichiometric equations of the other reactions.

Example: Are the following sets of reactions independent?

Set 1: $A+B \rightarrow C$
Set 2: $\mathrm{A}+\mathrm{B} \rightarrow \mathrm{C}$
$2 \mathrm{~A} \rightarrow \mathrm{~B}$
$2 \mathrm{~A} \rightarrow \mathrm{~B}$
$3 \mathrm{~A} \rightarrow \mathrm{C}$
Independent Species: Species (whether molecular or atomic) are independent if they do not move through the process so as to be always in the same ratio. If two species are independent, the balance equations they provide are independent as well. Molecular species refers to molecules (e.g. $\mathrm{H}_{2}, \mathrm{O}_{2}$, toluene, water...). Atomic species refers to atoms comprising the molecules (e.g. C, H, O, N, S...).

In the below example, which molecular species are independent? Which atomic species are independent?


## Material Balances on Reactive vs Nonreactive Processes

When we earlier considered material balances on nonreactive processes (processes in which no chemical reactions are taking place), we wrote the balance equations in terms of the molecular species flowing through the process. For example, if A and B type molecules were moving through the process, we would write a material balance on A molecules and on B molecules. Possibly, we may also write an overall balance on total number of moles or mass. This approach, referred to as the molecular species balance method, can still be made to work for reactive processes. In the presence of reactions, however, there would be generation and consumption terms in the molecular balances for the reacting species that would also need to be determined.

We will study two ways of solving material balances for reactive processes. The first, which is often the simplest to implement, is the method of atomic species balances. In this approach, balances are written on atomic species moving through the process, NOT on molecular species. Since atoms are neither created nor destroyed, the balance equations are simple:

Input of atom $i$ - output of atom $i=$ accumulation of atom $i$
Note that there are no generation or consumption terms in equation 8 .

The second approach uses extents of reaction to express flowrates of each reactive species according to the stoichiometries of the reactions taking place. In this approach, the extents of reaction are solved for as part of the solution process. Therefore, this approach may be advantageous if, as part of the solution, one wants to also derive the reaction extents.

Which approach one chooses to use does not matter in the sense that both yield the same answers (if no mistakes are made!). However, if the goal is to solely derive flowrates, usually the atomic species balance approach is most direct as it avoids calculating generation or reaction extents as part of the solution. On the other hand, if the extents of reaction are also needed, then the second approach is used.

No matter which method you use, the degree of freedom analysis still applies. It is always the case that the number of unknown variables you intend to determine as part of the solution must equal the number of independent equations that relate the unknown variables. Let's look at an example that illustrates the two material balance approaches mentioned above.

## Example 4.7-1 (Incomplete combustion of methane)

Methane is burned with air in a continuous combustion reactor that is at steady state. The reactions taking place are

$$
\begin{aligned}
& \mathrm{CH}_{4}+3 / 2 \mathrm{O}_{2} \rightarrow \mathrm{CO}+2 \mathrm{H}_{2} \mathrm{O} \\
& \mathrm{CH}_{4}+2 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}
\end{aligned}
$$

The feed to the reactor contains 7.80 mole $\% \mathrm{CH}_{4}, 19.4$ mole $\% \mathrm{O}_{2}$, and 72.8 mole $\% \mathrm{~N}_{2}$. The percentage conversion of methane is $90.0 \%$, and the gas leaving the reactor contains $8 \mathrm{~mol} \mathrm{CO} 2 / \mathrm{mol} \mathrm{CO}$. Carry out a degree of freedom analysis of the process, and calculate the molar composition of the product stream.

CBE2124, Levicky

CBE2124, Levicky

Recycling of reactant: If a process stream is recycled in order to increase the conversion of a reactant, we can define single-pass conversion and overall conversion as follows:

$$
\begin{equation*}
\text { Single-pass conversion }=\frac{\text { reactant input to reactor }- \text { reactant output from reactor }}{\text { reactant input to reactor }} \tag{9}
\end{equation*}
$$

Overall conversion $=\frac{\text { reactant input to process }- \text { reactant output from process }}{\text { reactant input to process }}$
Single-pass conversion gives the fraction of reactant converted on a single pass through the reactor. In contrast, overall conversion gives the fraction of reactant converted by the process, which may involve recycling reactant molecules many times through the reactor in order to increase their conversion.

## Example:



What are the single-pass and overall conversion of the above process?
What considerations might impact the decision to use a process with recycle as opposed to one based on single-pass conversion?

Purge Streams: Purge streams are used to rid a process of an undesirable material or waste. Purge streams are often encountered together with recycle streams, since recycling makes a process particularly susceptible to accumulation of undesired species.

## Combustion Reactions

Combustion: a combustion reaction is the reaction of a fuel with oxygen. Examples of fuels are coal, natural gas (i.e. methane or propane), fuel oil, and gasoline.
These reactions release a lot of energy, and so are widely encountered in the production of electricity and heat. They are also used to burn waste. Combustion of carbon based fuels, such as those listed above, involves mostly $\mathrm{C}, \mathrm{H}$, and S atoms. When the fuel is reacted with oxygen, the carbon is converted to $\mathrm{CO}_{2}$ or CO , the hydrogen to $\mathrm{H}_{2} \mathrm{O}$, and the
sulfur is primarily oxidized to $\mathrm{SO}_{2}$. Formation of CO (carbon monoxide) indicates partial combustion. Complete combustion would realize the fully oxidized species $\mathrm{CO}_{2}$ (carbon dioxide).

$$
\begin{array}{ll}
\mathrm{C}_{3} \mathrm{H}_{8}+5 \mathrm{O}_{2} \rightarrow 3 \mathrm{CO}_{2}+4 \mathrm{H}_{2} \mathrm{O} & \text { (complete combustion of propane) } \\
\mathrm{C}_{3} \mathrm{H}_{8}+7 / 2 \mathrm{O}_{2} \rightarrow 3 \mathrm{CO}+4 \mathrm{H}_{2} \mathrm{O} & \text { (partial combustion of propane) } \\
\mathrm{CS}_{2}+3 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{SO}_{2} & \text { (complete combustion of carbon disulfide) }
\end{array}
$$

Most often the source of oxygen in combustion reactions is air, which has approximately the following molar composition on a dry basis:
$78.03 \% \mathrm{~N}_{2}$
$20.99 \% \mathrm{O}_{2}$
00.94 \% Ar
$00.03 \% \mathrm{CO}_{2}$
00.01 \% other gases

Average molecular weight $=29.0$
In material balance calculations, it is usually acceptable to simplify the dry basis composition of air as $21 \% \mathrm{O}_{2}$ and $79 \% \mathrm{~N}_{2}$ (why?). Note that "composition on a dry basis" refers to mole fractions calculated with exclusion of water, i.e. as if no water vapor were present in the gas. Composition on a wet basis, on the other hand, would include any water vapor that may be present. In this case, the mole fractions of each gas species would depend on the humidity (i.e. water vapor content) of the air.

Combustion reactions are usually run with an excess of oxygen, since the air providing the oxygen is free and since an excess of the oxygen reactant helps drive the combustion reaction forward. Theoretical oxygen is the amount of $\mathrm{O}_{2}$ needed for complete combustion of the fuel, assuming that all carbon is converted to $\mathrm{CO}_{2}$ and all hydrogen to $\mathrm{H}_{2} \mathrm{O}$. Theoretical air is, then, the amount of air that contains the theoretical oxygen. Excess air is the amount by which the air input into the combustion furnace exceeds the theoretical air:

$$
\begin{equation*}
\text { percent excess air }=\frac{\left(\text { moles air }_{\text {fed }}-(\text { moles air })_{\text {theorerical }}\right.}{\left(\text { moles air }_{\text {Itheorereical }}\right.} \times 100 \% \tag{11}
\end{equation*}
$$

## Example 4.8-3 (Combustion of ethane)

Ethane is burned with $50 \%$ excess air. The percentage conversion of the ethane is $90 \%$.
From the ethane that is converted, $25 \%$ reacts to form CO and the rest reacts to form $\mathrm{CO}_{2}$.

What is the molar composition of the stack gas on a dry basis? What is the mole ratio of water to dry stack gas?

