Performing Reactive Mass and Energy Balances

When reactions occur, material balances become more difficult, and energy balances are often more important.How do we handle generation and consumption of molecular species ? What if we don 't even *know* the stoichiometry ?

- Calculate quantities necessary for reaction / chemistry benchmarking
  # Calculate the limiting reactant, excess reactants, percent excess, and fractional conversion in a given reaction
  # Define and calculate the yield and selectivity for reaction networks
  # Define and calculate the "atom economy" of a process proposal
- Perform reactive mass balances(degree - of - freedom plus calculations)
  # Write extent - of - reaction expressions from stoichiometry
  # Utilize equilibrium expressions to determine equilibrium compositions and extents of reaction
  # Perform atomic species balances

What effect do reactions have on energy balances ? How do we handle fictitious paths of material that is generated or consumed ?

- Perform reactive energy balances
  # Explain how chemical reactions are handled in the General Energy Balance
  # Use Hess 's Law to determine the heat of reaction of given reactions

Reactive Systems Review (?)

So far, no reaction. How do things change now?

Stoichiometric relations become important, for one!

A->B(1 mole of B made from 1 mole of A)
2B->C(it takes 2 moles of B to make one mole of C)
How many moles of A are necessary to make a mole of C (if no B is fed to the reactor and the reaction goes to completion)

Generation, Consumption terms NOT equal to zero

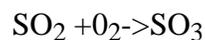This makes mass balances more complicated. Need to review/introduce some ideas about reactions.

Stoichiometry

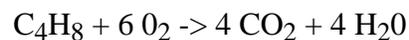Represents molar participation in a reaction.

How do you do it?

Like a mini mass balance! (Can only balance atomic species NOT total moles or moles (mass) of compounds!)
Left hand side is inlet, right hand side is outlet.

$$SO_2 + O_2 -> SO_3$$

Left side 1 S = Right side 1 S (OK so far)
Left side (2 O + 2 O), Right side 3 O (NOT BALANCED!)

$$C_4H_8 + 6\ O_2 -> 4\ CO_2 + 4\ H_2O$$

Left side 4 C = Right side 4 C (OK so far)
Left side 8 H = Right side 8 H (OK so far)
Left side 12 O = Right side (8 O + 4 O)(BALANCED!)

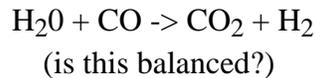So, it takes 6 moles of oxygen (diatomic) to completely combust 1 mole of butane!

Another way to look at it is using a ratio.

6 mole O_2 consumed/1 mole C_4H_8 consumed

OR 4 mole H_2O generated/6 Mole O_2 consumed

Reactions and Stoichiometry

So, if we had the following reaction:

$$H_2O + CO \rightarrow CO_2 + H_2$$
(is this balanced?)

and we tried to react 28g of CO completely, How many grams of H_2O would we need? (Recall that $MW_{CO}=28$ g/mol; $MW_{H_2O}=18$ g/mol; $MW_{CO_2}=44$ g/mol; $MW_{H_2}= 2$ g/mol)

How many grams of total products would we get?

What happens if we only have 9g of H_2O?

DEFINITION

> *The **limiting reactant (reagent)** is the one which would run out if we tried to have the reaction proceed to completion. The limiting reactant is present in LESS THAN STOICHIOMETRIC PROPORTIONS!*

DEFINITION

> *The **excess reactants (reagents)** are the ones which are left over.*

How do we quantify the excess?

DEFINITION

> *The **fractional excess** is the ratio of the amount by which the feed exceeds stoichiometric requirements (in moles) divided by the stoichiometric requirement (in moles).*

It is given (mathematically) by:

$XS = (n_{A_{real}} - n_{A_{stoichiometric}}) / n_{A_{stoichiometric}}$

Where does $n_{A_{stoichiometric}}$ come from? [cheat]

OUTCOMES:

> Calculate the limiting reactant, excess reactants, percent excess, and fractional conversion in a given reaction

DEFINITION

> *The **conversion** is the ratio of the moles that react to the moles that are fed to a reactor. ($f_{CO}=25$ mol/mol in our example)*

Multiple Reactions

It is often the case that additional (unwanted) reactions may occur in our reactor that either divert reactants to something else or use our product after it is made.

A -> B (desired product)
2B -> C
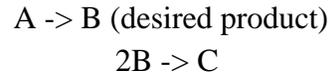
Because there is now multiple possible outcomes, we need some terminology to describe the products we get. In other words, if the world were perfect, we would always only have the reactions we *want* happening. But the world is not perfect (that's why we ChE's have to strive to get it closer!), so we must quantify *how close* to perfect we can get!

DEFINITION

> The **yield** of a reaction is the ratio of the desired product formed (in moles) to the total amount that could have been made (if conversion of limiting reactant was 100% and no side reactions occurred).

DEFINITION

> The **selectivity** of a reaction is the ratio of the desired product formed (in moles) to the undesired product formed (in moles).

OUTCOMES:

> Define and calculate the yield and selectivity for reaction networks

Atom Economy

As should have been clear from our earlier discussion of product design, we can think of product design as taking a "step back" from a process and analyzing the bigger picture. Previously, we saw this as defining our product for what it *does* rather than for the specific material that it *is*, so that we might step out of the box and perhaps choose a better material for the job.

In the context of designing/choosing reaction networks, another characteristic of product engineering is to step back and ask ourselves what is the best possible scenario, given the process being considered. Instead of focusing on what the current reaction network for making our material is, we focus on what the *material itself* is, and consider multiple networks that might get us there. In this way, we might first maximize our "best case" before we actually do the process engineering necessary to attempt to get as close as we can to that ideal.

DEFINITION

> The **atom economy** of a process is the theoretical maximum percentage of our feedstock's atoms that could become product if both our yield and our conversion were 100%.
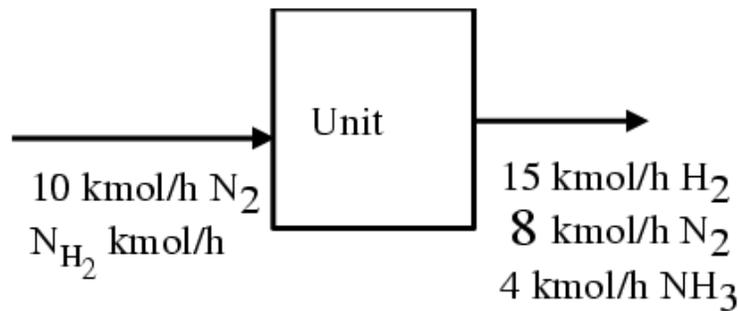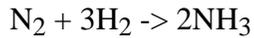
OUTCOMES:

Define and calculate the "atom economy" of a process proposal

Reactive Processes

Performing material balances on reactive systems is slightly more complex than for non-reactive systems

$N_2 + 3H_2 \rightarrow 2NH_3$

While we can still do a balance on total mass, this is often not particularly useful (as we would like to know component compositions). What differs now is that a balance on total moles will *not* work (in general).

While the book notes three types of reactive balances, there are really only two types that are clearly distinct: a molecular species/extent of reaction balance; and a balance on atomic species.

For simplicity, this course will only focus on reactive processes that are open systems which are run at steady state. This yields a simplified balance equation of:

$$0 = \dot{M}_I - \dot{M}_O + G - C$$

Molecular/Extent of Reaction Balances

In this balance method we will examine each molecular species individually, and will typically rearrange our balance equation to be in the form:

$$\dot{M}_O = \dot{M}_I + G - C$$

The G and C terms will then come directly from a combination of stoichiometry and the concept of the *extent of reaction*.

DEFINITION

> The **extent of reaction** (ξ) is a method of quantifying how many "times" a reaction has occurred. It has units of moles/time and numerically, it is chosen such that the stoichiometric coefficient times ξ is equal to the quantity of species reacted.

Using the above definition of the extent of reaction, it is a simple matter to write G and C in terms of this quantity simply using stoichiometry.

Let's write the expressions for our figure above:

$$\dot{M}_{N_{2_O}} = 8kmol/h = \dot{M}_{N_{2_I}} + G_{N_2} - C_{N_2} = 10kmol/h + 0 - 1\xi$$

$$\dot{M}_{H_{2_O}} = 15kmol/h = \dot{M}_{H_{2_I}} + G_{H_2} - C_{H_2} = \dot{M}_{H_{2_I}} + 0 - 3\xi$$

$$\dot{M}_{NH_{3_O}} = 4kmol/h = \dot{M}_{NH_{3_I}} + G_{NH_3} - C_{NH_3} = 0 + 2\xi - 0$$

NOTE:

Typically "reactants" have G=0, while "products" have a zero initial concentration and have C=0. This obviously becomes more complex when multiple reactions take place.

Using the extent of reaction method for systems with multiple reactions involves including a new value of ξ for each reaction, and then calculating C and G as the sum of applicable ξ's.

EXAMPLE

Consider the reaction network:

A -> B

2B -> C
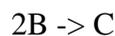
If we assign ξ_1 to the first reaction and ξ_2 to the second, we get expressions that look like:

$$\dot{M}_{A_O} = \dot{M}_{A_I} + G_A - C_A = \dot{M}_{A_I} + 0 - \xi_1$$

$$\dot{M}_{B_O} = \dot{M}_{B_I} + G_B - C_B = \dot{M}_{B_I} + \xi_1 - 2\xi_2$$

$$\dot{M}_{C_O} = \dot{M}_{C_I} + G_C - C_C = \dot{M}_{C_I} + \xi_2 - 0$$

OUTCOME

Write extent of reaction expressions from stoichiometry

Due to the introduction of the new variables ξ our degrees of freedom analysis must change:

Molecular Balance Degrees of Freedom

- Number of unknowns
- + (yes, plus!) the number of independent reactions
- - number of independent species
- - other equations (physical constraints, process specifications, etc.)

NOTE:

Equations are not independent if they can be obtained through algebraic manipulation of the other (already deemed independent) equations! (This includes multiplying an equation by a constant factor.)

Methane and oxygen react in the presence of a catalyst to form formaldehyde. In a parallel reaction, methane is oxidized to carbon dioxide and water:

$$CH_4 + O_2 \rightarrow HCHO + H_2O$$
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
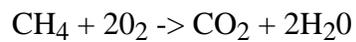
The feed to the reactor contains equimolar amounts of methane and oxygen. Assume a basis of 100 mol feed/s.

Draw and label a flowchart. Derive expressions for the product stream components in terms of the extents of reaction, ξ_1 and ξ_2.

The fractional conversion of methane is 0.900 and the fractional yield of formaldehyde is 0.855. Calculate the molar composition of the reactor output stream and the selectivity of the formaldehyde production relative to carbon dioxide production.

Equilibrium

Reactions don't proceed instantly, in fact, predicting the rate at which a reaction occurs is very important to ChEs.

Furthermore, reactions do not necessarily happen independently, in fact, often the reverse of the reaction we are interested in also happens!

DEFINITION

Chemical equilibrium *is reached when the rates of the forward and reverse reactions are equal to each other (i.e., compositions no longer change with time!)*

While we will not *calculate* rates in this course, we need to know what affects them (because this will affect the equilibrium!). Things that we must consider that effect reaction rates (and hence equilibrium) are:

- Temperature
- concentrations (pressure)

So how do we do equilibrium calculations? I'd wager you have already done them in a chemistry class a long time ago (in a galaxy far far away...) when dealing with acid-base chemistry.

Despite the fact that an equilibrium reaction can occur both forward and backward, we simply define **one** extent of reaction to that expression (forward and backward are not independent of each other, after all).

You then plug either known equilibrium concentrations or extent of reaction expressions (reactive material balances based on extents) directly into the equilibrium expression.

NOTE

The equilibrium expression will serve as one additional equation in your degrees of freedom analysis (you could call it a process specification or a physical law).

EXAMPLE

Consider the reaction of methane with oxygen:

$2CH_4 + O_2 \leftrightarrow 2CH_3OH$

We are given that, at equilibrium, the compositions of the components satisfy:

$$K(T) = \frac{y^2_{CH_3OH}}{y^2_{CH_4} y_{O_2}}$$

If you are given the feed compositions (n_{CH_4}, n_{O_2}, and n_{CH_3OH}), and the equilibrium constant, $K(T)$, how do you determine the equilibrium compositions?
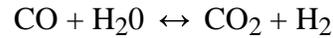
Utilize equilibrium expressions to determine equilibrium compositions and extents of reaction

Try an example yourselves:

At low to moderate pressures, the equilibrium state of the water-gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

is approximately described by the relation:

$$K(T) = 0.0247e^{[4020/T(K)]} = \frac{y_{H_2}y_{CO_2}}{y_{CO}y_{H_2O}}$$

where T is the reactor temperature, K, is the reaction equilibrium constant, and y, is the mole fraction of the species in the reactor at equilibrium.

The feed to a batch shift reactor contains 20.0 mole% CO, 10.0% CO_2, 40.0% water, and the balance inert gas. The reactor is maintained at T 1123 K.

Assume a basis of 1 mol/hr feed and draw and label a flowchart. Calculate the total moles of gas in the reactor at equilibrium and then the equilibrium mole fraction of hydrogen in the product.

Atomic Balances

In certain problems an extent of reaction balance method is simply not practical (or even possible). This can happen if the number of total reactions (and therefore necessary extent variables) is large, or if we don't even know exactly what reactions take place (for example, when burning coal or some other complex material).

In this case, there is another technique which proves to be quite simple for solving reactive balances.

DEFINITION

> *An **atomic** balance is one in which we balance each individual atomic species rather than each independent molecular species (i.e., instead of balancing water we note that it contains two H's and one O, and balance those).*

How does our differential material balance simplify in this case?! Note that performing an atomic species balance is much like balancing a stoichiometric expression.

IMPORTANT:

> *Both reactive balance methods should **always** give you the same answer! We simply learn two because sometimes one is easier than the other!*

Obviously our degrees of freedom analysis will change relative to the extent of reaction balances:

Atomic Balance Degrees of Freedom

- Number of unknowns
- - number of independent atomic species
- - number of independent NONREACTIVE molecular species
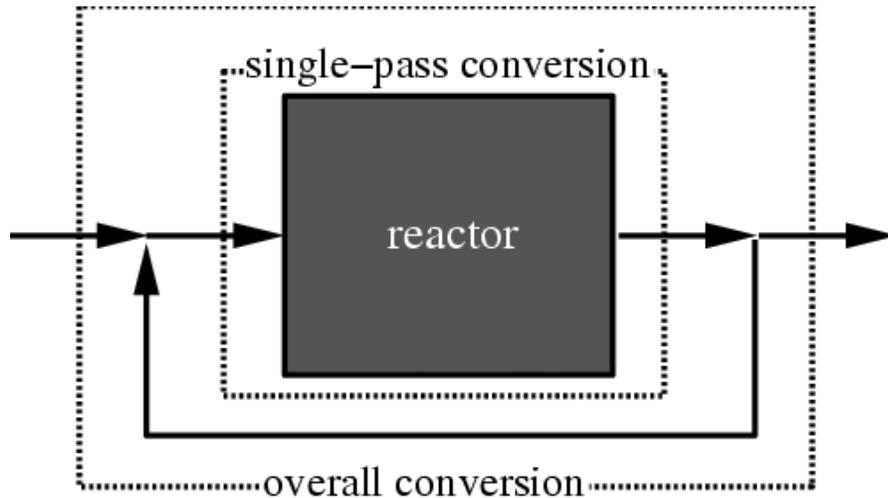- - other equations (physical constraints, process specifications, etc.)

OUTCOMES:

> Perform atomic species balances

TEST YOURSELF

> *Re-do the yield example and make certain an atomic balance gives the same answer*

Recycle Revisited

We need to revisit our definition of conversion now that we have looked at reactive process, as this could lead to a degree of ambiguity.

DEFINITION

*The **overall conversion** ignores the fact that recycle is occurring and is calculated purely on the basis of the difference between the **process** inputs and outputs (i.e., "outside" the reactor/ recycle).*

DEFINITION

*The **single-pass conversion** is based on the difference between the **reactor** input and output (i.e. "inside" the reactor/recycle).*
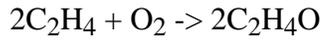
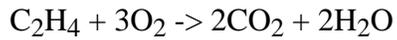**OUTCOMES:**

Perform reactive balances with recycle

TEST YOURSELF

Let's try one together...

Reactive Recycle Example

Ethylene oxide is produced by burning ehtylene

$$2C_2H_4 + O_2 \rightarrow 2C_2H_4O$$

an undesired side reaction is the complete combustion of ethylene

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

The feed to the reactor (not the process!) contains 3 moles of ethylene per mole of oxygen. The single-pass conversion of ethylene is 20% and for every 100 moles of ethylene consumed in the reactor 90 moles of ethylene oxide are produced. A complex separation system is used so that ethylene and oxygen may be recycled to the reactor, while carbon dioxide and water are discarded and ethylene oxide is packaged and sold.

Assume a 100 mol/hr feed rate of ethylene to the *reactor*.

ATOMIC DEGREES OF FREEDOM ANALYSIS

How many Unknowns are there?
How many different (reactive)
Atomic Species are there?
How many Process Specifications are we given?
How many Physical Constraints are there?
The total number of Degrees of Freedom is

Reactive Energy Balances

Our previous methods for solving energy balances equations is no longer strictly valid for reactive systems. In particular, the issue with our technique lies in our previous statement regarding choosing reference states. For non-reactive systems, we can **arbitrarily** choose a reference state *for each species*, this is simply not the case for reactive systems. Let's take a look...

Using our old method, we could simply choose CH_4 and O_2's reference points to be at 100C and 1 atm, while we choose CO_2 and H_2O's reference points to be at 250C and 1 atm. This would lead us to conclude that ΔH was zero, which we know from experience is clearly not true! (Can you prove this to yourself?)

In order to solve this dilemma, we can choose one of two (equivalent) methods for solving reactive systems (much like we chose one of two methods to do reactive **mass balances**):

- Heat of Formation Method
- Heat of Reaction Method

Heat of Formation Method

In the heat of formation method we change our previous procedure in two very significant (but rather simple) ways:

- Reference states are chose as **elemental species** at standard temperature and pressure (STP; 298K and 1atm). This is somewhat similar to doing an atomic material balance for reactive systems.
- First step in calculating $\hat{H}$ is to **form** the molecular species from their elemental species (the reference states).

Following that first step (once our molecular species is formed at STP), we then simply follow our fictitious path, stepwise, summing $\hat{H}$ for each step as we go (changes in T, P, and phase).

An example $\hat{H}$, might therefore include (with first formation and them a T change and then a P change):

$$\hat{H}_{CH_4} = \Delta^o_{f\,CH_4} + \int_{298K}^{373K} c_{P\,CH_4} dT + \hat{V} \Delta P$$

Heat of Reaction Method

In the heat of reaction method we now follow a trend more analogous to the extent of reaction method of reactive material balances. Again, our previous (nonreactive) energy balance procedure changes in three very significant (but rather simple) ways:

- We must first look up the heat of reaction *for each reaction taking place* and note under what conditions the reaction takes place for the tabulated data (usually STP; 298K and 1atm). (NOTE that this does **not** mean that all reactions listed can actually *happen* at STP, simply that if they **did** happen at STP that this would be their heat of reaction).
- Use the T, P, and state of aggregation from the heat of reaction formula as the reference state for each species.
- Calculate $\hat{H}$'s following our fictitious path, stepwise, summing $\hat{H}$ for each step as we go (changes in T, P, and phase), but **now we add the extent of reaction times the heat of reaction to the total Δ H expression** (or add multiple extents of reaction of heats of reaction if multiple reactions take place).

An example $\hat{H}$, and ΔH calculation might therefore look like (for the example above):

$$\hat{H}_{CH_4} = \int_{298K}^{373K} c_{P\,CH_4} dT + \hat{V} \Delta P$$

$$\Delta H = \hat{H}_{CO_2} \dot{n}_{CO_2} + \hat{H}_{H_2O} \dot{n}_{H_2O} - (\hat{H}_{CH_4} \dot{n}_{CH_4} + \hat{H}_{O_2} \dot{n}_{O_2}) + \dot{\xi} \Delta \hat{H}^o_{rxn}$$

OUTCOME:

Explain how chemical reactions are handled in the General Energy Balance

Hess's Law

It should come as no surprise that you will obtain the same answer to a reactive energy balance problem regardless of whether you chose to do a *heat of formation* or a *heat of reaction* balance.

Therefore, your choice of method will often be dictated by convenience, much like your choice of atomic versus extent methods for reactive mass balances. In fact, some of the same reasoning goes into both decisions (an extent of reaction energy balance is usually only performed when you have done an extent of reaction mass balance, for example, since you already know the extent values).

Setting these two energy balance methods equal to each other yields...
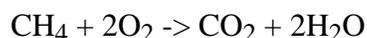
DEFINITION

> **Hess's Law** *directly relates the heat of reaction to the heats of formation of the reactants and products.*

A mathematical expression for Hess's Law is

$$\Delta \hat{H}^o_{rxn} = \Sigma P_i \Delta \hat{H}^o_f - \Sigma R_i \Delta \hat{H}^o_f$$

where P_i are the stoichiometric coefficients for the products being summed and R_i are the coefficients of the reactants.

Recalling again the reaction

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Here, the heat of reaction may be calculated as:

$$\Delta \hat{H}^o_{rxn} = (2 \Delta \hat{H}^o_{f\,H_2O} + \Delta \hat{H}^o_{f\,CO_2}) - (\Delta \hat{H}^o_{f\,CH_4} + 2 \Delta \hat{H}^o_{f\,O_2})$$

NOTE

> This method is particularly useful when we have novel reactions occurring whereby heats of reaction may be difficult or impossible to find in tables. Also, recall that $\Delta \hat{H}^o_{f\,O_2} = 0$.

OUTCOME:

> Use Hess's Law to determine the heat of reaction of given reactions