UCH 1201 Principles of Chemical Engineering

Stoichiometry

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June 3, 2021

Contents

Physico-Chemical Calculations - Energy - Equivalent mass - Concept of material and Energy balance.

Objectives

- To give an overview of mass and energy balance calculations.
- To understand the role of various process streams in a chemical industry.
- To give an overview of various terminologies about conversions and yield of chemical reactions.

Material / Energy Balance Calculations

The problems encountered in process calculations are combination of the following categories:

- Material balance
- Energy balance

- Without chemical reaction
- With chemical reaction

- Steady state
- Unsteady state

Material / Energy Balance Calculations (contd..)

- Steady State Processes:
  - Of course, this is the desired mode of operation for a majority of the processes in use today.
  - It optimizes production and minimizes costs for large commodity products when you have a stable feedstock.
- Unsteady Processes—these are extremely important in the following situations:
  - Batch processes.
  - Start-up/shut down of continuous systems.
  - Continuous processes with changes in operating conditions or unplanned fluctuations due to control problems.

Mass Balance

$$\boxed{\text{input} + \text{generation} - \text{output} - \text{consumption} = \text{accumulation}}$$

where,

(i) input is the material entering through the system. This will include feed and makeup streams.

(ii) generation is the material produced within the system, such as the reaction products in a reactor;

(iii) output is the material that leaves through the system boundaries. These will typically be the product streams of the process.

(iv) consumption is the material consumed within the system, such as the reactants in a reactor;

(v) accumulation is the amount of material that builds up within the system.

'Energy balance' also has the same form of equation.

Mass Balance (contd..)

In a steady-state continuous process, the accumulation is zero, which leads to a more simple mass balance equation:

$$\text{input} + \text{generation} = \text{output} + \text{consumption}$$

Further, in the case of systems with no reaction, where mass is neither generated nor consumed, the result is even simpler:

$$\text{input} = \text{output}$$

In a unsteady-state process, the accumulation is **nonzero**. Here, conditions are changing with time.

Mass Balance (contd..)

Atom Balance:
Since atom can NOT be created or destroyed, for any process, a number of atoms entering the process must be equal to that leaving the process.

input (of some species of atom) = output (of the same species of atom)

The chemical reactions that take place in a complicated process can be solved by atom balances without knowing the actual chemical reactions taking place in that.

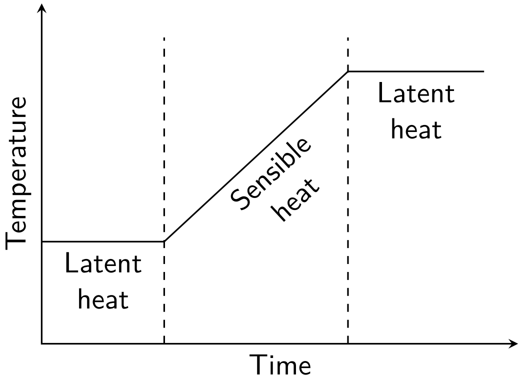
Converting Mole Fraction to Mass Fraction

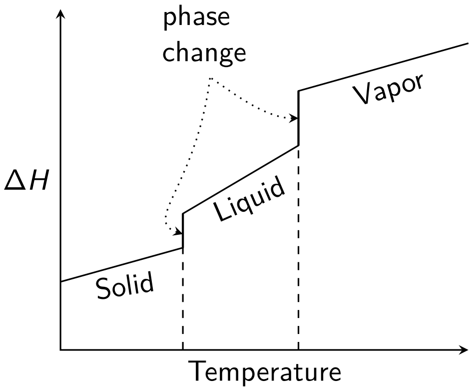
Air contains 21 mol% oxygen (O_2), and 79 mol% nitrogen (N_2). Express the same in mass%.

Sensible and Latent Heats

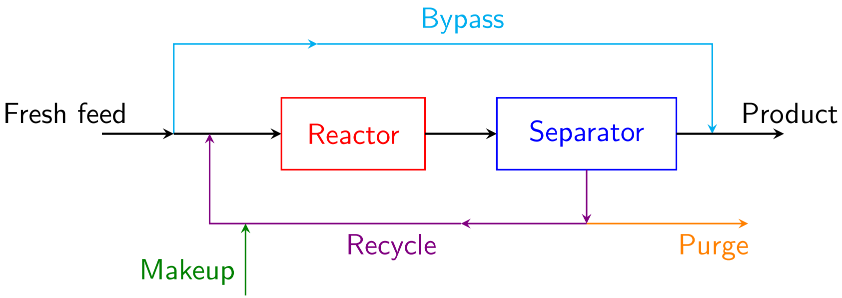
There are two types of heat:

- Sensible heat: heat transfer arising from the change in temperature, while the state of a substance does NOT change.
- Latent heat: heat transfer when the state of a substance changes, while the temperature remains constant.


Temperature
Latent heat
Sensible heat
Latent heat
Time


phase
change
Vapor
Liquid
ΔH
Solid
Temperature

Process Streams



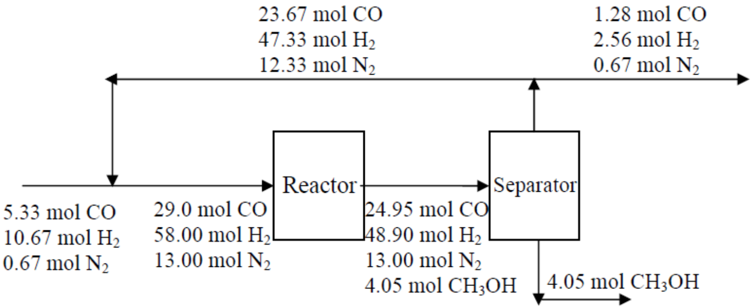
Process Streams (contd..)

There are various streams entering / leaving a process, namely: feed, product, recycle, bypass, purge, makeup, as shown in previous page.

- **Recycle** is the operation or a process step whereby a part or fraction of the products from the reactor is returned and mixed with the incoming fresh feed to the reactor.
  In a reactive process, there is generally some unreacted feed material found in the product mixture. In order to reduce cost and increase the overall conversion, the unreacted material is often separated and reused in a recycle loop. 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.

Process Streams (contd..)

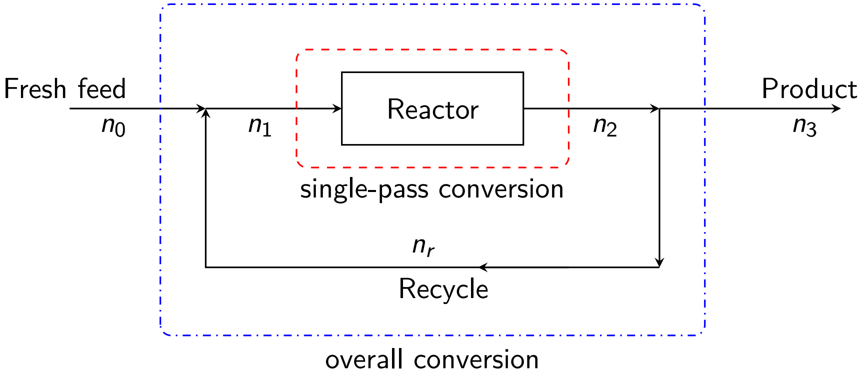
- **Bypass Stream**—one that skips one or more stages of the process and goes directly to another downstream stage. Bypass is useful, for example, for decreasing the extent of conversion of input materials or for providing improved control over stream temperatures.
- **Purge Stream**—a stream bled off to remove an accumulation of inerts or unwanted material that might otherwise buildup in the recycle stream.
  Purge streams are often encountered together with recycle streams, since recycling makes a process particularly susceptible to accumulation of undesired species. This purge fraction is generally only a few percent of the recycle flow rate.



$$CO + 2\,H_2 \rightarrow CH_3OH$$

Methanol is made by reacting carbon dioxide and hydrogen. The fresh feed to the process contains 0.67 mol of N_2, which is an inert material because it does not react. Hence, it should be purged or bled from the recycle stream. If feed to the process does not contain N_2, there is no need for purge.

Conversion



Fresh feed
n_0
n_1
Reactor
n_2
Product
n_3
single-pass conversion
n_r
Recycle
overall conversion

Conversion (contd..)

$$\text{Overall conversion} = \frac{\begin{pmatrix}\text{reactant input}\\ \text{to process}\end{pmatrix} - \begin{pmatrix}\text{reactant output}\\ \text{from process}\end{pmatrix}}{\text{reactant input to process}}$$

$$= \frac{n_0 - n_3}{n_0}$$

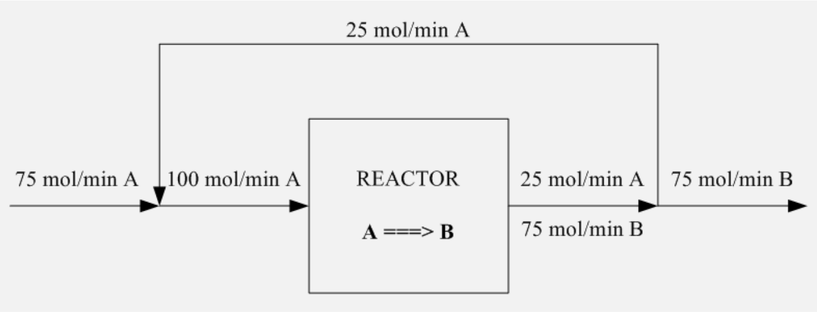
$$\text{Single-pass conversion} = \frac{\begin{pmatrix}\text{reactant input}\\ \text{to reactor}\end{pmatrix} - \begin{pmatrix}\text{reactant output}\\ \text{from reactor}\end{pmatrix}}{\text{reactant input to reactor}}$$

$$= \frac{n_1 - n_2}{n_1}$$

Conversion calculation is based on the limiting reactant. Single-pass conversion is also called as once-through conversion, or conversion per pass. Because of the recycle, the overall conversion—which is based on the fresh feed, will be higher than the conversion per pass—which is based on the mixed feed to the reactor.

$$\text{single pass conversion of CO} = \frac{29.00 \text{ mol CO} - 24.95 \text{ mol CO}}{29.00 \text{ mol CO}} = 14\%$$

$$\text{Overall conversion of CO} = \frac{10.67 \text{ mol CO} - 1.28 \text{ mol CO}}{10.67 \text{ mol CO}} = 88\%$$



Single pass conversion = 75%
Overall conversion = 100%

Limiting and Excess Reactants

- **Limiting and Excess Reactants**: The reactant that is completely consumed when a reaction is run to completion is known as the limiting reactant. The other reactants are termed as excess reactants.
  - To find the limiting reactant: First, balance the stoichiometric equation. Then, take the ratio of the reactant feed rate to their stoichiometric coefficients. The limiting reactant is the reactant that has the lowest ratio.
- **Fractional Excess**: The fractional excess of a reactant is the ratio of excess to the stoichiometric requirement.

$$\text{Fractional excess of } A = \frac{n_A \text{ in feed} - n_A \text{ stoichiometric}}{n_A \text{ stoichiometric}} \quad (1)$$

'n_A' is the number of moles of A—the reactant. 'n_A stoichiometric' is the amount of A needed, to react completely with the limiting reactant.

Example:

Two moles of nitrogen (N_2) react with four moles of hydrogen (H_2) to form ammonia (NH_3). The reaction is:

$$\mathrm{N_2 + 3H_2 \rightarrow 2NH_3}$$

The ratio of reactant amount to their stoichiometric coefficients:

$$\mathrm{N_2} = \frac{2}{1} = 2 \qquad \mathrm{H_2} = \frac{4}{3} = 1.33$$

The ratio for H_2 is the least; therefore, H_2 is the limiting reactant. Stoichiometric N_2 requirement: 3 mole of H_2 demands 1 mole of N_2. Therefore, for 4 mole of H_2, the requirement of $N_2 = 4/3$ mole.

$$\%\text{excess of } \mathrm{N_2} = \frac{2 - \frac{4}{3}}{\frac{4}{3}} \times 100 = 50\%$$

Yield and Selectivity

- Yield: The actual amount of products formed relative to what is actually expected from the reaction.

$$\% \text{ Yield} = \frac{\text{actual amount of product formed}}{\text{theoretical amount of product expected}} \times 100$$

- Selectivity: The ratio of the moles of the desired product produced to the moles of undesired product (by-product).

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

Yield and Selectivity (contd..)

For example, methanol (CH_3OH) can be converted into ethylene (C_2H_4) and propylene (C_3H_6) by the reactions:

$$2\,CH_3OH \rightarrow C_2H_4 + 2\,H_2O$$
$$3\,CH_3OH \rightarrow C_3H_6 + 3\,H_2O$$

If the desired product is ethylene, then the selectivity is computed as:

$$\text{Selectivity} = \frac{\text{moles of ethylene formed}}{\text{moles of propylene formed}}$$

Quiz

1. Write down the mass balance equation for unsteady non-reactive systems.
2. Convert the composition of air from mole basis to mass basis. On mole basis, air is: 21% O_2, and 79% N_2. Molecular weights: $O_2 = 32$; $N_2 = 28$.