

Material Balances

“Solving the derived equations is usually a matter of simple algebra, but deriving them from a description of a process and a collection of process data may present considerable difficulties. It may not be at all obvious from the problem statement just what is known and what is required, for example, and it is not uncommon to find students (particularly on quizzes) scratching their heads and staring vacantly for an hour at a problem that should take five minutes to solve completely.” (Felder & Rousseau)

“Engineering is solving story problems where you often have to make up the story.”

“Bookkeeping is just arithmetic and definitions, but it needs to be done correctly.”

First define your system.

Transient

The values of process variables are changing with time.

Steady State

The values of process variables do not change with time but may change with position. (What EE's call a DC steady state)

Batch (closed)

Throw stuff in. Wait. Pull products out.

Semibatch

Neither batch nor continuous.

Continuous (open)

Continually throw stuff in and pull stuff out.

The General Balance Equation

All entities which can enter or exit a system are subject to the general balance equation.

$$\text{Input} + \text{Generation} = \text{Output} + \text{Consumption} + \text{Accumulation}$$

For conserved quantities (energy, mass, atoms) the consumption and generation terms are zero

For steady-state systems the accumulation is zero.

Differential Balances

All terms in the balance are rate terms *e.g.*, mol/s, gal/hr, pg/yr.

Usually used for continuous processes.

Integral Balances

All terms in the balance are amounts *e.g.*, mol, gal, pg.

Usually used for batch processes.

Definitions

PFD

Process Flow Diagram or flowsheet. A schematic drawing of the mixers, dividers, separators and reactors used in the process.

Recycle

Part of a product stream is returned to the feed of a process.

Bypass

Part of the feed is routed around a process and mixed with the product.

Purge

A stream used to prevent buildup of trace components in a recycle loop.

Tie Components

A component of the feed which is unchanged by a process. Often useful for calculations but never necessary.

Overall Balance

Treating a PFD as a black box with only inputs and outputs.

One Useful Solution Technique for Mass Balance Problems

1. Draw a flowchart and fill in all given variable values.
2. Choose a basis of calculation (usually an amount or flow rate of one of the process streams).
3. Label unknown stream variables on the chart. Use a consistent system of labeling.
4. Convert stream volumes or volumetric flow rates to mass or molar flow rates.
5. Convert mixed mass and mole units to either all mass or all mole units.
6. Write material balance equations.
7. Write other problem constraints as equations.
8. Do a Degree-of-Freedom analysis. Count the number of unknowns and the number of independent equations. Are they equal? What did you forget?
9. Solve the equations.
10. Convert the answers to the desired units.

Speed tips:

1. Don't solve for everything.
2. Write equations in order of number of unknowns from fewest to most.
3. Try overall balances first.
4. Check out tie components.
5. Remember mole fractions or mass fractions add up to 1.
6. Usually, solving a recycle loop requires a complete set of equations around the loop.

Chemical Reactors

Reactants \rightarrow Products



ν_i – stoichiometric coefficient for component i .

(ν_i is positive for products and negative for reactants)

In a differential balance, if \dot{n}_i is the rate of *production* of species i

$$\frac{\dot{n}_A}{\nu_A} = \frac{\dot{n}_B}{\nu_B} = \frac{\dot{n}_P}{\nu_P} = \frac{\dot{n}_Q}{\nu_Q} = \dot{\xi}$$

$\dot{\xi}$ is the *extent of reaction* (a rate *e.g.*, mol/s)

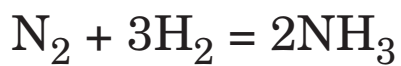
In an integral balance, if n_i is the *amount* of species i *produced*

$$\frac{n_A}{\nu_A} = \frac{n_B}{\nu_B} = \frac{n_P}{\nu_P} = \frac{n_Q}{\nu_Q} = \xi$$

ξ is the *extent of reaction* (an amount *e.g.*, mol)

The advantage is that ξ does not depend on the reactant chosen or the way the equation is written.

Example (differential balance)



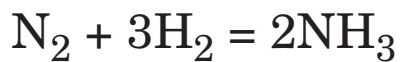
$$\text{if } \dot{n}_{\text{NH}_3} = 2 \text{ mol/s}$$

$$\dot{n}_{\text{N}_2} = -1 \text{ mol/s}$$

$$\dot{n}_{\text{H}_2} = -3 \text{ mol/s}$$

$$\dot{\xi} = 1 \text{ mol/s}$$

Example (integral balance)



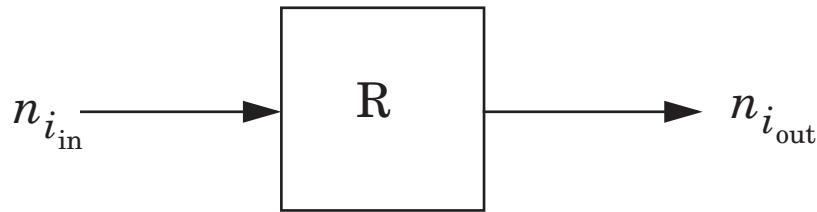
$$\text{if } n_{\text{NH}_3} = 6 \text{ mol}$$

$$n_{\text{N}_2} = -3 \text{ mol}$$

$$n_{\text{H}_2} = -9 \text{ mol}$$

$$\xi = 3 \text{ mol}$$

Reactor Mass Balance Equations



Differential Balance

$$\dot{n}_{i_{\text{out}}} = \dot{n}_{i_{\text{in}}} + v_i \dot{\xi}$$

$$\dot{n}_{\text{out}} = \dot{n}_{\text{in}} + v \dot{\xi}$$

$$\text{where } \dot{n}_{\text{in}} = \sum \dot{n}_{i_{\text{in}}}, \dot{n}_{\text{out}} = \sum \dot{n}_{i_{\text{out}}}, \text{ and } v = \sum v_i$$

Integral Balance

$$n_{i_{\text{final}}} = n_{i_{\text{initial}}} + v_i \xi$$

$$n_{\text{final}} = n_{\text{initial}} + v \xi$$

$$\text{where } n_{\text{initial}} = \sum n_{i_{\text{initial}}}, n_{\text{final}} = \sum n_{i_{\text{final}}}, \text{ and } v = \sum v_i$$

Remember

v_i — positive for product

v_i — negative for reactant

v_i — 0 for inert

e.g.



$$\nu_{\text{O}_2} = -2$$

$$\nu_{\text{C}} = -4$$

$$\nu_{\text{CO}} = 4$$

$$\nu_{\text{N}_2} = -8 + 8 = 0$$

$$\nu = 8 + 4 - 8 - 2 - 4 = -2$$

Fractional Conversion (of Reactant k)

Differential Balance

$$\begin{aligned}f_k &= \frac{\dot{n}_{k_{in}} - \dot{n}_{k_{out}}}{\dot{n}_{k_{in}}} \\&= \frac{-v_k \dot{\xi}}{\dot{n}_{k_{in}}} \\ \Rightarrow \dot{\xi} &= \frac{\dot{n}_{k_{in}} f_k}{-v_k}\end{aligned}$$

Integral Balance

$$\begin{aligned}f_k &= \frac{n_{k_{\text{initial}}} - n_{k_{\text{final}}}}{n_{k_{\text{initial}}}} \\&= \frac{-v_k \xi}{n_{k_{\text{initial}}}} \\ \Rightarrow \xi &= \frac{n_{k_{\text{initial}}} f_k}{-v_k}\end{aligned}$$

Limiting Reactant



If we had 100% conversion of A

$$\xi = \frac{\dot{n}_{A_{\text{in}}}}{-\nu_A} \text{ or } \xi = \frac{n_{A_{\text{initial}}}}{-\nu_A}$$

If we had 100% conversion of B

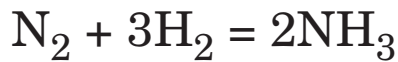
$$\xi = \frac{\dot{n}_{B_{\text{in}}}}{-\nu_B} \text{ or } \xi = \frac{n_{B_{\text{initial}}}}{-\nu_B}$$

Reactant yielding smallest value for ξ or ξ is the *limiting reactant*. All other reactants are *excess reactants*. The *fractional excess* is the fraction in excess of stoichiometric.

$$\text{frac. xs} = \frac{n_{i_{\text{feed}}} - n_{i_{\text{stoic}}}}{n_{i_{\text{stoic}}}}$$

Important note: These numbers are calculated regardless of the actual extent of reaction or fractional conversion in the process.

e.g.



If

$$\dot{n}_{\text{N}_{2in}} = 100 \text{ mol/s and } \dot{n}_{\text{H}_{2in}} = 200 \text{ mol/s}$$

then

$$\frac{200}{3} < \frac{100}{1}$$

and H_2 is the limiting reactant.

Also

$$\dot{\xi} = \frac{200}{3}$$

for 100% conversion of H_2 . And

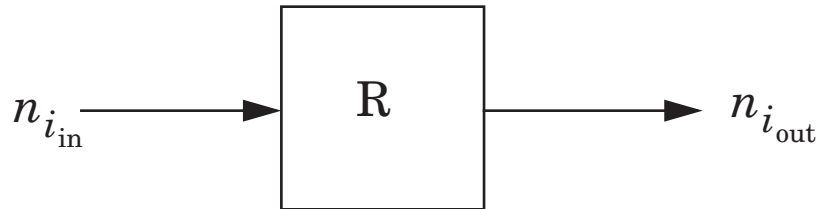
$$\dot{n}_{\text{N}_{2\text{stoic}}} = \dot{\xi}(-\nu_{\text{N}_2}) = \frac{200}{3}(1)$$

So the fractional excess of N_2 is

$$\frac{\dot{n}_{\text{N}_{2in}} - \dot{n}_{\text{N}_{2\text{stoic}}}}{\dot{n}_{\text{N}_{2\text{stoic}}}} = \frac{100 - \frac{200}{3}}{\frac{200}{3}} = \frac{1}{2} = 50\%$$

Mass Balance for multiple reactions

$$j = 1 \dots J$$



Differential Balance

$$\dot{n}_{i_{\text{out}}} = \dot{n}_{i_{\text{in}}} + \sum_{j=1}^J v_{ij} \dot{\xi}_j$$

Integral Balance

$$n_{i_{\text{final}}} = n_{i_{\text{initial}}} + \sum_{j=1}^J v_{ij} \xi_j$$

where

v_{ij} is the stoichiometric coefficient for reactant i in reaction j .

$\dot{\xi}_j$, ξ_j is the extent of reaction j .

Usually there is one desired product and one or more undesired products. We then define

Yield

$$\text{Yield} = \frac{n_{\text{product}_{\text{actual}}}}{n_{\text{product}_{\text{possible}}}}$$

Selectivity

$$\text{Selectivity} = \frac{n_{\text{product}_{\text{desired}}}}{n_{\text{product}_{\text{undesired}}}}$$

The goal is almost always high selectivity and high yield.

Combustion Reactions

Combustion reactions are rapid oxidation reactions. One usually burns a *fuel* (typically coal, oil or natural gas) in air (or rarely pure oxygen). The principal atomic species in combustion reactions are carbon, hydrogen, sulfur and oxygen.

Complete combustion

If all of the fuel is completely oxidized, we have complete combustion. For the principal species the combustion products are CO_2 , H_2O , and SO_2 .

Partial or incomplete combustion

If not all of the fuel is completely oxidized, or if some is not oxidized at all, we have partial or incomplete combustion. A typical product of incomplete combustion is CO .

Stack or Flue gas

The combustion products along with any remaining reactants are referred to as *stack gas* or *flue gas*. The composition of the flue gas is reported in one of two bases.

Wet basis

Wet basis includes the water vapor in the flue gas composition.

Dry basis (Orsat analysis)

Dry basis does not include water vapor in the flue gas composition. One apparatus for measuring flue gas composition was

named after Orsat. It reports compositions on a dry basis.

Theoretical air

Theoretical air is the amount of air containing the stoichiometric oxygen needed for complete combustion.

Excess air

Excess air is calculated in the same manner as any excess reactant. It is the fraction above stoichiometric.

Burning in excess air does not guarantee complete combustion.

Burning with less than theoretical air is known as burning rich (as in fuel rich).

Burning with excess air is known as burning lean.

Reaction Equilibria

Extents of reaction are limited by two things

Thermodynamics

Kinetics

From Thermodynamics, equilibrium is reached when the total Gibbs Energy is minimized. Mathematically the criterion is

$$\sum v_i G_i^\circ + RT \sum \ln(\hat{a}_i)^{v_i} = 0$$

or rearranged

$$\prod (\hat{a}_i)^{v_i} = \exp\left(\frac{-\sum v_i G_i^\circ}{RT}\right) \equiv K$$

The \hat{a}_i are the *activities* of the various species where

$$\hat{a}_i \equiv \frac{\hat{f}_i}{f_i^\circ}.$$

\hat{f}_i is the *fugacity* of species i in solution and f_i° is the *reference fugacity* of species i .

$\sum v_i G_i^\circ$ is often written ΔG° and is similar to ΔH° .

K is the *equilibrium constant*. It varies **only** with temperature. What are its units?

For ideal gases (see Cpt. 5 & Cpt. 8) the fugacity in solution is numerically equal to the partial pressure, and the reference fugacity is the ideal gas state at the system T and a pressure of 1 atm (1 bar). With these substitutions

$$K = \prod \left(\frac{p_i}{1 \text{ atm}} \right)^{v_i}$$

or

$$K(1 \text{ atm})^v = \prod (p_i)^{v_i}$$

K is still dimensionless but may not appear to be.

Often problems are posed in mole fractions instead of partial pressures. Since for an ideal gas

$$y_i = \frac{p_i}{P}$$

then

$$p_i = y_i P$$

Substituting

$$K(1 \text{ atm})^v = \prod (y_i P)^{v_i} = P^v \prod (y_i)^{v_i}$$

or

$$K(1 \text{ atm})^v P^{-v} = \prod (y_i)^{v_i}$$

which is where the book begins. Again, K depends only on temperature but the equilibrium composition depends on total pressure and the presence of inerts.

With a fair amount of calculus one can show that

$$\frac{d\ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

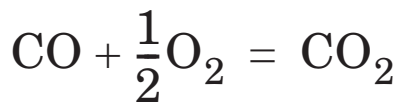
which if ΔH° is constant with temperature integrates to

$$\ln \frac{K}{K_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right)$$

Example

Carbon monoxide and oxygen are fed in equimolar ratios to an isothermal combustor. If the reaction proceeds to equilibrium calculate the fractional conversion of CO and O₂ as the reactor temperature varies from 300 K to 2500 K.

Setup



$$\Delta G^\circ = -281885 + 85.678T \text{ [J/mol]}$$

$$v_{\text{CO}} = -1$$

$$v_{\text{O}_2} = -\frac{1}{2}$$

$$v_{\text{CO}_2} = 1$$

$$\nu = -1 - \frac{1}{2} + 1 = -0.5$$

$$K \text{ atm}^\nu P^{-\nu} = \prod (y_i)^{v_i}$$

$$\frac{y_{\text{CO}_2}}{y_{\text{CO}} y_{\text{O}_2}^{0.5}} = K \text{ atm}^{-0.5} P^{0.5}$$

$$y_{\text{CO}} = \frac{n_{\text{CO}_{\text{out}}}}{n_{\text{out}}} = \frac{n_{\text{CO}_{\text{in}}} + v_{\text{CO}} \xi}{n_{\text{in}} + \nu \xi}$$

$$y_{\text{CO}_2} = \frac{n_{\text{CO}_{2\text{out}}}}{n_{\text{out}}} = \frac{n_{\text{CO}_{2\text{in}}} + v_{\text{CO}_2} \xi}{n_{\text{in}} + \nu \xi}$$

$$y_{\text{O}_2} = \frac{n_{\text{O}_{2\text{out}}}}{n_{\text{out}}} = \frac{n_{\text{O}_{2\text{in}}} + v_{\text{O}_2} \xi}{n_{\text{in}} + \nu \xi}$$

What is missing?

P and $n_{\text{O}_{2\text{in}}}$ or $n_{\text{CO}_{\text{in}}}$.

Pick a basis of 1 mol/s

Assume $P = 1 \text{ atm}$.

$$\frac{\left(\frac{0 + \xi}{2 - 0.5\xi}\right)}{\left(\frac{1 - \xi}{2 - 0.5\xi}\right)\left(\frac{1 - 0.5\xi}{2 - 0.5\xi}\right)^{0.5}} = K(1 \text{ atm})^{-0.5}(1 \text{ atm})^{0.5}$$

$$\frac{(2 - 0.5\xi)^{0.5}}{(1 - 0.5\xi)^{0.5}} \frac{\xi}{1 - \xi} = K$$

As an approximation

$$\xi = \frac{\frac{K}{\sqrt{3}}}{1 + \frac{K}{\sqrt{3}}} \text{ or } 1 - \xi = \frac{1}{1 + \frac{K}{\sqrt{3}}}$$

Results

