Basics of balance equations

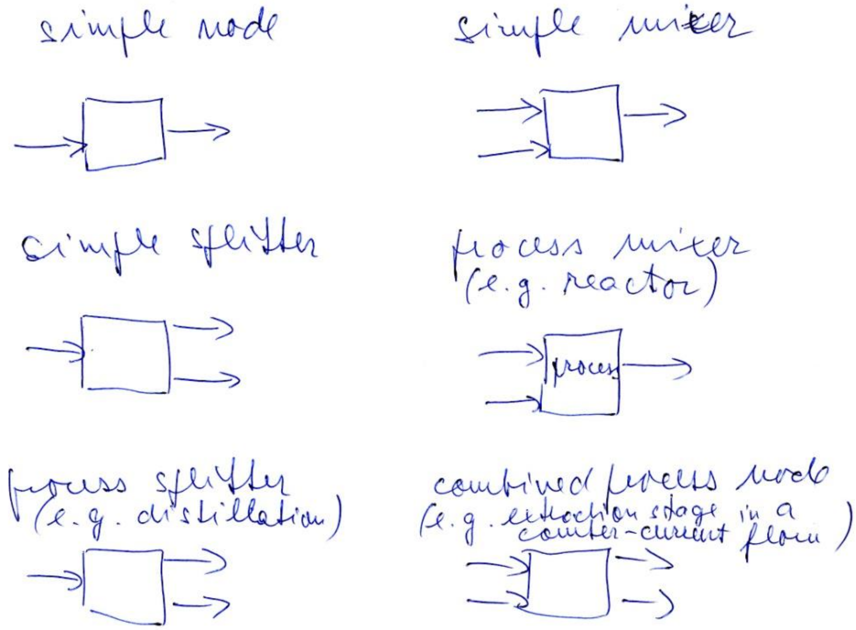
Balance equations are based on preservation of basic physical quantities, such as mass, moles (amount of substance), energy and momentum. All quantities amenable to balancing must be extensive, which means that the quantity is proportional to the size of the system. On the other hand, intensive quantities, such as pressure, temperature, density, velocity etc. are independent of the size of the system.

General formulation o the balance equation for an extensive quantity:

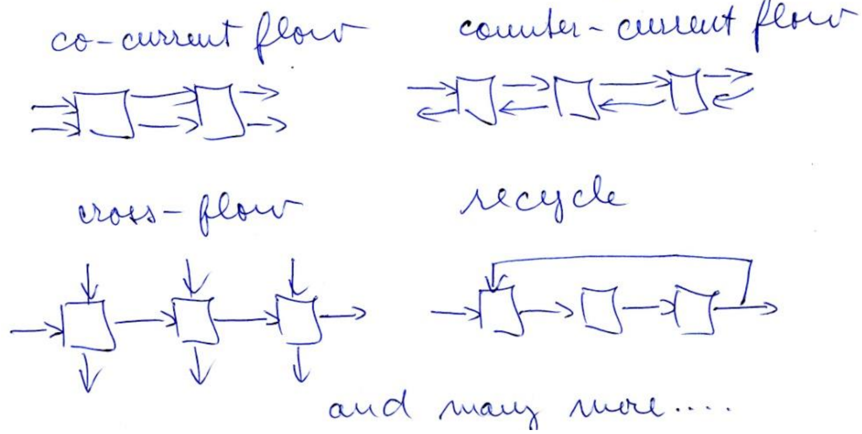
inititial amount + sum of inputs + sum of generations – sum of consumptions = final amount + sum of outputs

This holds for a system (finite or differentially small) over a time period (finite or differrential).

The types of systems interesting in chemical engineering are:



Nodes could be arranged as:



and many more....

The balance equation can be simplified by introducing the terms:

accumulation = final amount – initial amount

source = sum of generations – sum of consumptions

The balance equation then becomes (omitting the word sum)

input + source = out + accumulation

For a quantity B, the equation reads:

$$\sum_{j}^{over\ inputs} B_j + \left(\sum_{j}^{over\ generations} B_j - \sum_{j}^{over\ consuptions} B_j \right) = \sum_{j}^{over\ outputs} B_j + \left(B_{final} - B_{initial}\right)$$

For flow systems, it is convenient to consider balancing within a differential time dτ during which the quantity B changes only differrentially, i.e by dB. Then it is useful to apply balancing of B per time unit, i.e. $\frac{dB}{d\tau} = \dot{B}$. Hence the balance equation is

$$\sum_{j}^{over\ inputs} \dot{B}_j + \left(\sum_{j}^{over\ generations} \dot{B}_j - \sum_{j}^{over\ consuptions} \dot{B}_j \right) = \sum_{j}^{over\ outputs} \dot{B}_j + \frac{dB}{d\tau}$$

Material balances (balance equations for mass or moles)

A distinct feature is that there may be many components making up a mixture; material balance can be then applied to each component separately as well as to the entire mixture. For that purpose, it is useful to introduce mass and molar fractions:

$w_{i,j} = \frac{m_{i,j}}{m_j}$; $m_{i,j}$... mass of the component i in j-th stream, $m_{,j}$... total mass in j-th stream (mas of the mixture)

$x_{i,j} = \frac{n_{i,j}}{n_j}$; n ... symbol for moles

The sum of fractions **over all components** is equal to **one**

$$\sum_i w_{i,j} = 1, \qquad \sum_i x_{i,j} = 1;$$

Remarks:

1) for ideal gaseous mixtures: $x_{i,j} = \frac{p_{i,j}}{p_j}$, where $p_{i,j}$ is partial pressure and p_j is (overall) pressure in stream j
2) conversion between $w_{i,j}$ and $x_{i,j}$:

$$x_{i,j} = \frac{n_{i,j}}{\sum_i n_{i,j}} = \frac{w_{i,j}/M_i}{\sum_i w_{i,j}/M_i}; w_{i,j} = \frac{x_{i,j}M_i}{\sum_i x_{i,j}M_i}$$

3) sometimes **mean/average molar mass** is used: $\overline{M_i} = \sum_i x_{i,j}M_i = \frac{1}{\sum_i w_{i,j}/M_i}$

Material balances without chemical reactions

Source terms are zero in this case, because mass of a component can be generated or consumed only by chemical reaction (no relativistic effects are assumed).

Balance of total mass (=mixture):

$$m_{initial} + \sum_j^{inputs} m_j = \sum_j^{outputs} m_j + m_{final}$$

Balance of each of the components (i=1 ... N):

$$m_{init}w_{i,init} + \sum_j^{inputs} m_j\, w_{i,j} = \sum_j^{outputs} m_j w_{i,j} + m_{fin}w_{i,fin}$$

Important remark: For N components there is N+1 mass balance equations, but only N of them are linearly independent! So, in calculations one of them (usually the most inconvenient) must be left out!

Other remarks:

a) mass of the component *i* in the stream *j*, $m_{i,j}$ is according to the definition of the mass fraction $m_{i,j}=m_jw_{i,j}$ which is the basis of the component balances written above. Another way of writing a component balance is

$$m_{i,init} + \sum_j^{inputs} m_{i,j} = \sum_j^{outputs} m_{i,j} + m_{i,fin}$$

which avoids mass fractions – this form is useful for computerized solutions.

b) The initial and final amount can be formally thought of as being an input and output, respectively. Then they are called **fictitious input/output** and the equations can be formally written as if there were only inputs and outputs

$$\sum_j^{all\ inputs} m_{i,j} = \sum_j^{all\ outputs} m_{i,j};\quad \sum_j^{all\ inputs} m_j\, w_{i,j} = \sum_j^{all\ outputs} m_j w_{i,j}$$

c) At **steady state no accumulation** takes place and then

$m_{init} = m_{fin}$ and $m_{init}w_{i,init} = m_{fin}w_{i,fin}$ and they can be left out from the equations altogether

Material balances for moles are analogous to those for mass:

$$n + \sum_{j}^{inputs} n_j = \sum_{j}^{outputs} n_j + n_{final}$$

$$n_{init} x_{i,init} + \sum_{j}^{inputs} n_j \, x_{i,j} = \sum_{j}^{outputs} n_j x_{i,j} + n_{fin} x_{i,fin}$$

Material balances with chemical reactions

Here the **generation/consumptions terms** are in general **nonzero**. This holds in particular for those components, which are either produced or consumed by **chemical reaction(s)**. However, mass of all reactants must equal that of all products, thus total **balance of mass does not have source terms**. On the other hand, a total balance of moles admits a nonzero source term. Source terms must obey **stoichiometric relations** given by chemical equations for the occuring reactions.

There are two principal ways how to write down source terms, either via **reaction extent** ot via **fictitious inputs/outputs.**

The use of reaction extent (also degree of advancement):

assume a chemical reaction expressed by a stoichiometric equation:

$$|\nu_A|\mathrm{A} + |\nu_B|\mathrm{B} \rightarrow |\nu_C|C + |\nu_D|\mathrm{D}$$

where ν_i are the stoichiometric coefficients (dimensionless), which are **negative for reactants** and **positive for products.**

The **extent** of the chemical reaction is

$$\xi = \frac{n_i - n_{i,0}}{\nu_i} \qquad i = \mathrm{A, B, C, D} \ldots$$

$n_{i,0}$ ... amount of moles of species i at the beginning of the reaction

n_i ... amount of moles of species i at the end of the reaction

The units of ξ are **moles of reaction turnover**. Notice that $n_i - n_{i,0} < 0$ for reactants, thus ξ is always positive. Moreover, ξ **is the same regardless of the chosen species *i*.**

Therefore we can express the source for species i as follows:

$$\sum^{\substack{over\ all \\ reactions}} sources = \frac{sum\ of}{generations} - \frac{sum\ of}{consuptions} = \sum_{j}^{gener.} n_{i,j} - \sum_{j}^{consupt.} n_{i,j} = \sum_{j}^{\substack{over \\ reactions}} \nu_{i,j}\, \xi_j$$

The balance equations are:

- **for moles**

  Total balance:

$$\sum_{j}^{\substack{inputs\\+initial}} n_j + \underbrace{\sum_{i}^{\substack{over\\components}} \; \sum_{j}^{\substack{over\\reactions}} \nu_{i,j}\,\xi_j}_{\text{in general nonzero}} = \sum_{j}^{\substack{outputs\\+final}} n_j$$

  component balances (i = 1 ... N):

$$\sum_{j}^{\substack{inputs\\+initial}} n_j\,x_{i,j} + \sum_{j}^{react.} \nu_{i,j}\,\xi_j = \sum_{j}^{\substack{outputs\\+final}} n_j\,x_{i,j}$$

- **for mass**

  Total balance:

$$\sum_{j}^{\substack{inputs\\+initial}} m_j + \mathbf{0} = \sum_{j}^{\substack{outputs\\+final}} m_j$$

  component balance (i = 1 ... N):

$$\sum_{j}^{\substack{inputs\\+initial}} m_j\,w_{i,j} + \boldsymbol{M_i} \sum_{j}^{react.} \nu_{i,j}\,\xi_j = \sum_{j}^{\substack{outputs\\+final}} m_j\,w_{i,j}$$

In practical calculations the extent ξj (ξj depends on the reaction j but not on the species i) may be inconvenient and then the concept of fictitious streams may be used.

The use of fictitious streams:

Total balance :

$$\sum_{j}^{\substack{inputs\\+initial\\+generation}} n_j = \sum_{j}^{\substack{outputs\\+final\\+consumption}} n_j$$

Component balance:

$$\sum_{j}^{\substack{inputs \\ +initial \\ +generation}} n_j \, x_{i,j} = \sum_{j}^{\substack{outputs \\ +final \\ +consumption}} n_j \, x_{i,j}$$

Fictitious streams corresponding to consumption terms are **positive** on the right hand side of equation. At steady state $n_{initial} = n_{final}$ and $n_{initial} x_{i,init} = n_{final} x_{i,final}$.

The fictitious generation or consumption terms correspond to the products or reactants in each reaction, respectively, and $x_{i,j}$ for the "chemical" fictitious stream are:

fictitious output stream: $$x_{i,j} = \frac{|\nu_{i,j}|}{\sum_i^{\substack{all \\ reactants}} |\nu_{i,j}|}$$

fictitious input stream: $$x_{i,j} = \frac{\nu_{i,j}}{\sum_i^{\substack{all \\ products}} \nu_{i,j}}$$

where *j* refers to j-th reaction.

Thus for each reaction, there are **two fictitious streams**, one for the **consumption** (left hand side of the chemical stoichiometric equation) and the other for the **generation** (right hand side of the chemical equation).

Example:

Stream 1 $C + \frac{1}{2} O_2 \rightarrow CO$ Stream 2

components: A ... C; B ... O_2; C...CO

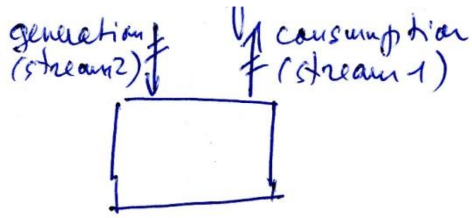
stoichiometric coefficients: ν_A = -1; ν_B=-1/2; ν_C=1

consumption term (=stream 1): contains two components A and B in the stoichimetric ratio 1:1/2; therefore

$$x_{A1} = \frac{|\nu_A|}{|\nu_A| + |\nu_B|} = \frac{1}{1 + \frac{1}{2}} = \frac{2}{3}; \; x_{B1} = \frac{|\nu_B|}{|\nu_A| + |\nu_B|} = \frac{\frac{1}{2}}{1 + \frac{1}{2}} = \frac{1}{3}$$

generation term (= stream 2): contains only one compound C; therefore x_{C2} = 1.

In schemes, the fictitious reaction stream are marked as follows:



The amounts n_1 and n_2 corresponding to the fictitiousstreams are actually:

$$n_1 = moles\ of\ \mathrm{C} + moles\ of\ \mathrm{O_2}\ \ that\ reacted$$

$$n_2 = moles\ of\ \mathrm{CO}\ \ that\ was\ produced$$

Then, of course $n_1 x_{A1}$ = moles of C that reacted

$n_1 x_{B1}$ = moles of O_2 that reacted

$n_2 x_{C2}$ = moles of CO produced (in this case $n_2 x_{C2} = n_2$)

In addition to the molar balances, there is an **extra relation** that expresses the **stoichiometric relation betwee fictitious streams** for generation and consuption. Namely,

$$\frac{n_1}{n_2} = \frac{|\nu_A| + |\nu_B|}{\nu_C} = \frac{3}{2}$$

or generally

$$\frac{n_{consumption}}{n_{generation}} = \frac{\sum^{reactants} |\nu_i|}{\sum^{products} \nu_i}$$

Remark: Note that $n_1 \neq n_2$, i.e. here more moles were consumed than produced (this depends on the reaction considered). For mass $\boldsymbol{m_1 = m_2}$ **holds always.**

Balance equations with fictitious streams for mass

total balance: unlike moles, mass is special in that the mass of all reactants must equal that of all products, i.e.

$$m_{generation} = m_{consumption}$$

Therefore in total balance, the fictitious reaction input and output is cancelled out.

$$\sum_{j}^{\substack{init+\\inputs}} m_j = \sum_{j}^{\substack{final+\\output}} m_j$$

For steady state also $m_{init} = m_{final}$

Component balance: (here generation and consumption terms do NOT cancel)

$$\sum_{j}^{\substack{init+\\inputs+\\generation}} m_j w_{i,j} = \sum_{j}^{\substack{final+\\output+\\consumption}} m_j w_{i,j}$$

For steady state $m_{init} w_{i,init} = m_{final} w_{i,final}$.

For fictitious streams the composition is given by:

a) **output/reactant:** $w_{i,j} = \frac{M_i |\nu_{i,j}|}{\sum^{reactants} M_i |\nu_{i,j}|}$

b) **input/product:** $w_{i,j} = \frac{M_i \nu_{i,j}}{\sum^{products} M_i \nu_{i,j}}$

here M_i is molar mass of component *i*.

In conclusion, below is an outline of a systematic approach to problems involving material balances:

1) Draw balance scheme, denote nodes (usually by capital Roman numbers) and streams (usually by Arabic numbers).
2) If there is accumulation in the system (i.e, unsteady operation), draw a pair of fictitious streams for initial and final amount of material – this is rather rare.
3) If there are chemical reactions, write the chemical stoichiometric equations and for each reaction draw a pair of fictitious streams.
4) Denote all components that occur in the system (by capital letters in alphabetical order, or by using chemical formula). Components may be chemical species or elements or even chemically undefined stuff, such as ashes, impurities, inerts, etc.
5) Determine whether to use mass or molar balance – depends on convenience.
6) Recalculate data so as to conform with our choice of the balanced quantity (i.e, convert data to moles + molar fractions or masses + mass fractions, including the fictitious streams.
7) All inout data should be arranged in an input data matrix (including zero values). Unknown values are denoted by their symbols. If there is no extensive quantity provided (i.e mass or moles of at least one stream) then one must choose mass or moles of a convenient stream (e.g. input stream) – this is called a **basis of calculations**.
8) From the input data matrix we can determine the number of unknowns. Write down all independent material balances plus all additional relations, such as
   - sum of mass/molar fractions over all components in a stream is equal to 1
   - stoichiometric relation between input and output fictitious streams in each reaction, for mass $\frac{m_{gener}}{m_{consump}} = 1$, for moles $\frac{n_{gener}}{n_{consump}} = \frac{\sum^{products} |\nu_i|}{\sum^{reactants} |\nu_i|}$
   - definition of stoichiometric surplus (excess):

$$P_{i,j} = \frac{m_{i,real} - m_{i,theor}}{m_{i,theor}} = \frac{n_{i,real} - n_{i,theor}}{n_{i,theor}}$$

where "real" refers to actual amount and "theor" refers to exact amount given by stoichiometry (Remark: flows $\dot{m}$, $\dot{n}$ can be used instead of m, n)

- definition of conversion for j-th reaction

$$\zeta_{i,j} = \frac{n_{i,initial} - n_{i,final}}{n_{i,initial}} \text{ for unsteady operations}$$

$$\zeta_{i,j} = \frac{\dot{n}_{i,initial} - \dot{n}_{i,final}}{\dot{n}_{i,initial}} \text{ for steady state flow operations}$$

9) Solve the system of equation whose number must equal to the number of unknows.
10) Double check the results and formulate answers to given questions in the problem solved.

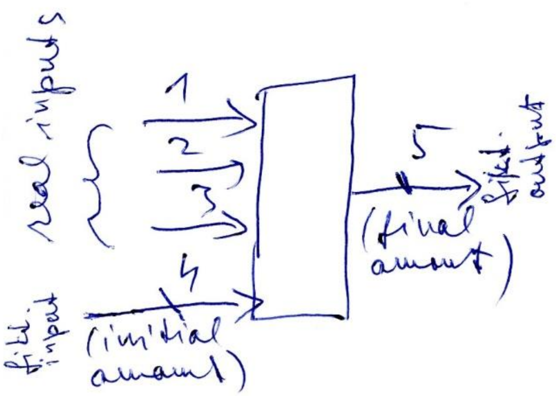
Remark: The form of input data matrix is as follows

	stream 1	*stream 2*	*stream 3*	*stream 4*	*stream 5*
mass/moles					
mass/mole fraction					
mass/mole fraction					
mass/mole fraction					
mass/mole fraction					

Example

Mixing of three streams in a container with initial mass different than the final one (nonzero accumulation = unsteady operation). There is no real output stream

Scheme:



Input data matrix:

	1	*2*	*3*	*4*	*5*
m	m_1	m_2	m_3	*300*	*500*
w_A	*0.9*	*0*	*0*	*0.1*	*0.2*
w_B	*0.1*	*0.08*	*1*	*0.1*	*0.3*
w_C	*0*	*0.92*	*0*	*0.8*	*0.5*

Clearly, there are three independent mass balances for three unknown masses m1, m2, m3. No additional relation is needed in this case

Components: A,B,C