

Matter balances in steady state with generation

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1. Summary

In this article, we show how to work with **matter balances** that include the term of **generation**. Our goal is to offer an overview of the management of this tool in systems in which a chemical reaction occurs.

2. Introduction

Balances are used to quantify the data in processes, perform calculations and make predictions of the behavior of a system under determined conditions, contrast hypotheses, or determine a concrete datum in a flow diagram. They are based on the **Law of conservation of matter**, or Law of Lomonósov-Lavoisier, or **First Principle of thermodynamics**, which establishes that matter and energy are neither created nor destroyed, but transformed (Figure 1). For example, a mass in an isolated system is not created or destroyed by means of chemical reactions or physical transformations. Therefore, the mass of the products in a chemical reaction is equal to the mass of the reagents. This principle has been fundamental for the significant progress made in the field of physics. It was the basis upon which Albert Einstein developed the theory of relativity, describing matter and energy as interchangeable against conservation ($E=mc^2$).

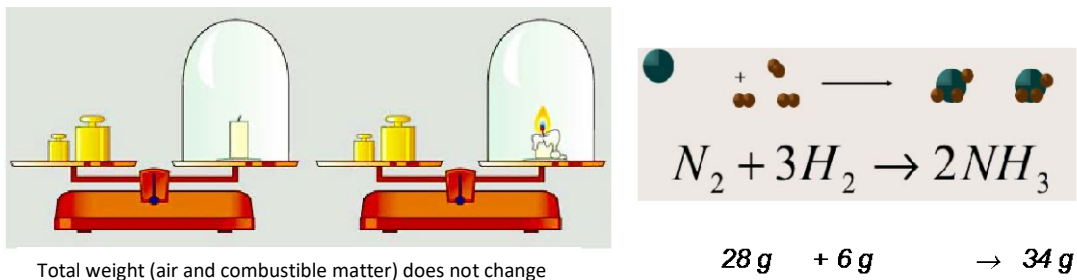


Figure 1. Examples of the law of conservation of matter which shows that the sum of the mass of the reagents is equal to the mass of the products

The balances (of mass and energy) always have the same general structure:

$$\text{INCOME} + \text{GENERATION} = \text{OUTCOME} + \text{ACCUMULATION}$$

If we think of a system (control volume) as the one represented in Figure 2, the different terms of the general equation of the balances refer to the following:

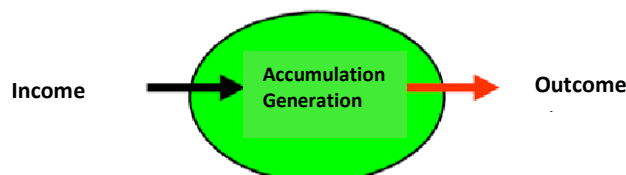


Figure 2. Graphical representation of the general equations of the balances.

- **Income/outcome:** the streams that pass through the system boundaries, either coming in or going out
- **Accumulation:** the variation in a determined time of what is in the interior of the system
- **Generation:** the term refers to what appears or disappears within the system boundaries, having neither been present from the beginning nor transferred

across the system boundaries, and being associated with chemical, biochemical, microbiological, mechanical or nuclear reactions

Thus, the matter balances are useful for the following purposes:

- Measurement-free calculation of the components coming in or going out of a process
- Analysis-free estimation of the composition of the streams
- Evaluation of the yield and efficacy of a process
- Process design

From the general equation of the matter balances, we must take into account that, if the time variable does not affect the physicochemical properties when working in the steady state, the accumulation term will not be considered. On the other hand, if the onset or loss of a chemical species in the process is not produced, the generation term will not be considered either. However, in some processes, such as fermentation, hydrolysis or isomerization, the generation term is considered since chemical species appear or disappear.

In this article, we will focus on the resolution of matter balances with generation in steady state, i.e. with no accumulation.

3. Objectives

Once you have carefully read this document, you will be able to:

- Apply the analysis of the degrees of freedom of the data and unknown variables that take part in the streams of a process
- State the balances of total matter and the balances of the compounds of a system
- Manage the generation term in a balance
- Solve systems of equations that are needed in order to deduce the unknown variables, and in this way, enable the adequate design of an industrial process with streams circulation and the characterization of its flow and composition.

4. Development

In order to quantify the flows and compositions of the streams in a process that works in the steady state with generations, we will use the following parameters:

m : mass flows (kg/h) of each stream

x_i : mass fraction of the component i (kg _{i} /kg total)

G_i : mass flow (kg/h) of the generation of the component i

The matter balances that are stated in this situation are:

Balance of total matter: $\sum m_{\text{outcome}} - \sum m_{\text{income}} = 0$

Balance of matter of each compound: $\sum (m \cdot x_i)_{\text{outcome}} - \sum (m \cdot x_i)_{\text{income}} = G_i^*$

* If the chemical species is created, G is positive, while G is negative if the species is consumed in the chemical reaction

The balance statement will be performed through a series of mathematical equations that we can solve, taking into account a number of conditions that will subsequently be explained. In order to discover the sequence of resolution of the whole process, we will apply the degrees of freedom study. This study indicates whether a control volume has a single solution. To perform this study, we will first need to identify and adapt the available information and modify the variables and equations so as to discard the existing dependence relations.

4.1. Study of independent variables

A system of equations can be solved as long as two conditions are fulfilled:

- 1st) Variables are independent of each other
- 2nd) Equations are determined

When analyzing any process, there are three conditions that cause part of the variables of the system to be dependent on each other and part of the obtained equations resulting from the balance statement to be undetermined:

- **Condition 1.** In each stream, the sum of all the mass fractions is 1, so all the mass fractions of streams with more than one compound are related with each other ($\sum x = 1$), and consequently they are dependent.

Solution: we will consider all the mass fractions as independent variables, except one. If a stream is pure, i.e. made of one compound only, this will be considered as an independent variable in the system.

- **Condition 2.** When applying the 1st principle of thermodynamics in each chemical reaction, the sum of the generations of the consumed compounds is equal to the sum of the produced compounds, so they are dependent: $\sum G_{\text{consumed}} = \sum G_{\text{produced}}$.

Solution: One term per chemical reaction in the system will not be considered

- **Condition 3.** The sum of all the compound balances is the balance of total matter, so if we consider a system of equations with the balances of all the compounds and the balance of total matter, it will be undetermined.

Solution: the matter balance of one compound, preferably the same one for which the mass fraction has not been considered in the system of equations, will not be considered

Taking into account these considerations, the system of equations will become determined and solely composed of variables and equations that are independent of each other.

4.2. Stating the balances with generation

In order to work adequately with the term "generation" in the matter balances, we need to know the STOICHIOMETRY of the chemical relations involved in each of the basic operations of the process.

As mass is a preservative magnitude, the sum of the generation terms of the produced and consumed compounds is equal. This means that in the general equation of the total mass balances no generation term is considered. However, we will consider generation terms in the compound balances, taking into account the mathematical relation established by the stoichiometry. For example, in the reaction $A \rightarrow B+C$, we will have $G_A = G_B + G_C$

Let's see an example: An industry produces Paracetamol® in a 3-stage process. The first is a reactor (R1) into which 100 kg/h of a mixture of nitrobenzene (N) (at 92%) and water (W) are introduced, and hydrogen (H) is aggregated on demand, to produce the chemical reaction (Reaction 1) with a nitrobenzene yield of 90%. The product of this reaction is mixed in a second reactor (R2) with acetic anhydride (AHA) on demand to carry out the second chemical reaction (Reactor 2), in which the paracetamol (P) produced along with water will be split on the one hand, and, the acetic acid (AA) with the residual nitrobenzene on the other. The wet paracetamol is submitted to a dehydration process (D) in which water is removed until paracetamol capsules containing 2% water are obtained.

Data:

Reaction1 ($\eta = 90\%$): nitrobenzene (123 g/mol) + 2 H₂ (2 g/mol) → aminophenol (109 g/mol) + H₂O (18 g/mol)

Reaction2 ($\eta = 100\%$): aminophenol + acetic anhydride (102 g/mol) \rightarrow paracetamol (151 g/mol) + acetic acid (60 g/mol)

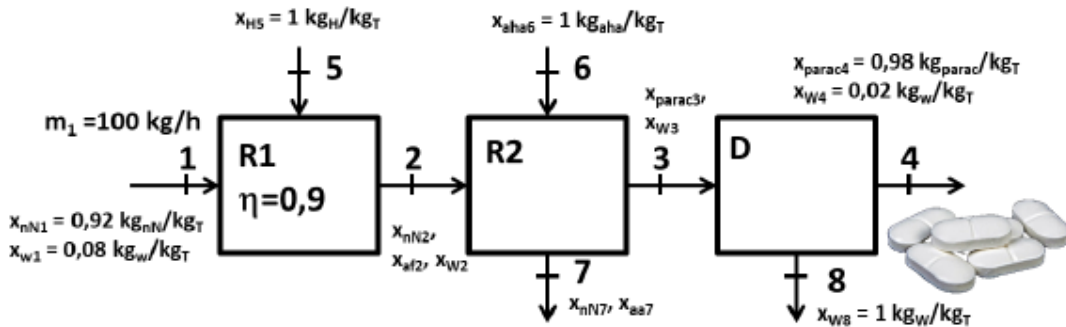


Figure 3. Flowchart of the above example: paracetamol production

According to the statement, we will organize the available information in Table 1.

Table 1. Known data in the example of paracetamol production

	Streams							
	1	2	3	4	5	6	7	8
m (kg/h)	100							
x_{nN} (kg/kg _{total})	0.08		0	0				0
x_w (kg/kg _{total})	0.92			0.02		0		1
x_{af} (kg/kg _{total})					0		0	
x_{aHa} (kg/kg _{total})			0	0		1		
x_{aa} (kg/kg _{total})	0	0						0
x_{parac} (kg/kg _{total})				0.98		0	0	
x_H (kg/kg _{total})			0	0	1			

In order to complete all the cells in this table and, in this way, estimate the compound composition and mass flows in every stream of the process, we must state a system of equations based on the matter balances and the relations/restrictions imposed in the process. To perform the degrees of freedom analysis, we first need to carry out a study of the independent variables. This can be simply done by compiling all the existing variables in the system in a table (Table 2).

Table 2. Variables in the example process of paracetamol production

Stream	Variables							Generations (kg/h)	
1	m_1	x_{nN}	x_w						G^1_{nN}
2	m_2	x_{nN}	x_w		x_{af}				G^1_H
3	m_3		x_w			x_{parac}			G^1_{af}
4	m_4		x_w			x_{parac}			G^1_w
5	m_5			x_H					G^2_{aHa}
6	m_6						x_{aHa}		G^2_{aa}
7	m_7	x_{nN}					x_{aa}		G^2_{parac}
8	m_8		x_w					G^2_{af}	

Following the previously explained steps, we will eliminate one fraction per stream with more than one compound from the system of variables (streams 1, 2, 3, 4 and 7). In this case, we should select the water fraction in every stream, except in stream 7 which does not contain it, in order to facilitate the upcoming choice of the balance to eliminate from the system of equations. Furthermore, we will eliminate one generation per reaction. In this case, we will consider the generation of water as the dependent variable in the first reaction, and that of acetic acid in the second. The following data are displayed in the above table as follows:

- In bold: known variables
- In red: variables considered as dependent; thus, not taken into account
- In purple: generations in the first chemical reaction, excluding the generation of water (crossed) as a dependent variable
- In green: the generations in the second chemical reaction, excluding the generation of acetic acid (crossed) as a dependent variable

Now all the variables of the system are independent!

From Table 2 we deduce there are 17 unknown independent variables: m_2 , m_3 , m_4 , m_5 , m_6 , m_7 , m_8 , X_{nN2} , X_{af2} , X_{parac3} , X_{nN7} , G^1_{nN} , G^1_H , G^1_{af} , G^2_{af} , G^2_{parac} , G^2_{aha} ; and 5 unknown dependent variables: X_{w2} , X_{w3} , X_{w4} , G^1_w , G^2_{aa} .

In addition to eliminating the water balance for the purposes of stating a compatible and determined system of equations, those stoichiometric relations implying generation terms considered as dependent variables should not be considered either; this is highlighted in red in Table 3.

Table 3. Mathematical stoichiometric relations of the chemical reactions

Reaction 1	Reaction 2
$\frac{G^1_{nN}}{123} = \frac{G^1_H}{2 \cdot 2}$	$\frac{G^2_{af}}{109} = \frac{G^2_{aha}}{102}$
$\frac{G^1_{nN}}{123} = \frac{G^1_{af}}{109}$	$\frac{G^2_{af}}{109} = \frac{G^2_{parac}}{151}$
$\frac{G^1_{nN}}{123} = \frac{G^1_w}{18}$	$\frac{G^2_{af}}{109} = \frac{G^2_{aa}}{60}$

Finally, according to the yield of reaction 1, we know that:

$$G^1_{nN} = 0.9 \cdot m_1 \cdot X_{nN1}$$

Now the system of equations is determined and can be solved. Specifically, it is composed of the equations that we can obtain from each of the environments (or control volumes) in the flow diagram, which are the following:

Reactor 1. Data: m_1 , X_{nN1} , X_{H5} . Unknown variables: m_2 , m_5 , X_{nN2} , X_{af2} , G^1_{nN} , G^1_H , G^1_{af}

- Equation 1: Balance of total matter: $m_2 = m_1 + m_5$
- Equation 2: Balance of nitrobenzene: $(m_1 \cdot X_{nN1}) - G_{nN1} = m_2 \cdot X_{N2}$
- Equation 3: Balance of aminophenol: $G^1_{ap} = m_2 \cdot X_{af2}$
- Equation 4. Balance of hydrogen: $(m_5 \cdot X_{H5}) - G_H = 0$
- Equation 5. Stoichiometric relation between nN and H in Reaction 1: $4 \cdot G^1_{nN} = 123 \cdot G^1_H$
- Equation 6: Stoichiometric relation between nN and af in Reaction 1: $109 \cdot G^1_{nN} = 123 \cdot G^1_{af}$
- Equation 7: yield of Reaction 1: $G^1_{nN} = 0.9 \cdot m_1 \cdot X_{nN1}$

Reactor 2. Data: X_{aha6} . Unknown variables: m_2 , m_6 , m_7 , m_3 , X_{nN2} , X_{nN7} , X_{ap2} , X_{ap3} , G^2_{af} , G^2_{parac} , G^2_{aha}

- Equation 8: Balance of total matter: $m_2 + m_6 = m_3 + m_7$
- Equation 9: Balance of nitrobenzene: $m_2 \cdot X_{nN2} = m_7 \cdot X_{N7}$
- Equation 10: Balance of aminophenol: $(m_2 \cdot X_{af2}) - G^2_{af} = 0$
- Equation 11: Balance of acetic anhydride: $(m_6 \cdot X_{ahaA6}) - G^2_{aha} = 0$
- Equation 12: Balance of paracetamol: $G^2_{af} = m_3 \cdot X_{af3}$
- Equation 13: Balance of acetic acid: $G^2_{af} + G^2_{aha} - G^2_{af} = m_7 \cdot (1 - X_{N7})$
- Equation 14: $102 \cdot G^2_{af} = 109 \cdot G^2_{aha}$
- Equation 15: $151 \cdot G^2_{af} = 109 \cdot G^2_{parac}$

Dehydrator. Data: x_{p4} . Unknown variables: $m_3, m_4, m_8, X_{\text{parac}3}$

- Equation 16: Balance of total matter: $m_3 = m_4 + m_8$
- Equation 17: Balance of paracetamol: $m_3 \cdot X_{\text{parac}3} = m_4 \cdot X_{\text{parac}4}$

On the basis of all this information, we can go ahead and carry out the degrees of freedom analysis, which will let us know the calculation itinerary to follow.

4.3. Degrees of freedom analysis

Frequently, industrial processes are made up of a series of successive stages that transform raw materials in the targeted processed products, also giving rise to other streams of sub-products that have to be managed. For this reason, using the degrees of freedom (d.f.) analysis can be of great help to find out if there is sufficient information to design the process, as well as to establish a calculation sequence. The number of degrees of freedom is calculated as follows:

Degrees of freedom = Σ independent variables - Σ known m, G and x_i - Σ balances - Σ relations

According to the value obtained, we will be able to determine whether the system/stage/environment:

- Can be solved: if the d.f. = 0
- Has missing information: if the d.f. >0, and, thus, there are infinite solutions
- Has too much information: if the d.f. <0; thus, there is no possible solution
- Can be solved by using a calculation basis (in terms of mass flow): if the d.f. = 1 and as long as there is no established flow in the available information.

The use of a table (Table 4) is recommended when performing the degrees of freedom study. We will have a column per control volume or stage of the process, also including the "global", which represents the control volumes in which the balances will be applied. Furthermore, we will use an additional column for the "process", which includes all the information regarding data, variables and equations. This column will be used to find out whether the system of equations has a solution or not. In the rows in this table, we will list the independent variables, mass flows, generation flows and mass fractions that we know, the balances that can be stated in each case, and the possible mathematical relations (stoichiometric, yield...), in order to calculate the degrees of freedom in the last row.

Table 4. Degrees of freedom analysis in the example of paracetamol production.

	Reactor 1	Reactor 2	Dehydrator	Global	Process
Indep. Variables	10	12	6	18	23
Balances	4	6	2	6	12
m, G	1	0	0	1	1
X	2	1	2	5	5
Relations	3	2	0	5	5
d.f.	0	3	2	1	0

To complete the Reactor 1 column, we have counted the independent variables displayed according to Table 3, which are: $m_1, m_2, m_5, X_{\text{N}1}, X_{\text{H}4}, X_{\text{N}2}, X_{\text{af}2}, G^1_{\text{N}}, G^1_{\text{H}}, G^1_{\text{af}}$, which concern streams 1, 2 and 5. In this environment, we can state four balances: balance of total matter, and the balances of nitrobenzene, hydrogen and acetic anhydride. Additionally, we know m_1 and $X_{\text{N}1}$. As regards relations, we will consider the 2 relations indicated in Table 3, which relate nitrobenzene with hydrogen and with acetic anhydride, as well as the yield of the operation. For the rest of the environments, the same procedure will be followed.

In the column corresponding to the process, all the independent variables of the process will be considered. As far as balances are concerned, we add up the balances that are in each cell of each environment, except the global environment. The known variables will be established considering the sum of all the known independent variables of the whole process (Table 2), as well as the relations (Table 3). Provided that the number of degrees of freedom is 0 in the process column, we know that the problem is correctly approached, as it will have a single solution. Furthermore, we deduce that the first environment or control volume to work out is Reactor 1, because it has 0 d.f. as well. Once Reactor 1 is solved, we will obtain the value of the variables that will enable the recalculation of the d.f. in the other environments (Table 5), until all the unknown variables of the process have been worked out (Tables 6 and 7).

Table 5. Calculation itinerary based on the degrees of freedom analysis.

Reactor 1	Reactor 2	Dehydrator
<p>1) G_{nN}^1 from eq. 7 2) G_H^1 from eq. 5 3) G_{af}^1 from eq. 6 4) m_5 from eq. 4 5) m_2 from eq. 1 6) x_{af2} from eq. 3 7) x_{nN2} from eq. 2 Besides: $G_w^1 = G_{nN}^1 + G_H^1 - G_{af}^1$ $x_{w2} = 1 - x_{af2} - x_{nN2}$ knowing m_2, x_{nN2} y x_{af2}, we will be able to solve reactor 2.</p>	<p>8) G_{af}^2 from eq. 10 9) G_{aha}^2 from eq. 14 10) G_{parac}^2 from eq. 15 $G_{aa}^1 = G_{af}^2 + G_{aha}^2 - G_{parac}^2$ 11) m_6 from eq. 11 12 and 13) m_7 and x_{nN7} solving the system formed by eq. 9 and 13 eq. 9: $m_7 = \frac{m_2 \cdot x_{nN2}}{x_{nN7}}$ eq. 13: $m_7 = \frac{G_{aa}^2}{1 - x_{nN7}}$ equaling both: $x_{nN7} = \frac{m_2 x_{nN2}}{(G_{aa}^2 + m_2 x_{nN2})}$ 14) m_3 from eq. 8 15) x_{parac3} from eq. 12 $x_{w3} = 1 - x_{parac3}$ y $x_{aa7} = 1 - x_{nN7}$ knowing m_3 and x_{parac3}, we will be able to solve the dehydrator</p>	<p>16) m_4 from eq. 17 17) m_8 from eq. 16</p>

By working out the control volumes, we will obtain the following results:

Table 6. Results of mass flows and mass fractions in the example of paracetamol production

	Streams							
	1	2	3	4	5	6	7	8
m (kg/h)	100	102.7	121.8	103.7	2.7	68.7	49.6	18.0
x_{nN} (kg nitrobenzene/kg total)	0.92	0.090	0	0			0.186	0
x_w (kg water/kg totals)	0.08	0.196	0.165	0.02		0		1
x_{af} (kg aminophenol/k total)		0.715			0		0	
x_{aha} (kg acetic anhydride/kg total)			0	0		1		
x_{aa} (kg acetic acid/kg total)	0	0					0.814	0
x_{parac} (kg paracetamol/kg total)			0.835	0.98		0	0	
x_H (kg hydrogen/kg total)			0	0	1		0	

Data are indicated in red

Table 7. Results of generations in the example of paracetamol

G¹_{nN} (kg/h)	82.8	G²_{af} (kg/h)	73.4
G¹_H (kg/h)	2.7	G²_{aha} (kg/h)	68.7
G¹_{af} (kg/h)	73.4	G²_{parac} (kg/h)	101.6
G¹_w (kg/h)	12.1	G²_{aa} (kg/h)	40.4

5. Closing statement

Through this learning object, we have learnt to obtain the mass flows and compositions of the different streams involved in an industrial process, in which chemical, biochemical or microbial reactions take place. To do so, we have used matter balances with generation and in the steady state. In addition, we have been able to state the sequential resolution of the equations of the system by means of the degrees of freedom analysis, a tool with great practical applications.

6. References

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