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MASS BALANCES FOR CHEMICAL ENGINEERS

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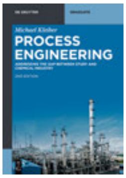

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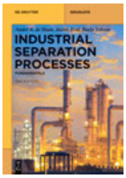

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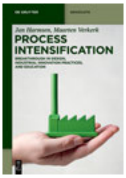

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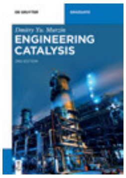

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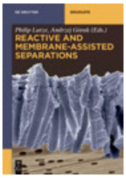

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1 Conservation principles

1.1 The law of conservation of mass

Conservation laws define the fundamentals of science and engineering. The most common statements of these laws express that “mass (or energy) cannot be created or destroyed,” “the mass (or energy) of the universe is constant,” “the mass (or energy) of an isolated system is constant” and so forth. That is, there are certain characteristics of matter that remain constant when a physical or chemical change takes place in a system. The constancy of these properties, that is, their conservation, is the main object of the study of the so-called principles of conservation.

Although the ancient Greeks first proposed the idea that the total amount of matter in the universe is constant, the French chemist Lavoisier[1] enunciated the law of conservation of mass based on countless experiments where he measured the mass of all the components of a wide range of chemical reactions. This law states that, despite chemical reactions or physical transformations, mass is conserved – that is, it cannot be created or destroyed – within an isolated system. In other words, in a chemical reaction, the mass of the products will always be equal to the mass of the reagents.

Therefore, chemical reactions can be visualized as a rearrangement of atoms and bonds, while the number of atoms involved in a reaction remains unchanged. This assumption allows us to represent a chemical reaction as a balanced equation, in which the number of moles of any element involved is the same on both sides of the equation.

A more general statement of this law consists in pointing out that matter is neither created nor destroyed, it is only transformed. This fact is valid for practically all physical and chemical changes, with the exception of nuclear reactions, where part of the matter is transformed into energy.

1.2 General balance equation

The calculation and design of industrial unitary equipment requires the resolution of equations that describe the systems under study and relate the variables involved to each other (flow rate, T, P, composition, energy, etc.).

Using the conservation principle of matter, a series of equations (=balances) can be formulated between the various units, systems and flows of the processes. Accordingly, it is possible to:

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[1] Antoine-Laurent de Lavoisier (1743–1794): French scientist considered the father of modern chemistry.

https://doi.org/10.1515/9783110624304-001

1. Calculate mass flows by reducing in situ measurements.
2. Close the mass flows (=close the mass balances) to describe the system comprehensively or compare the actual (measured) values with the target values.

These balances give an idea of “how much” the change in a given system meant. Now, we cannot solve these equations without some knowledge and interpretation of the transport mechanism. That is, in addition to “how much,” we need to know “at which rate” the change occurs. This value is given by kinetic laws:

- Physical kinetics: friction (motion), conduction–convection and radiation (energy), and diffusion (matter).
- Chemical kinetics: for systems where a chemical reaction occurs.

A third important element to take into account is the information about natural and/or nonnatural restrictions. These restrictions can take the form of the following:

- physical equilibrium,
- chemical equilibrium,
- boundary conditions,
- other (economic, safety, legislation, etc.).

The knowledge of all this information is the first step for the definition of a mathematical model from which it is possible to analyze, simulate, design a system and/or process.

The basic principle used in modeling of chemical engineering process is based on the concept of balances (momentum, mass and energy). The application of balances must refer to a system defined by a control volume, perfectly delimited in space by a control surface. Generally speaking, any balance can be expressed in a general form as follows (Figure 1.1):

$$Input + Generation = Output + Accumulation$$

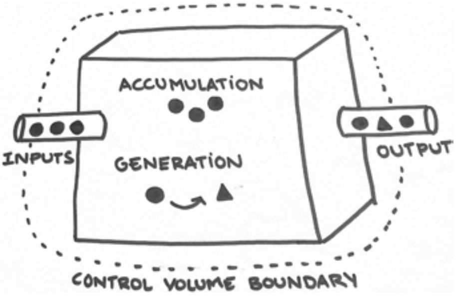

Figure 1.1: Mass balance scheme.

- *Input/Output*: This corresponds to the flow of property (mass and/or energy) that crosses the limits of the system in a given time.
- *Accumulation*: This corresponds to the amount of property within the system after a time t, so it can be both positive and negative.
- *Generation*: This corresponds to the amount of property that appears or disappears within the system without initially being present or having been transferred across the system boundaries.

The extent of description of the balances can be defined at various scales:

- *Macroscopic balance* (also called *integral*): It is applied to a volume element and allows to know what happens between two instants of time. It is characterized by the knowledge of only one value of each variable, which will be the mean value of the whole system.
- *Microscopic balance* (also called *differential*): A differential element of volume is applied and allows to know what happens in an instant of time; therefore, there is a variation of the property (mass/energy) with space (x, y, z) and time (t).

At the same time, the existence of chemical reaction (generation term) or nonstationary state (accumulation term) implies notorious differences in the type of equation of the balances and, therefore, in their resolution. Appendices C, D and E show the basic mathematical aspects and their application in Excel for solving systems of linear and nonlinear equations.

The synoptic description of a process is usually represented through flow diagrams, which help to understand how the flow of materials or energy is carried out in a process or in an equipment. Different representation options are considered: block diagram, process flow diagram and piping and instrumentation diagram (P&ID).

The block diagram is represented by means of boxes or rectangles in which the input and output flows are identified (usually with an identifying number in a rhombus over each process line). Process flow diagrams include symbols representing major equipment items and process lines (including bypass and recycle streams). The physical properties, quantities, temperatures and pressures of the materials can be indicated for each process line in the stream table that typically compiles an inventory of the different flows. More exhaustive information is included in the P&ID such as instrumentation and control details, vents and drains and relief and safety valves.

2 Balances in systems without chemical reaction

2.1 Formulation of the general equation of macroscopic mass balance

2.1.1 Overall balance

The rigorous formulation of the mass balance for a control volume (V) delimited by a control surface (A) (Figure 2.1) in which the density (ρ) of the system varies continuously with position and over time is presented in the following expression:

$$\left\{\begin{matrix}\text{mass accumulation}\\ \text{rate}\end{matrix}\right\} = \left\{\begin{matrix}\text{mass input}\\ \text{rate}\end{matrix}\right\} - \left\{\begin{matrix}\text{mass output}\\ \text{rate}\end{matrix}\right\}$$

Applying it to the entire control volume,

$$\int_A \rho \cdot \left(\vec{v} \cdot \vec{n}\right) \cdot dA + \frac{d}{dt} \cdot \int_V \rho \cdot dV = 0 \tag{2.1a}$$

$$\Delta m + \frac{dM}{dt} = 0 \tag{2.1b}$$

where m is the mass flow rate expressed in mass units (kg/s) and M, mass of the system in mass units (kg).

In eqs. (2.1a) and (2.1b), the term generation is null, because mass is a conserved magnitude. Therefore, in that arbitrary volume, mass is continuously entering and exiting, the difference between the two is accumulating.

In many cases it is interesting to know the total flows of input/output material without it being essential to know the value of the velocity at each point of the input/output surfaces. In these cases, the average velocity $<v>$ can be used. In addition, if the density is uniform across each step surface, a simple form of the above equations is obtained:

$$\Delta(\rho \cdot \langle v \rangle \cdot A) + \frac{dM}{dt} = 0 \tag{2.2}$$

If the balance is established in moles instead of units of mass, it must be taken into account that the generation may not be null. For example, if there is a chemical reaction, the number of moles of product may be different than the number of reactants. By calling "g" the amount of mass, in moles, produced or consumed per unit of time and volume, the moles generated per unit of time will be

$$\int_V g \cdot dV = 0 \tag{2.3}$$

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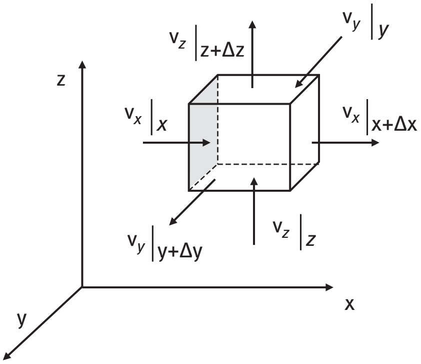


Side	Input	Output
x	$\rho v_x\|_x \Delta y \Delta z$	$\rho v_x\|_{x+\Delta x} \Delta y \Delta z$
y	$\rho v_y\|_y \Delta x \Delta z$	$\rho v_y\|_{y+\Delta y} \Delta x \Delta z$
z	$\rho v_z\|_z \Delta x \Delta y$	$\rho v_z\|_{z+\Delta z} \Delta x \Delta y$

- ρv_x is the density of mass flow in the direction x: (kg/m^{2}s)
- $\Delta y \Delta z$ delimits the surface perpendicular to the direction of flow for which the flow density is defined

Figure 2.1: Density of material flow in the control volume for each of the control surfaces that delimit it.

If the molar density or system concentration (moles/volume) is denoted as "C," the overall balance of mass in molar units would be as follows:

$$\int_A C \cdot \left(\vec{v} \cdot \vec{n}\right) \cdot dA + \frac{d}{dt} \cdot \int_V C \cdot dV = \int_V g \cdot dV \tag{2.4a}$$

$$\Delta n + \frac{dN}{dt} = \int\limits_V g \cdot dV \tag{2.4b}$$

where n is the mass flow expressed in molar units (kmol/s) and N, mass of the system in molar units (kmol).

2.1.2 Component balance

The mass balance is applicable not only to all the material that enters, exits, accumulates or is generated in the system, but also to any component. Thus, although it must be borne in mind that in the case of a chemical reaction, the term *generation* will not be zero, not even working in units of mass. The generation can be negative (when the component is a reactant) or positive (if the component is a product).

The formulation of the balance of the component "i" is obtained from eqs. (2.1a) and (2.1b) by replacing ρ by c_i (mass concentration), m by m_i and M by M_i. Strictly speaking $\vec{v}$ should also be replaced by $\vec{v_i}$, because if there are concentration gradients the individual components will not move with the same velocity $\vec{v}$. However, in systems considered from a macroscopic point of view, this difference is not significant:

$$\int_A c_i \cdot \left(\vec{v} \cdot \vec{n}\right) \cdot dA + \frac{d}{dt} \cdot \int_V c_i \cdot dV = \int_V G_i \cdot dV \tag{2.5a}$$

$$\Delta m_i + \frac{dM_i}{dt} = \int_V G_i \cdot dV \tag{2.5b}$$

Equation (2.5b) can be expressed as a function of the mass fraction, w_i (kg component/kg total mass), or molar, x_i (mol component/total moles):

$$\Delta(w_i \cdot m) + \frac{d(w_i \cdot M)}{dt} = \int_V G_i \cdot dV \tag{2.6a}$$

$$\Delta(x_i \cdot n) + \frac{d(x_i \cdot N)}{dt} = \int_V g_i \cdot dV \tag{2.6b}$$

2.2 Macroscopic mass balances for systems without chemical reaction at steady state

If, in a stationary process, each output and input flow can be measured and analyzed, the usefulness of the macroscopic balance is limited, except for checking the consistency of the experimental data. However, if there are one or more points where it is not practical or possible to take the necessary data, they can be calculated applying the mass balances. In addition, another usefulness of the mass balances is their application to carry out the previous calculations in the design of units and the simulation of processes.

For systems in stationary state without chemical reaction, both the accumulation and generation term are zero in the total balance and in the component balances.

2.2.1 Overall balance

Equation (2.2) would be simplified to

$$\Delta(\rho \cdot \langle v \rangle \cdot A) = 0 \tag{2.7}$$

Equation (2.7) can also be expressed as a function of mass flow or volume flow:

$$\Delta(\rho \cdot \langle v \rangle \cdot A) = \Delta m = \Delta(q \cdot \rho) = 0 \tag{2.8}$$

Therefore, if subindexes 1 and 2 refer to input and output, respectively,

$$\Sigma(\rho \cdot \langle v \rangle \cdot A)_1 = \Sigma(\rho \cdot \langle v \rangle \cdot A)_2 \tag{2.9a}$$

$$\Sigma m_1 = \Sigma m_2 \tag{2.9b}$$

$$\Sigma(q \cdot \rho)_1 = \Sigma(q \cdot \rho)_2 \tag{2.9c}$$

2.2.2 Component balance

Equations (2.6a) and (2.6b) would be simplified to

$$\Delta(w_i \cdot m) = 0 \quad \Rightarrow \quad \Sigma(w_i \cdot m)_1 = \Sigma(w_i \cdot m)_2 \tag{2.10a}$$

$$\Delta(x_i \cdot n) = 0 \quad \Rightarrow \quad \Sigma(x_i \cdot n)_1 = \Sigma(x_i \cdot n)_2 \tag{2.10b}$$

If the density remains constant, the balance of a component can also be defined from volumetric flow and mass concentration:

$$\Sigma(q \cdot c_i)_1 = \Sigma(q \cdot c_i)_2 \tag{2.11}$$

2.3 Heuristic rules for the solution of problems on mass balance

The following steps can be defined to solve mass balance problems (Figure 2.2):

1. Representation of the system scheme or process flow diagram with identification and enumeration of the different streams and selection of the suitable basis of calculation: The basis of calculation is defined as the numerical value of an extensive quantity, which is arbitrarily chosen to facilitate calculations and on which other resulting extensive quantities are referred to. In general, different priority criteria are considered for the choice of the calculation basis: (i) a quantity of one of the components of the system, which does not react chemically and which enters and leaves the system as part of a single stream; (ii) a quantity of one of the flows entering or leaving the system, usually the one for which more information is available and (iii) a time interval.
2. Mass balance calculations can be made on the basis of any conventional set of flow quantities or flow velocities. Therefore, when balancing a process, one must select an overall quantity or one of the components (e.g., mass, number of moles, etc.), in such a way that all unknowns are determined in a way that they are consistent with this basis. Guidelines for choice:
    i. If the value of a flow or a flow velocity is provided as data from the problem statement, it is usually convenient to use that quantity as a basis for calculation.
    ii. If the flow or flow velocities of any of the streams are not known, one value should be assumed. In this case, a quantity of flow is chosen for which the composition is known. If the composition data are in mass or molar fraction, the most appropriate calculation basis will be the total mass or number of total moles, respectively.

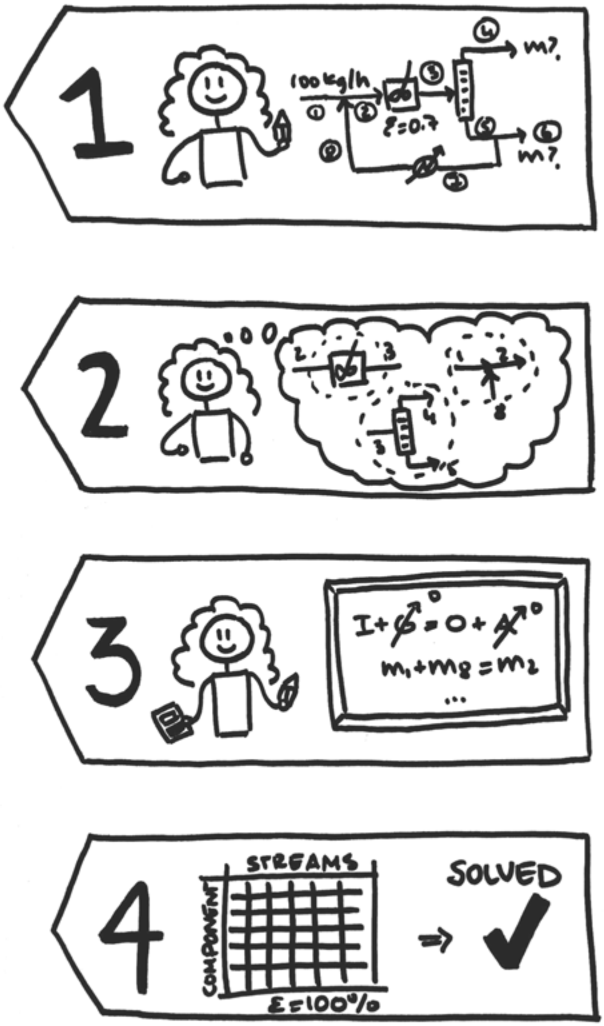


Figure 2.2: Steps on the path to the solution of mass balances.

iii. If the result or objective of the calculation are relative values, for example, the mass ratio between two streams, the final value is independent of the calculation basis.

3. Definition of system boundaries and formulation of the mass balances: For the solution of this type of problems the technique of the "black box" can be used, that is to say, a line is drawn around the process and it is considered exclusively what enters or leaves it. This procedure defines the "system boundary conditions" over which the balance sheets are defined. It should be noted that

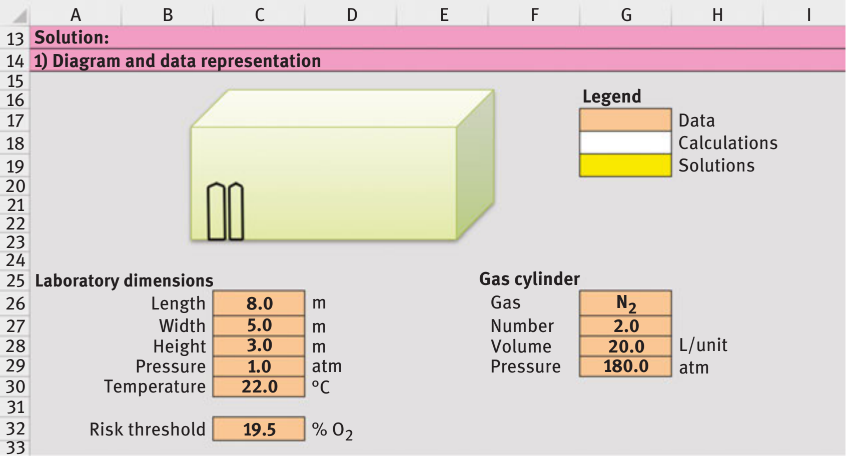
not all balances are independent, so when formulating the balances of the "*i*" components of the system and then an overall balance, the latter will be the sum of the simple balances. Therefore, the number of independent equations in each environment (number of degrees of freedom) will be equal to "*i*," the total number of components.

4. Solving the system of "*i*" linear or nonlinear equations that correctly represent the "*i*" unknown values of the problem.

Example 2.1: Normally the air we breathe contains 20.8% (by volume) of O_2, when in a confined space, this percentage is below 19.5% of its total atmosphere, and the atmosphere is considered to be oxygen deficient. In these conditions, no worker can enter without auxiliary breathing apparatus, since below this threshold there is an increase in breathing, accelerated beats and poor coordination. Calculate whether there is a potential risk from a suboxygenated atmosphere in a laboratory when two gas cylinders of 20 L of N_2 (at 180 atm) are leaking. The dimensions of the laboratory are 8 m long, 5 m wide and 3 m high. Consider atmospheric pressure and 22 °C.

Solution:

Step 1: Diagram and data representation (Figure 2.3)



Solution:

1) Diagram and data representation

Legend

🟧 Data
⬜ Calculations
🟨 Solutions

Laboratory dimensions

Length	**8.0**	m
Width	**5.0**	m
Height	**3.0**	m
Pressure	**1.0**	atm
Temperature	**22.0**	°C
Risk threshold	**19.5**	% O_2

Gas cylinder

Gas	**N_2**	
Number	**2.0**	
Volume	**20.0**	L/unit
Pressure	**180.0**	atm

Figure 2.3: Process scheme and data representation.

Step 2: Basis of calculations

The objective of this problem is to determine whether the leakage of nitrogen gas cylinders can cause a suboxygenated atmosphere in the laboratory; therefore, the volume of nitrogen confined in the gas cylinder: 40 L will be considered as the basis for calculation.

Step 3: Definition of system boundaries and formulation of the mass balances

In this problem the system boundary is the laboratory and the balances are formulated from eq. (2.10b), where subindexes 1 and 2 refer to the initial and final instant (after the leak):

$$\Sigma(x_i \cdot n)_1 = \Sigma(x_i \cdot n)_2$$

$$\text{Balance for } O_2\text{:} \quad (n_{O_2})_2 = (n_{O_2})_1 = (n_{O_2})_{\text{lab}}$$

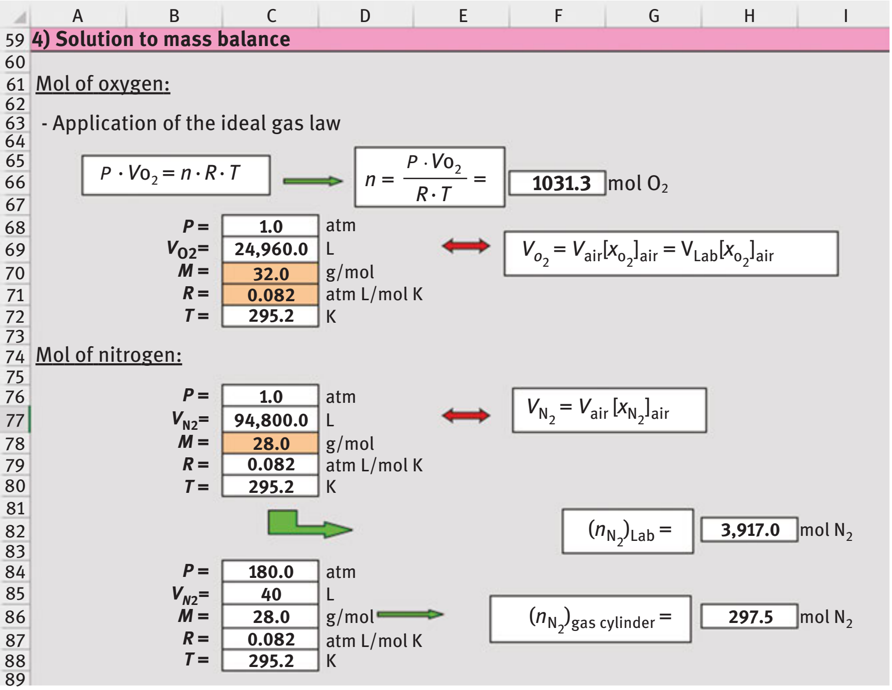
$$\text{Balance for } N_2\text{:} \quad (n_{N_2})_2 = (n_{N_2})_1 = (n_{N_2})_{\text{lab}} + (n_{N_2})_{\text{gas cylinder}}$$

So, the new oxygen concentration will be calculated by

$$(x_{O_2})_2 = \frac{(n_{O_2})_2}{(n_{O_2})_2 + (n_{N_2})_2}$$

Step 4: Resolution of the mass balances

The number of moles of oxygen and nitrogen is calculated by applying the law of ideal gases (Figure 2.4).



4) Solution to mass balance

Mol of oxygen:

- Application of the ideal gas law

$P \cdot V_{O_2} = n \cdot R \cdot T$ → $n = \dfrac{P \cdot V_{O_2}}{R \cdot T} =$ 1031.3 mol O_2

$P =$ 1.0 atm

$V_{O2} =$ 24,960.0 L

$M =$ 32.0 g/mol

$R =$ 0.082 atm L/mol K

$T =$ 295.2 K

$V_{O_2} = V_{\text{air}}[x_{O_2}]_{\text{air}} = V_{\text{Lab}}[x_{O_2}]_{\text{air}}$

Mol of nitrogen:

$P =$ 1.0 atm

$V_{N2} =$ 94,800.0 L

$M =$ 28.0 g/mol

$R =$ 0.082 atm L/mol K

$T =$ 295.2 K

$V_{N_2} = V_{\text{air}}[x_{N_2}]_{\text{air}}$

$(n_{N_2})_{\text{Lab}} =$ 3,917.0 mol N_2

$P =$ 180.0 atm

$V_{N2} =$ 40 L

$M =$ 28.0 g/mol

$R =$ 0.082 atm L/mol K

$T =$ 295.2 K

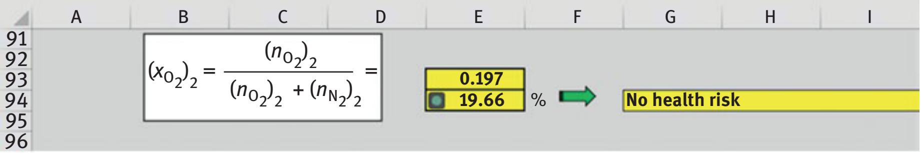
$(n_{N_2})_{\text{gas cylinder}} =$ 297.5 mol N_2

Figure 2.4: Calculation of the number of moles of oxygen and nitrogen.

In this way, the final oxygen concentration can be calculated in the laboratory after the nitrogen in the bottles has leaked. In addition, the *IF* function in Excel can be used:

=IF(logic_test;[true_if_value];[false_if_value])

A text message that “warns” of the health risk can be related to the threshold value that is set (Figure 2.5):



$$(x_{O_2})_2 = \frac{(n_{O_2})_2}{(n_{O_2})_2 + (n_{N_2})_2} =$$

0.197

● 19.66 %

No health risk

Figure 2.5: Calculation of the oxygen concentration and application of the Excel SI function.

> G94: =IF(E94 < C32; “There is a risk to health”; “no health risk”). The threshold value of 19.5% is defined in cell C32.

In complex sheets it may be of interest to introduce rules in some cells that allow “alerting” a discrepancy between the physical meaning and the mathematical result; for example, the existence of negative values in variables that represent mass flows.

In this problem, the alert would be related to the potential risk, in such a way that values above the threshold would have a “green” icon or otherwise a “red” icon. Thus, to introduce a rule in cell E94 where it is calculated as the result of the final percentage of oxygen (Figure 2.4), proceed as follows:

i. Select the cell in which to enter the rule, that is, E94.
ii. Conditional Format > New rule.
iii. In the display of format style select the option “set of icons.” In the icon style you will choose “3 semaphores with frame.”
iv. In the type choose formula.
v. In the value you enter 19.6 and 19.5 to set the condition of each icon.

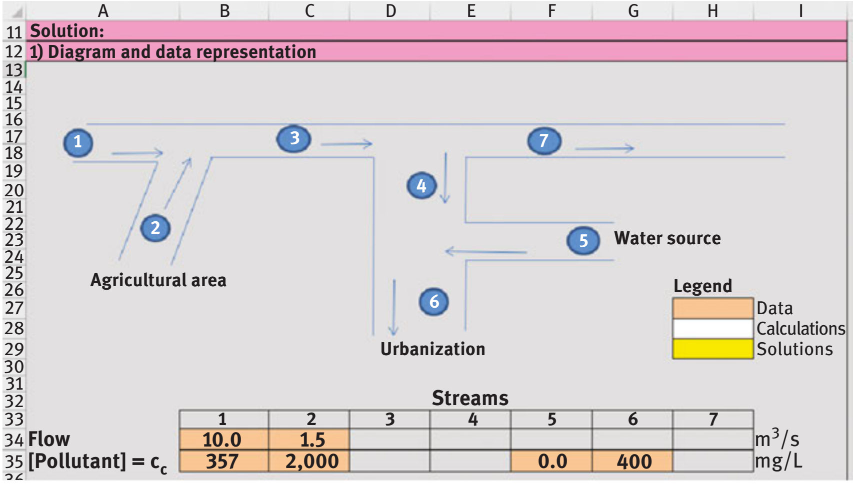
Questions/simulations:

i. *Design calculation*: The mass balance allows us to simulate design/operation situations. Thus, if in this laboratory increased from 2 to 3 gas cylinder of nitrogen, we would have a potentially dangerous situation if there were a complete leak of the nitrogen confined within them. For example, if the value of 3 is entered in the cell G27, this would result in an oxygen concentration of 19.12% and therefore a health risk (the “red” icon in the cell would be shown).

Example 2.2: A river with 357 mg/L of a contaminant and a flow of 10 m^3/s receives an agricultural discharge of 1.5 m^3/s carrying 2,000 mg/L of that contaminant. The contaminating compound dissolves quickly and evenly in the river water. Downstream, water is extracted for consumption from an urban nucleus, where it is previously mixed with water from another source so that the final content of the contaminant does not exceed 400 mg/L. What should be the mixing ratio of the source water with the river water?

Solution:

Step 1: Flowchart with identification and enumeration of streams (Figure 2.6)



Solution:

1) Diagram and data representation

🟧	Data
☐	Calculations
🟨	Solutions

Streams

	1	2	3	4	5	6	7	
Flow	**10.0**	**1.5**						m^3/s
[Pollutant] = c_c	**357**	**2,000**			**0.0**	**400**		mg/L

Figure 2.6: Scheme of the process data representation.

Step 2: Basis of calculations
The objective of this problem is the calculation of the q_5/q_4 ratio; therefore, the final value will not depend on the quantity selected as the calculation base. In this case, in the first instance a value of 5 m^3/s will be chosen for the flow of water that will finally be supplied to the urban nucleus, q_6.

Step 3: Definition of system boundaries and formulation of the mass balances
In this problem, the most suitable systems to define the balances would correspond to the points of mixing (mixer) and division (divider) of streams (Figure 2.7).

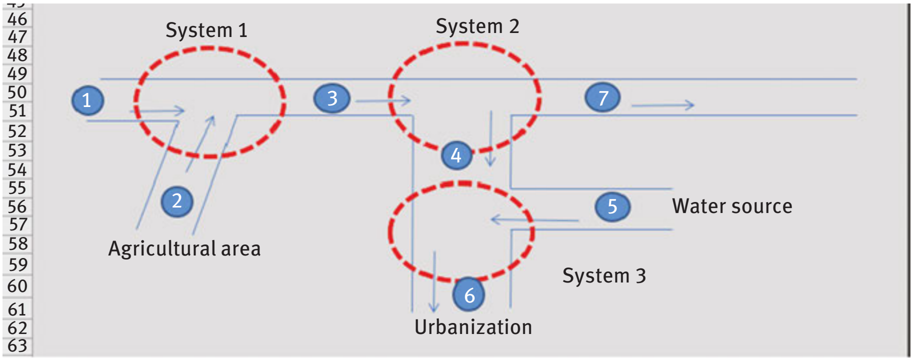


Figure 2.7: Definition of control volumes.

If you consider “system 1” to define the overall balance you can calculate the value of q_3. Applying the global balance (eq. (2.9c)) and taking into account that density can be considered constant and equal in all streams:

$$\begin{array}{c} \Sigma(q\cdot\rho)_{\text{input}} = \Sigma(q\cdot\rho)_{\text{output}} \\ \Sigma q_{\text{input}} = \Sigma q_{\text{output}} \end{array} \quad \Rightarrow \quad q_1 + q_2 = q_3$$

Consequently, the value of $q_3 = 10 + 1.5 = 11.5\ \text{m}^3/\text{s}$.

Applying the component balance (eq. (2.11)) the value of the salt concentration in stream 3 will be determined:

$$q_1\cdot(c_{\text{salt}})_1 + q_2\cdot(c_{\text{salt}})_2 = q_3\cdot(c_{\text{salt}})_3 \quad \Rightarrow \quad (c_{\text{salt}})_3 = \frac{q_1\cdot(c_{\text{salt}})_1 + q_2\cdot(c_{\text{salt}})_2}{q_3}$$

The value of the concentration will be

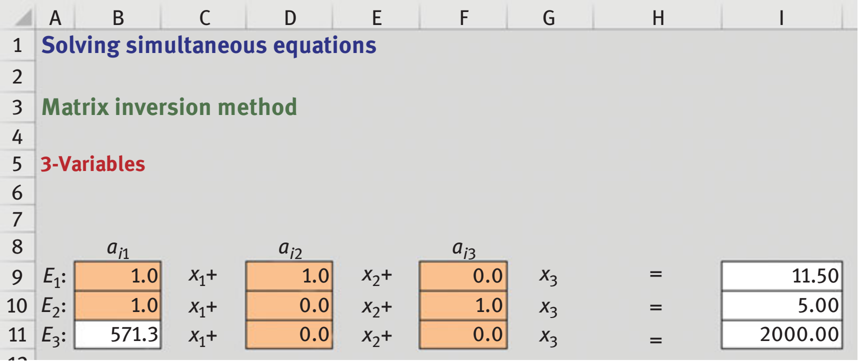
$$(c_{\text{salt}})_3 = \frac{q_1\cdot(c_{\text{salt}})_1 + q_2\cdot(c_{\text{salt}})_2}{q_3} = \frac{(10\cdot 357) + (1.5\cdot 2000)}{11.5} = 571.3\ \frac{\text{mg}}{\text{L}}$$

When considering the system “2” and “3” we formulate a system of 3 linearly independent equations with 3 unknown variables, where two of them are adequate for the final objective of the problem:

– System “2”		
Overall balance	Parameters	Coded Equation
$q_3 = q_4 + q_7$	$x_1 = q_4$ $x_2 = q_7$	$x_1 + x_2 = q_3$
– System “3”		
Overall balance		
$q_4 + q_5 = q_6$	$x_3 = q_5$	$x_1 + x_3 = q_6$
Component balance – outlet		
$q_4\cdot(c_{\text{salt}})_4 = q_6\cdot(c_{\text{salt}})_6$		$(c_{\text{salt}})_4\cdot x_1 = q_6\cdot(c_{\text{salt}})_6$

Step 4: Solving the simultaneous equations

In a first stage, a copy of the “3 variables” sheet from the “Appendix D_Inversion Matrix” (see Appendix D) to the book where the solution to the problem is being elaborated. Both sheets are then “connected” with the input of the coefficients as data (for those not dependent on the problem data) or as a formula (when dependent on the problem data; Figure 2.8).



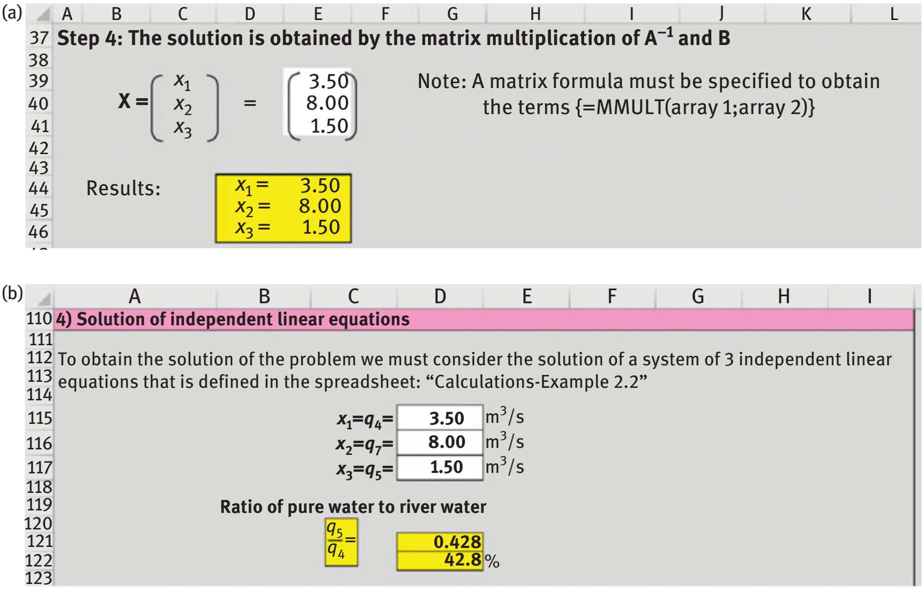
	A	B	C	D	E	F	G	H	I
1	Solving simultaneous equations								
2									
3	Matrix inversion method								
4									
5	3-Variables								
6									
7									
8		a_{i1}		a_{i2}		a_{i3}			
9	E_1:	1.0	x_1+	1.0	x_2+	0.0	x_3	=	11.50
10	E_2:	1.0	x_1+	0.0	x_2+	1.0	x_3	=	5.00
11	E_3:	571.3	x_1+	0.0	x_2+	0.0	x_3	=	2000.00

Figure 2.8: Spreadsheet with the solution of the system of linear equations from Example 2.2.

For example,

B9: = 1,0 (coefficient).
I9: = ‘Example 2.2’!F77 (is entered as a formula since it depends on the data of the problem).

When you finish entering the coefficients, the calculation of the solution will be automatically produced, which we can, in turn, connect to the main sheet of the problem (Figure 2.9a, b).



Step 4: The solution is obtained by the matrix multiplication of A^{-1} and B

$$\mathbf{X} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} 3.50 \\ 8.00 \\ 1.50 \end{pmatrix}$$

Note: A matrix formula must be specified to obtain the terms {=MMULT(array 1;array 2)}

Results:
$x_1 =$ 3.50
$x_2 =$ 8.00
$x_3 =$ 1.50

4) Solution of independent linear equations

To obtain the solution of the problem we must consider the solution of a system of 3 independent linear equations that is defined in the spreadsheet: “Calculations-Example 2.2”

$x_1=q_4=$ 3.50 m^3/s
$x_2=q_7=$ 8.00 m^3/s
$x_3=q_5=$ 1.50 m^3/s

Ratio of pure water to river water

$\frac{q_5}{q_4}=$ **0.428**
42.8 %

Figure 2.9: (a) System solution using the reverse matrix method. (b) Solution of the problem.

Accordingly,

D115: = ‘Calculations-Example 2.2’!E44
D116: = “Calculations-Example 2.2’!E45
D117: = “Calculations-Example 2.2’!E46

Consequently, the solution to the problem will be 42.8% in the flow ratio.

Questions/simulations:

i. *Effect of the calculation basis*: The result of the problem (relation between streams) does not depend on the value of the calculation base. Thus, if another value is entered in cell C39, for example, 3.5 m^3/s, the final value will not change even if the flow values vary.

ii. *Effect of an overload*: If the concentration in the agricultural waste is increased by 25%, therefore, the concentration would be 2,500 mg/L (cell C35), and the value of the ratio would be 59.1%. Obviously, it will be necessary to increase the flow from the water source in order to maintain the same characteristics of the water that reaches the urbanization.

2.4 Recirculation, purge or bypass

2.4.1 Recirculation/recycle and purge streams

In many operations and to improve the conversion of the process into reversible reactions or to recover specific components of the product stream such as solvents, it is necessary to introduce a scheme that considers the possibility of recirculation. A recirculation/recycle stream is simply a flow that is taken from the discharge of a unit (it may or may not have the same concentration as the product stream) and returned as feed to a unit located upstream in the process (Figure 2.10). From a mathematical point of view, it is necessary to pose the balance equations to the whole system, to each process block and to the mixing point.

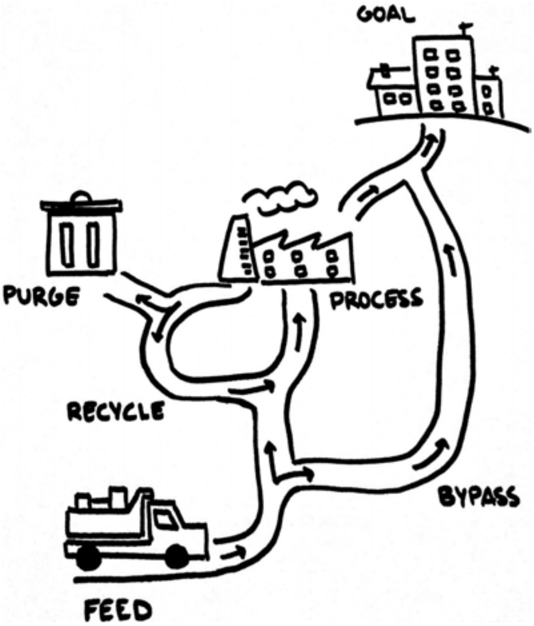


Figure 2.10: Recycle, purge and bypass streams in a process.

The purge stream is defined as the flow separated from the system, typically corresponding to a fraction of the recirculation stream, in order to remove certain substances that would otherwise accumulate inside the system. This is done by balancing the entire system around each block at the mixing point and at the purge extraction point.

A recirculating unit can be viewed as a process of three units: mixer, system and a stream divider (Figure 2.11).

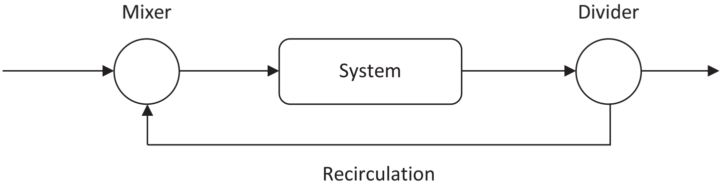
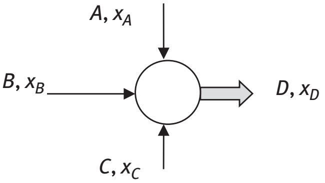


Figure 2.11: Diagram of a process with recirculation.

The mixer is a device within which two or more streams are joined together to form a single main stream (Figure 2.12). As the mixing is carried out solely on the basis of the flow, the main stream has a flow equal to the sum of the flows of each of the streams.

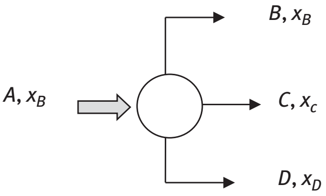


$$D = A + B + C$$

$$x_D = \frac{A \cdot x_A + B \cdot x_B + C \cdot x_C}{D}$$

Figure 2.12: Overall balance and component balance in a stream mixer.

A divider is a device within which the input flow is divided into two or more streams. As this division is made only as a function of flow, the composition of all the streams into which the mainstream is divided will be identical (Figure 2.13).



$$A = B + C + D$$

$$x_A = x_B = x_c = x_D$$

Figure 2.13: Balance in a stream divider.

There are three ways or types of recirculation so that raw materials that have not been used (reacted in a chemical reactor, absorbed in an absorption tower, etc.) can be recycled upstream in a process:

1. Separate and purify the output stream and recirculate them at the beginning of the process.
2. Partially recirculate the output stream using a purge stream to avoid accumulations.
3. Partially recirculate the output stream without considering a purge stream.

Example 2.3: The biogas generated in the anaerobic digestion of sludge from a wastewater treatment plant, which contains 74% CH_4 and 26% CO_2 (percentages by volume), is to be used in a cogeneration system. Its previous conditioning consists of two absorption columns (Figure 2.14) by recirculating methanol as an extractive separating agent (consider that for the purposes of the process it is nonvolatile; therefore, it is not found in any of the gas streams of the process units). In the absorption column T-102, it is possible to extract 90% of the CO_2 from the stream 3: (i) recirculation flow (stream 4), (ii) flow of stream 3 and molar fraction of CO_2 and (iii) fractional extraction of CO_2 expressed as absorbed moles/moles in the feed.

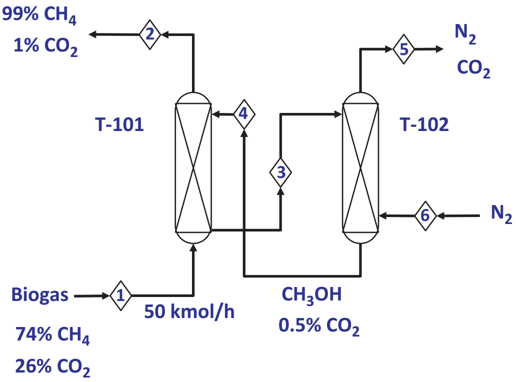


Figure 2.14: Process of conditioning biogas prior to its use in a cogeneration system.

Solution:

Step 1: Flowchart and stream table

The statement of the problem already has the flow diagram; therefore, it is only necessary to indicate and enumerate the data of molar flow and molar fraction of each of the streams. Two aspects should be highlighted: (i) the % by volume coincides with the % molar and (ii) the composition of stream 4 is 0.5% CO_2 and, therefore, 99.5% CH_3OH.

	1	2	3	4	5	6	
Flow rate	50.0						kmol/h
CH_4	74.0	99.0	0.0				% molar
CO_2	26.0	1.0		0.5			% molar
CH_3OH				99.5	0.0		% molar
N_2				0.0		100.0	% molar

Step 2: Basis of calculations

The calculation basis will be the feed flow rate: $n_1 = 50$ kmol/h.

Step 3: Definition of system boundaries and formulation of the mass balances

- If the absorption column T-101 is considered as the control volume to define the balance of CH_4, the value of n_2 can be calculated. Applying the component balance (eq. (2.10b)),

$$(x_{CH_4})_1 \cdot n_1 = (x_{CH_4})_2 \cdot n_2 \quad \Rightarrow \quad n_2 = \frac{(x_{CH_4})_1 \cdot n_1}{(x_{CH_4})_2} = \frac{0.74 \cdot 50}{0.99} = 37.37 \ \frac{\text{kmol}}{h}$$

  If you consider the CO_2 balance and the overall balance, you will get two equations with three unknown variables:

CO_2 Balance	Unknown parameters	Coded equation
$(x_{CO_2})_1 \cdot n_1 + (x_{CO_2})_4 \cdot n_4 = (x_{CO_2})_2 \cdot n_2 + (x_{CO_2})_3 \cdot n_3$	$x_1 = n_3$ $x_2 = (x_{CO_2})_3$ $x_1 = n_4$	$x_1 \cdot x_2 - (x_{CO_2})_4 \cdot x_3 + (x_{CO_2})_2 \cdot n_2 - (x_{CO_2})_1 \cdot n_1 = 0$
Overall Balance		
$n_1 + n_4 = n_2 + n_3$		$x_1 - x_3 + n_2 - n_1 = 0$

- The third equation is obtained from the CO_2 balance by considering the absorption column T-102 as the control volume, taking into account the efficiency of the CO_2 recovery of this column:

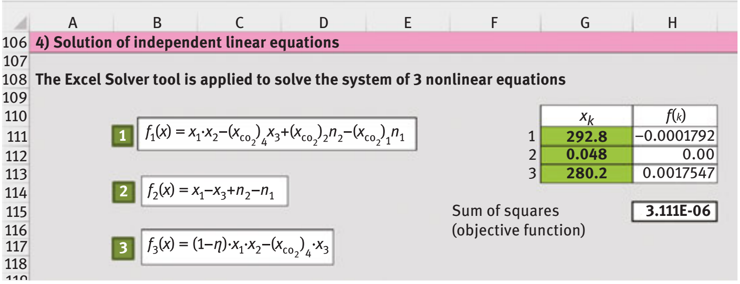
$$\begin{aligned} (x_{CO_2})_3 \cdot n_3 &= (x_{CO_2})_4 \cdot n_4 + (x_{CO_2})_5 \cdot n_5 \\ (x_{CO_2})_5 \cdot n_5 &= \eta \cdot (x_{CO_2})_3 \cdot n_3 \end{aligned} \quad \Rightarrow \quad (1-\eta) \cdot (x_{CO_2})_3 \cdot n_3 = (x_{CO_2})_4 \cdot n_4$$

  If this last equation is coded,

$$(1-\eta) \cdot x_1 \cdot x_2 - (x_{CO_2})_4 \cdot x_3 = 0$$

  From these balances we have obtained a system of three independent nonlinear equations with three unknown variables, which will allow us to calculate the objectives of the problem.

Step 4: Solving the system of nonlinear equations
As noted in Appendix E on solving systems of nonlinear equations, the application of Excel Solver tool is a suitable technique to obtain the solution to a system of nonlinear equations (Figure 2.15).



4) Solution of independent linear equations

The Excel Solver tool is applied to solve the system of 3 nonlinear equations

1 $f_1(x) = x_1 \cdot x_2 - (x_{co_2})_4 x_3 + (x_{co_2})_2 n_2 - (x_{co_2})_1 n_1$

2 $f_2(x) = x_1 - x_3 + n_2 - n_1$

3 $f_3(x) = (1-\eta) \cdot x_1 \cdot x_2 - (x_{co_2})_4 \cdot x_3$

	x_k	$f(k)$
1	**292.8**	−0.0001792
2	**0.048**	0.00
3	**280.2**	0.0017547

Sum of squares (objective function) **3.111E-06**

Figure 2.15: Definition of the balance sheet and solution of Example 2.3.

Therefore, it is now possible to respond to each of the sections of the problem:

a. recirculation flow rate (stream 4): $n_4 = 280.2$ kmol/h,
b. flow of stream 3 and molar fraction of CO_2:

$$n_3 = 293.8\,\text{kmol/h}$$

$$(x_{CO_2})_3 = 0.048$$

c. fractional extraction of CO_2 expressed as absorbed moles/moles in the feed: 97.12%

$$\frac{(x_{CO_2})_3 \cdot n_3 - (x_{CO_2})_4 \cdot n_4}{(x_{CO_2})_1 \cdot n_1} = 0.9712$$

Example 2.4: The galvanizing industry has been one of the first for which a BREF[2] document has been defined, where the best available techniques (BAT) are collected for each sector under study, due to the degree of pollution of the effluents. One of the BATs defined in this document is the increase in the internal recycling of baths (with a high metal content) until they get more exhausted. Thus, in a given metal surface treatment facility, there is a problem with its discharge effluent due to the high concentration of zinc and nickel. A process is proposed (Figure 2.16) where recirculation streams play a key role in the final effectiveness of the process.

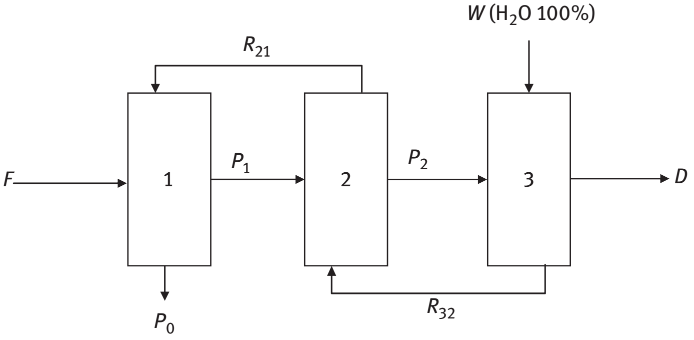


Figure 2.16: Zn and Ni recovery process in a galvanizing industry to apply in Example 2.4.

Table 2.1 lists the concentrations of several of the streams, all of which contain water. Calculate (in L/h) the flow rate of the recycling stream R_{32}.

---

[2] Best available techniques reference document: https://eq.europa.eu/jrc/en.

Table 2.1: Data from the design process streams for the recovery of Zn and Ni in the galvanizing industry (Example 2.4).

Stream	**Zn (g/L)**	**Ni (g/L)**
F	100.0	10.00
P_0	190.1	17.02
P_2	3.50	2.19
R_{32}	4.35	2.36
D	0.10	1.00

Solution:

Step 1: Flowchart and stream table

The statement of the problem already has the flow diagram; therefore, it is only necessary to indicate the flow and concentration of each of the streams.

	Stream								
	F	P_0	P_1	P_2	W	D	R_{21}	R_{32}	
Flow rate									L/h
Zn	100.00	190.10		3.50	0.00	0.10		4.35	g/L
Ni	10.00	17.02		2.19	0.00	1.00		2.36	g/L

Step 2: Basis of calculations

The feed flow rate shall be taken as the basis for calculation: $q_F = 1$ L/h.

Step 3: Definition of control volumes and formulation of the mass balances

In problems with recirculation it is often appropriate that one of the control volumes encompass recirculation; therefore, from a black box perspective the recirculation variable will not be reflected in the balances. Obviously, another of the control volumes to consider will be that in which the recirculation stream is reflected as its input or output.

Equations (2.9c) and (2.11) will be applied for the overall balance and component balance, respectively, taking into account that density can be considered constant and equal in all streams.

– Control volume encompassing all 3 units		
Overall balance	Unknown	Coded equation
$q_F + q_W = q_{P_0} + q_D$	$x_1 = q_W$ $x_2 = q_{P_0}$ $x_3 = q_D$	$x_1 - x_2 - x_3 = -q_F$
Component balance: Zn		
$q_F (c_{\text{Zn}})_F = q_{P_0} (c_{\text{Zn}})_{P_0} + q_D (c_{\text{Zn}})_D$		$(c_{\text{Zn}})_{P_0} x_2 + (c_{\text{Zn}})_D x_3 = q_F (c_{\text{Zn}})_F$
Component balance: Ni		
$q_F (c_{\text{Ni}})_F = q_{P_0} (c_{\text{Ni}})_{P_0} + q_D (c_{\text{Ni}})_D$		$(c_{\text{Ni}})_{P_0} x_2 + (c_{\text{Ni}})_D x_3 = q_F (c_{\text{Ni}})_F$

– Control volume corresponding to unit “3”		
Overall balance		
$q_W + q_{P_2} = q_{R_{32}} + q_D$	$x_4 = q_{P_2}$ $x_5 = q_{R_{32}}$	$x_1 - x_3 + x_4 - x_5 = 0$
Component balance – Zn		
$q_{P_2}(c_{Zn})_{P_2} = q_{R_{32}}(c_{Zn})_{R_{32}} + q_D(c_{Zn})_D$		$(c_{Zn})_D x_1 - (c_{Zn})_{P_2} x_4 + (c_{Zn})_{R_{32}} x_5 = 0$

Consequently, a system of five linear equations has to be solved to calculate the flow rate of the recirculation stream R_{32}.

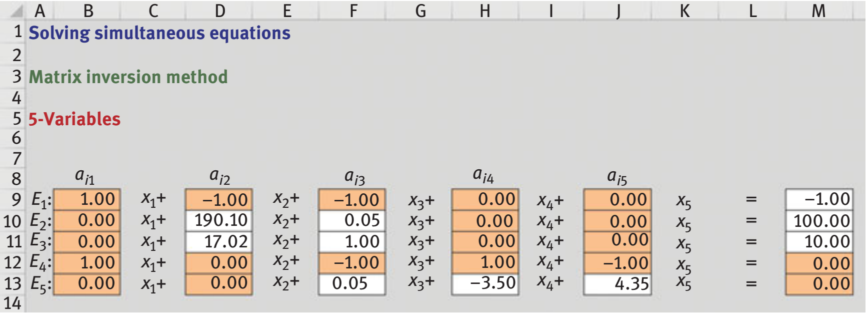
Step 4: Solving the system of equations

Application of the matrix inversion method

First, a copy of the “5 variables” sheet from the ““Appendix_D_Matrix Inversion” file (see Appendix D) to the book where the solution to the problem is being elaborated. Both sheets are then “connected” with the input of the coefficients as data or as a formula (Figure 2.17):

B9: = 1.0 (entered as a number, as it does not depend on the data in the problem statement).

D10: = ‘Example 2.4’!C70 (is entered as a formula since it depends on the data of the problem).



	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Solving simultaneous equations												
2													
3	Matrix inversion method												
4													
5	5-Variables												
6													
7													
8		a_{i1}		a_{i2}		a_{i3}		a_{i4}		a_{i5}			
9	E_1:	1.00	x_1+	−1.00	x_2+	−1.00	x_3+	0.00	x_4+	0.00	x_5	=	−1.00
10	E_2:	0.00	x_1+	190.10	x_2+	0.05	x_3+	0.00	x_4+	0.00	x_5	=	100.00
11	E_3:	0.00	x_1+	17.02	x_2+	1.00	x_3+	0.00	x_4+	0.00	x_5	=	10.00
12	E_4:	1.00	x_1+	0.00	x_2+	−1.00	x_3+	1.00	x_4+	−1.00	x_5	=	0.00
13	E_5:	0.00	x_1+	0.00	x_2+	0.05	x_3+	−3.50	x_4+	4.35	x_5	=	0.00
14													

Figure 2.17: Connection of sheet containing the data of the problem with the solution of the system of linear equations of Example 2.4.

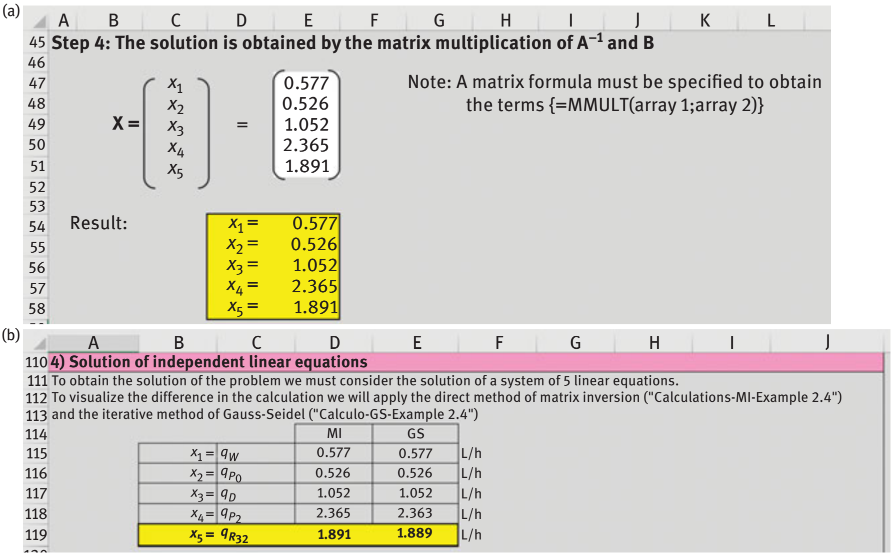
When you finish entering the coefficients, the calculation of the solution will be automatically produced, which we can, in turn, connect to the main sheet of the problem (Figure 2.18a, b).

Thus, D122: = ‘Calculations-IM-Example 2.4’! E58. Consequently, the recirculation stream R_{32} has a flow rate of 1.83 L/h.

Application of the Gauss–Seidel iterative method

Similarly, a copy of the sheet “5 variables” from the file ““Appendix_D_Gauss Seidel” (see Appendix D) is made to the book where the solution to the problem is being elaborated. Both sheets are then “connected.” The value of three significant figures is entered in cells Q13, R13, S13, T13 and U13 to consider the maximum error in the calculation.

When you finish entering the coefficients will automatically produce the calculation of the solution that we can, in turn, connect to the main sheet of the problem (Figure 2.20b), where E122: = ‘Calculations-GS-Example 2.4’!U32.



(a)

Step 4: The solution is obtained by the matrix multiplication of A^{-1} and B

$$X = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \end{pmatrix} = \begin{pmatrix} 0.577 \\ 0.526 \\ 1.052 \\ 2.365 \\ 1.891 \end{pmatrix}$$

Note: A matrix formula must be specified to obtain the terms {=MMULT(array 1;array 2)}

Result:

$x_1 =$ 0.577
$x_2 =$ 0.526
$x_3 =$ 1.052
$x_4 =$ 2.365
$x_5 =$ 1.891

(b)

4) Solution of independent linear equations

To obtain the solution of the problem we must consider the solution of a system of 5 linear equations.
To visualize the difference in the calculation we will apply the direct method of matrix inversion ("Calculations-MI-Example 2.4")
and the iterative method of Gauss-Seidel ("Calculo-GS-Example 2.4")

	MI	GS	
$x_1 = q_W$	0.577	0.577	L/h
$x_2 = q_{P_0}$	0.526	0.526	L/h
$x_3 = q_D$	1.052	1.052	L/h
$x_4 = q_{P_2}$	2.365	2.363	L/h
$x_5 = q_{R32}$	**1.891**	**1.889**	L/h

Figure 2.18: (a) System solution using the matrix inversion method. (b) Solution of the problem.

Questions/simulations:

i. *Accuracy of calculation*: The Gauss–Siedel iterative method is less precise than the reverse matrix method, but more universal in its application.

ii. *Effect of recirculation*: If the concentration of Zn at the output (stream D) is to be reduced to 0.05 g/L (cell G70), the flow rate of the recirculation stream must be increased to 1.89 L/h; the value of flow rate that can be varied operationally.

iii. *Feed/recirculation ratio*: There is a proportional ratio between supply and recirculation R_{32} so if the inlet flow (calculation basis) is increased by 5 times (5 L/h in cell C75); the value of R_{32} will be 5*1.83 = 9.15 L/h.

iv. *Function between the final concentration of Zn and the recirculation ratio*: For each value of Zn in the stream D a value of the recirculation ratio (q_{R32}/q_F) is obtained. By representing both values (Figure 2.19), a trend line can be obtained, which in this case is of the linear type.

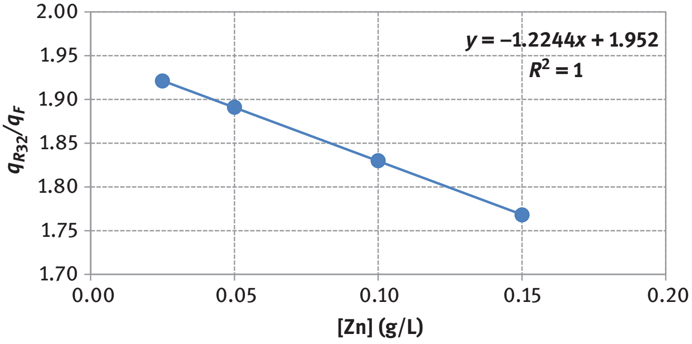


Figure 2.19: Relationship between the final concentration of Zn and the recirculation ratio.

2.4.2 Bypass stream

A derivation (or “Bypass”) consists of dividing a mainstream into two others: one undergoes the physical or chemical transformation and the other is mixed with the stream resulting from the transformation. The bypass stream is fed back directly to a subsequent stage at the so-called mixing point to obtain a desired final composition. The purpose of this flow is to avoid an overload of some process units in relation to their initial design capacity and/or to control the composition of the mixed stream. Accordingly, it is often used in cases where only a small change in the supply stream is desired because from a control point of view, it is easier to control a large change in a small portion of the fluid than a small change in a large stream.

Example 2.5: Fresh orange juice contains on average 12% solids in aqueous solution (percentage in mass). To reduce relocation costs, juice is concentrated before packing and then reconstituted upon arrival at its destination. The concentration process is carried out in specially designed evaporators that operate with short residence times and lower atmospheric pressures to reduce losses of flavor and aroma components present in very small quantities, which are very volatile and heat sensitive. Since it is very difficult to avoid losses in these traces, a common practice is to concentrate the juice a little more than necessary, and then add a small amount of fresh juice to the concentrate to obtain a product with a better aroma and taste. If the bypass stream is 10% of the feed and the evaporator outlet contains 80% solids in solution, calculate the water evaporation rate and the composition of the final product if fresh feed is 10,000 kg/h.

Solution:
Step 1: Flowchart and stream table (Figure 2.20)

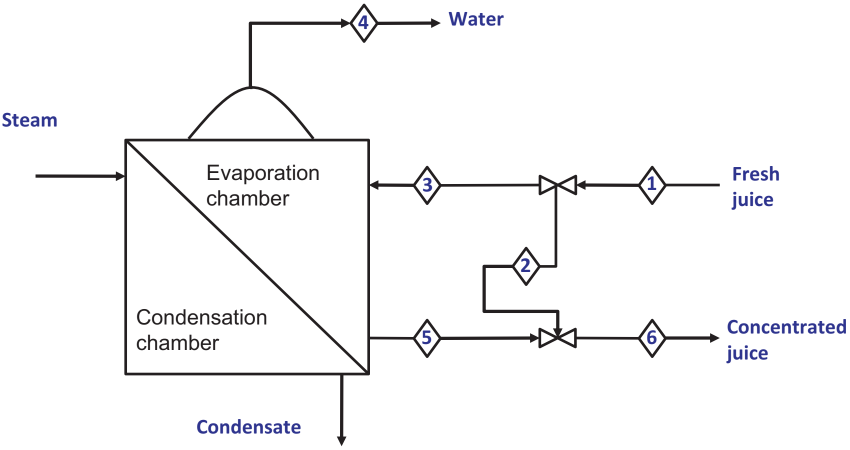


Figure 2.20: Process scheme.

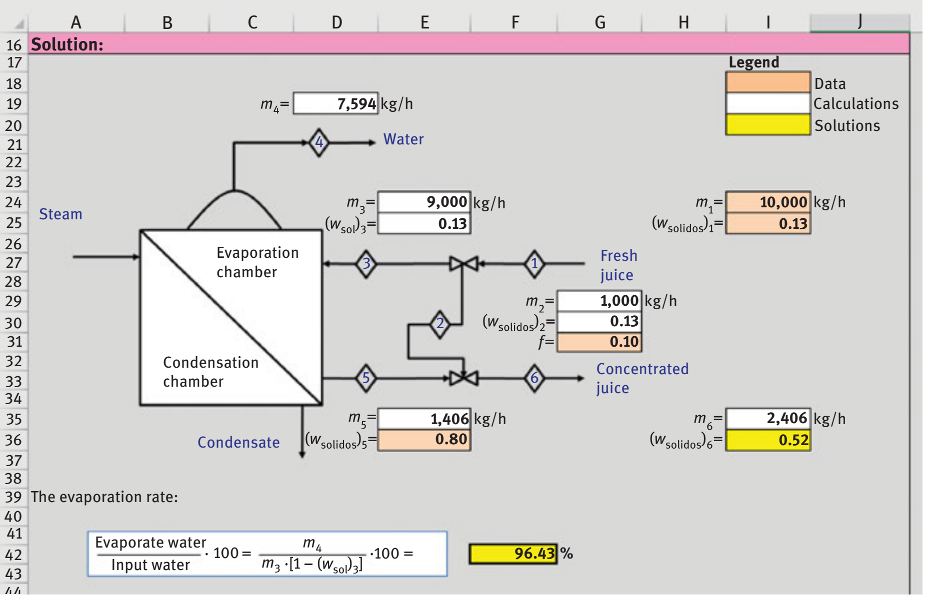
	Stream						
	1	**2**	**2**	**4**	**5**	**6**	
Flow rate	10,000						k/h
Solids	12.0				80.0		%

Step 2: Basis of calculations
The fresh feed flow rate shall be taken as the calculation basis: $m_1 = 10{,}000$ kg/h.

Step 3: Definition of control volumes and formulation of the mass balances
Equations (2.9b) and (2.10a) will be applied for the overall balance and component balance, respectively:

– Control volume at the bypass valve	
Bypass	Unknown
$m_2 = f \cdot m_1$ (f is the derived fraction)	m_2
Overall balance	
$m_1 = m_2 + m_3$	m_3
Component balance – stream divider	
$w_1 = w_2 = w_3$	w_2 and w_3
– Control volume in the evaporation chamber	
Component balance – solids	
$(w_{\text{solidos}})_3 \cdot m_3 = (w_{\text{solidos}})_5 \cdot m_5$	m_5
Overall balance	
$m_3 = m_4 + m_5$	m_4
– Control volume in the mixing valve of the streams	
Overall balance	
$m_2 + m_5 = m_6$	m_6
Component balance	
$(w_{\text{sol}})_2 \cdot m_2 + (w_{\text{sol}})_5 \cdot m_5 = (w_{\text{sol}})_6 \cdot m_6$	$(w_{\text{sol}})_6$

Step 4: Solving the system of equations
Since these are equations of a single unknown parameter, the corresponding equation can be entered directly into each cell (Figure 2.21).



Solution:

Legend
Data
Calculations
Solutions

m_4= 7,594 kg/h

m_3= 9,000 kg/h
$(w_{sol})_3$= 0.13

m_1= 10,000 kg/h
$(w_{solidos})_1$= 0.13

m_2= 1,000 kg/h
$(w_{solidos})_2$= 0.13
f= 0.10

m_5= 1,406 kg/h
$(w_{solidos})_5$= 0.80

m_6= 2,406 kg/h
$(w_{solidos})_6$= 0.52

The evaporation rate:

$$\frac{\text{Evaporate water}}{\text{Input water}}\cdot 100 = \frac{m_4}{m_3 \cdot [1-(w_{sol})_3]}\cdot 100 =$$ 96.43 %

Figure 2.21: Solution of the mass balances.

Accordingly:

G29: = I24*G31
E24: = I24–G29
G30: = I24
E25: = I24
E35: = (E25*E24)/E36
D19: = E24–E35
I35: = G29 + E35
I36: = (G29*G30 + E35*E36)/I35

Questions/simulations:

i. *Effect of the calculation basis*: If the value of the calculation basis is changed, the results of the total mass flows will change, but the concentration and the evaporation ratio will not change. Test in cell I24 with a value of 20,000 kg/h.
ii. *Effect of the bypass stream*: The value of the fraction of fresh feed that is derived has a direct effect on the final solids concentration that is achieved. Thus, for a factor of 0.12 (cell G31) the concentration is reduced to 0.48. However, it has no effect on the evaporation ratio.

2.5 Air–water balance

The air–steam water system is the most frequently used of all two-phase systems. Its study is important in the design and operation of air conditioning systems, refrigeration towers, dehumidifiers and, in general, in any industrial process where it is necessary to control the water vapor content of the air.

2.5.1 Absolute and relative humidity

The composition of a given wet air sample can be described in several different ways, for example, in terms of the moles of dry air and water vapor present in the mixture or in terms of their molar fractions.

Specific humidity: Specific humidity, also called *absolute* or *simply humidity*, is defined as the quotient between the masses of water vapor and dry air (eq. (2.12a)):

$$\varpi = \frac{\text{steam mass}}{\text{dry air mass}} = \frac{m_v}{m_a} \tag{2.12a}$$

It can also be expressed as a function of partial pressures and molecular weights by applying the equation of ideal gases to eq. (2.12b):

$$\varpi = \frac{M_v \cdot p_v}{M_a \cdot p_a} = \left(\frac{18}{28.93}\right) \cdot \frac{p_v}{P - p_v} = 0.622 \cdot \frac{p_v}{P - p_v} \tag{2.12b}$$

Relative humidity: It is defined as the quotient between the mole fraction of water vapor in a given humid air sample and the mole fraction of water vapor in a humid air sample saturated at the same temperature and pressure as the mixture (eq. (2.13)):

$$\varpi_r = \left.\frac{y_v}{y_{v,\text{sat}}}\right|_{T,P} = \left.\frac{p_v}{p_{v,\text{sat}}}\right|_{T,P} \tag{2.13}$$

Both specific and relative humidity can be measured experimentally, with the hygrometer being the instrument capable of measuring the degree of humidity of the air or other gas.

Dew point

An important aspect of humid air behavior is that partial condensation of water vapor can occur when the temperature is reduced. A gas is saturated with vapor at a determined temperature (referred to as dew temperature) when an infinitesimal decrease in temperature causes vapors condensation.

2.5.2 Psychometric diagrams

Psychrometric diagrams or humidity charts (Figure 2.22) provide graphical representation of various characteristic properties of humid air:

- Dry bulb temperature (°C) indicated on the abscissa axis refers to the temperature measured by a common thermometer.
- Moisture content (specific humidity (kg of water vapor per kg of dry air)) is represented on the ordinate axis.
- Relative humidity (%) corresponds to the exponential curves.

- Spray temperature: Since the dew point is the state in which the mixture is saturated by cooling it under constant vapors pressure, the dew temperature of a given humid air state can be determined by tracing a constant specific humidity line to the saturation line (100% relative humidity). The dew and dry bulb temperatures coincide for the states above the saturation curve.
- Wet bulb or saturation temperature (T_{bh}) is the dynamic equilibrium temperature obtained on a water surface when the heat transfer rate by convention to it is equal to the rate of transfer of matter leaving such a surface. It is measured in an ordinary glass liquid thermometer whose bulb is surrounded by a cloth moistened with water. The constant temperature lines run from the upper left side to the lower right side of the diagram.
- Specific volume (m^3/kg dry air): The lines of constant volume also go from the left side to the right side but have a greater slope.
- In addition, in this type of diagram the specific enthalpy of the humid air (kJ/kg dry air) is added, whose lines coincide approximately with the temperature lines of the humid bulb.

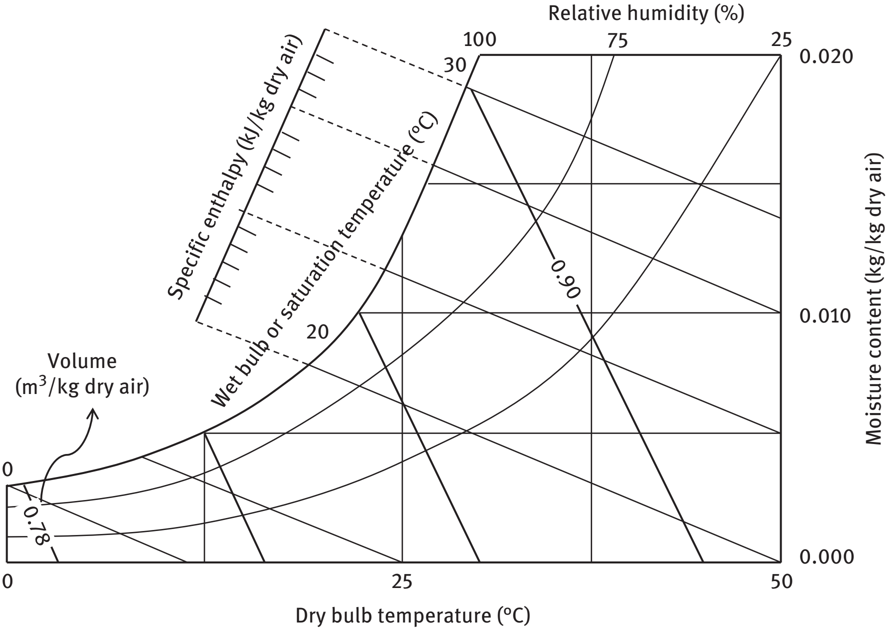


Figure 2.22: Psychometric diagram.

Example 2.6: Timber boards used in construction should be dried from 18% (by weight) moisture to 1% by circulating hot air over them. The inlet air is at 55 °C and has a relative humidity of 20%. The air at the exit of the tray dryer has a temperature of 47 °C and a relative humidity of 90%. How many m^3 of dry air (measured under normal conditions) would be needed per ton of wood?

Solution:

Step 1: Flowchart and stream table (Figure 2.23)

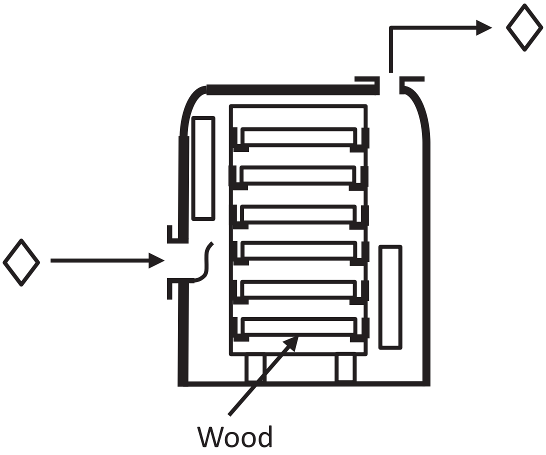


Figure 2.23: Diagram of the tray dryer.

The data of the problem is:

	Stream			
	1	**2**	**Initial**	**Final**
Wood				
Moisture (% weight)			18	1
Air				
Temperature (°C)	55	47		
Relative moisture (%)	20	90		

Using the psychrometric diagram, the specific or absolute moisture of the air is obtained from the dry bulb temperature and the relative moisture (Figure 2.24): 0.020 and 0.060 kg water per kg dry air for stream 1 and 2, respectively.

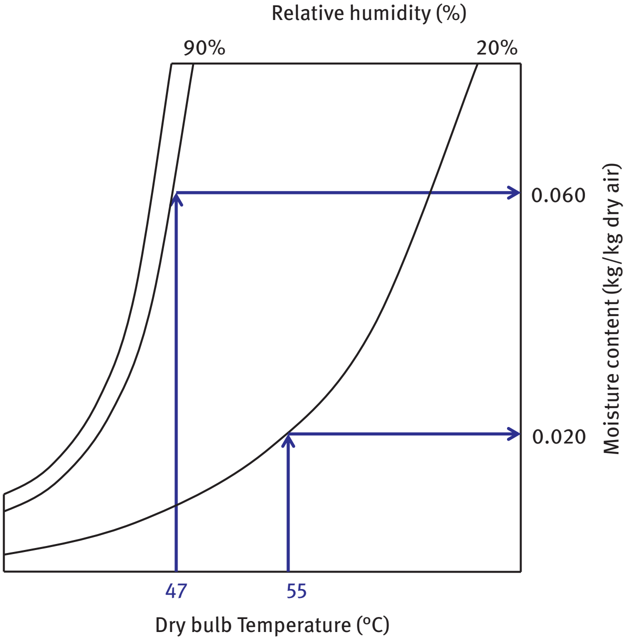


Figure 2.24: Specific or absolute moisture knowing the dry bulb temperature and relative moisture.

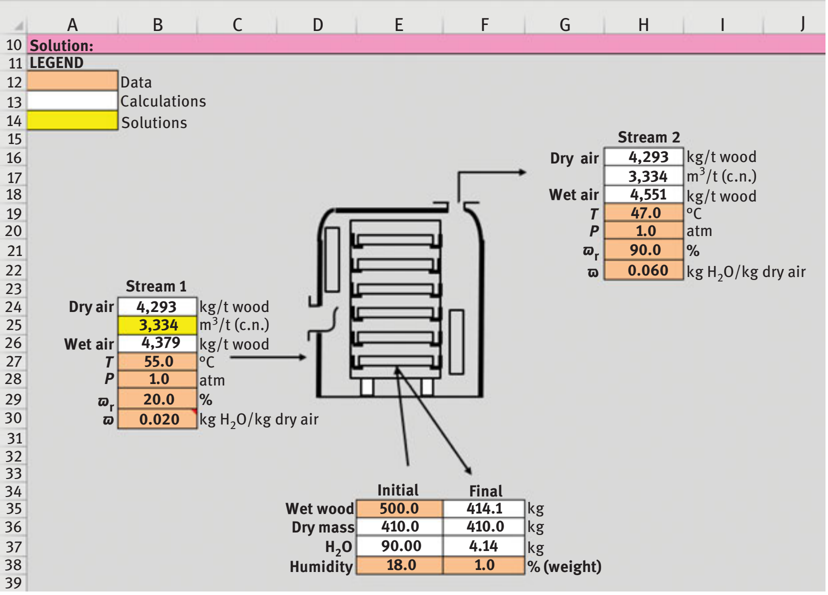
Step 2: Basis of calculations
The load of 500 kg of wood to the tray dryer shall be considered as the basis for calculation.

Step 3: Definition of control volumes and formulation of the mass balances
Equation (2.10a) corresponding to the component balance shall be applied in the only control volume of the system, that is, the tray dryer:

– Balance of dry material in wood boards	Unknown
$(w_{\text{dry mass}})_{\text{initial}} \cdot m_{\text{initial}} = (w_{\text{dry mass}})_{\text{final}} \cdot m_{\text{final}}$	Mass of the wet wood at the end: m_{final}
– Water balance in the tray dryer	
$(w_{H_2O})_{\text{initial}} \cdot m_{\text{initial}} + \varpi_1 \cdot m_1 = (w_{H_2O})_{\text{final}} \cdot m_{\text{final}} + \varpi_2 \cdot m_2$	Mass of dry air: $m_1 = m_2$

Step 4: Solving the system of equations
Since these are equations of a single unknown, the corresponding equation can be entered directly into each cell (Figure 2.25). Accordingly,

F35: = E35*((1–(E38/100))/((1–(F38/100))))
B24: = ((((E38/100)*E35)–((F38/100)*F35))/(H22–B30)/E35)*1000



Solution:

LEGEND

🟧	Data
☐	Calculations
🟨	Solutions

	Stream 1	
Dry air	4,293	kg/t wood
	3,334	m^3/t (c.n.)
Wet air	4,379	kg/t wood
T	55.0	°C
P	1.0	atm
ϖ_r	20.0	%
ϖ	0.020	kg H_2O/kg dry air

	Stream 2	
Dry air	4,293	kg/t wood
	3,334	m^3/t (c.n.)
Wet air	4,551	kg/t wood
T	47.0	°C
P	1.0	atm
ϖ_r	90.0	%
ϖ	0.060	kg H_2O/kg dry air

	Initial	Final	
Wet wood	500.0	414.1	kg
Dry mass	410.0	410.0	kg
H_2O	90.00	4.14	kg
Humidity	18.0	1.0	% (weight)

Figure 2.25: Solution of the mass balances.

To obtain the volume of dry air (m^3) in normal conditions (0 °C and 1 atm) it is enough to apply the law of ideal gases ($PV = n\,R\,T$). The result of the problem is 3,334 m^3 per ton of wood:

B25: = ((B24*0.082*273.15)/(28.84*$B$28))

2.6 Study of the nonstationary state

In this case the flows and operating conditions will vary over time, and so we have to operate with the full expression of the balance. The procedure of solving matter balances in these systems is analogous to the one already defined, but with the consideration of two additional important aspects: the formulation of the equation in nonstationary regime and the solution of the same; that is to say, our objective will be to transfer the problem in one or more differential equations of the form:

$$\frac{dx}{dt} = f(x,t) \tag{2.14}$$

Therefore, to solve this type of equations it is necessary to know the initial conditions or some value of x for a known time. The stages to follow will be the following:

1. Represent a diagram and place the known data in it.
2. Choose dependent and independent variables, taking into account that time is an independent variable.

3. Specify the initial conditions or the value of x for a time t.
4. Establish the necessary balances and solve the differential equations.

No internal generation

A fairly common situation corresponds to the study of homogeneous systems where there is a variation in the concentration of one of the components over time due to dilution, absorption phenomena and so on; in these cases when applying eq. (2.5a) it is necessary to take into account:

$$\int_A c_i\left(\vec{v}\cdot\vec{n}\right)\cdot dA+\frac{d}{dt}\cdot\int_V c_i\cdot dV=\int_V G\cdot dV \tag{2.15}$$

- The term generation is null: $\int_V G\cdot dV=0$.
- The concentration c_i is uniform, due to being a perfectly homogenized system, for all the volume and the areas of input and output: $\frac{d}{dt}\int_V c_i\cdot dV=\frac{dc_i}{dt}\int_V dV=\frac{d}{dt}(c_i\cdot V)$.
- $\left(\vec{v}\cdot\vec{n}\right)=<v>$, the vector representative of the input area has the same direction that $\vec{v}$(although the sense is the same in the output but inverse in the input):

$$\int_A c_i(\vec{v}\cdot\vec{n})dA=[\langle v\rangle c_iA]_{\text{output}}-[\langle v\rangle c_iA]_{\text{input}}$$

Therefore, the balance equation is simplified to eq. (2.15):

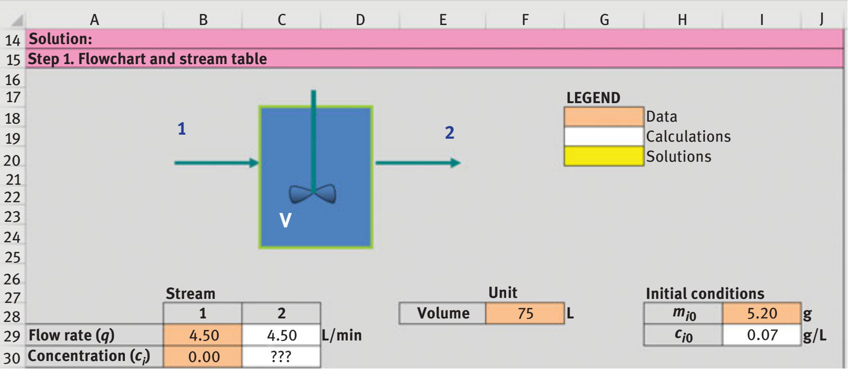
$$\begin{aligned}[\langle v\rangle c_iA]_{\text{output}}-[\langle v\rangle c_iA]_{\text{input}}+\frac{d}{dt}(c_i\cdot V)=0\\ [q\cdot c_i]_{\text{output}}-[q\cdot c_i]_{\text{input}}+\frac{d}{dt}(c_i\cdot V)=0\end{aligned} \tag{2.16}$$

Example 2.7: A tank contains 75 L of a salt solution in water, in which 5.2 g of salt are dissolved. The water enters the tank with a flow rate of 4.5 L/min and the output stream has the same flow rate. If the mixture in the tank is adequate to achieve uniformity in salt concentration at all times, how much salt will remain in the tank after 42 min? Assume that the density of the input water, the dissolution in the tank and the output stream are equal to each other.

Step 1: Flowchart with stream table (Figure 2.26)

Step 2: Definition of dependent and independent variables
As previously indicated, in this type of problem, time should always be considered as an independent variable. The salt content in the tank or its concentration can be considered as a dependent variable.

Step 3: Initial or contour conditions
At initial time the amount of salt in the tank is 5.20 g, that is, a salt concentration of 0.069 g/L.



Solution:

Step 1. Flowchart and stream table

LEGEND
🟧 Data
⬜ Calculations
🟨 Solutions

	Stream 1	Stream 2	
Flow rate (q)	4.50	4.50	L/min
Concentration (c_i)	0.00	???	

Unit

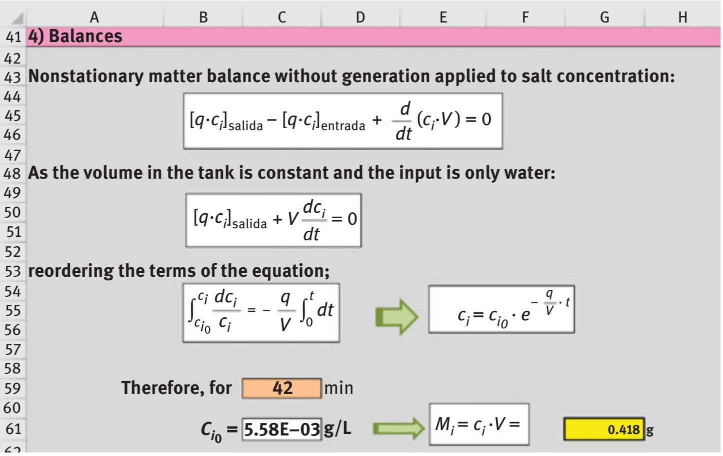
Volume	75	L

Initial conditions

m_{i0}	5.20	g
c_{i0}	0.07	g/L

Figure 2.26: Flowchart and data representation.

Step 4: Establishing the balances and solving the system of equations
The component balance is the one defined in eq. (2.42), in which it must be taken into account that the input is exclusively water and the volume in the tank is constant, from which a first-order differential equation will be obtained where the variables c_i and t (Figure 2.27).



4) Balances

Nonstationary matter balance without generation applied to salt concentration:

$$[q\cdot c_i]_{\text{salida}} - [q\cdot c_i]_{\text{entrada}} + \frac{d}{dt}(c_i\cdot V) = 0$$

As the volume in the tank is constant and the input is only water:

$$[q\cdot c_i]_{\text{salida}} + V\frac{dc_i}{dt} = 0$$

reordering the terms of the equation;

$$\int_{c_{i0}}^{c_i}\frac{dc_i}{c_i} = -\frac{q}{V}\int_0^t dt \Rightarrow c_i = c_{i0}\cdot e^{-\frac{q}{V}\cdot t}$$

Therefore, for 42 min

C_{i_0} = 5.58E−03 g/L ⇒ $M_i = c_i\cdot V =$ 0.418 g

Figure 2.27: Definition of the mass balance and resolution of Example 2.7.

2.7 Proposed problems

2.7.1 Balances to units and systems

2.1 The conventional method of separation of ethyl alcohol from an ethanol–water mixture is by distillation. However, the highest concentration that can be obtained in the distillate is 95% by volume of alcohol, because ethanol and water form a mixture with a constant boiling point, called *azeotrope*. In order to purify the alcohol, it is necessary to add a third component that forms an azeotrope of minimum boiling point with water. Industrially one of the most employed is benzene. It is desired to obtain 1,850 kg/h of ethyl alcohol by azeotropic distillation from a feed stream containing 42% (by weight) of alcohol from an ethanol–water mixture. It is estimated that the distillate will contain 76% benzene, 23% water, with the remaining 1% ethanol (all percentages by weight). Pure ethanol is obtained from the bottoms. Calculate (a) flow rate of feed, benzene and distillate (b) the efficiency of the column represented as the ratio of ethanol lost in the distillate to the value fed.

Solution: (a) 4,686, 8,981 and 11,817 kg/h, respectively; (b) 6.0%.

2.2 A stream of 1,000 mol/h of hydrocarbons with the following composition (% molar): 20% propane, 30% isobutane, 20% isopentane and 30% pentane; separated into two fractions by distillation. The distillate contains all the propane entering the unit, as well as 80% of the isopentane and with an isobutane composition of 40%. The stream from the bottoms must contain all the pentane that is fed to the unit. Calculate the stream compositions of top and bottom of the column.

Solution: Top: 33.30% C_3, 40.00% i-C_4 and 26.64% i-C_5; bottom: 14.96% i-C_4, 75.11% C_5 and 9.95% i-C_5.

2.3 There is a system of two distillation columns arranged in series to separate a binary mixture formed by the generic components denoted by A and B (Figure P2.3). Calculate the flows and compositions of streams 3, 5 and 7.

Solution: (3) 60 kg/h and 23.3% A; (5) 90 kg/h and 25.6% A; (7) 60 kg/h and 8.3% A.

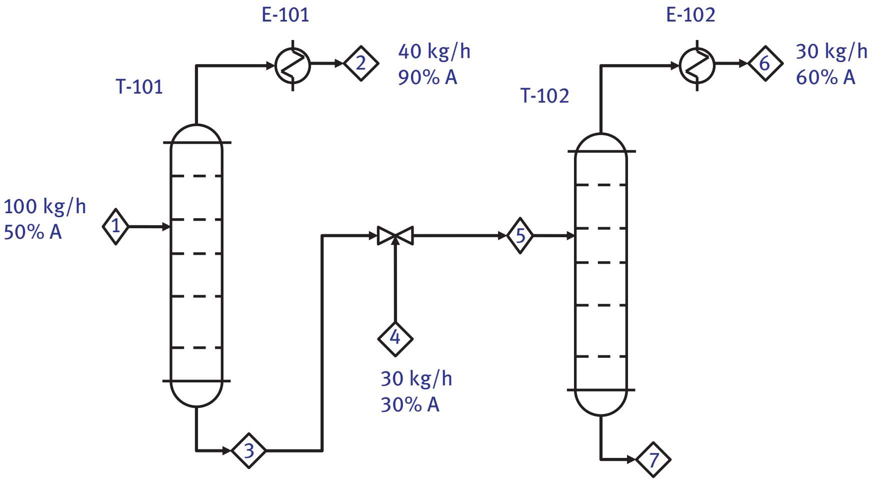


Figure P2.3

2.4 In a wastewater treatment plant (WWTP) there are three tanks for the preparation of a suitable coagulant solution (Figure P2.4). Calculate the concentration in each tank (perfectly mixed and in stationary state), where the flows are expressed in L/s.

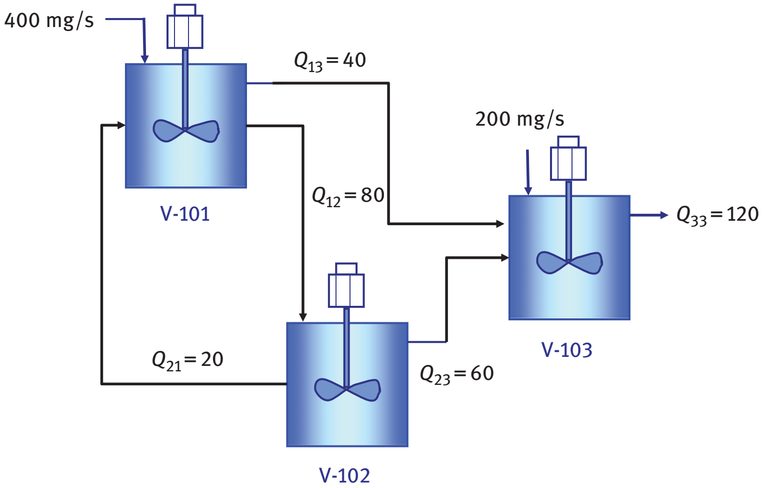


Figure P2.4

Solution: $c_1 = c_2 = 4$ mg/L; $c_3 = 5$ mg/L.

2.5 A reverse osmosis plant has been installed with three membrane separation units connected in series without recirculation (Figure P2.5) to obtain water of a purity (less than 25 ppm -in weight of NaCl) such that it can be used as boiler feed. Sea water containing 3.5% by weight of NaCl is used as a feed. The membrane modules of 40 m^2 work at 75 atm and reach a flow of 0.4 m^3/m^2 d when the permeate pressure is 1.8 atm. A value of 75% is considered as a safety factor.

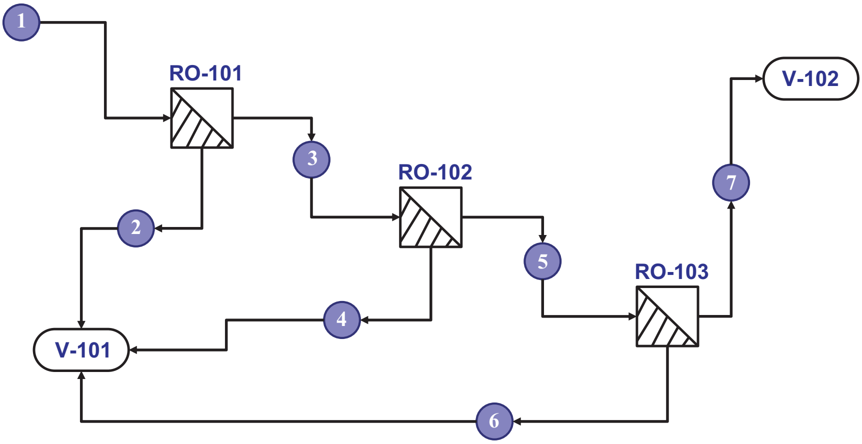


Figure P2.5

If each membrane module has a 96% rejection of the salt that has been fed, determine:

(a) The water recovery factor expressed as m_{H_2O} permeate after the third unit divided by m_{H_2O} in the feed.

(b) The flow of seawater that must be fed to the installation to obtain 5,000 m^3/d.

Notes

i. A concentration of 25 ppm is equal to 0.0025% by weight.

ii. Effect of the safety factor

$$[\%\text{Salt}]_{\text{operation}} = F_{\text{safety}} \cdot [\%\text{Salt}]_{\text{equilibrium}}$$

iii. Osmotic pressure data for sea salt and sodium chloride solutions at 40 °C have been published by Stoughton and Lietzke (1965).

$P_{osmotic}$ (atm)	Salts (% weight)	$P_{osmotic}$ (atm)	Salts (% weight)
7.41	1.00	86.46	10
14.88	2.00	146.6	15
26.17	3.45	225.1	20
38.96	5.00	331.0	25
61.40	7.50		

iv. The osmotic pressure is equal to the pressure of the retained minus the pressure in the permeate

Solution: (a) 48.2%; (b) 120 kg/s.

2.6 If the water flows between each of the vessels of the drinking water treatment plant are known (Figure P2.6), determine the chlorine concentration in each by means of the corresponding balances.

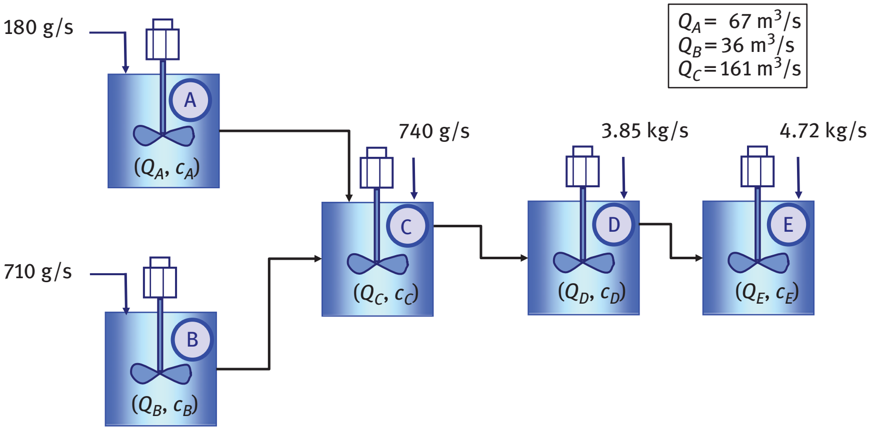


Figure P2.6

Solution: $c_A = 2.69$; $c_B = 19.72$; $c_C = 10.12$; $c_D = 30.11$; $c_E = 48.11$ (all in ppm).

2.7.2 Balances with recirculation, bypass and/or purge

2.7 A nitrogen oxide absorber is fed by a fresh feed stream with a volume composition of 49% NO_2, 49% NO_3 and 2% CO_2, mixed with a recycled stream from the volume composition output of 45% NO_2, 45% NO_3 and 10% CO_2, with half of the incoming NO_2 and NO_3 being separated in the absorber. From the outlet stream, a part is recycled at the inlet and the rest is purged. Taking as a base calculation 100 mol/h of mixture entering the absorption tower, calculate:

(a) Recycled moles.
(b) Purged moles.
(c) If the packing of the column is changed, the separation efficiency increases to 65%. What would be the recirculation molar flow rate?

Solution: (a) 40.79 mol/h; (b) 11.84 mol/h; (c) 21.79 mol/h.

2.8 In a process to concentrate 1,000 kg of orange juice containing 12.5% by weight of solids, the juice is filtered giving 800 kg of liquid and 200 kg of wet pulp. The filtrate is concentrated in an evaporator to obtain an evaporated juice with 58% solids. About 200 kg of wet pulp is taken out of the evaporator and mixed with the evaporated juice to improve the taste. This final juice has 42% solids by weight. Calculate:

(a) The concentration of solids in the filtered juice.
(b) Kilograms of final concentrated juice.
(c) The concentration of solids in the juice stream.
(d) Evaluate the effect of the concentration of solids in the final juice with the quantity produced. Consider that it increases from 42 to 50%.
(e) Evaluate the effect of the concentration of solids in the final juice on the concentration of solids in the recirculation stream. Analyze the same case when going from 42 to 50%.

Solution: (a) 7.1%, (b) 297.6 kg/h, (c) 34.2%; (d) the variation is inversely proportional, given that this 19% increase also means a 19% reduction in the quantity produced, given that it drops from 297.6 to 250 kg/h; (e) in this case the proportional variation, given that it goes from 34.2 to 48%.

2.9 Figure P2.9 shows the flow diagram of a stationary process for the recovery of crystalline potassium chromate (K_2CrO_4) from an aqueous solution of this salt. About 4,500 kg/h of a solution containing 1/3 K_2CrO_4 in mass is combined with a recirculation flow containing 36.36% K_2CrO_4; the combined flow is fed to an evaporator. The concentrated flow out of the evaporator contains 49.4% K_2CrO_4; this flow feeds a crystallizer, where it cools (precipitation of K_2CrO_4 crystals occurs from dissolution) and then filters out. The filtrate consists of K_2CrO_4 crystals and a solution containing 36.36% K_2CrO_4; the crystals represent 95% of the total filtrate mass.

Calculate:

(a) Quantity of water extracted in the evaporator.
(b) The production rate of crystalline K_2CrO_4.

(c) Ratio between the kilograms of flow recycled per kilogram of fresh feed.
(d) The feed rates at which the evaporator and crystallizer must be designed.

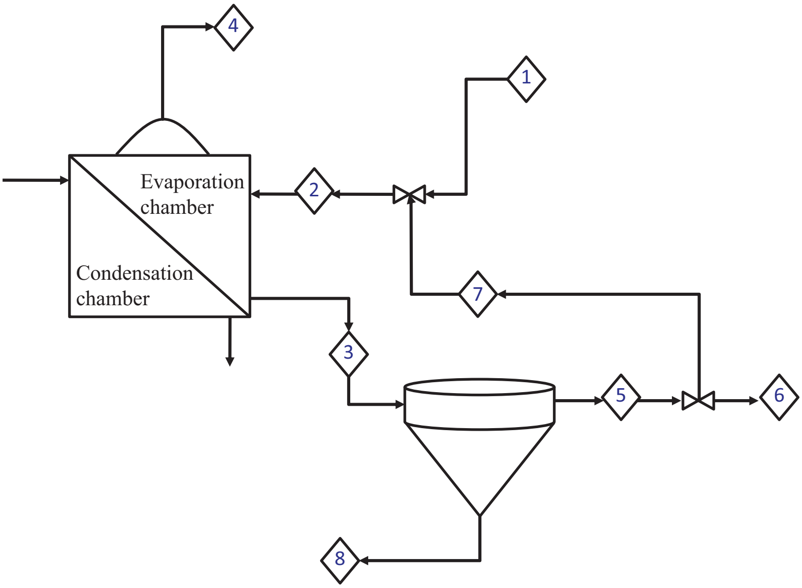


Figure P2.9

Solution: (a) 2,950.7 kg/h; (b) 1,471.8 kg/h; (c) 1.25; (d)10,113.8 kg/h and 7,183.1 kg/h.

2.10 In biotechnological processes it is common to concentrate the product after the fermentation stage in order to reach a level of purity suitable for marketing (Figure P2.10). Thus, the production of vitamin B12 by *Streptomyces* (see

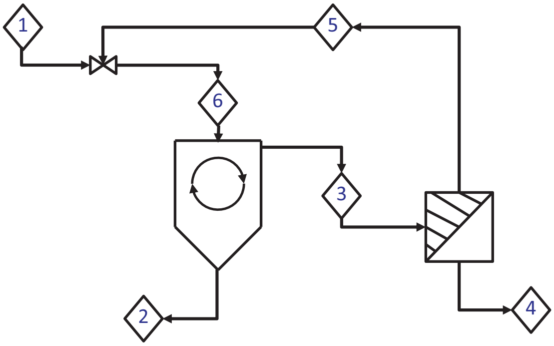


Figure P2.10

figure) requires an initial stage of centrifugation followed by filtration to reach 97% vitamin concentration. Calculate the mass flow of product stream and recirculation:

Stream	B12 Vitamin	Water
1	18%	82%
2	–	100%
3	60%	40%
4	97%	3%
5	0.35 kg/kg water	

Solution: Based on a calculation of 1,000 kg/h of fermentation broth in stream 1, the results would be 185.6 and 201.5 kg/h for the product stream and recirculation, respectively.

2.11 One of the strategies for providing the Mediterranean basin with drinking water has been the implementation of various seawater desalination plants. Figure P2.11 reflects a basic scheme of its operation, where the quality of the desired drinking water should not exceed 475 ppm of salt. If you consider a design flow rate of 1,000 kg/h of seawater (stream 1), calculate:
(a) Brine flow.
(b) Production of drinking water.
(c) Recirculating brine fraction.

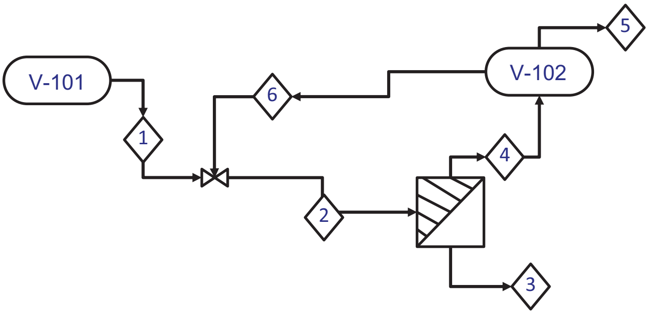


Figure P2.11

Stream	Salt
1	3%
2	4%
3	475 ppm
5	5.25%

Solution: (a) 567.5 kg/h; (b) 432.5 kg/h; (c) 58.5%.

2.12 A distillation column (Figure P2.12) separates 5,000 kg/h from a mixture of benzene (45%) and toluene (55%). The distillate contains 95.5% benzene, and the glue stream has a concentration of toluene of 96.2%. The distillate stream entering the condenser has a flow rate of 3,500 kg/h. If a fraction of the distillate, once condensed, returns to the distillation column as reflux, calculate the ratio of reflux or recirculation of the column.

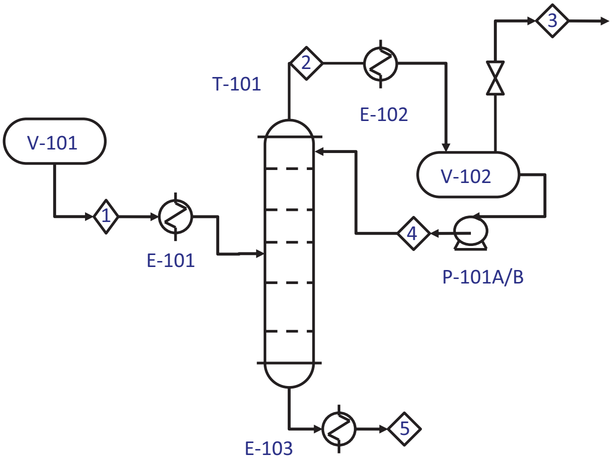


Figure P2.12

Solution: 55.8%.

2.13 A continuous evaporation–crystallization system operates in stationary mode according to the scheme shown in Figure P2.13. The concentrations of the streams are as follows:

i. Stream 1: 22% (by weight) from KNO_3.
ii. Stream 3: 54% (by weight) of KNO_3.

iii. Stream 5: The crystals separated in the crystallizer have 3.8 kg of water/ 100 kg total.
iv. Stream 6: 0.63 kg KNO_3/kg water

Calculate: (a) kilograms of water evaporated/h in the evaporator; (b) mass flow rate (kg/h) of streams 3 and 6.

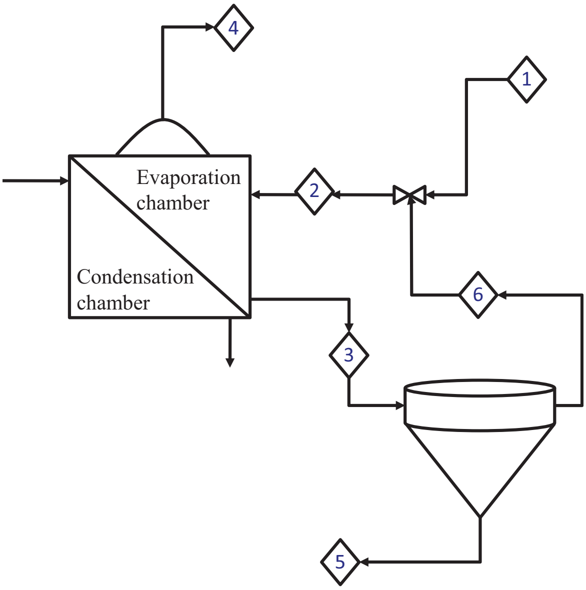


Figure P2.13

Solution: (a) 7,713.1 kg/h; (b) m_3 = 8,574.1 kg/h and m_6 = 6,287.2 kg/h.

2.14 The depleted bath of a galvanizing industry contains 5.35% (by weight) of Cr. Part of it is recovered (94%) in a treatment unit (maximum capacity of 5,200 kg/h), while the wastewater poor in Cr is treated prior to discharge. If the flow from the plant exceeds 5,200 kg/h, a bypass of the Cr recovery unit is activated and directly diverted to the wastewater treatment plant (WWTP) (Figure P2.14).
Evaluate:
(a) If the flow to the system is 6,500 kg/h, calculate the flow rate of the wastewater to the WWTP, and the mass fraction of Cr in this stream.
(b) Obtain the equation that represents the mass fraction of Cr at the input of the WWTP as a function of the flow of the stream of Cr to be recovered. Make a representation of its evolution between 1,000 and 20,000 kg/h of raw water to be treated.

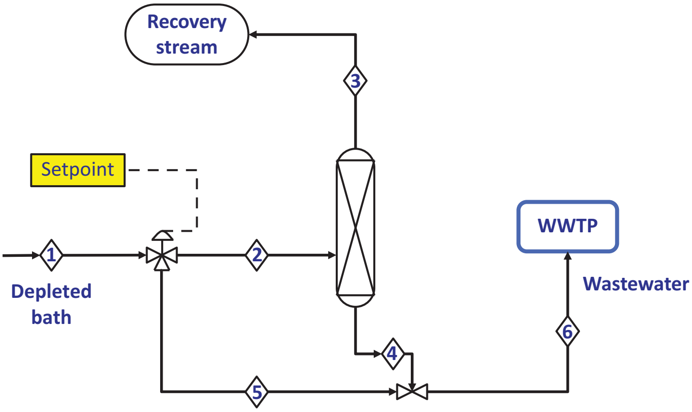


Figure P2.14

Solution: 6,238.5 kg/h and 1.38%.

2.15 A biogas contains (by volume) 96% CH_4 and 4% SH_2, the use of which implies a reduction to values less than 0.1%. Therefore, an amine absorption (molecular mass of 112 g/mol) is designed in a closed circuit thanks to a second column with steam entrainment (Figure P2.15). The SH_2 between stream 2 and 4 is in equilibrium: K_{Henry} = 20 KPa at a total pressure of 120 kPa. The concentration in weight of stream SH_2 in stream 4 and 6 is: 0.021% and 6.1%, respectively. Calculate the flows and compositions of all streams for a feed stream of 15,000 kg/h.

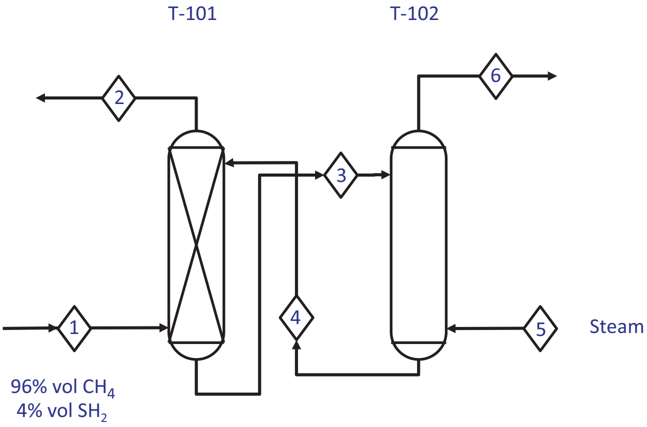


Figure P2.15

Solution: n_3 = 116.3 kmol/h; $(x_{\mathrm{SH2}})_3$ = 0.308; n_4 = 80.5 kmol/h.

2.16 A particular industry must prevent the discharge of a pollutant, C, through a three-step separation process (Figure P2.16). The m_8/m_7 ratio is 3, the m_6/m_5 ratio is 1 and the ratio of compound A to B in stream 6 is 4 to 1. Calculate the composition of the stream flow 4, bypass and the percentage of each of the components in it.

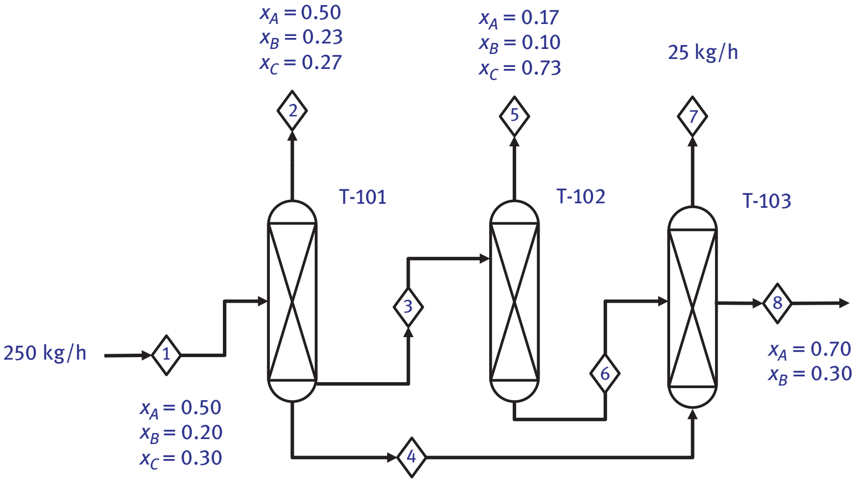


Figure P2.16

Solution: 32.5 kg/h, $x_A = 0.484$, $x_B = 0.312$ and $x_C = 0.204$.

2.17 The extraction of vegetable oils generally uses hexane as a solvent. Due to its toxicity potential, it is necessary to design process lines that incorporate the best available techniques, so that hexane can be used in a “closed” circuit and, therefore, minimize the feed of fresh hexane. The case study consists of using sunflower oil (Figure P2.17) using 1,800 kg/h of crushed sunflower seeds (10.3% oil and the rest of solids) as feed, which together with hexane (2.85 kg of hexane/kg of sunflower) allows the oil to be effectively separated in the extraction column (T-101). The output of the extractor passes through a filter (F-101). The precipitate contains 76.8% by weight of solids, and the rest of oil and hexane (both compounds maintain the same proportion as in the output stream of the extraction column). The cake is conditioned so that it can be used as a food supplement in the formulation of animal feed (based on the principles of circular economy). The filtered stream is fed to a vacuum evaporator, where the oil is separated and the hexane is recovered for recirculation after condensation. Calculate:

(a) Sunflower oil yield (kilograms of oil/kilograms of seeds in feed).
(b) Feeding pure hexane per kilogram of sunflower.
(c) The degree of recirculation of the hexane.
(d) Composition of the suspension leaving the extraction tower and the cake after filtration.

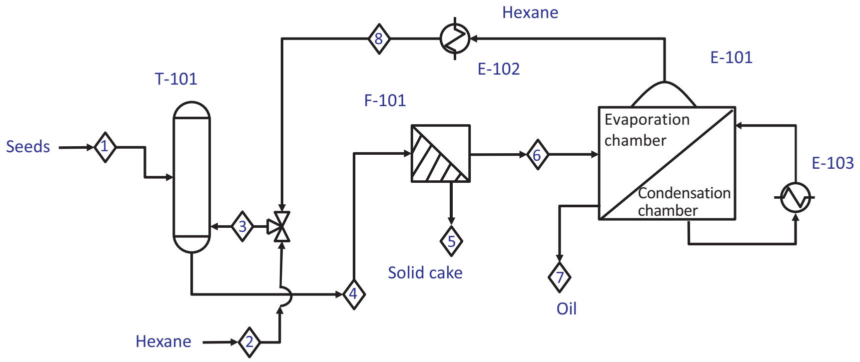


Figure P2.17

Solution: (a) 9.35%; (b) 0.26 kg C_6H_{14} per kg of seeds; (c) 9.90 kg C_6H_{14} recirculated per kilogram C_6H_{14} fresh; (d) stream 4: 6,930 kg/h, 2.7% oil, 23.3% solids and 74% C_6H_{14}; stream 5: 2,102.3 kg/h, 0.8% oil, 76.8% solids and 22.4% C_6H_{14}.

2.7.3 Balances in the air–water balance

2.18 In order to condition the air in an office building during the winter, 1,500 m^3 of humid air at 101.3 kPa and 25 °C and with a dew point of 12.5 °C are introduced into the process. The air leaves the process at 98 kPa and a dew point of 59.5 °C. How many kilograms of water vapor are added to each kilogram of moist air entering the process?

Solution: 0.145 kg water/kg humid air.

2.19 Soils contaminated with recalcitrant organic compounds can be treated with hot air and water vapor to release contaminants. If 45 m^3 of air at 95 °C and 99.2 kPa with a dew point of 32 °C are introduced into the soil, and in the soil the air is cooled to 16 °C at a pressure of 108 kPa, what fraction of the water in the gas at 95 °C is separated by condensation in the soil?

Solution: 66.62%.

2.20 A granular solid (250 kg/h) with a moisture of 2.4 kg H_2O/kg of dry matter should be dried until its moisture is 1.5 kg H_2O/kg dry matter (Figure P2.20). For this purpose, fresh air with a specific humidity of 0.015 kg H_2O/kg dry air is introduced as backward stream in the dryer, while the air entering the unit (after joining the recirculation stream) has a relative humidity of 20% and a temperature of 55 °C. If the air outlet temperature is 95 °F and the relative humidity is 85%, calculate:

(a) The amount of wet fresh air to be supplied to the dryer.
(b) The amount of humid air entering the dryer.
(c) The fraction of the recirculated air with respect to that entering the dryer.

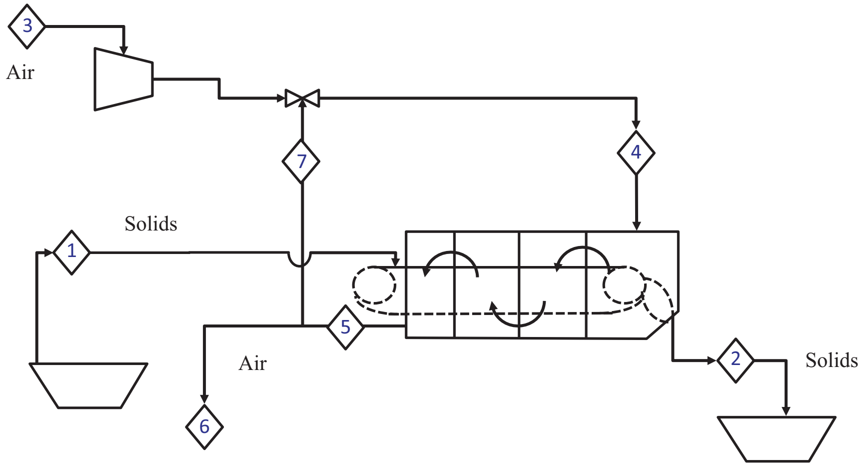


Figure P2.20

Solution: (a) 4,478 kg/h;(b)6,750 kg/h;(c)34.3%.

2.21 An aqueous suspension with 10% (by weight) of solids is introduced into a vacuum rotary filter, where a cake with 60% (by weight) of water is obtained. This cake then enters a rotary dryer from which it comes out with a moisture content of 0.09 kg of water/kg of dry solid. If the process has been designed for a throughput of 1,000 kg/h, calculate:

(a) Amount (kilograms) of water removed in the filter.
(b) Amount (kilograms) of dry air to be introduced into the dryer.
(c) Fraction of the recirculated air with respect to that entering the dryer.

Data: Characteristics of humid air

Stream	Relative humidity (%)	Dry bulb temperature
Fresh air	20%	85 °F
Dryer input	50%	78 °F
System output	90%	71 °F

Solution: (a) 750 kg/h; (b) 28,200 kg/h; (c) 50.75%.

2.22 It is desired to filter 1,500 kg of a suspension containing 12.5% by weight of $CaCO_3$ in a vacuum rotary filter. The cake that is taken out of the filter contains 58% water. This cake is placed in a dryer and dried until it has a moisture content of 8.75 kg H_2O/100 kg $CaCO_3$. If the humidity of the fresh air entering the dryer is 0.002 kg of water/kg of dry air and the humidity of the air leaving the dryer is 0.017 kg of water/kg of dry air, calculate:

(a) The amount of water removed in the filter and in the dryer (in kilograms).
(b) The amount of moist air entering the dryer (in kilograms).
(c) If part of the air from the dryer to the outlet is recirculated to it, the resulting stream would have an absolute humidity of 0.005 kg of water/kg of dry air. In this case the moisture content is reduced to 7.55 kg H_2O/100 kg $CaCO_3$. Calculate the kilograms of humid air entering the dryer and the amount of water removed from the dryer.

Solution: (a) 1,053.6 and 242.5 kg/h; (b) 16,200.5 kg/h; (c) 20,499.7 kg of dry air/h and 244.8 kg of water/h.

2.23 The transport of sludge from a wastewater treatment plant (WWTP) is one of the important costs to be taken into account in its management, so it is necessary to significantly reduce the percentage of water from them prior to transport. For this purpose, a two-stage process is designed: filtration and drying. A WWTP produces 3,200 kg of wet sludge per day with 3% by weight of dry sludge entering a vacuum rotary filter. The cake that is taken out of the filter contains 45% water. This cake is placed in a dryer from which it comes out with a moisture content of 8.5 kg H_2O/100 kg dry sludge. The humidity of the fresh air entering the dryer is 0.002 kg of water per kg of dry air and the humidity of the air leaving the dryer is 0.018 kg of water/kg of dry air. It is possible to recirculate part of the air from the dryer (the resulting stream would have an absolute humidity of 0.005 kg of water/kg of dry air). In this case the moisture content is reduced to 7.10 kg H_2O/100 kg dry sludge. If the transport cost is 0.15 €/kg wet sludge, which is the difference in annual cost and therefore savings between both operating conditions.

Solution: Annual cost without recirculation 7,223 €/year and with recirculation 7,130 €/year and, therefore, a saving of 103 €/year.

2.24 One of the principles of the circular economy is to achieve maximum efficiency of a process, that is, the complete transformation of raw materials into products without the generation of waste, for example, by defining closed-loop systems for the separating agents. A 10,000 kg/feed of flax seed (*Linum usitatissimum*) is processed in three stages (Figure P2.24). The feed contains (% weight): 35.0% protein, 27.1% carbohydrates, 9.4% fiber and ash, 10.5% moisture and 18% oil. In the first stage, the flax is macerated and pressed to extract the oil, obtaining oil streams and pressed pulp that still contains 6% oil. In the second stage the pressed paste is treated with hexane (2.85 kg of hexane in stream 6 per load in stream 1) to obtain a linen extract stream (containing 0.5% oil and 0.1% hexane) and an oil–hexane stream. Finally, the extract is dried to obtain a product with 8% humidity by weight. Calculate:

(a) The kilograms of flax paste that comes out of the first stage.

(b) The kilograms of flax extract obtained in the second stage.

(c) The kilograms of final dry matter and % by weight of protein in the dry product.

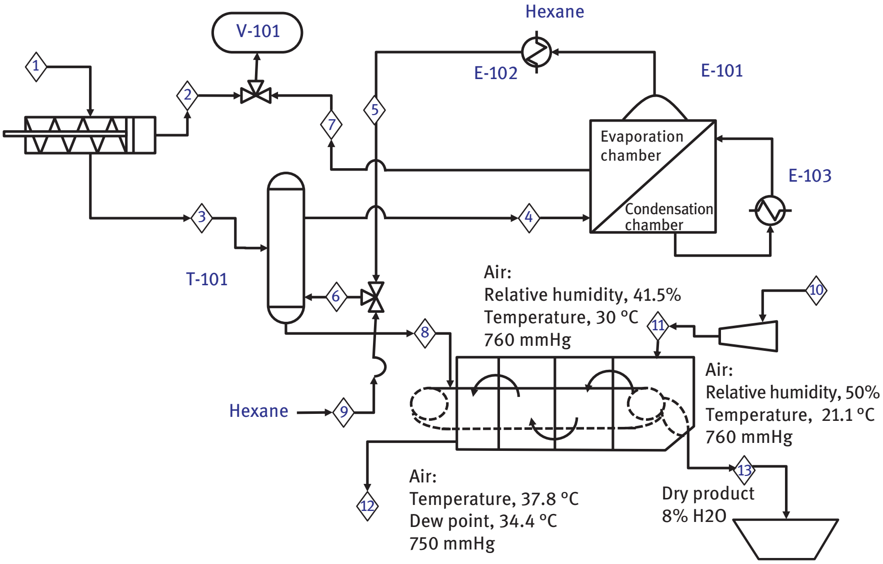


Figure P2.24

Solution: (a) 8,723.4 kg; (b) 8,249.5 kg; (c) 7,825.5 kg and 44.7% of protein.

2.7.4 Mass balances in nonstationary state

2.25 Water is pumped, with a flow rate of 325 L/min, to a cylindrical tank of 2.75 m in diameter. Water flows through a pipe from the tank with a flow rate that depends on the height of the liquid (h) in the tank, which complies with the following ratio:

$$q_{\text{output}} = a \cdot h$$

where
- flow rate is expressed in L/min;
- the height in m;
- a is an empirical coefficient.

Graphically represent the evolution of the liquid height in the tank over time. Calculate the height of the water in the tank after 60 min of operation, if the initial height of the water is half a meter and the empirical coefficient has a value of 185.

Solution: 1.56 m.

2.26 A compound A is dissolved in water at a rate proportional to the product of the amount of compound remaining undissolved, m_A, by the difference between the mass fraction of the saturated solution, $(w_A)_{\text{sat}}$, and the actual concentration of the solution at that time, w_A. In an experiment, 12.5 kg of compound A with 70 kg of pure water has been initially arranged, observing that after 3.5 h 1.88 kg of A were dissolved. Data: $(w_A)_{\text{sat}}$ is 0.311.

Graphically represent the evolution of the dissolved amount of A, n_A, and the undissolved amount, m_A, over time. Determine also the dissolved quantity of compound A after 12 h.

Solution: 5.01 kg.

3 Balances in systems with chemical reaction

When considering the modeling of systems with chemical reaction, it is necessary to take into account the controlling “mechanism” of the reaction (Figure 3.1). Three controlling factors are addressed in this chapter: (1) stoichiometry, (2) equilibrium and (3) kinetics.

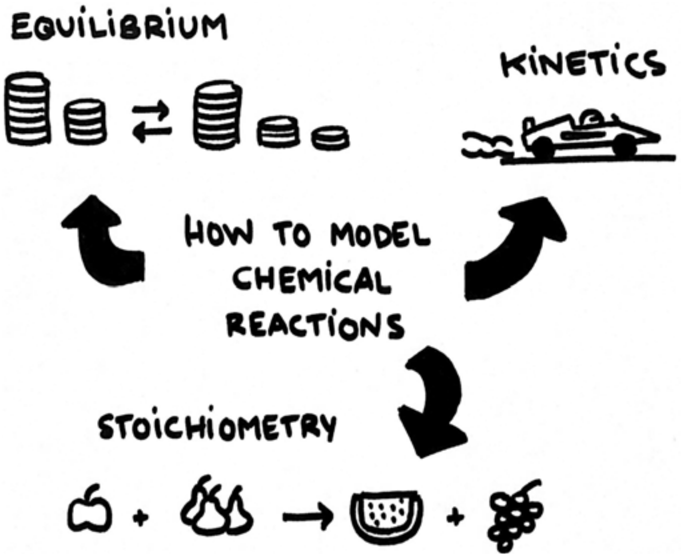


Figure 3.1: Limiting mechanisms in the modeling of a chemical reaction from the point of view of mass balances.

3.1 Stoichiometry

In 1792 the German chemist J.B. Richter defined the law of proportional equivalents, which can be expressed by saying that the weight of substance A that is combined with a certain quantity of another substance B is the same that would be combined with a substance C that enters in combination with the same quantity of substance B. Richter called this new field of research *stoichiometry* (from the Greek στοιχειον, stoicheion, “element” and μετρον, metric, “measure”).

In 1799 Proust formulated the law of defined proportions: “when two elements react to form a compound, they always do so in a constant weight relationship.” In 1808 Dalton published another ponderal law, the so-called multiple proportions: if from the combination of two elements several compounds can arise, it is fulfilled

https://doi.org/10.1515/9783110624304-003

that, while the weight of one remains constant, the weights of the other vary according to a simple numerical relationship.

These laws led Dalton to define his atomic theory in 1803. Their essential postulates are as follows:

1. Chemical elements consist of individual atoms that are indivisible.
2. Chemical compounds are formed by the union of atoms of different elements in proportions of simple integers.

According to Dalton's theory, the elements are conserved in a chemical reaction and, therefore, balances in weight can be taken, both elementary and global. Thus, the chemical equation provides both quantitative and qualitative information for calculating the quantities of substances that are combined in a chemical process. For example, the reaction of ammonia synthesis

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

tells us which are the stoichiometric relationships (once balanced). In this case, for each mole of nitrogen we can obtain two moles of ammonia, for which you will have to react with 3 moles of hydrogen. The relationships obtained from the numerical coefficients of the chemical equation are the stoichiometric coefficients.

3.1.1 Algebraic formulation

For the chemical reaction of ammonia synthesis, if we call $A_1 \equiv N_2$, $A_2 \equiv H_2$, $A_3 \equiv NH_3$, it can be represented:

$$A_1 + 3A_2 \rightleftarrows 2A_3$$

It is convenient to write all chemical compounds on the same side of the equation, and give the negative sign to those that are reactants and positive to the products. Therefore, the direct and inverse reaction could be expressed as follows:

$$2A_3 - 3A_2 - A_1 = 0 \qquad\qquad A_1 + 3A_2 - 2A_3 = 0$$

The numbers 2, −3, −1 (direct reaction) and 1, 3, −2 (reverse reaction) are called *stoichiometric coefficients* (α) and the natural way of writing these reactions would be the following:

$$\sum_{j=1}^{3} \left(\alpha_j \cdot A_j\right) = \alpha_1 \cdot A_1 + \ \alpha_1 \cdot A_1 + \alpha_3 \cdot A_3 = 0 \tag{3.1}$$

Equation (3.1) can be generalized to "w" compounds, so that

$$\sum_{j=1}^{w} \left(\alpha_j \cdot A_j\right) = 0 \tag{3.2}$$

where α_j represents the stoichiometric coefficients (positive value for the products and negative value for the reactants) and A_j are each of the compounds.

The general notation of writing of a chemical reaction can easily be extended to simultaneous reactions. Let us consider the synthesis reaction of methanol:

$$CO + 2H_2 \rightleftarrows CH_3OH$$

with the secondary reaction:

$$CO_2 + H_2 \rightleftarrows H_2O + CO$$

If we call $A_1 \equiv CH_3OH$, $A_2 \equiv CO$, $A_3 \equiv H_2$, $A_4 \equiv CO_2$ and $A_5 \equiv H_2O$, both reactions can be written:

$$\begin{array}{ll} \text{Reaction 1:} & A_1 - A_2 - 2A_3 = 0 \\ \text{Reaction 2:} & A_2 - A_3 - A_4 + A_5 = 0 \end{array}$$

where $\alpha_{11} = \alpha_{22} = \alpha_{25} = 1$, $\alpha_{12} = \alpha_{23} = \alpha_{24} = -1$, $\alpha_{21} = \alpha_{14} = \alpha_{15} = 0$ and $\alpha_{13} = -2$. Therefore, in a compact form it could be represented:

$$\sum_{j=1}^{5} \left(\alpha_{ji} \cdot A_j\right) = 0 \tag{3.3}$$

If instead of five compounds there were “w” and instead of two reactions there were “h,” the way to represent the system of equations would be

$$\sum_{j=1}^{w} \left(\alpha_{ji} \cdot A_j\right) = 0 \qquad i = 1, 2, \ldots, h \tag{3.4}$$

Example 3.1: The adjustment of biological reactions can be more complex due to the formation of biomass, where the resolution of a system of linear equations corresponding to the balances of the chemical elements is necessary. The ANAMMOX[3] process is a biological process consisting of the anaerobic oxidation of ammonium ion to nitrogen gas according to the reaction:[4]

$$NH_4^+ + \alpha_1 NO_2^- + \alpha_2 HCO_3^- + \alpha_3 H^+ \rightarrow N_2 + \alpha_4 NO_3^- + \alpha_5 CH_2O_{0.5}N_{0.15} + \alpha_6 H_2O$$

This reaction is carried out by *Planctomycetes* bacteria with a nitrification capacity (NO_3^-/NO_2^-) of 0.225.

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[3] ANAMMOX, acrónimo de ANAerobic AMMonium Oxidation.

[4] Jetten et al. (2009). Critical Reviews in Biochemistry and Molecular Biology, 44(2–3):65–84.

Solution:
Elementary balances:

$$
\begin{aligned}
&\text{N:} && 1+\alpha_1 = 2+\alpha_4+0.15\alpha_5\\
&\text{H:} && 4+\alpha_2+\alpha_3 = 2\alpha_5+2\alpha_6\\
&\text{O:} && 2\alpha_1+3\alpha_2 = 3\alpha_4+0.5\alpha_5+\alpha_6\\
&\text{C:} && \alpha_2 = \alpha_5
\end{aligned}
$$

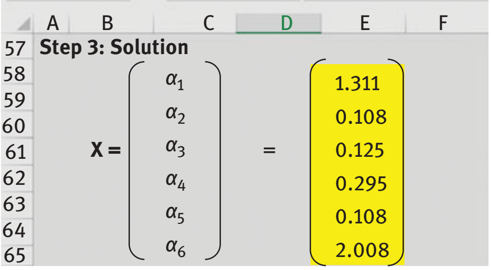
Coefficient balance:

$$1-\alpha_1-\alpha_2+\alpha_3 = -\alpha_4$$

Nitrification capacity:

$$\frac{\alpha_4}{\alpha_1} = 0.225$$

Resolution of the mass balances:
For solving the system of linear equations, the method of matrix inversion is applied (see Appendix D), with the results shown in Figure 3.2.



Step 3: Solution

$$X = \begin{pmatrix}\alpha_1\\ \alpha_2\\ \alpha_3\\ \alpha_4\\ \alpha_5\\ \alpha_6\end{pmatrix} = \begin{pmatrix}1.311\\ 0.108\\ 0.125\\ 0.295\\ 0.108\\ 2.008\end{pmatrix}$$

Figure 3.2: Stoichiometric coefficients to adjust the reaction.

Example 3.2: One of the most commonly used physicochemical parameters in the characterization of the organic matter content of wastewater is the chemical oxygen demand (COD). This is defined as the amount of oxygen necessary for a complete oxidation of organic matter. The calculation of the theoretical COD for an organic compound can be obtained from the adjustment of the complete oxidation reaction to CO_2 and H_2O:

$$C_xH_yO_z + \alpha_1 O_2 \rightarrow \alpha_2 CO_2 + \alpha_3 H_2O$$

where stoichiometric coefficients would be:

$$\alpha_1 = \frac{1}{4}(4x+y-2z)$$

$$\alpha_2 = x$$

$$\alpha_3 = \frac{y}{2}$$

Consequently, the theoretical COD would be obtained as follows:

$$COD_T = \frac{8(4x+y-2z)}{(12x+y+16z)} \left(\frac{mg\ O_2}{mg\ C_xH_yO_z} \text{or} \frac{mg\text{COD}}{mg\ C_xH_yO_z}\right)$$

With this in mind, calculate:

a. The concentration, expressed as g COD/L, of wastewater composed of 2 g/L glucose, 1,500 ppm acetic acid, 1,800 ppm propionic acid and 0.5 g/L butyric acid.
b. If the flow of wastewater was 500 m^3/d, what would be the equivalent number of inhabitants of a city with a similar organic load.[5]

Solution:

For the calculation of (a) it is necessary to first know the COD_T for each of the compounds present in the wastewater, applying the equation of the reaction adjustment of the complete oxidation (Figure 3.3).

D38: = 8*(4*D34 + D35−2*D36)/(12*D34 + D35 + 16*D36) [COD_T value for glucose]

The values for acetic acid, propionic acid and butyric acid are calculated analogously in cells E38, F38 and G38. The concentration value (in g COD/L) is calculated in cells F46, F47, F48 and F49; the sum of which (cell F50) makes it possible to determine the COD_T value of wastewater:

F46: = D46*E46 [g COD/L for glucose]
F50: = SUM(F46:F49) [COD_T value of the wastewater]

Since the organic load of a wastewater is defined as the product of flow by concentration (expressed in terms of COD), (b) is calculated as follows:

$$\text{p.e.} = \frac{OL}{60\left(\frac{g\text{COD}}{d\text{p.e.}}\right)} = \frac{Q\left(\frac{L}{d}\right)\cdot\left(\frac{g\text{COD}}{L}\right)}{60\left(\frac{g\text{COD}}{d\text{p.e.}}\right)} = \frac{5\cdot 10^5 \times 7.367}{60} = 61,392$$

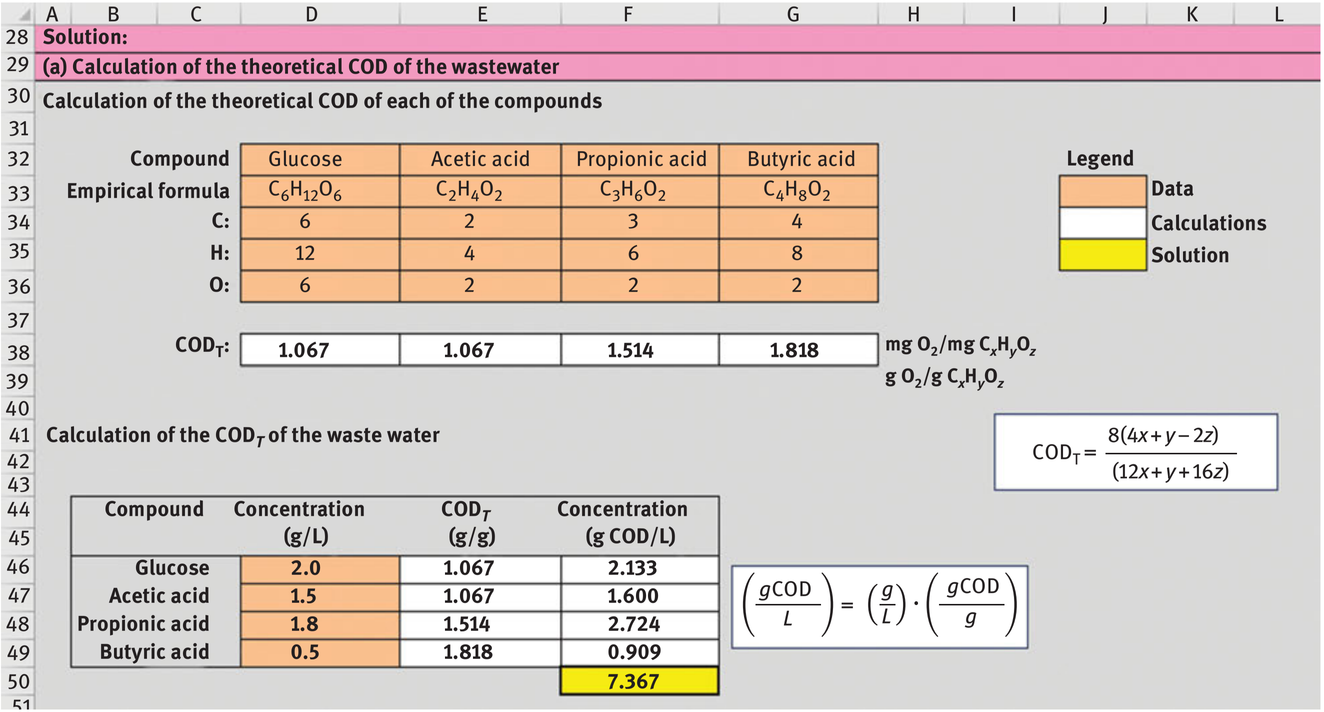
3.1.2 Conversion

When a chemical reaction takes place, the quantities of the components that existed initially change (increasing or decreasing) and, in the end, different quantities are obtained from those that existed initially. In order to measure the evolution of the reaction, different variables have been defined, both intensive and extensive, referring to some of the components or independent of them.

If N_j is the number of moles of A_j at any time, N_{jo} is the number present in an arbitrary determined time and if the composition only changes due to the chemical reaction, the molar conversion is defined according to eq. (3.5):

---

[5] Directive 91/271/EEC (https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A31991L0271) concerning urban waste water treatment plays a major role in the management of urban waste water and in the protection of receiving surface waters and the aquatic environment. The Directive states that 1 p.e. (population equivalent)' means the organic biodegradable load having a five-day biochemical oxygen demand (BOD_5) of 60 g of oxygen per day.



Solution:

(a) Calculation of the theoretical COD of the wastewater

Calculation of the theoretical COD of each of the compounds

Compound	Glucose	Acetic acid	Propionic acid	Butyric acid
Empirical formula	$C_6H_{12}O_6$	$C_2H_4O_2$	$C_3H_6O_2$	$C_4H_8O_2$
C:	6	2	3	4
H:	12	4	6	8
O:	6	2	2	2
COD_T:	**1.067**	**1.067**	**1.514**	**1.818**

mg O_2/mg $C_xH_yO_z$
g O_2/g $C_xH_yO_z$

Legend
- 🟧 **Data**
- ☐ **Calculations**
- 🟨 **Solution**

$$COD_T = \frac{8(4x+y-2z)}{(12x+y+16z)}$$

Calculation of the COD_T of the waste water

Compound	**Concentration (g/L)**	**COD_T (g/g)**	**Concentration (g COD/L)**
Glucose	**2.0**	**1.067**	**2.133**
Acetic acid	**1.5**	**1.067**	**1.600**
Propionic acid	**1.8**	**1.514**	**2.724**
Butyric acid	**0.5**	**1.818**	**0.909**
			7.367

$$\left(\frac{gCOD}{L}\right) = \left(\frac{g}{L}\right)\cdot\left(\frac{gCOD}{g}\right)$$

Figure 3.3: Calculation of the COD_T of each compound and of the residual water.

$$X = \frac{N_j - N_{jo}}{\alpha_j} \tag{3.5}$$

which has the same value for the “S” components. From eq. (3.5) we obtain the quantity of component at a given time:

$$N_j = N_{jo} + \alpha_j \cdot X \tag{3.6}$$

The molar conversion, X, is an extensive variable, measured in moles, and its main property is that it is a variable that depends exclusively on the reaction and not on the choice of any arbitrary A_j compound.

If there are several reactions, a molar conversion can be defined for each of them X_i. If X_i is the conversion of the reaction i, this reaction would increase (or decrease) the number of moles of the compound A_j by an amount of $\alpha_{ij}\,X_i$:

$$N_j = N_{jo} + \sum_i \alpha_{ji} \cdot X_i \tag{3.7}$$

The equations are also valid for dynamic systems, where it is normal to use molar flows, n, instead of quantities. So, for a reaction:

$$X = \frac{n_j - n_{jo}}{\alpha_j} \tag{3.8a}$$

$$n_j = n_{jo} + \alpha_j \cdot X \tag{3.8b}$$

In the rest of the chapter the equations will be expressed with the terminology of the molar quantity, N, which is logically equivalent for dynamic systems with molar flows, n.

3.1.2.1 Intensive conversion

If the volume remains constant, we can divide eq. (3.6) by V for a single reaction:

$$\begin{gathered} \frac{N_j}{V} = \frac{N_{jo}}{V} + \alpha_j \cdot \frac{X}{V} \\ c_j = c_{jo} + \alpha_j \cdot \xi \end{gathered} \tag{3.9}$$

where ξ is the intensive conversion of the reaction (moles/volume) and c_{jo} is the composition of the component A_j in the initial conditions.

3.1.2.2 Degree of Conversion

For a given reaction scheme the degree of conversion of a given component, A_k (always reactant), can be defined as the number of moles that have reacted of that component for each mole of reactant present in the initial mixture. The definition applies to both static and dynamic systems. In the former, the initial mixture should be understood for a reaction time $t = 0$, and in the latter, the initial mixture should be understood at the input of the system.

The conversion degree symbol is usually provided with a subscript that refers to the key component or component for which it was defined, although in the case of systems in which a single reaction takes place, the subscript is usually not considered, although it must be made very clear to which component or chemical species it refers.

Therefore, if we work with quantity of moles (N):

$$\zeta_k = \frac{N_{ko} - N_k}{N_{ko}} \tag{3.10}$$

Therefore,

$$N_k = N_{ko}(1 - \zeta_k) \tag{3.11}$$

If the density of the system remains constant throughout the process (this hypothesis is valid for most liquid reactions and gas reactions where the number of products is equal to the number of moles of reactants, i.e., when $\sum\alpha_j = 0$), expression (3.11) can be divided by the volume:

$$\frac{N_k}{V} = \frac{N_{ko}}{V}(1 - \zeta_k) \qquad \Rightarrow \qquad c_k = c_{ko}(1 - \zeta_k) \tag{3.12}$$

The degree of conversion, ζ, is an intensive magnitude and refers to one component (reactant) and therefore does not have to be the same for all reactants. In any case it is evident that its value can oscillate between 0 (null conversion) or 1 (complete conversion).

In the reaction,

$$\alpha_k A_k + \alpha_j A_j + \alpha_e A_e = 0$$

where A_k and A_j are the reactants, it must be fulfilled that

$$\frac{(N_{ko} - N_k)}{\alpha_k} = \frac{(N_{jo} - N_j)}{\alpha_j}$$

Substituting the value of N_k for the value obtained in eq. (3.11), the expression for the calculation of N_j is obtained from the degree of conversion:

$$N_j = N_{jo} - N_{ko} \cdot \zeta_k \cdot \frac{\alpha_j}{\alpha_k} \tag{3.13}$$

If in addition the volume remains constant, dividing expression (3.13) by the volume:

$$c_j = c_{jo} - c_{ko} \cdot \zeta_k \cdot \frac{\alpha_j}{\alpha_k} \tag{3.14}$$

The above relationships are equally valid for molar flows.

3.1.2.3 Relationship between molar conversion and degree of conversion

From eqs. (3.6) and (3.13) it must be fulfilled that

$$\alpha_j \cdot X = -N_{ko} \cdot \zeta_k \cdot \frac{\alpha_j}{\alpha_k}$$

The relationship between the molar conversion, X, and the degree of conversion, ζ_k, is therefore immediately deduced:

$$X = -\frac{N_{ko}}{\alpha_k} \cdot \zeta_k \tag{3.15}$$

3.1.3 Limiting reactant and excess

It is said that A_k is a limiting reactant is the one that is in less quantity than that of stoichiometric proportion, that is, to say:

$$\left|\frac{N_{ko}}{\alpha_k}\right| < \left|\frac{N_{jo}}{\alpha_j}\right|_{j=1,2,\ldots,S} \tag{3.16}$$

Generally, the degree of conversion refers to the limiting reactant.

It is said that a reactant is in excess on the limiting reactant if it is found in greater quantity than that which would correspond to it stoichiometrically. Excess is defined as

$$\%A_j = \frac{N_{jo}/\alpha_j - N_{ko}/\alpha_k}{N_{ko}/\alpha_k} \cdot 100 \tag{3.17}$$

Example 3.3: The empirical formula of gasoline is approximately C_7H_{15} and has a specific weight of 750 Km/m^3. If all the carbon is emitted in the form of CO_2 when burned calculate:

a. For a Euro 4 car – whose average consumption is 10 L per 100 km – that travels about 300,000 km before being scrapped, how much carbon will it emit during its useful life?
b. If the car weighs 1,800 kg and travels 25,000 km/year, what is the relationship between the emitted carbon sink and the weight of the vehicle?
c. If vehicles were subject to the Kyoto protocol and therefore had to access the carbon market (average cost of the Tm of CO_2 of 20 euros), what would be the annual cost and the cost per liter consumed?
d. If you switched to a car that complies with the Euro 5 Directive, with an average consumption of 7.5 L per 100 km, what would be the reduction in emissions that would be achieved in its useful life?
e. If an electricity company were to accept as carbon credits the subsidy on the purchase of Euro 5 vehicles to remove old vehicles from circulation, how much should it be willing to pay to incentivize its owners to purchase a new vehicle?

Solution:

Step 1: Scheme of the process with identification of data

The reaction that takes place in the car:

$$C_7H_{15} + \frac{43}{2}O_2 \rightarrow 7CO_2 + \frac{15}{2}H_2O$$

If we call $A_1 \equiv C_7H_{15}$, $A_2 \equiv O_2$, $A_3 \equiv CO_2$, $A_4 \equiv H_2O$ the reaction can be expressed:

$$\frac{15}{2}A_4 + 7A_3 - \frac{43}{2}A_2 - A_1 = 0$$

It is worth noting:

i. The limiting reactant will be the fuel since the amount of air is at least stoichiometric, that is, $k = 1$.
ii. Conversion rate equal to 1 (full conversion).
iii. In this problem it is necessary to use molecular masses, since many of the sections the emissions are needed.

Step 2: Basis of calculations

The basis of calculation shall be the mileage of the vehicle.

Step 3: Definition of control volumes and formulation of the mass balances

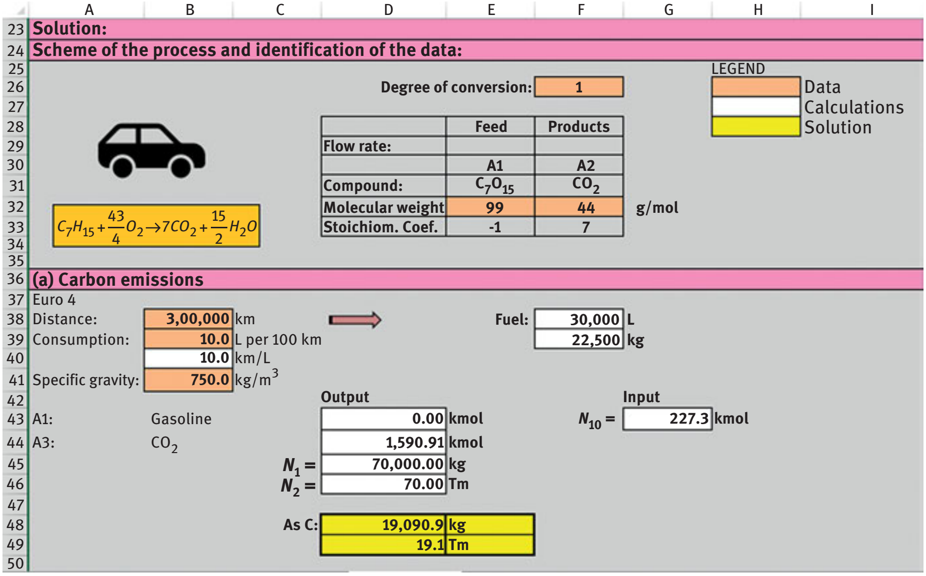
In this case, the only volume is the vehicle where the mass balances with chemical reactions are raised, which corresponds to the application of eqs. (3.11) and (3.13):

Balance for the limiting reactant: $N_1 = N_{1o} \cdot (1 - \zeta_1)$

Balance for CO_2: $N_3 = N_{3o} - N_{1o} \cdot \zeta_1 \cdot \frac{\alpha_3}{\alpha_1}$

Step 4: Solving the system of equations

The calculations for section (a) are shown in Figure 3.4.



Solution:

Scheme of the process and identification of the data:

LEGEND
▨ Data
□ Calculations
🟨 Solution

Degree of conversion: 1

	Feed	Products
Flow rate:		
	A1	**A2**
Compound:	C_7O_{15}	CO_2
Molecular weight	**99**	**44**
Stoichiom. Coef.	-1	7

g/mol

$C_7H_{15}+\frac{43}{4}O_2\rightarrow 7CO_2+\frac{15}{2}H_2O$

(a) Carbon emissions

Euro 4
Distance: **3,00,000** km
Consumption: **10.0** L per 100 km
10.0 km/L
Specific gravity: **750.0** kg/m^3

Fuel: **30,000** **L**
22,500 **kg**

Output
0.00 **kmol**
1,590.91 **kmol**
N_1 = **70,000.00** **kg**
N_2 = **70.00** **Tm**

Input
N_{10} = **227.3** **kmol**

A1: Gasoline
A3: CO_2

As C: **19,090.9** **kg**
19.1 **Tm**

Figure 3.4: Calculation of the composition of the combustion gases.

H44: = –(G43*$F$26*($F$33/$E$33)) [moles of CO_2 formed; the initial amount of CO_2 is 0]
H45: = D44*$F$32 [from the molecular weight of CO_2, its value in weight can be obtained]
H48: = –($H$47*$C$31*(C37/$C$34)) [from the weight of C in the CO_2 molecule, the kg of C can be obtained]

For the calculation of section (b), it is sufficient to replace the value of 300,000 km by 25,000 km and the value obtained by dividing it by 1,800 kg. The result is 0.88.

Section (c) is obtained directly by multiplying the annual tons of CO_2 produced in section (b) by the value of 20 €, that is, 116.67 €. If this value is divided by the liters of annual fuels (2,500 L/year), the cost would be 5 cents per liter.

Section (d) implies changing the value of the consumption, by a value of 7.5 km per 100 km, which will allow the vehicle to travel 13.3 km per liter. In this case, the kg of CO_2 that would be formed would be 52,500 kg; therefore, the emission reduction would be: 70,000–52,500 = 17,500 kg. This reduction would entail a cost (section e) of €350, which should be the subsidy provided by the electricity company.

Example 3.4: In a boiler, propane is burned as fuel in the presence of air. Determine the molar composition (dry and wet basis) of the combustion products if the operating conditions are as follows:

a. 100% conversion and supply of stoichiometric air.
b. 100% conversion and supply of enriched air (23% oxygen) in stoichiometric quantities.
c. 100% conversion and 20% excess air.
d. 90% conversion and 20% excess air.

Solution:

Step 1: Flowchart with identification of data

The flow diagram is very simple as it is a single unit (furnace) where propane is burned (Figure 3.5).

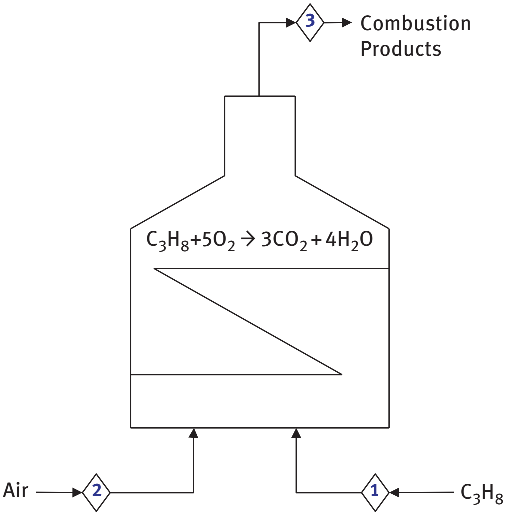


Figure 3.5: Process scheme.

If we call $A_1 \equiv C_3H_8$, $A_2 \equiv O_2$, $A_3 \equiv N_2$, $A_4 \equiv CO_2$, $A_5 \equiv H_2O$ the reaction can be expressed as follows:

$$4A_5 + 3A_4 - 5A_2 - A_1 = 0$$

The degree of conversion will vary for each section. As far as stream data is concerned, it is worth noting:

i. The limiting reactant will be the fuel (stream 1) since the amount of air is at least stoichiometric, that is, $k = 1$.
ii. The average air composition can be assimilated to 21% oxygen and 79% molar nitrogen; therefore, the nitrogen flow at the furnace inlet, stream 2 – indicated by the subindex outside the parentheses, will be $(n_3)_2 = (n_2)_2 \cdot \left(\frac{0.79}{0.21}\right)$.
iii. The number of moles of oxygen at the inlet will depend on the excess to be considered with respect to the fuel (for stoichiometric conditions the value of the excess will obviously be zero). The equation applied is (3.17)

$$\%A_2 = \frac{(n_2)_2/\alpha_2 - (n_1)_1/\alpha_1}{(n_1)_1/\alpha_1} \cdot 100 \Rightarrow (n_2)_2 = \frac{\alpha_2}{\alpha_1}(n_1)_1\left[1 + \left(\frac{\%A_2}{100}\right)\right]$$

Step 2: Basis of calculations
The basis of calculation shall be the fuel flow: $(n_{1o})_1 = 100$ mol/h.

Step 3: Definition of control volumes and formulation of the mass balances
In this case, the only control volume is the furnace where the mass balances with chemical reactions are raised, which corresponds to the application of eqs. (3.11) and (3.13) in molar units.

Balance for the limiting reactant: $(n_1)_3 = (n_1)_1 \cdot (1 - \zeta_1)$
Balances for all other reactants and products: $(n_j)_3 = (n_j)_2 - (n_1)_1 \cdot \zeta_1 \cdot \frac{\alpha_j}{\alpha_1}$
Balance for inerts (N_2): $(n_3)_3 = (n_3)_2$

Step 4: Solving the system of equations
The composition of the combustion gases for section (a) is presented in Figure 3.6.

H21: = H47*(1–C31) [limiting reactant])
H22: = B47–($H$47*$C$31*(C35/$C$34)) [oxygen moles]
H23: = B48 [moles of nitrogen, inert in reaction]
H24: = –($H$47*$C$31*(C37/$C$34)) [moles of CO_2 formed, value at input is zero]
H25: = –($H$47*$C$31*(C38/$C$34)) [moles of H_2O formed, the value at the input is zero]

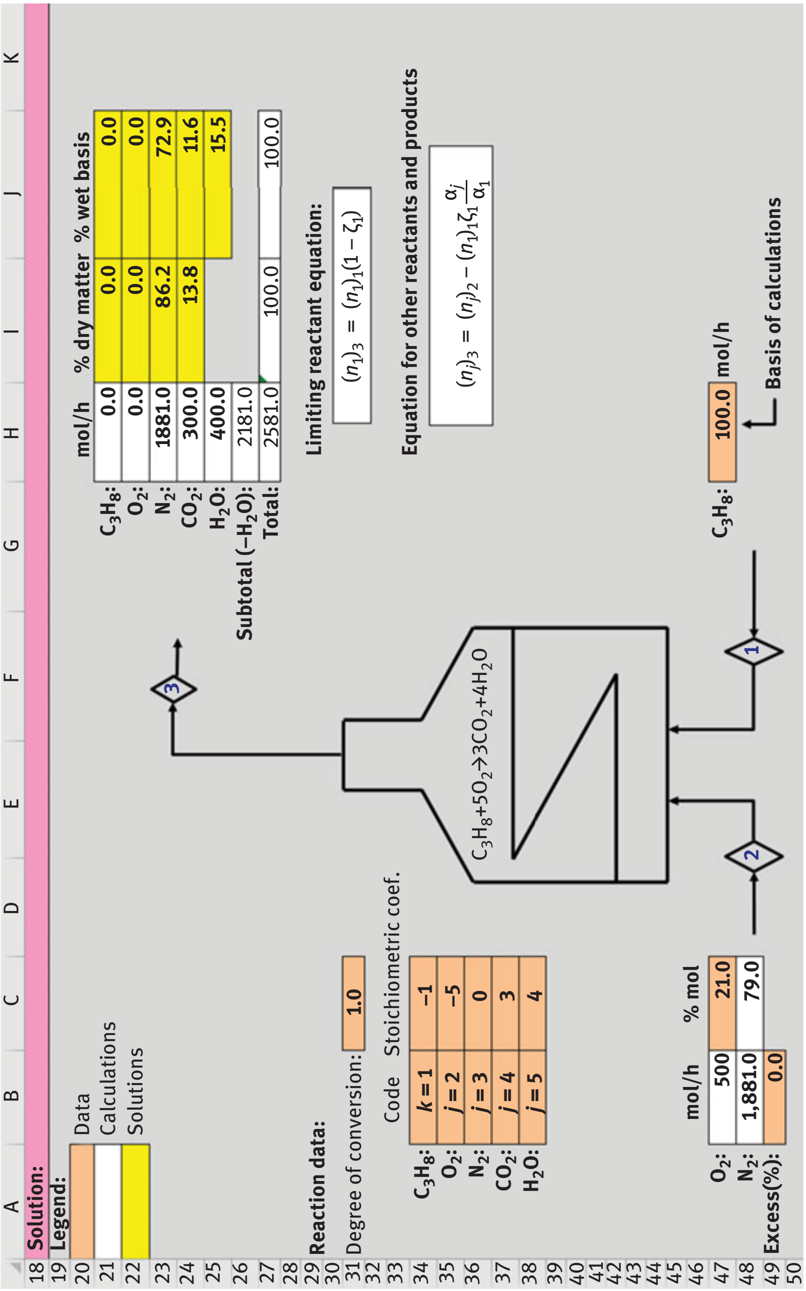
In cells H26 and H27 the moles of products are added, whether or not the quantity of H_2O is taken into account, since both quantities are necessary for the calculation of the percentage on a dry or wet basis of the combustion gases composition of the furnace:

$$\text{\% on a dry matter:} \quad \%\text{DM} = \frac{\text{mol}_{\text{component}}}{\text{total mol}_{\text{without } H_2O}} \cdot 100$$

$$\text{\% on a wet basis:} \quad \%\text{w.b.} = \frac{\text{mol}_{\text{component}}}{\text{total mol}} \cdot 100$$

Questions/simulations:

i. *Effect of the calculation base*: If the calculation basis is changed, the concentration of the combustion products will not change. Thus, if cell H47 is changed to 25 mol/h, the same values will be obtained in the percentage of each of the compounds.
ii. *Enriched air (section b)*: If enriched air is used, cell C47 with a value of 23, the amount of N_2 will be lower and the relative concentrations of the other gases will increase.
iii. *Simulation of boiler operation*: Sections (c) and (d) of the problem correspond to different boiler operating conditions. For its calculation it is enough to replace in cell C31 the degree of advance of the reaction and in cell B49 the excess of air that is used.



Solution:

Legend:

🟧	Data
☐	Calculations
🟨	Solutions

Reaction data:

Degree of conversion: 1.0

	Code	Stoichiometric coef.
C_3H_8:	$k = 1$	−1
O_2:	$j = 2$	−5
N_2:	$j = 3$	0
CO_2:	$j = 4$	3
H_2O:	$j = 5$	4

	mol/h	% mol
O_2:	500	21.0
N_2:	1,881.0	79.0
Excess(%):	0.0	

	mol/h	% dry matter	% wet basis
C_3H_8:	0.0	0.0	0.0
O_2:	0.0	0.0	0.0
N_2:	1881.0	86.2	72.9
CO_2:	300.0	13.8	11.6
H_2O:	400.0		15.5
Subtotal ($-H_2O$):	2181.0		
Total:	2581.0	100.0	100.0

Limiting reactant equation:

$$(n_1)_3 = (n_1)_1(1-\zeta_1)$$

Equation for other reactants and products

$$(n_j)_3 = (n_j)_2 - (n_1)_1\zeta_1\frac{\alpha_j}{\alpha_1}$$

C_3H_8: 100.0 mol/h

Basis of calculations

Figure 3.6: Calculation of the composition of the combustion gases.

Example 3.5: Figure 3.7 shows part of the methanol production process with a stoichiometric CO and H_2 feed (stream 1) to achieve a step conversion in the reactor (R-101) of 27.5%. In the separation tower (T-101) all the methanol formed comes out as a product, with a maximum stream of 0.5% H_2 from which the tower is fed. The recirculation ratio is 7.0. Calculate the overall conversion, molar flow and composition of all streams.

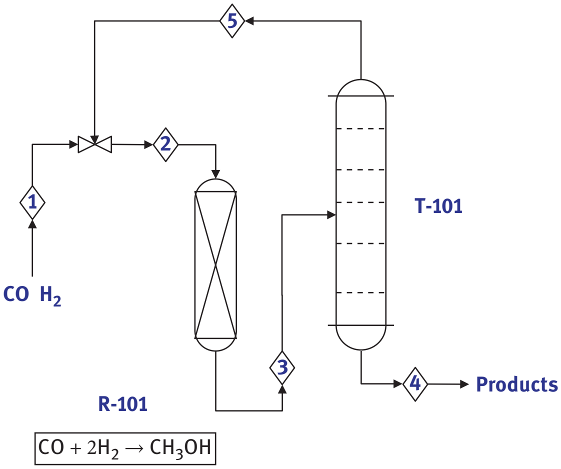


Figure 3.7: Methanol production process.

Solution:

Step 1: Flowchart with identification of data

Reaction data: If we call $A_1 \equiv CO$, $A_2 \equiv H_2$, $A_3 \equiv CH_3O$, the reaction can be expressed:

$$A_3 - 2A_2 - A_1 = 0$$

CO being the limiting reactant (in this case since both reactants are in stoichiometric ratio, H_2 could also be considered); therefore, $k = 1$ and a degree of conversion of 0.275.

Process data:

i. The recirculation ratio, $r = (n_{total})_5/(n_{total})_1 = 7.0$.
ii. Hydrogen in product stream, $\varphi = 0{,}005$:

$$(n_2)_4 = \varphi \cdot (n_2)_3$$

Step 2: Basis of calculations

The flow rate of CO feed shall be considered as the calculation basis: $(n_1)_1 = 100$ mol/h; therefore, the quantity of hydrogen (stoichiometric) will be $(n_2)_1 = 200$ mol/h.

Step 3: Definition of control volumes and formulation of the mass balances

To calculate the molar flow of the components in each stream (obviously, this will allow the immediate calculation of the molar fraction), eq. (2.10b) for the component balance without chemical reaction and eqs. (3.11) and (3.13) for the mass balances with chemical reactions will be applied:

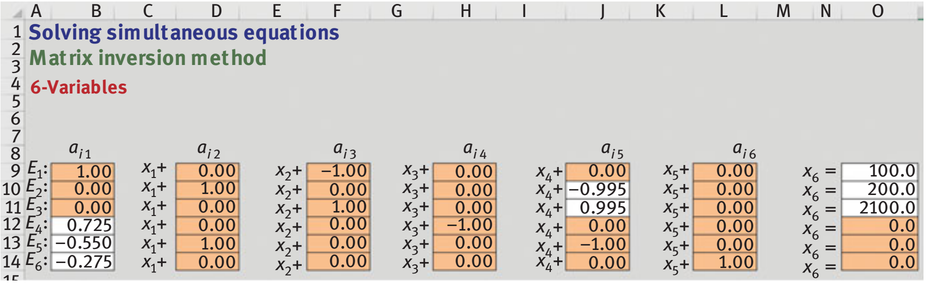
– Volume control to the mixing point of the feed and recirculation	
CO balance	$(n_1)_1 + (n_1)_5 = (n_1)_2$
H_2 balance	$(n_2)_1 + (n_2)_5 = (n_2)_2$
Recirculation ratio	$r = \frac{(n_{\text{total}})_5}{(n_{\text{total}})_1} = \frac{(n_1)_5 + (n_2)_5}{(n_{\text{total}})_1}$
– Control volume corresponding to reactor R-101	
CO balance (limiting reactant)	$(n_1)_3 = (n_1)_2 \cdot (1 - \zeta_1)$
H_2 balance	$(n_2)_3 = (n_2)_2 - (n_1)_2 \cdot \zeta_1 \cdot \frac{\alpha_2}{\alpha_1}$
CH_3OH balance (*stream 2 does not contain methanol*)	$(n_3)_3 = -(n_1)_2 \cdot \zeta_1 \cdot \frac{\alpha_3}{\alpha_1}$
– Control volume for separation column T-101	
CO balance	$(n_1)_3 = (n_1)_4 + (n_1)_5$
H_2 balance and recovery	$(n_2)_3 = (n_2)_4 + (n_2)_5$ $(n_2)_4 = \varphi \cdot (n_2)_3$
CH_3OH balance	$(n_3)_3 = (n_3)_4$

Step 4: Solving the system of equations
From the above equations, the system is defined by six linearly independent equations:

Equations	Unknowns	Coded equations
[1] $(n_1)_1 + (n_1)_5 = (n_1)_2$	$x_1 = (n_1)_2$	[1] $x_1 - x_3 = (n_1)_1$
[2] $(n_2)_1 + (1-\varphi)(n_2)_3 = (n_2)_2$	$x_2 = (n_2)_2$	[2] $x_2 - (1-\varphi) \cdot x_5 = (n_2)_1$
[3] $r = \frac{(n_{\text{total}})_5}{(n_{\text{total}})_1} = \frac{(n_1)_5 + (1-\varphi)(n_2)_3}{(n_{\text{total}})_1}$	$x_3 = (n_1)_5$	[3] $x_3 + (1-\varphi) \cdot x_5 = r \cdot (n_{total})_1$
[4] $(n_1)_3 = (n_1)_2 \cdot (1 - \zeta_1)$	$x_4 = (n_1)_3$	[4] $(1-\zeta_1)x_1 - x_4 = 0$
[5] $(n_2)_3 = (n_2)_2 - (n_1)_2 \cdot \zeta_1 \cdot \frac{\alpha_2}{\alpha_1}$	$x_5 = (n_2)_3$	[5] $\zeta_1 \cdot \frac{\alpha_2}{\alpha_1} x_1 - x_2 + x_5 = 0$
[6] $(n_3)_3 = -(n_1)_2 \cdot \zeta_1 \cdot \frac{\alpha_3}{\alpha_1}$	$x_6 = (n_3)_3$	[6] $\zeta_1 \cdot \frac{\alpha_3}{\alpha_1} x_1 + x_6 = 0$

First, a copy of the “6 variables” sheet from the “Appendix_D_Linear_Equations” (see Appendix D) to the book where the solution to the problem is being elaborated. Both sheets are then “interconnected” with the introduction of the coefficients of the linear equations as data or as a formula when related to the spreadsheet of the problem (Figure 3.8):

B11: = 0 (entered as a number, since it does not depend on the data in the problem statement).
B12: = (1-’Example 3.5’!C42) (introduced as a formula by relating it to the spreadsheet where the data on the problem are indicated).



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	Solving simultaneous equations														
2															
3	Matrix inversion method														
4	6-Variables														
5															
6															
7															
8		a_{i1}		a_{i2}		a_{i3}		a_{i4}		a_{i5}		a_{i6}			
9	E_1:	1.00	x_1+	0.00	x_2+	−1.00	x_3+	0.00	x_4+	0.00	x_5+	0.00		x_6 =	100.0
10	E_2:	0.00	x_1+	1.00	x_2+	0.00	x_3+	0.00	x_4+	−0.995	x_5+	0.00		x_6 =	200.0
11	E_3:	0.00	x_1+	0.00	x_2+	1.00	x_3+	0.00	x_4+	0.995	x_5+	0.00		x_6 =	2100.0
12	E_4:	0.725	x_1+	0.00	x_2+	0.00	x_3+	−1.00	x_4+	0.00	x_5+	0.00		x_6 =	0.0
13	E_5:	−0.550	x_1+	1.00	x_2+	0.00	x_3+	0.00	x_4+	−1.00	x_5+	0.00		x_6 =	0.0
14	E_6:	−0.275	x_1+	0.00	x_2+	0.00	x_3+	0.00	x_4+	0.00	x_5+	1.00		x_6 =	0.0

Figure 3.8: Connection of sheet containing the data of the problem with the solution of the system of linear equations of Example 3.5.

When you finish entering the coefficients you will automatically get the calculation of the solution that we can, in turn, transfer to the corresponding cells in the main spreadsheet of the problem (Figure 3.9).

Questions/simulations:

i. *Effect of the degree of conversion or step conversion in the reactor (R-101)*: The overall conversion depends to a large extent on the recirculation system with separation. Thus, if a (more expensive) catalyst change were to take place that would allow a step conversion of 30% (cell C42), the overall conversion would not change.

ii. *Separation efficiency in tower T-101*: If the separation efficiency is reduced so that the output stream is 1% H_2 (cell L40), two effects occur: (a) the purity of the methanol is reduced and (b) the overall conversion is reduced to 90%.

3.1.4 Multiple reactions: yield and selectivity

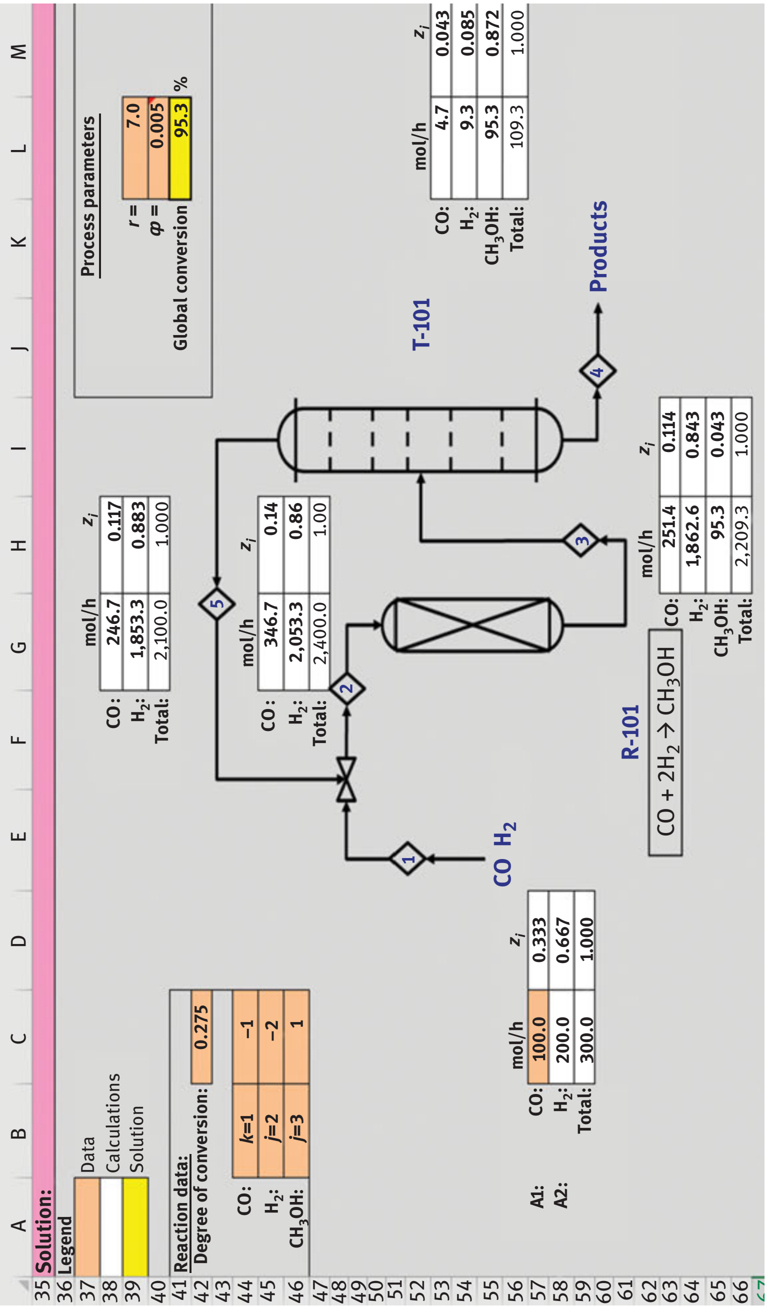
For multiple reactions the molar conversion of each of them, X_i, is defined so that the equation that relates the initial and final moles for all the components of the reaction corresponds to eq. (3.18):

$$N_j = N_{jo} + \sum_{i=1}^{h} (\alpha_{ji} \cdot X_i) \tag{3.18}$$

In moles per unit of time,

$$n_j = n_{jo} + \sum_{i=1}^{h} (\alpha_{ji} \cdot X_i) \tag{3.19}$$

Similarly, it is necessary to define intensive conversion for each of them, to obtain the concentration of each of the components of the reaction:



Solution:

Legend

- 🟧 Data
- ⬜ Calculations
- 🟨 Solution

Reaction data:

Degree of conversion: 0.275

CO:	*k*=1	−1
H_2:	*j*=2	−2
CH_3OH:	*j*=3	1

A1:
A2:

	mol/h	z_i
CO:	100.0	0.333
H_2:	200.0	0.667
Total:	300.0	1.000

	mol/h	z_i
CO:	246.7	0.117
H_2:	1,853.3	0.883
Total:	2,100.0	1.000

	mol/h	z_i
CO:	346.7	0.14
H_2:	2,053.3	0.86
Total:	2,400.0	1.00

	mol/h	z_i
CO:	251.4	0.114
H_2:	1,862.6	0.843
CH_3OH:	95.3	0.043
Total:	2,209.3	1.000

	mol/h	z_i
CO:	4.7	0.043
H_2:	9.3	0.085
CH_3OH:	95.3	0.872
Total:	109.3	1.000

Process parameters

r = 7.0
φ = 0.005
Global conversion 95.3 %

Figure 3.9: Solution to Example 3.5.

$$\xi_i = -\frac{X_i}{V} \tag{3.20}$$

$$c_j = c_{jo} + \sum_{i=1}^{h} \left(\alpha_{ji} \cdot \xi_i\right) \tag{3.21}$$

If the degree of conversion were used, the moles of the limiting reactant (3.11) and of the other reactants and products (3.13) would be calculated by

$$N_k = N_{ko}\left(1 - \sum_{i=1}^{h} \zeta_{ki}\right) \tag{3.22}$$

$$N_j = N_{jo} - \sum_{i=1}^{h} \left(N_{k_0 i} \cdot \zeta_{ki} \cdot \frac{\alpha_{ji}}{\alpha_{ki}}\right) \tag{3.23}$$

For both single and multiple reactions, the performance of an A_j product is defined, always with reference to the limiting reactant A_k as

$$R_j = \frac{\text{kmol } \mathrm{A}_j \text{ output}}{\text{kmol } \mathrm{A}_k \text{ input}} \cdot \frac{\alpha_k}{\alpha_j} = \frac{N_{jo} - N_j}{N_{ko}} \cdot \frac{\alpha_k}{\alpha_j} \tag{3.24}$$

The *selectivity* of an A_j product is a term usually used only in multiple reaction systems. It is usually defined as

$$S_j = \frac{\text{kmol } \mathrm{A}_j \text{ generated}}{\text{kmol } \mathrm{A}_k \text{ that reacted}} \cdot \frac{\alpha_k}{\alpha_j} = \frac{N_{jo} - N_j}{N_{ko} - N_k} \cdot \frac{\alpha_k}{\alpha_j} \tag{3.25}$$

Being A_k, the limiting reactant from which A_j can be obtained.

Example 3.6: In the combustion chamber of a boiler, propane is introduced with 200% excess air. If 80% is converted to carbon dioxide and 10% to carbon monoxide, calculate the composition of the combustion gases on a dry and wet basis.

Solution:

Step 1: Flowchart with identification of data

The flow diagram is identical to Example 3.4 (Figure 3.5) except that two reactions take place in this case:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

$$C_3H_8 + \frac{7}{2}O_2 \rightarrow 3CO + 4H_2O$$

If we call $A_1 \equiv C_3H_8$, $A_2 \equiv O_2$, $A_3 \equiv N_2$, $A_4 \equiv CO_2$, $A_5 \equiv H_2O$, $A_6 \equiv CO$ the reactions can be expressed:

$$4A_{51} + 3A_{41} - 5A_{21} - A_{11} = 0$$

$$3A_{62} + 4A_{52} \qquad - \frac{7}{2}A_{22} - A_{12} = 0$$

where $\alpha_{11} = -1$, $\alpha_{21} = -5$, $\alpha_{41} = 3$, $\alpha_{51} = 4$, $\alpha_{12} = -1$, $\alpha_{22} = -3{,}5$, $\alpha_{52} = 4$ and $\alpha_{62} = 3$.

The degree of conversion will vary for each section. As far as stream data is concerned, it is worth noting:

i. The limiting reactant will be the fuel (stream 1) since the amount of air is in excess; therefore, $k = 1$ for both reactions.
ii. The average air composition can be assimilated to 21% oxygen and 79% molar nitrogen; therefore, the nitrogen flow at the furnace inlet, stream 2 – indicated by the subindex outside the parentheses, will be $(n_3)_2 = (n_2)_2 \cdot \left(\frac{0.79}{0.21}\right)$.
iii. The amount of moles of oxygen at the inlet will depend on the excess considered over the fuel. Equation (3.17) is applied to each of the reactions to obtain the number of moles of oxygen in stream 2:

$$(n_2)_2 = \left(\frac{\alpha_{21}}{\alpha_{11}} + \frac{\alpha_{22}}{\alpha_{12}}\right) \cdot (n_1)_1 \cdot \left[1 + \left(\frac{\%\, A_2}{100}\right)\right]$$

Step 2: Basis of calculations
The basis of calculation shall be the fuel flow: $(n_{1o})_1 = 100$ mol/h.

Step 3: Definition of control volumes and formulation of the mass balances
In this case, the only control volume is the furnace where the mass balances with chemical reactions are raised, which corresponds to the application of eqs. (3.22) and (3.23) in molar units:

Balance for the limiting reactant: $(n_1)_3 = (n_1)_1 \cdot (1 - \zeta_{11} - \zeta_{12})$
Balances for all other reactants and products: $(n_j)_3 = (n_j)_2 - (n_1)_1 \cdot \zeta_{11} \cdot \frac{\alpha_{j1}}{\alpha_{11}} - (n_1)_1 \cdot \zeta_{12} \cdot \frac{\alpha_{j2}}{\alpha_{12}}$
Balances for inerts: (N_2): $(n_3)_3 = (n_3)_2$

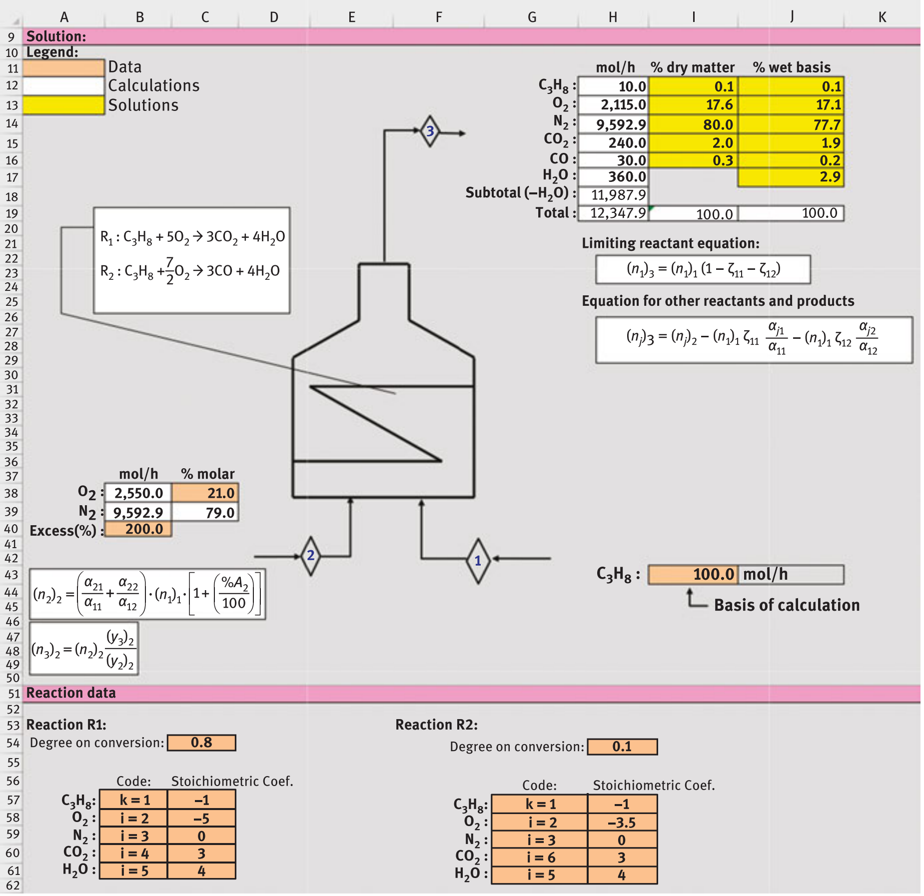
Step 4: Solving the system of equations
The composition of the combustion gases is presented in Figure 3.10:

H12: = I43*(1–C54–H54) [limiting reactant])
H13: = B38–(\$I\$43*\$C\$54*(C58/\$C\$57))–(\$I\$43*\$H\$54*(H58/\$H\$57 [oxygen moles]
H14: = B39 [moles of nitrogen, inert in reaction]
H15: = –(\$I\$43*\$C\$54*(C60/\$C\$57) [moles of CO_2 formed, value at input is zero, in the first reaction]
H16: = –(\$I\$43*\$H\$54*(H60/\$H\$57)) [moles of CO_2 formed, value at input is zero, in the second reaction]
H17: = –(\$I\$43*\$C\$54*(C61/\$C\$57))–(\$I\$43*\$H\$54*(H61/\$H\$57)) [moles of H_2O formed, the value at the input is zero in both reactions]

In cells H18 and H19 the moles of products are added, whether or not the quantity of H_2O is taken into account, since both quantities are necessary for the calculation of the percentage on a dry or wet basis of the combustion gases composition of the furnace:

$$\text{\% on a dry matter:} \qquad \%\text{DM} = \frac{\text{mol}_{\text{component}}}{\text{total mol}_{\text{without H}_2\text{O}}} \cdot 100$$

$$\text{\% on a wet basis:} \qquad \%\text{wet basis} = \frac{\text{mol}_{\text{component}}}{\text{total mol}} \cdot 100$$



Solution:

Legend:

🟧	Data
☐	Calculations
🟨	Solutions

	mol/h	% dry matter	% wet basis
C_3H_8 :	10.0	0.1	0.1
O_2 :	2,115.0	17.6	17.1
N_2 :	9,592.9	80.0	77.7
CO_2 :	240.0	2.0	1.9
CO :	30.0	0.3	0.2
H_2O :	360.0		2.9
Subtotal ($-H_2O$) :	11,987.9		
Total :	12,347.9	100.0	100.0

$R_1 : C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

$R_2 : C_3H_8 + \frac{7}{2}O_2 \rightarrow 3CO + 4H_2O$

Limiting reactant equation:

$$(n_1)_3 = (n_1)_1\,(1 - \zeta_{11} - \zeta_{12})$$

Equation for other reactants and products

$$(n_j)_3 = (n_j)_2 - (n_1)_1\,\zeta_{11}\,\frac{\alpha_{j1}}{\alpha_{11}} - (n_1)_1\,\zeta_{12}\,\frac{\alpha_{j2}}{\alpha_{12}}$$

	mol/h	% molar
O_2 :	2,550.0	21.0
N_2 :	9,592.9	79.0
Excess(%) :	200.0	

C_3H_8 : 100.0 mol/h

Basis of calculation

$$(n_2)_2 = \left(\frac{\alpha_{21}}{\alpha_{11}} + \frac{\alpha_{22}}{\alpha_{12}}\right)\cdot(n_1)_1\cdot\left[1 + \left(\frac{\%A_2}{100}\right)\right]$$

$$(n_3)_2 = (n_2)_2\,\frac{(y_3)_2}{(y_2)_2}$$

Reaction data

Reaction R1:

Degree on conversion: 0.8

	Code:	Stoichiometric Coef.
C_3H_8:	k = 1	−1
O_2 :	i = 2	−5
N_2 :	i = 3	0
CO_2 :	i = 4	3
H_2O :	i = 5	4

Reaction R2:

Degree on conversion: 0.1

	Code:	Stoichiometric Coef.
C_3H_8:	k = 1	−1
O_2 :	i = 2	−3.5
N_2 :	i = 3	0
CO_2 :	i = 6	3
H_2O :	i = 5	4

Figure 3.10: Calculation of the composition of the combustion gases (multiple reactions).

3.2 Chemical equilibrium in systems with chemical reactions

3.2.1 Chemical equilibrium with gas-phase reactions

Most reactions are, to some extent, reversible, acting in both directions at once. When the reaction rates are the same, the reaction is said to have reached equilibrium, and the equilibrium constant of the reaction, K, can be defined by eq. (3.26):

$$aA + bB \rightleftarrows cC + dD$$

$$K = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} = e^{-\frac{\Delta G^o}{RT}} \tag{3.26}$$

where

- a, activity
- ΔG^o, standard Gibbs free energies of formation[6]
- R, constant of ideal gases
- T, temperature.

The standard Gibbs free energy of a reaction is defined as

$$\Delta G^0 = \sum_{j=1}^{S} \alpha_j \cdot G_j^0 \tag{3.27}$$

As $G^o{}_i$ energy is a property of the pure species i in its standard state at fixed pressure, it depends only on the temperature, and both the free Gibbs energy exchange standard of a reaction and the equilibrium constant will also be unique functions of its temperature.

Starting from Gibbs' dependence of free energy on temperature, eq. (3.28)[7] signals the effect of temperature on the equilibrium constant. If the reaction is exothermic, $\Delta H^o < 0$, the equilibrium constant decreases as the temperature increases. In contrast, the value of K increases with T for an endothermic equation:

$$\frac{d \ln K}{dT} = -\frac{d(\Delta G^0/RT)}{dT} = \frac{\Delta H^0}{RT^2} \tag{3.28}$$

Taking into account the definition of activity (as the quotient of the fugacity of species j and the value of the fugacity of the standard state, $\hat{f}_j$ see Section 2.5 of Chapter 2) and of the fugacity coefficient (relationship between fugacity and pressure, $\hat{\phi}_j$):

$$a_j = \frac{\hat{f}_j}{f_j^o} = \frac{\hat{\phi}_j \cdot p_j}{f_j^o} \tag{3.29}$$

---

[6] **J. Willard Gibbs** (1839–1903): American chemist.

[7] Commonly referred to as the *van't Hoff equation*, in honor of **Jacobus van't Hoff** (1852–1911)

If Dalton's law applies

$$a_j = \frac{\hat{\phi}_j \cdot y_j \cdot P}{f_j^o} \tag{3.30}$$

Equation (3.30) can be simplified for ideal gases (usually at sufficiently low pressures or sufficiently high temperatures) as indicated in eq. (3.31), as it is verified:

i. Fugacity in its standard state is equal to its pressure, $f_j^o = P^o$.
ii. The standard state for a gas is the ideal state of pure gas at the pressure of the standard state P^o of 1 atm.
iii. The fugacity coefficient is 1:

$$a_j = \frac{y_j \cdot P}{P_j^o} = y_j \cdot P \tag{3.31}$$

By replacing this definition of activity in the definition of the equilibrium constant (3.26):

$$K = \frac{y_C^c \cdot y_D^d}{y_A^a \cdot y_B^b} \cdot P^{c+d-a-b} \tag{3.32}$$

Considering the algebraic formulation of a chemical reaction, the general expression that defines the equilibrium for gas phase reactions would be

$$\ln K = \sum_{j=1}^{w} \alpha_j \ln\left(y_j \cdot P\right) \tag{3.33}$$

Example 3.7: One of the reactions involved in the production of hydrogen is as follows:

$$CO_{(g)} + H_2O_{(v)} \rightleftarrows CO_{2(g)} + H_{2(g)}$$

Calculate the degree of conversion in the equilibrium as well as the molar fraction of each component with a stoichiometric feed. The pressure is atmospheric, and the temperature is 500 K, for which the standard Gibbs free energy is −20.784,63 J/mol.

Solution:

Step 1: Flowchart with identification of data

The flow diagram is very simple as it is a single unit where hydrogen is produced (Figure 3.11).

If we call $A_1 \equiv CO$, $A_2 \equiv H_2O$, $A_3 \equiv CO_2$, $A_4 \equiv H_2$, the direct reaction can be expressed as

$$A_4 + A_3 - A_2 - A_1 = 0$$

As far as stream data is concerned, it is worth noting:

i. The limiting reactant will be CO, that is, $k = 1$.
ii. In equilibrium the eq. (3.33) should be verified:

$$\ln K = \alpha_1 \ln(y_1 \cdot P) + \alpha_2 \ln(y_2 \cdot P) + \alpha_3 \ln(y_3 \cdot P) + \alpha_4 \ln(y_4 \cdot P)$$

Step 2: Choice of the calculation base

The calculation basis shall be the flow rate of CO in the input stream: $(n_1)_1 = 100$ mol/h.

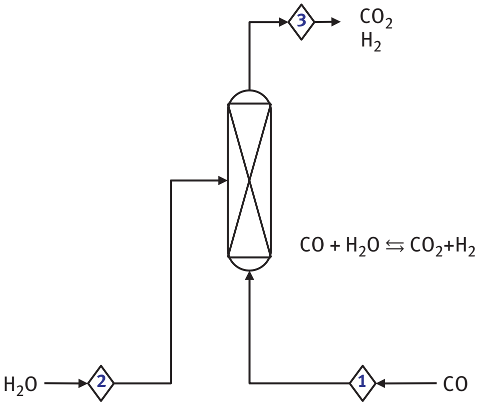


Figure 3.11: Scheme of the process.

Step 3: Definition of control volumes and formulation of the mass balances
In this case, the only control volume is the unit where the mass balances with chemical reaction are raised, which corresponds to the application of eqs. (3.11) and (3.13) for molar flows with the degree of equilibrium conversion.

Balance for the limiting reactant: $(n_1)_3 = (n_1)_1 \cdot (1 - \zeta_{eq})$
Balances for all other reactants and products: $(n_j)_3 = (n_j)_i - (n_1)_1 \cdot \zeta_{eq} \cdot \frac{\alpha_j}{\alpha_1}$

Step 4: Solving the system of equations
The idea is to solve a nonlinear equation (equilibrium condition) as a function of the degree of conversion that determines the molar fractions obtained from the mass balance with chemical reaction. This nonlinear equation will be solved by the "Goal Seek" technique (see Appendix C), for which a spreadsheet should be developed where the target function will be the difference between the actual value of K and the value obtained in the iteration of the calculation as a function of the degree of conversion (Figure 3.12).

The molar flow and composition in the output stream is obtained from the mass balance with chemical reaction (cells H15:I18). So, for the CO:

H15: = I41*(1–C25) [limiting reactant in the output stream]
I15: = H15/$H$19 [mole fraction of CO in the output stream]

The estimate of the equilibrium constant from the equilibrium conversion (cell C25) is calculated in cell I32:

I32: = C28*LN(I15*I31) + C29*LN(I16*I31) + C30*LN(I17*I31) + C31*LN(I18*I31)

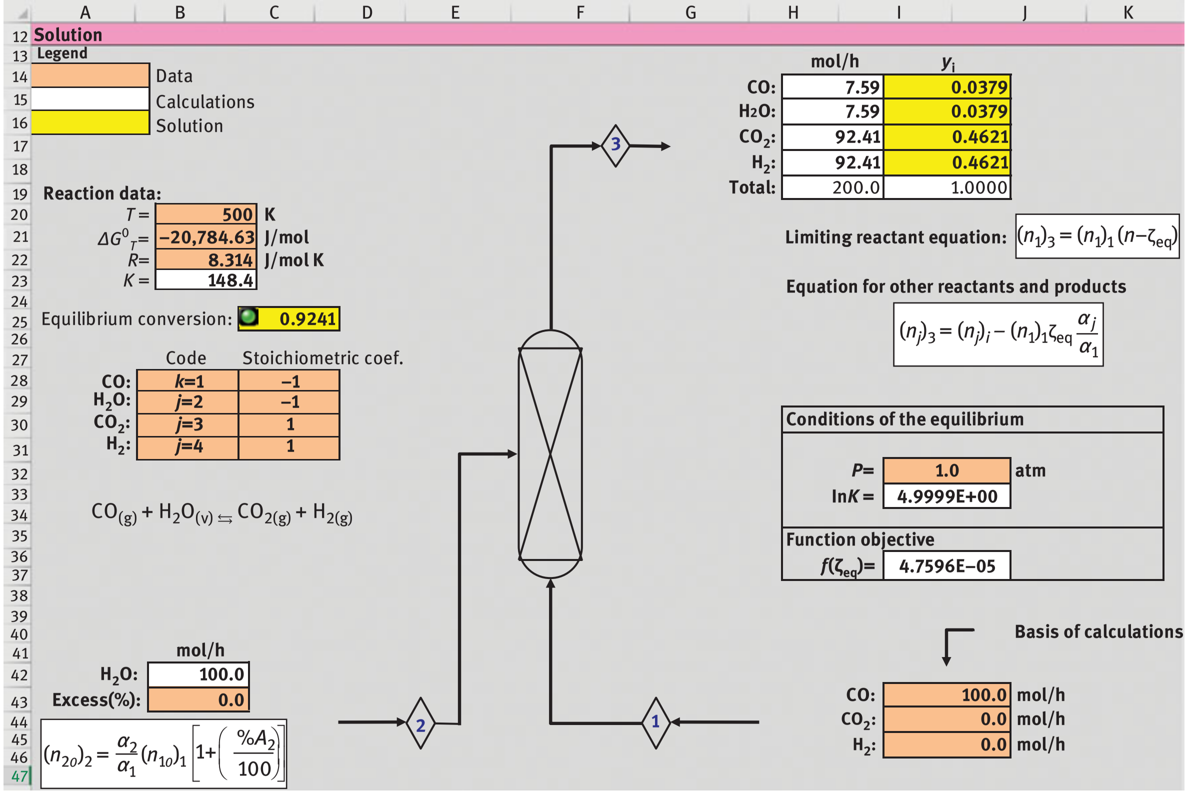
The actual value of the equilibrium constant is calculated in cell B23 from eq. (3.26):

B23: = EXP(–1*B21/(B22*B20))

The problem will be solved as soon as the value of the real equilibrium constant and the estimated equilibrium constant are equal, that is, the objective function of cell I35:

I35: = LN(B23)–I32

When considering the function "Goal Seek" it will be specified the following:
- Target cell: I35
- With a value of 0
- To change the cell: C25 (equilibrium conversion)



Solution

Legend

▨	Data
☐	Calculations
🟨	Solution

Reaction data:

$T =$ 500 K

$\Delta G^0_T =$ −20,784.63 J/mol

$R =$ 8.314 J/mol K

$K =$ 148.4

Equilibrium conversion: ● 0.9241

	Code	Stoichiometric coef.
CO:	$k=1$	−1
H_2O:	$j=2$	−1
CO_2:	$j=3$	1
H_2:	$j=4$	1

$$CO_{(g)} + H_2O_{(v)} \leftrightarrows CO_{2(g)} + H_{2(g)}$$

	mol/h
H_2O:	100.0
Excess(%):	0.0

$$(n_{20})_2 = \frac{\alpha_2}{\alpha_1}(n_{10})_1\left[1+\left(\frac{\%A_2}{100}\right)\right]$$

	mol/h	y_i
CO:	7.59	0.0379
H2O:	7.59	0.0379
CO_2:	92.41	0.4621
H_2:	92.41	0.4621
Total:	200.0	1.0000

Limiting reactant equation: $(n_1)_3 = (n_1)_1(n - \zeta_{eq})$

Equation for other reactants and products

$$(n_j)_3 = (n_j)_i - (n_1)_1\zeta_{eq}\frac{\alpha_j}{\alpha_1}$$

Conditions of the equilibrium

$P =$ 1.0 atm

$\ln K =$ 4.9999E+00

Function objective

$f(\zeta_{eq}) =$ 4.7596E−05

Basis of calculations

CO:	100.0	mol/h
CO_2:	0.0	mol/h
H_2:	0.0	mol/h

Figure 3.12: Calculation of the equilibrium conversion.

Automatically the result of the problem will be obtained, where 0.9241 being the degree of conversion in the equilibrium. A rule with icons has been inserted in the cell, such that if the convergence value was negative, a red traffic light would be obtained.

Questions/simulations:

i. *Excess in one of the reactants*: If an excess of water vapor is introduced, for example, 50% in cell B43, and the "Find Target" function is reapplied, the conversion to equilibrium will be 0.9872. If an excess of water vapor is introduced, for example, 50% in cell B43, and the "Find Target" function is reapplied, the conversion to equilibrium will be 0.9872. This data is explained by the principle of Le Châtelier; the balance has been displaced in the sense of the direct reaction.

ii. *Presence of products in the feed*: If an amount of carbon dioxide is present in the feed stream (e.g., 25 mol/h in cell I42), the conversion to equilibrium would obviously be lower (0.9152).

Example 3.8: Analyze the appropriate P and T conditions, from a thermodynamic point of view, to define the operating conditions of a reactor where ethanol is produced from ethylene hydration with a steam/ethylene feed ratio of 4:

$$C_2H_{4(g)} + H_2O_{(g)} \rightleftarrows C_2H_5OH_{(g)}$$

Data: (a) ΔG^O = 6,730.02 J/mol at 145 °C; (b) ΔG^O = 20,021.36 J/mol at 250 °C; (c) consider the operating pressure of 20 and 40 atm.

Solution:

Step 1: Flowchart with identification of data

The flow diagram is similar to Example 3.7, since it is a single unit, the reactor.

If we call $A_1 \equiv C_2H_4$, $A_2 \equiv H_2O$, $A_3 \equiv C_2H_5OH$, the direct reaction can be expressed as

$$A_3 - A_2 - A_1 = 0$$

As far as stream data is concerned, it is worth noting:

i. The limiting reactant will be C_2H_4, that is, $k = 1$.

ii. In equilibrium the eq. (3.33) should be verified:

$$\ln K = \alpha_1 \ln(y_1 \cdot P) + \alpha_2 \ln(y_2 \cdot P) + \alpha_3 \ln(y_3 \cdot P)$$

Step 2: Basis of calculations

The calculation basis will be the flow rate of C_2H_4 in the input stream: $(n_1)_1 = 100$ mol/h.

Step 3: Definition of control volumes and formulation of the mass balances

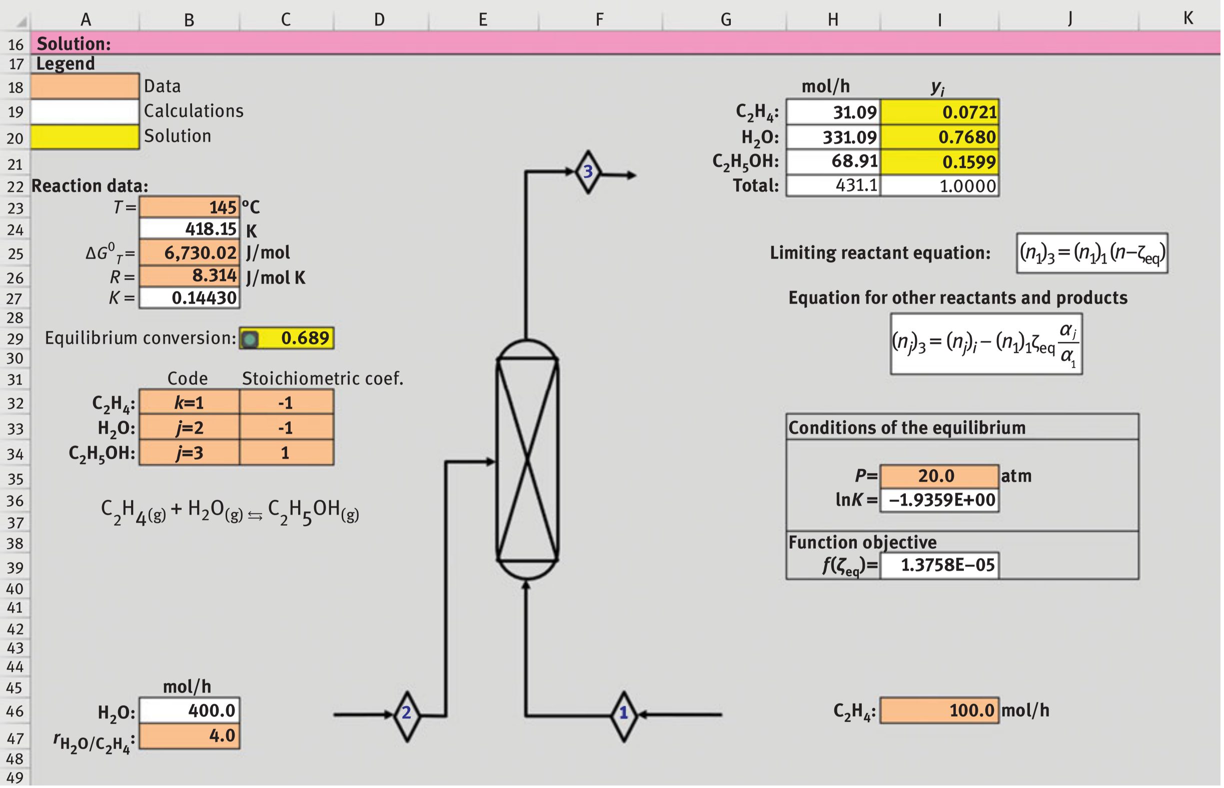
In this case, the only control volume is the unit where the mass balances with chemical reaction are raised, which corresponds to the application of eqs. (3.11) and (3.13) for molar flows with the degree of equilibrium conversion:

Balance for the limiting reactant: $(n_1)_3 = (n_1)_1 \cdot \left(1 - \zeta_{eq}\right)$

Balances for all other reactants and products: $\left(n_j\right)_3 = \left(n_j\right)_i - (n_1)_1 \cdot \zeta_{eq} \cdot \frac{\alpha_j}{\alpha_1}$

Step 4: Solving the system of equations

The idea is to solve a nonlinear equation (equilibrium condition) as a function of the degree of conversion that determines the molar fractions obtained from the mass balance with chemical reaction. This nonlinear equation will be solved by the "Goal Seek" technique (see Appendix C), for which a spreadsheet must be developed where the target function will be the difference between the actual value of K and the value obtained in the iteration of the calculation as a function of the degree of conversion. Figure 3.13 shows the results obtained for a temperature of 145 °C and a pressure of 20 atm.



Solution:

Legend

🟧	Data
☐	Calculations
🟨	Solution

Reaction data:

T = 145 °C

418.15 K

$\Delta G^0{}_T$ = 6,730.02 J/mol

R = 8.314 J/mol K

K = 0.14430

Equilibrium conversion: ● 0.689

	Code	Stoichiometric coef.
C_2H_4:	k=1	-1
H_2O:	j=2	-1
C_2H_5OH:	j=3	1

$C_2H_{4(g)} + H_2O_{(g)} \leftrightarrows C_2H_5OH_{(g)}$

	mol/h
H_2O:	400.0
r_{H_2O/C_2H_4}:	4.0

	mol/h	y_i
C_2H_4:	31.09	0.0721
H_2O:	331.09	0.7680
C_2H_5OH:	68.91	0.1599
Total:	431.1	1.0000

Limiting reactant equation: $(n_1)_3 = (n_1)_1\,(n - \zeta_{eq})$

Equation for other reactants and products

$$(n_j)_3 = (n_j)_i - (n_1)_1 \zeta_{eq} \frac{\alpha_j}{\alpha_1}$$

Conditions of the equilibrium

P= 20.0 atm

ln$K$ = −1.9359E+00

Function objective

$f(\zeta_{eq})$= 1.3758E−05

C_2H_4: 100.0 mol/h

Figure 3.13: Calculation of the equilibrium conversion.

The molar flow and composition in the output stream is obtained from the mass balances with chemical reaction in cells H19:I21. So, for C_2H_4:

H19: = I46*(1–C29) [limiting reactant in output stream]
I19: = H19/$H$22 [mole fraction of C_2H_4 in output stream]

The estimate of the equilibrium constant from the equilibrium conversion (cell C29) is calculated in cell I36:

I36: = C32*LN(I19*I35) + C33*LN(I20*I35) + C34*LN(I21*I35)

The actual value of the equilibrium constant is calculated in cell B27 from eq. (3.26):

B27: = EXP(–B25/(B24*B26))

The problem will be solved as soon as the value of the real equilibrium constant and the estimated equilibrium constant are equal, that is, the objective function of cell I39:

I39: = LN(B27)–I36

When considering the function "Goal Seek" it will be specified:

- Target cell: I39
- With a value of 0
- To change the cell: C29 (equilibrium conversion)

The result of the problem will be obtained automatically, 0.689 being the degree of conversion in the equilibrium. A rule with icons has been inserted in the cell, such that if the convergence value was negative, a red traffic light would be obtained.

By entering the pressure and temperature data in the corresponding cells and applying the "Find Target" function, the following results will be obtained:

T(cell B19)	*K*(cell B27)	*P*(cell I31)	ζ_{eq}(cell C25)
145 °C	$14.43 \cdot 10^{-2}$	20 atm	0.689
	$14.43 \cdot 10^{-2}$	40 atm	0.815
250 °C	$10.02 \cdot 10^{-3}$	20 atm	0.137
	$10.02 \cdot 10^{-3}$	40 atm	0.240

In this reaction when the temperature increases the *K* decreases and consequently the conversion. As the pressure increases, so does the conversion. Because of this, thermodynamic considerations suggest that the operating pressure should be as high as possible (no phase change) and the temperature as low as possible.

Example 3.9: The synthesis of Haber–Bosch[8] for ammonia made it possible to obtain this compound in large quantities for the production of fertilizers, explosives and so on:

$$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)} \quad K = 0.05$$

A 220 atm catalytic reactor with unreacted nitrogen and hydrogen recirculation is used, previously separated in a condenser (Figure 3.14). Stream 4 contains 98% ammonia and 5% nitrogen and hydrogen present in stream 3. Calculate the degree of conversion in equilibrium as well as the mole fraction of each component with a fresh 1/3 N_2/H_2 feed.

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[8] **Fritz Haber (1868–1934):** German chemist. **Carl Bosch (1874–1940):** German engineer and chemist.

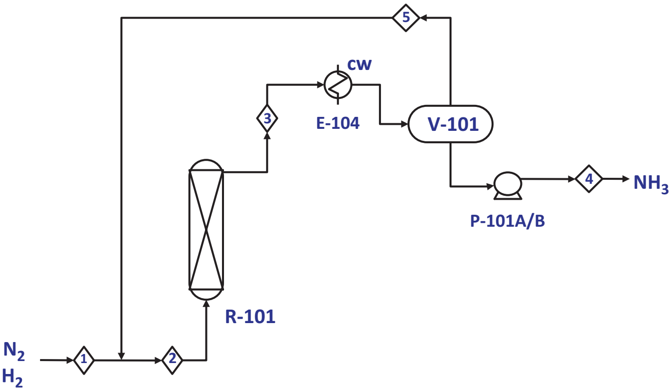


Figure 3.14: Flowchart of NH_3 production.

Solution:
Step 1: Flowchart with identification of data
Reaction data:

If we call $A_1 \equiv N_2$, $A_2 \equiv H_2$, $A_3 \equiv NH_3$ the reaction can be expressed as

$$2A_3 - 3A_2 - A_1 = 0$$

with N_2 being the limiting reactant (in this case, since both reactants are in stoichiometric relation, H_2 could also be considered); therefore, $k = 1$. In addition, eq. (3.33) should be verified in the equilibrium:

$$\ln K = \alpha_1 \ln(y_1 \cdot P) + \alpha_2 \ln(y_2 \cdot P) + \alpha_3 \ln(y_3 \cdot P)$$

Process data:
Condenser recovery of $\varphi_1 = 0.005$, $\varphi_2 = 0.005$, $\varphi_3 = 0.98$,

$$(n_1)_4 = \varphi_1 \cdot (n_1)_3$$
$$(n_2)_4 = \varphi_2 \cdot (n_2)_3$$
$$(n_3)_4 = \varphi_3 \cdot (n_3)_3$$

Step 2: Basis of calculations
The feed flow rate of N_2 shall be taken as the calculation basis: $(n_1)_1 = 100$ mol/h; hence the quantity of hydrogen (stoichiometric) will be $(n_2)_1 = 300$ mol/h.

Step 3: Definition of control volumes and formulation of the mass balances
To calculate the molar flow of the components in each stream (obviously, this will allow the immediate calculation of the molar fraction), eq. (2.10b) for the component balance without chemical reaction and eqs. (3.11) and (3.13) for the mass balances with chemical reaction will be applied:

– Volume control to the mixing point of the feed and recirculation	
Balance for N_2	$(n_1)_1 + (n_1)_5 = (n_1)_2$
Balance for H_2	$(n_2)_1 + (n_2)_5 = (n_2)_2$
Balance for NH_3	$(n_3)_5 = (n_3)_2$

– Control volume corresponding to reactor R-101	
Balance for N_2 (limiting reactant)	$(n_1)_3 = (n_1)_2 \cdot (1 - \zeta_1)$
Balance for H_2	$(n_2)_3 = (n_2)_2 - (n_1)_2 \cdot \zeta_1 \cdot \frac{\alpha_2}{\alpha_1}$
Balance for NH_3	$(n_3)_3 = (n_3)_2 - (n_1)_2 \cdot \zeta_1 \cdot \frac{\alpha_3}{\alpha_1}$
– Control volume for separation column T-101	
N_2 balance and recovery	$(n_1)_3 = (n_1)_4 + (n_1)_5$ $(n_1)_4 = \varphi_1 \cdot (n_1)_3$
H_2 balance and recovery	$(n_2)_3 = (n_2)_4 + (n_2)_5$ $(n_2)_4 = \varphi_2 \cdot (n_2)_3$
NH_3 balance and recovery	$(n_3)_3 = (n_3)_4 + (n_3)_5$ $(n_3)_4 = \varphi_3 \cdot (n_3)_3$

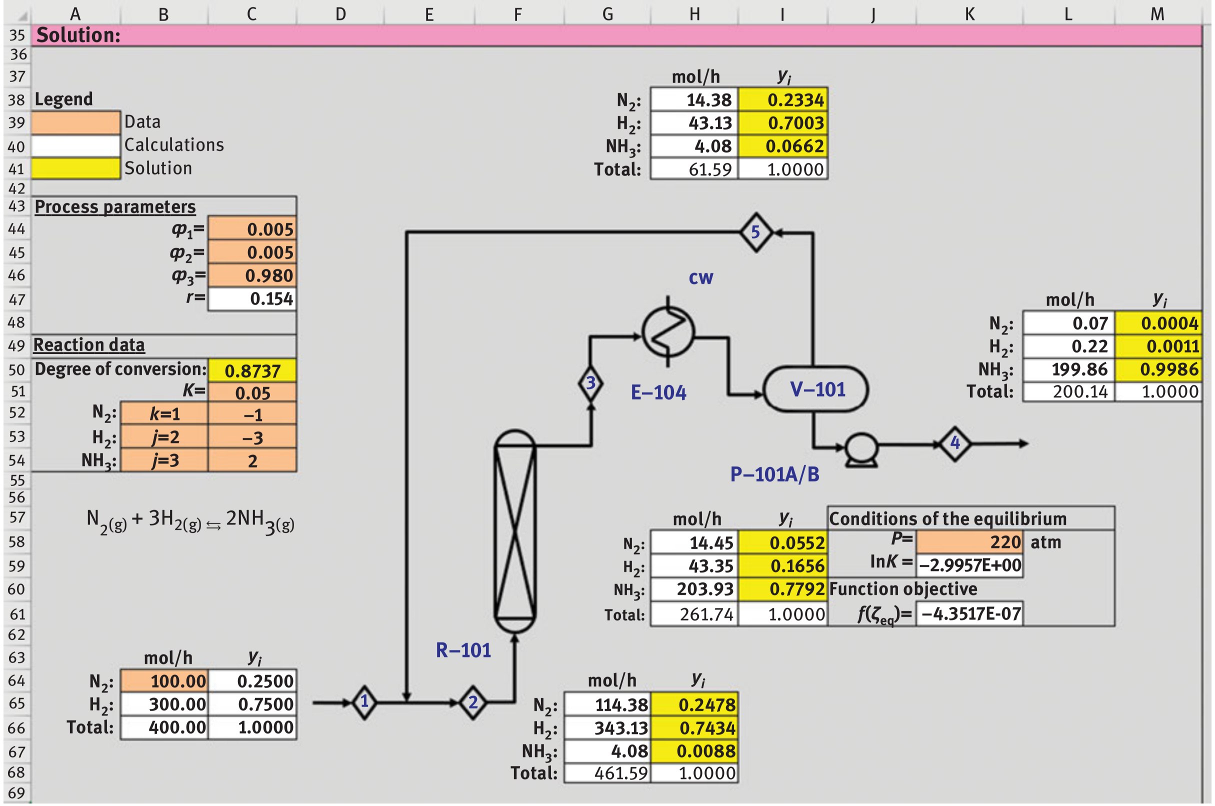
Step 4: Solving the system of equations
It is about solving in a combined way the nonlinear equation that defines the equilibrium condition as a function of the degree of conversion that in turn defines the flows and molar fractions that are obtained when solving the balances of matter with chemical reaction (in this case it supposes a system of six linearly independent equations).

Equations	Unknowns	Coded equations
[1] $(n_1)_1 + (1 - \varphi_1)(n_1)_3 = (n_1)_2$	$x_1 = (n_1)_2$	[1] $x_1 - (1 - \varphi_1) \cdot x_4 = (n_1)_1$
[2] $(n_2)_1 + (1 - \varphi_2)(n_2)_3 = (n_2)_2$	$x_2 = (n_2)_2$	[2] $x_2 - (1 - \varphi_2) \cdot x_5 = (n_2)_1$
[3] $(1 - \varphi_3)(n_3)_3 = (n_3)_2$	$x_3 = (n_3)_3$	[3] $x_3 - (1 - \varphi_3) \cdot x_6 = 0$
[4] $(n_1)_3 = (n_1)_2 \cdot (1 - \zeta_1)$	$x_4 = (n_1)_3$	[4] $(1 - \zeta_1) x_1 - x_4 = 0$
[5] $(n_2)_3 = (n_2)_2 - (n_1)_2 \cdot \zeta_1 \cdot \dfrac{\alpha_2}{\alpha_1}$	$x_5 = (n_2)_3$	[5] $\zeta_1 \cdot \dfrac{\alpha_2}{\alpha_1} x_1 - x_2 + x_5 = 0$
[6] $(n_3)_3 = (n_3)_2 - (n_1)_2 \cdot \zeta_1 \cdot \dfrac{\alpha_3}{\alpha_1}$	$x_6 = (n_3)_3$	[6] $\zeta_1 \cdot \dfrac{\alpha_3}{\alpha_1} x_1 - x_3 + x_6 = 0$

To solve the linear equations, proceed in the same way as Example 3.5. The nonlinear equation will be solved by applying the Solver function (see Appendix C), for which a spreadsheet must be prepared where the objective function will be the difference between the real value of K and the value obtained in the iteration of the calculation as a function of the degree of conversion (Figure 3.15).

When considering the function “Solver” it will be specified:
- Target cell: K61
- With a value of 0
- Changing cells: C50
- Restrictions: C50 ≥ 0 and C50 ≤ 1

Automatically the result of the problem will be obtained, with the degree of conversion in equilibrium of 0.8737.



Solution:

Legend

- 🟧 Data
- ☐ Calculations
- 🟨 Solution

Process parameters

φ_1= 0.005
φ_2= 0.005
φ_3= 0.980
r= 0.154

Reaction data

Degree of conversion: 0.8737
K= 0.05

N_2:	k=1	−1
H_2:	j=2	−3
NH_3:	j=3	2

$N_{2(g)} + 3H_{2(g)} \leftrightarrows 2NH_{3(g)}$

	mol/h	y_i
N_2:	100.00	0.2500
H_2:	300.00	0.7500
Total:	400.00	1.0000

	mol/h	y_i
N_2:	114.38	0.2478
H_2:	343.13	0.7434
NH_3:	4.08	0.0088
Total:	461.59	1.0000

	mol/h	y_i
N_2:	14.38	0.2334
H_2:	43.13	0.7003
NH_3:	4.08	0.0662
Total:	61.59	1.0000

	mol/h	y_i
N_2:	14.45	0.0552
H_2:	43.35	0.1656
NH_3:	203.93	0.7792
Total:	261.74	1.0000

Conditions of the equilibrium

P= 220 atm
ln$K$ = −2.9957E+00

Function objective

$f(\zeta_{eq})$= −4.3517E-07

	mol/h	y_i
N_2:	0.07	0.0004
H_2:	0.22	0.0011
NH_3:	199.86	0.9986
Total:	200.14	1.0000

Figure 3.15: Spreadsheet for combined resolution of matter balances with chemical reaction and equilibrium condition.

Example 3.10: H_2 is typically produced by reforming natural gas with steam over a catalyst at atmospheric pressure in the range of 700–1,000 °C:

$$CH_{4(g)} + H_2O_{(v)} \rightleftarrows CO_{(g)} + 3H_{2(g)}$$
$$CO_{(g)} + H_2O_{(v)} \rightleftarrows CO_{2(g)} + H_{2(g)}$$

Calculate the degree of conversion in the equilibrium as well as the mole fraction of each component with a feed of 6 mol/h of CH_4 and 5 mol/h of H_2O. The value of the equilibrium constant under these conditions is 0.54 and 2.49 for the first and second reaction, respectively.

Solution:

Step 1: Flowchart with identification of data

The flow diagram is identical to Example 3.5, except that two reactions take place in the unit.

If we call $A_1 \equiv CH_4$, $A_2 \equiv H_2O$, $A_3 \equiv CO$, $A_4 \equiv H_2$, $A_5 \equiv CO_2$, the direct reactions can be expressed as

$$3A_4 + A_3 - A_2 - A_1 = 0$$

$$A_5 + A_4 - A_3 - A_2 = 0$$

In the equilibrium eq. (3.33) should be verified for reaction A and B:

$$\ln K_A = [\alpha_1 \ln(y_1 \cdot P) + \alpha_2 \ln(y_2 \cdot P) + \alpha_3 \ln(y_3 \cdot P) + \alpha_4 \ln(y_4 \cdot P)]_A$$
$$\ln K_B = [\alpha_2 \ln(y_2 \cdot P) + \alpha_3 \ln(y_3 \cdot P) + \alpha_4 \ln(y_4 \cdot P) + \alpha_5 \ln(y_5 \cdot P)]_B$$

Step 2: Basis of calculations

The calculation basis will be the feed flow rates $(n_1)_1 = 6$ mol/h and $(n_2)_2 = 5$ mol/h.

Step 3: Definition of control volumes and formulation of the mass balances

In this case, the only control volume is the unit where the mass balances with chemical reaction are raised, which corresponds to the molar conversion application, eq. (3.19), for each of the reaction components.

Step 4: Solving the system of equations

Therefore, it is a question of solving two nonlinear equations (equilibrium condition) as a function of the molar conversion that defines the molar fractions obtained from the mass balance with chemical reaction. This nonlinear equation will be solved by applying the Solver function (see Appendix E), for which a spreadsheet should be developed where the objective function will be the difference between the actual value of K and the value obtained in the iteration of the calculation as a function of the molar conversion (Figure 3.16).

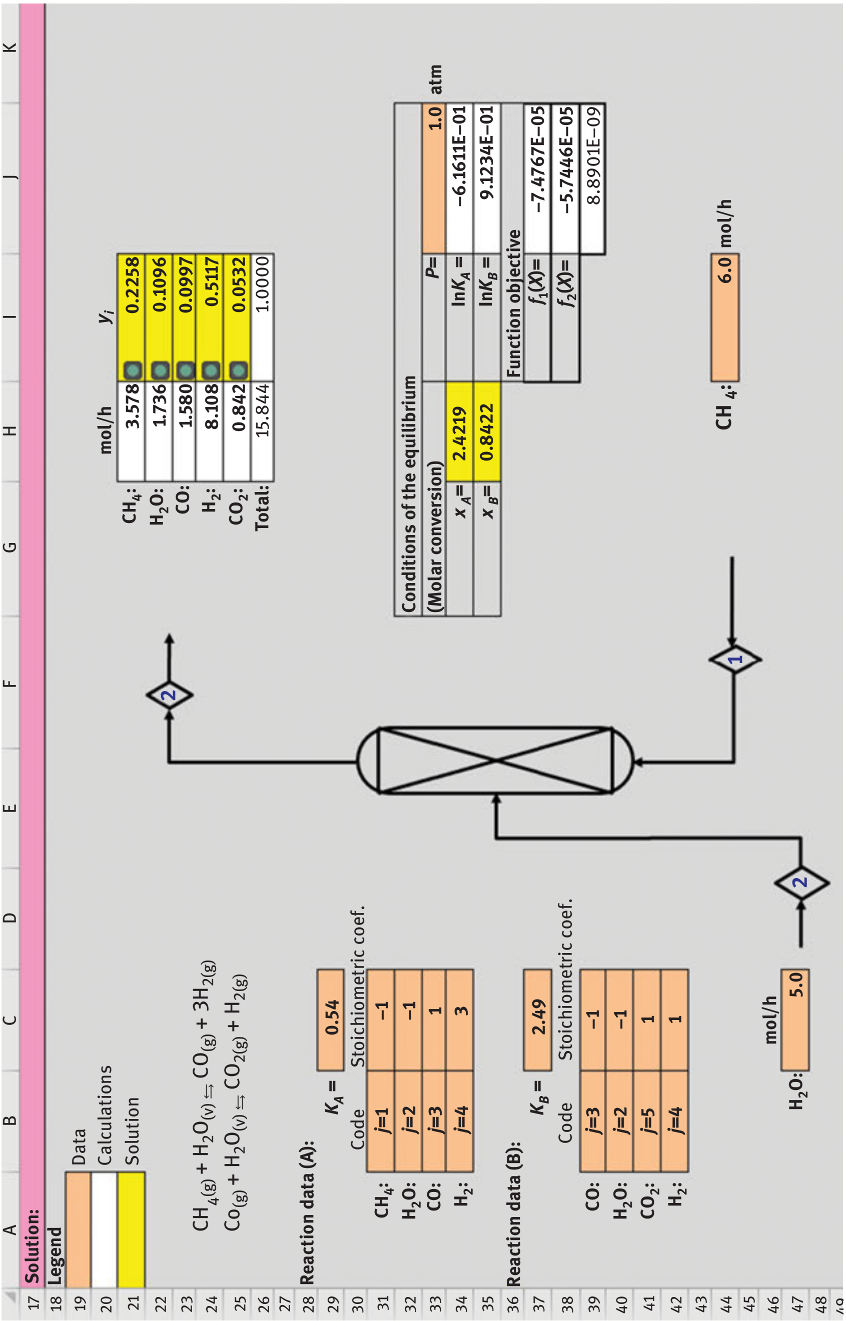
When considering the function "Solver" it will be specified:

- Target cell: J39
- With a value of 0
- Changing cells: H34:H35
- Restrictions: H34 ≥ 0 and H35 ≥ 0

Automatically the result of the problem will be obtained, being the molar conversions in equilibrium 2.4219 and 0.8422.

Questions/simulations:

i. *Importance of initial values for iteration*: A higher molar conversion of the main reaction than the secondary reaction is considered. A first set of values would be (0.8 and 0.2). The result is not



Solution:

Legend

🟧 Data
□ Calculations
🟨 Solution

$CH_{4(g)} + H_2O_{(v)} \leftrightarrows CO_{(g)} + 3H_{2(g)}$

$Co_{(g)} + H_2O_{(v)} \leftrightarrows CO_{2(g)} + H_{2(g)}$

Reaction data (A):

K_A = 0.54

	Code	Stoichiometric coef.
CH_4:	j=1	−1
H_2O:	j=2	−1
CO:	j=3	1
H_2:	j=4	3

Reaction data (B):

K_B = 2.49

	Code	Stoichiometric coef.
CO:	j=3	−1
H_2O:	j=2	−1
CO_2:	j=5	1
H_2:	j=4	1

H_2O: 5.0 mol/h

CH_4: 6.0 mol/h

	mol/h	y_i
CH_4:	3.578	0.2258
H_2O:	1.736	0.1096
CO:	1.580	0.0997
H_2:	8.108	0.5117
CO_2:	0.842	0.0532
Total:	15.844	1.0000

Conditions of the equilibrium
(Molar conversion)

x_A= 2.4219
x_B= 0.8422

P= 1.0 atm
lnK_A = −6.1611E−01
lnK_B = 9.1234E−01

Function objective
$f_1(X)$= −7.4767E−05
$f_2(X)$= −5.7446E−05
8.8901E−09

Figure 3.16: Calculation of equilibrium conditions.

valid as it leads to negative values of the water molar fraction. However, if the initial set is (1.0 and 0.2), the correct value of the equilibrium molar conversion and the composition in it is obtained.

	mol/h		y_i
CH_4:	2.000	🟢	0.1053
H_2O:	−1.204	🔴	−0.0634
CO:	1.796	🟢	0.0945
H_2:	14.204	🟢	0.7476
CO_2:	2.204	🟢	0.1160
Total:	19.000		1.0000

ii. *Extensive nature of molar conversion*: The molar conversion is an extensive property; it depends on the mass. Thus, if the amount at the reactor inlet is 60 and 50 moles for methane and water vapor, respectively, using Solver with the initial values obtained with a previous feed leads us to the calculation of $x_A = 24.2194$ and $x_B = 8.4218$, but the mole fraction of the components in the equilibrium will not vary, since the equilibrium constant does not depend on X.

3.2.2 Acid–base reactions

If the reaction takes place in an aqueous phase, the value of the activities of most chemical species can be considered approximately equal to the value of the concentrations; therefore, the expression for the equilibrium constant (eq. 3.26) would be expressed as follows:

$$aA + bB \rightleftarrows cC + dD$$

$$K = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} \cong \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} \tag{3.34}$$

A specific case of chemical equilibrium of reactions in aqueous phase corresponds to acid–base reactions. The dissociation or ionization constant is the equilibrium constant that refers to the process of dissociation into ions that many molecules suffer when dissolved in water. In acid–base reactions it is denoted by K_a, so that, for example, for acetic acid:

$$\begin{gathered} CH_3COOH \rightleftarrows CH_3COO^- + H^+ \\ K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \end{gathered} \tag{3.35}$$

Due to the high values of K_a the acidity constant is usually expressed by a logarithmic measure of the acidity constant, pK_a, such that

$$pK_a = -\log K_a \qquad \Leftrightarrow \qquad K_a = 10^{-pK_a} \tag{3.36}$$

The higher the pK_a value (Table 3.1), the smaller the extent of dissociation. Acids with pK_a values less than −2 are said to be strong acids; a strong acid is almost completely dissociated in aqueous solution to the extent that the concentration of the undissociated acid is undetectable.

Table 3.1: pK_a values for various acids.

Acid	Formula	pK_{a1}	pK_{a2}	pK_{a3}
Nitric acid	HNO_3	−1.30		
Hydrochloric acid	HCl	<0		
Sulfuric acid	H_2SO_4	<0	1.99	
Phosphoric acid	H_3PO_4	2.16	7.20	12.35
Arsenic acid	H_3AsO_4	2.24	6.76	
Citric acid	$C_3H_4OH(COOH)_3$	3.13	4.72	6.33
Acetic acid	CH_3COOH	4.76		
Carbonic acid	H_2CO_3	6.35	10.33	
Hydrogen sulfide	H_2S	6.99	12.92	
Hypochlorous acid	HOCl	7.60		
Ammonium ion	NH_4^+	9.26		
Silicic acid	H_4SiO_4	9.84	13.20	

Polyprotic acids are acids that can lose more than one proton. The dissociation constant for the first proton can be indicated as K_{a1}, the dissociation constants of successive protons as K_{a2} and so on. Phosphoric acid, H_3PO_4, is an example of polyprostide acid that can lose three protons:

$$H_3PO_4 \rightleftarrows H_2PO_4^- + H^+ \quad pK_{a1} = 2.16$$
$$H_2PO_4^- \rightleftarrows HPO_4^{-2} + H^+ \quad pK_{a2} = 7.20$$
$$HPO_4^{-2} \rightleftarrows PO_4^{-3} + H^+ \quad pK_{a3} = 12.35$$

The basicity constant or the ionization constant of the base can be established in the same way as the bases:

$$B_{(ac)} + H_2O_{(l)} \rightleftarrows BH^+_{(ac)} + OH^-_{(ac)}$$

$$K_b = \frac{[BH^+]\cdot[OH^-]}{[B]} \tag{3.37a}$$

$$pK_b = -\log K_b \tag{3.37b}$$

Weak bases have small K_b values (<1) for example, ammonia (NH_3), ethylamine ($C_2H_5NH_2$) and aniline ($C_6H_6NH_2$).

The relationship between the acidity and basicity constant of a conjugated acid–base is equal to the ionization product or water ionization constant:

$$K_a \cdot K_b = K_w = 10^{-14} \tag{3.38}$$

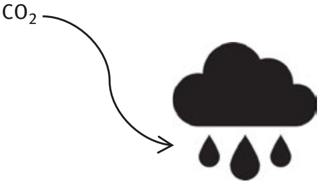
It is defined as the degree of ionization or dissociation ($\alpha_{a/b}$) as the relationship between the concentration of the ionized species in the state of equilibrium and the concentration of the species without ionizing:

$$\alpha_a = \frac{[\mathrm{A}^-]}{[\mathrm{AH}]_0}, \alpha_b = \frac{[\mathrm{BH}^+]}{[\mathrm{B}]_0} \tag{3.39}$$

Example 3.11: The concentration of CO_2 in the atmosphere before the Industrial Revolution was 275 ppm.[9] If the accumulation of CO_2 in the atmosphere continues at the rate of the first decade of the twenty-first century, according to data from the Mauna Loa[10] Observatory, by the middle of this century it will be close to 500 ppm.[11] Calculate the pH of rainwater (neglect the effects of any other gas) at 25 °C before the Industrial Revolution and its possible value in the middle of this century. Note: Henry's constant value for CO_2 is 0.033363 mol/L atm and the water dissociation constant 25 °C is 10^{-14}.

Solution:

Step 1: Flowchart with identification of data



$T = 25°C$
$P = 1$ atm
$K_W = 10^{-14}$ a 25°C
$pK_a1 = 6.35$ (Table 3.1)
$K_H = 0.033363$ mol/L atm

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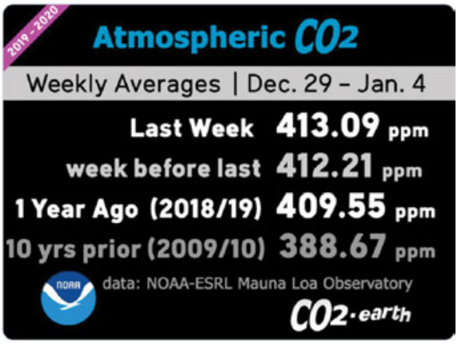
[9] IPCC – Intergovernmental Panel on Climate Change: www.ipcc.ch.

[10] http://www.esrl.noaa.gov/gmd/obop/mlo/

[11] The twitter account @CO$_2$_earth follows the world's latest data on atmospheric CO_2, almost in real time. An example of tweet.



2019 - 2020

Atmospheric CO2

Weekly Averages | Dec. 29 – Jan. 4

Last Week 413.09 ppm
week before last 412.21 ppm
1 Year Ago (2018/19) 409.55 ppm
10 yrs prior (2009/10) 388.67 ppm

data: NOAA-ESRL Mauna Loa Observatory

CO2·earth

7:15 p. m. · 6 ene. 2020 · Hootsuite Inc.

Step 2: Basis of calculations

The calculation base corresponds to the concentration of CO_2 in the atmosphere before the industrial revolution (275 ppm) and the forecast for the middle of the twenty-first century (500 ppm).

Step 3: Definition of control volumes and formulation of the mass balances.

Two simultaneous processes occur in the water drop: (i) water dissociation and CO_2 dissolution.

(i) water decoupling

$$H_2O \rightleftarrows H^+ + OH^-$$

(ii) CO_2 decoupling

$$CO_{2(aq)} + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^-$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^{-2}$$

If you consider load neutrality in raindrops, you must comply that

$$[H^+] = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-]$$

where the coefficient “2” that multiplies the concentration of the carbonate ion is due to the fact that it has two negative charges per mole. However, since rain has a slightly acidic pH, the balance is displaced to the formation of bicarbonate ion; therefore,

$$[H^+] = [HCO_3^-] + [OH^-]$$

If the concentration of OH^- is defined as a function of the water dissociation constant:

$$K_W = [H^+][OH^-] \Rightarrow [H^+] = [HCO_3^-] + \frac{K_W}{[H^+]}$$

$$[H^+] = \left([H^+][HCO_3^-] + K_W\right)^{1/2}$$

The concentration of bicarbonate ion can be expressed as a function of the equilibrium constant K_{a1} corresponding to the dissolution of CO_2:

$$K_{a_1} = 10^{-pKa_1} = \frac{[H^+][HCO_3^-]}{[CO_{2(aq)}]} \Rightarrow [H^+] = \left(K_{a_1}[CO_{2(aq)}] + K_W\right)^{1/2}$$

Henry’s law relates the partial pressure of CO_2 in the gas phase to its concentration in the liquid phase (eq. (2.21)):

$$p_{CO_2} = K_H \cdot [CO_{2(aq)}] \Rightarrow [H^+] = \left(K_{a_1} \cdot K_H \cdot p_{CO_2} + K_W\right)^{1/2}$$

Step 4: Solving the system of equations

This problem is about solving an equation with an unknown, the concentration of CO_2 in the atmosphere (Figure 3.17), where the partial pressure of CO_2 can be calculated from the concentration by applying Dalton’s Law:

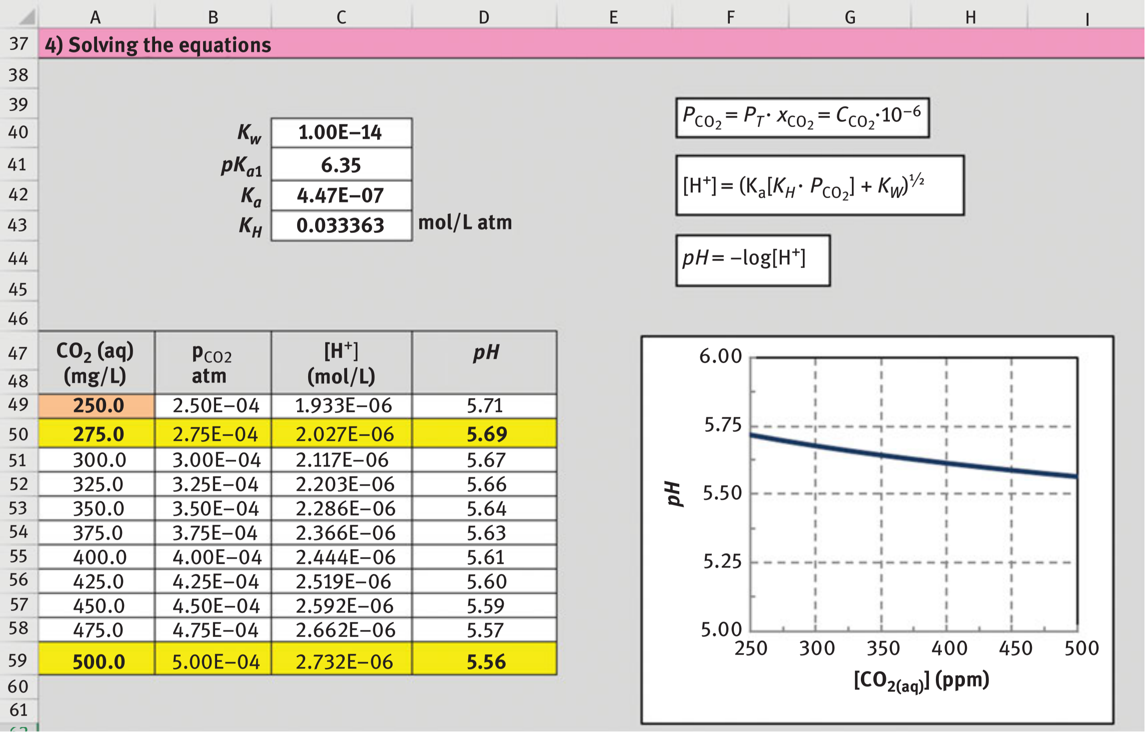
$$p_{CO_2} = P \cdot x_{CO_2} = c_{CO_2} \cdot 10^{-6}$$

First row:

B49: = A49*10^−6

C49: = ($C$42*$C$43*B49 + $C$40)^0,5

D49: = −1*LOG10(C49)



4) Solving the equations

K_w	1.00E−14
pK_{a1}	6.35
K_a	4.47E−07
K_H	0.033363 mol/L atm

$P_{CO_2} = P_T \cdot x_{CO_2} = C_{CO_2} \cdot 10^{-6}$

$[H^+] = (K_a[K_H \cdot P_{CO_2}] + K_W)^{1/2}$

$pH = -\log[H^+]$

CO_2 (aq) (mg/L)	p_{CO2} atm	$[H^+]$ (mol/L)	pH
250.0	2.50E−04	1.933E−06	5.71
275.0	2.75E−04	2.027E−06	5.69
300.0	3.00E−04	2.117E−06	5.67
325.0	3.25E−04	2.203E−06	5.66
350.0	3.50E−04	2.286E−06	5.64
375.0	3.75E−04	2.366E−06	5.63
400.0	4.00E−04	2.444E−06	5.61
425.0	4.25E−04	2.519E−06	5.60
450.0	4.50E−04	2.592E−06	5.59
475.0	4.75E−04	2.662E−06	5.57
500.0	5.00E−04	2.732E−06	5.56

Figure 3.17: Evolution of the pH of rainwater as a function of the concentration of CO_2.

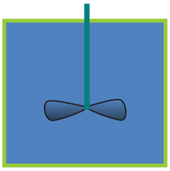
The rest of the rows are obtained with the “copy” and “paste” functions. The result does not indicate that the pH would be reduced from 5.69 to 5.56, when a CO_2 concentration of 500 ppm is reached in the atmosphere.

Example 3.12: Water is usually disinfected with chlorine gas, forming hypochlorous acid (HOCl), which is partially ionized to form ions of hydrogen and hypochlorite. The amount of HOCl depends on the *pH*. Calculate:

a. The portion of hypochlorous acid as a function of *pH*.
b. Which portion would be hypochlorous acid for a pH of 6 and 10?
c. At what pH should water be maintained so that at least 95% of the added chlorine is in the form of hypochlorous acid?

Solution:

Step 1: Scheme of the process and data representation



$T = 25°C$
$P = 1$ atm
$Pk_{a1} = 7.6$ (Table 3.1)

$HOCl \leftrightarrows OCl^- + H^+$

Step 2: Basis of calculations

The calculation basis corresponds to the pH, which will be the independent variable from which the portion of hyplochloric acid in the wastewater will be established.

Step 3: Definition of control volumes and formulation of the mass balances

The fraction of hypochlorous acid in the system is defined as

$$\alpha_{[HOCl]} = \frac{[HOCl]}{[HOCl]+[OCl^-]} = \frac{1}{1+[OCl^-]/[HOCl]}$$

The quotient between ion concentration and acid can be expressed as a function of the dissociation constant:

$$K_a = 10^{-pKa} = \frac{[OCl^-][H^+]}{[HOCl]} \quad \Rightarrow \quad \frac{[OCl^-]}{[HOCl]} = \frac{K_a}{[H^+]} = \frac{10^{-pKa}}{[H^+]}$$

Taking into account the definition of *pH*:

$$pH = -\log[H^+] \quad \Rightarrow \quad \frac{[OCl^-]}{[HOCl]} = \frac{10^{-pKa}}{10^{-pH}} = 10^{(pH-pKa)}$$

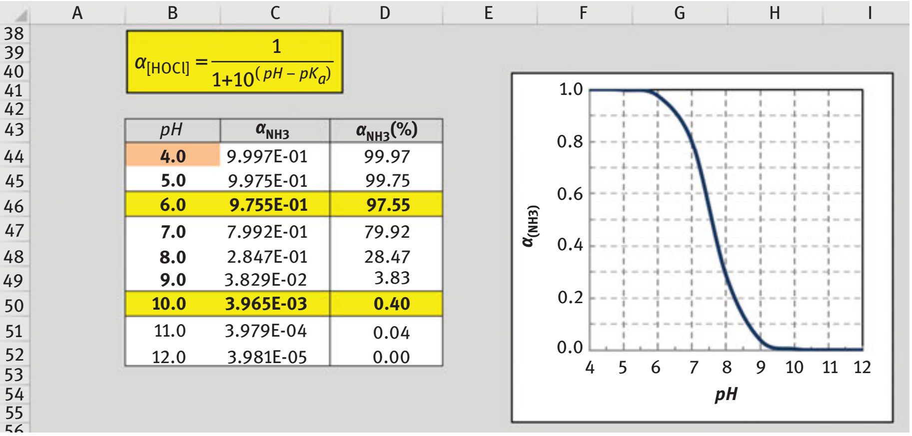
$$[H^+] = 10^{-pH}$$

Consequently, the fraction of hypochlorous acid as a function of *pH* and pK_a:

$$\alpha_{[HOCl]} = \frac{1}{1+10^{(pH-pKa)}}$$

Step 4: Solving the system of equations

This problem is about solving an equation with an unknown, the fraction of hypochlorous acid (Figure 3.18), which decreases as the pH increases, that is, to basic *pH*.



$$\alpha_{[HOCl]} = \frac{1}{1{+}10^{(pH-pK_a)}}$$

pH	α_{NH3}	α_{NH3}(%)
4.0	9.997E-01	99.97
5.0	9.975E-01	99.75
6.0	9.755E-01	97.55
7.0	7.992E-01	79.92
8.0	2.847E-01	28.47
9.0	3.829E-02	3.83
10.0	3.965E-03	0.40
11.0	3.979E-04	0.04
12.0	3.981E-05	0.00

Figure 3.18: Portion of hypochlorous acid as a function of *pH*.

First row:

C44: = 1/(1 + 10^(B44-$C$20)) [In cell C20, which is expressed as absolute direction, the value of the dissociation constant is indicated]

D44: = C44*100

The rest of the rows are obtained with the “copy” and “paste” functions. The value of the hypochlorous acid fraction for *pH* 6 and 10 is 97.55 and 0.40%, respectively.

If we consider the *pH* as a dependent variable and the fraction as an independent variable (Figure 3.19), we obtain that the *pH* necessary for the fraction to be 95% is 6.32:

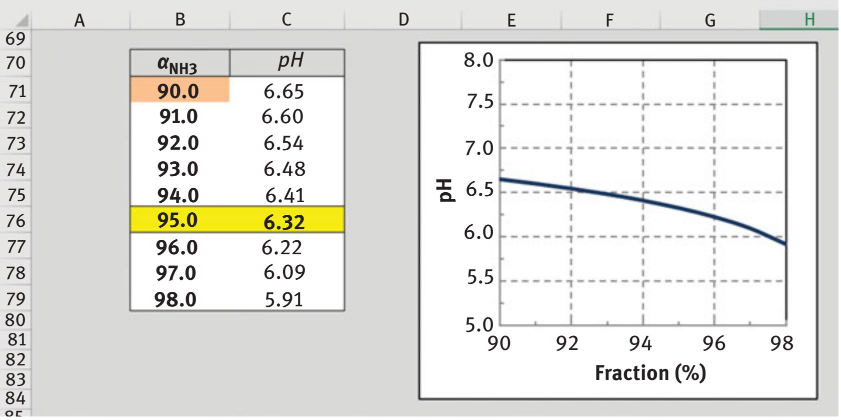
$$\alpha_{[HOCl]} = \frac{1}{1+10^{(pH-pK_a)}} \qquad \Rightarrow \qquad pH = -\log\left(\frac{10^{-pK_a}}{\frac{1}{\alpha_{[HOCl]}}-1}\right)$$

3.2.3 Solubility product

The solubility product (K_{ps}) of a compound is the product of the molar (equilibrium) concentrations of the constituent ions, each elevated to the potency of the stoichiometric coefficient in the equilibrium equation:

$$A_aB_b \rightleftharpoons aA + bB$$

$$K_{ps} = [A]^a[B]^b \tag{3.40}$$



α_{NH3}	*pH*
90.0	6.65
91.0	6.60
92.0	6.54
93.0	6.48
94.0	6.41
95.0	6.32
96.0	6.22
97.0	6.09
98.0	5.91

Figure 3.19: Portion of hypochlorous acid as a function of *pH*.

The value of K_{ps} indicates the solubility of a compound, and so the lower the value, the less soluble the compound will be (Table 3.2).

Table 3.2: Solubility product values for various compounds.

Compound	Equilibrium equation	K_{ps} at 25 °C
Silver bromide	$AgBr \rightleftharpoons Ag^+ + Br^-$	$5.41 \cdot 10^{-13}$
Calcium carbonate	$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$	$3.36 \cdot 10^{-9}$
Zinc carbonate	$ZnCO_3 \rightleftharpoons Zn^{2+} + CO_3^{2-}$	$1.46 \cdot 10^{-10}$
Silver chloride	$AgCl \rightleftharpoons Ag^+ + Cl^-$	$1.77 \cdot 10^{-10}$
Calcium fluoride	$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$	$3.45 \cdot 10^{-11}$
Aluminum phosphate	$AlPO_3 \rightleftharpoons Al^{3+} + PO_4^{3-}$	$9.84 \cdot 10^{-21}$
Aluminum hydroxide	$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$	$3.00 \cdot 10^{-34}$
Calcium hydroxide	$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$	$5.02 \cdot 10^{-6}$
Iron (III) hydroxide	$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$	$2.79 \cdot 10^{-39}$
Lead (II) hydroxide	$Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2OH^-$	$1.43 \cdot 10^{-20}$
Barium sulfate	$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$	$1.08 \cdot 10^{-10}$
Calcium sulfate	$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$	$4.93 \cdot 10^{-5}$
Calcium sulfate	$PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$	$1.80 \cdot 10^{-8}$
Silver iodide	$AgI \rightleftharpoons Ag^+ + I^-$	$7.92 \cdot 10^{-17}$

Table 3.3 lists different expressions between the solubility and the solubility product of a compound, depending on its empirical formula.

The solubility product plays an important role in precipitation reactions, which occur when dissolutions of soluble salts are mixed to form an insoluble product called *precipitate*. Fractionated precipitation consists of adding an ion that forms

Table 3.3: Relationship between solubility and solubility product.

Type of compound	Example	Expression of K_{ps}
AB	$NiS_{(s)} \rightleftarrows Ni^{2+}_{(ac)} + S^{2-}_{(ac)}$	$K_{ps} = [Ni^{2+}][S^{2-}] = s \cdot s = s^2$
A_2B	$Ag_2SO_{4(ac)} \rightleftarrows 2Ag^{+}_{(ac)} + SO^{2-}_{4(ac)}$	$K_{ps} = [Ag^{+}]^2[SO_4^{2-}] = (2s)^2 \cdot s = 4s^3$
AB_2	$Mg(OH)_{2(ac)} \rightleftarrows Mg^{2+}_{(ac)} + 2OH^{-}_{(ac)}$	$K_{ps} = [Mg^{2+}][OH^{-}]^2 = s \cdot (2s)^2 = 4s^3$
AB_3	$Fe(OH)_{3(ac)} \rightleftarrows Fe^{3+}_{(ac)} + 3OH^{-}_{(ac)}$	$K_{ps} = [Fe^{3+}][OH^{-}]^3 = s \cdot (3s)^3 = 27s^4$

insoluble salts with two or more ions between those present in the solution. For selective precipitation to occur, K_{ps} values must have sufficiently different values.

3.3 Kinetic aspects: reaction rate

The stoichiometric equation tells us in what proportion the reactants intervene in a given process. On the other hand, the reaction may have a greater or lesser degree of conversion, depending on the thermodynamics of the process and the time in which the reactants are kept in contact under favorable reaction conditions. In these cases, it is necessary to know the reaction time to obtain the determined conversion; once the thermodynamic data are known, we need information about the rate of the reaction and about the effects that modify it. This is the subject of chemical kinetics.

Thus, the term *generation* will depend on the rate of intensive reaction, which is defined for a component *Aj* (reactant or product) as the "number of moles" of that species that react (disappear or form) per unit of time and per unit of volume. The general expression of the kinetic equation:

$$G_i = r_i \cdot V$$

$$r_i = -\frac{1}{V}\frac{dN_i}{dt} = -\frac{dC_i}{dt}$$

3.3.1 Integrated equations of reaction rate

Order 0

The rate of the reaction does not depend on the concentration; it is equal to the kinetic coefficient, *k*:

$$r = -\frac{dC}{dt} = k \quad \Rightarrow \quad dC = -kdt \quad \Rightarrow \quad \int_{C_0}^{C} dC = -k\int_{o}^{t} dt$$

therefore,

$$C = C_0 - k \cdot t \tag{3.41}$$

The mean time is defined as the time in which the concentration is half of the initial one:

$$C = \frac{C_0}{2} \qquad \Rightarrow \qquad t_{1/2} = \frac{C_0}{2 \cdot k} \tag{3.42}$$

Order 1

The reaction rate is directly proportional to the concentration, $r = kC$:

$$\ln\left[\frac{C}{C_0}\right] = -k \cdot t \qquad \text{o} \qquad C = C_0 \cdot e^{-k \cdot t} \tag{3.43}$$

The expression for the mean time for a reaction of order 1:

$$t_{1/2} = \frac{\ln 2}{k} \tag{3.44}$$

Order 2

The reaction rate is directly proportional to the square of the concentration, $r = kC^2$:

$$\frac{1}{C} = \frac{1}{C_0} + k \cdot t \tag{3.45}$$

The expression for the mean time for a reaction of order 2:

$$t_{1/2} = \frac{1}{k \cdot C_0} \tag{3.46}$$

Figure 3.20 represents the relationship between concentration and time by reaction order, that is, eqs. (3.41), (3.43) and (3.45).

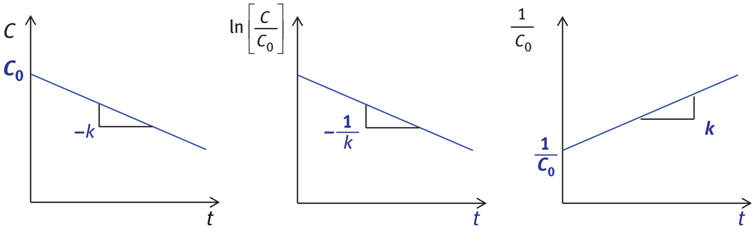


Figure 3.20: Representation of concentration versus time for reactions of order 0, 1 and 2.

3.3.2 Factors influencing reaction rate

3.3.2.1 Temperature

An increase in temperature (Figure 3.21) leads to an increase in reaction rate. The Arrhenius[12] equation relates the value of the kinetic coefficient to temperature (3.47):

$$k = A \cdot e^{-\frac{Ea}{RT}} \qquad \text{o} \qquad \ln k = \ln A - \frac{Ea}{RT} \tag{3.47}$$

- where k, kinetic coefficient;
- A, factor that takes into account the frequency of collisions;
- Ea, activation energy (J/mol);
- R, constant of ideal gases (8.31 J/K mol);
- T, temperature (K).

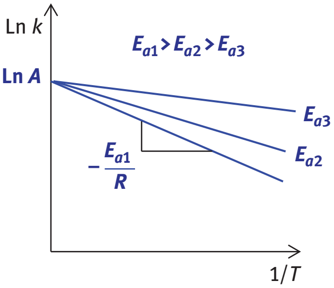


Figure 3.21: Representation of the Arrhenius equation.

For two given temperatures T_1 and T_2 of the same reaction, the relationship between their kinetic coefficients verifies that

$$\ln \frac{k_2}{k_1} = \frac{Ea}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \tag{3.48}$$

3.3.2.2 Catalysts

Catalysts are substances that modify the rate of a chemical reaction without being consumed during it (Figure 3.22). Positive catalysts reduce the activation energy and, therefore, increase the reaction rate. Negative catalysts (or inhibitors) increase the activation energy, thus slowing down the reaction rate.

Catalysis is defined as homogeneous when the reactants and the catalyst are in the same phase, and as heterogeneous if the reactants are in one phase (gaseous or liquid) and the catalyst in another phase (normally solid).

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[12] **Svante August Arrhenius (1859–1927):** Swedish chemist.

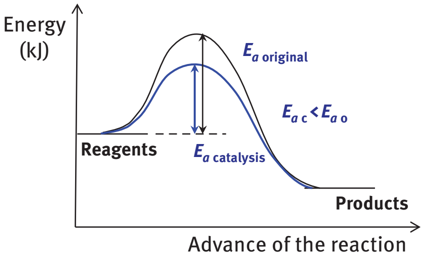


Figure 3.22: Energy diagram for a reaction with and without the presence of a catalyst.

For example, Fenton catalysis is a well-known and very good representative of homogeneous catalysis, which has been shown to be more efficient in terms of operating costs for the degradation of a wide range of organic compounds at low and high concentrations. The Fenton reaction starts with an electron transfer process, in which ferrous iron (Fe^{2+}) reacts with hydrogen peroxide (H_2O_2) to form ·OH (eq. 3.49), so that it oxidizes organic matter, ideally resulting in complete mineralization to carbon dioxide (CO_2) and water (H_2O). The ferric iron (Fe^{3+}) is then reduced to Fe^{2+} by H_2O_2, forming a hydroperoxyl radical (·OOH) (eq. 3.50).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + H^+ \tag{3.49}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH + H^+ \tag{3.50}$$

However, the conventional Fenton process has major drawbacks, the most notable being the impossibility of viable separation of the homogeneous catalyst (Fe^{2+}) from the treated effluent and, therefore, the need for treatment of the ferric hydroxide sludge produced. In this context, the cost associated with posttreatment can represent up to 50% of the total operating costs. To overcome these impediments, we can use the heterogeneous Fenton approach, using catalysts in solid phase that can be easily separated from the effiuent. However, heterogeneous catalysts have only a small fraction of iron on their surface, presenting slower reaction kinetics and mass transfer limitations compared to homogeneous catalysts. The link between heterogeneous and homogeneous catalysts can be accomplished using nanostructured materials.

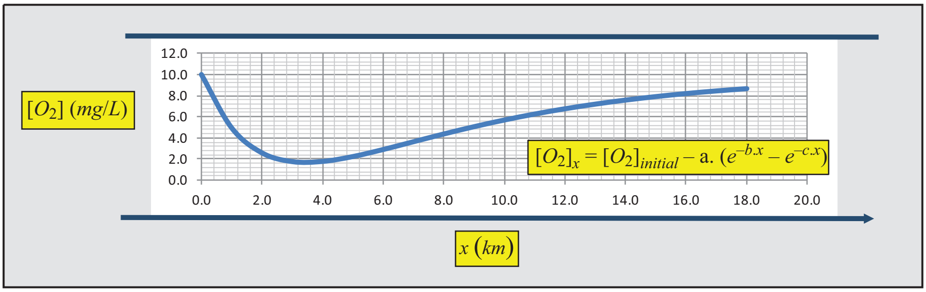
Example 3.13: The following equation is used to calculate the level of oxygen (mg/L) in a river below the discharge of a drain:

$$[O_2] = 10 - 20\left(e^{-0.15 \cdot x} - e^{-0.5 \cdot x}\right)$$

where x is the distance downstream in kilometers. Calculate:

a. The distance below the stream at which the oxygen level falls to a reading of 5 mg/L, at which detrimental effects are produced for certain species such as trout and salmon.
b. The distance downstream at which oxygen is at a minimum. What is the concentration at that location?

Solution:
The representation of the dissolved oxygen concentration (O_2) with the distance (x)



The distance in the river at which a value of 5 mg/L of oxygen will be observed can be obtained by solving the nonlinear equation by applying the Newton–Raphson method (see Appendix C). To do this, the derivative of the target function must be calculated:

$$f(x) = [O_2]_{\text{initial}} - a\left(e^{-b\cdot x} - e^{-c\cdot x}\right) - [O_2]_x$$

$$\frac{df(x)}{dx} = -a\left[-b\cdot e^{-bx} + c\cdot e^{-c\cdot x}\right]$$

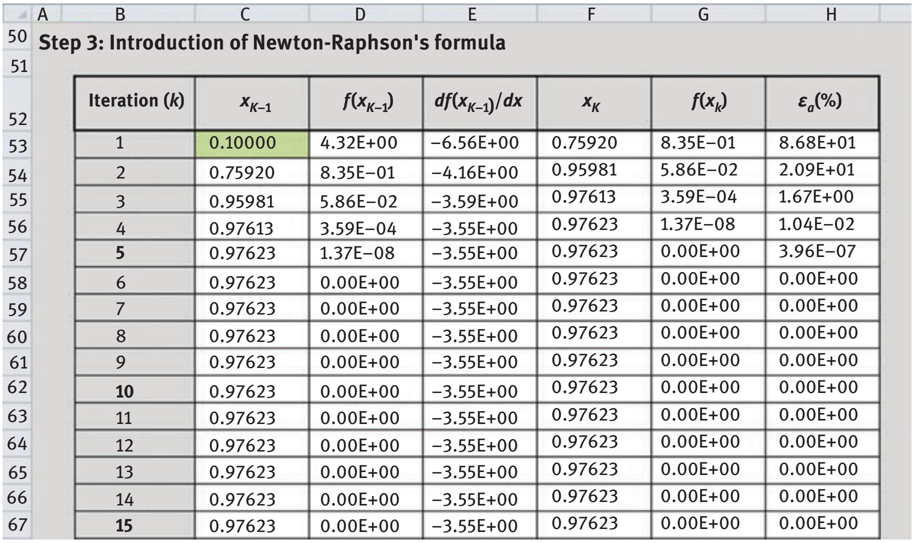
where parameters $[O_2]_{\text{initial}}$, a, b and c are known parameters. The initial value of the iteration would correspond to 0.1 (cell C53). The table for calculating the solution using Newton–Raphson is shown in Figure 3.23. By introducing six significant figures, convergence is obtained from the five iteration, with a value of 0.97623 km, that is, 976.2 m.

To obtain the distance at which the oxygen concentration will have a minimum value, the Solver function (See Appendix D) is applied by entering as the target cell value the search for a minimum. The results obtained are 1.643 mg/L at a distance of 3.44 km.

3.3.3 Application to Metabolic Engineering

Metabolic Engineering comprises a series of methodologies belonging to diverse disciplines that could be defined as the rational and directed improvement of the formation of a product, or a cellular property, through the modification of biochemical reactions proper to the microorganism or the introduction of new biosynthetic routes. Metabolic flow analysis (MFA) has become, since the 1990s, one of the most relevant tools of Metabolic Engineering, which consists of defining the stoichiometry of each of the most important reactions of a given metabolic network for the estimation of flows by means of the corresponding mass balances. The first metabolic networks consisted of 30–40 reactions, which, with the introduction of genomic aspects, involve the handling of thousands of equations, but always under the same principle.

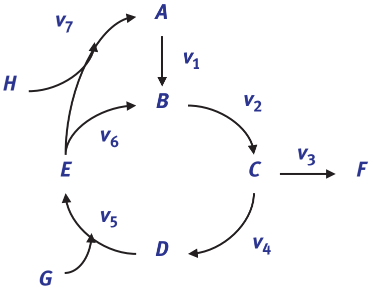
If one considers the metabolic network constituted by the biochemical reactions indicated in Figure 3.24, the concentration of all metabolites and the flows through all reactions can be represented by the following eight differential equations:



Step 3: Introduction of Newton-Raphson's formula

Iteration (k)	x_{K-1}	$f(x_{K-1})$	$df(x_{K-1})/dx$	x_K	$f(x_k)$	$\varepsilon_a(\%)$
1	0.10000	4.32E+00	−6.56E+00	0.75920	8.35E−01	8.68E+01
2	0.75920	8.35E−01	−4.16E+00	0.95981	5.86E−02	2.09E+01
3	0.95981	5.86E−02	−3.59E+00	0.97613	3.59E−04	1.67E+00
4	0.97613	3.59E−04	−3.55E+00	0.97623	1.37E−08	1.04E−02
5	0.97623	1.37E−08	−3.55E+00	0.97623	0.00E+00	3.96E−07
6	0.97623	0.00E+00	−3.55E+00	0.97623	0.00E+00	0.00E+00
7	0.97623	0.00E+00	−3.55E+00	0.97623	0.00E+00	0.00E+00
8	0.97623	0.00E+00	−3.55E+00	0.97623	0.00E+00	0.00E+00
9	0.97623	0.00E+00	−3.55E+00	0.97623	0.00E+00	0.00E+00
10	0.97623	0.00E+00	−3.55E+00	0.97623	0.00E+00	0.00E+00
11	0.97623	0.00E+00	−3.55E+00	0.97623	0.00E+00	0.00E+00
12	0.97623	0.00E+00	−3.55E+00	0.97623	0.00E+00	0.00E+00
13	0.97623	0.00E+00	−3.55E+00	0.97623	0.00E+00	0.00E+00
14	0.97623	0.00E+00	−3.55E+00	0.97623	0.00E+00	0.00E+00
15	0.97623	0.00E+00	−3.55E+00	0.97623	0.00E+00	0.00E+00

Figure 3.23: Application of the Newton–Raphson method for the calculation of the oxygen concentration.



$R_1 : A \to B$

$R_2 : B \to C$

$R_3 : C \to F$

$R_4 : C \to D$

$R_5 : D+G \to E$

$R_6 : E \to B$

$R_7 : E+H \to A$

Figure 3.24: Example of a metabolic network and its corresponding biochemical reactions. Symbols: A, B and so on represent metabolites; v_n represents metabolic fluxes or reaction rates.

$$\frac{d[A]}{dt} = v_7 - v_1 \qquad \frac{d[E]}{dt} = v_5 - v_6 - v_7$$

$$\frac{d[B]}{dt} = v_1 - v_2 + v_6 \qquad \frac{d[F]}{dt} = v_3$$

$$\frac{d[C]}{dt} = v_2 - v_3 - v_4 \qquad \frac{d[G]}{dt} = -v_5$$

$$\frac{d[D]}{dt} = v_4 - v_5 \qquad \frac{d[H]}{dt} = -v_7$$

The solution of this system of differential equations implies knowing the relationship between metabolic fluxes or reaction rates ($v_1, v_2, \ldots, v_n$) and the kinetic parameters of the enzymes involved and the concentrations of the metabolites. The AFM applies the steady-state principle, that is, it assumes that the concentrations of metabolites in a biological system remain practically constant over time, and thus $d[C]/dt = 0$. Mathematically, the problem is transformed from a system of differential equations to a system of linear equations, which in its matrix form is represented as a function of the stoichiometric coefficients of the reactions of the metabolic network.

$$\begin{array}{c} \\ \begin{bmatrix} \boldsymbol{d[A]/dt} \\ \boldsymbol{d[B]/dt} \\ \boldsymbol{d[C]/dt} \\ \boldsymbol{d[D]/dt} \\ \boldsymbol{d[E]/dt} \\ \boldsymbol{d[F]/dt} \\ \boldsymbol{d[G]/dt} \\ \boldsymbol{d[H]/dt} \end{bmatrix} \end{array} = \begin{array}{ccccccc} R_1 & R_2 & R_3 & R_4 & R_5 & R_6 & R_7 \\ -v_1 & 0 & 0 & 0 & 0 & 0 & v_7 \\ v_1 & -v_2 & 0 & 0 & 0 & v_6 & 0 \\ 0 & v_2 & -v_3 & -v_4 & 0 & 0 & 0 \\ 0 & 0 & 0 & v_4 & -v_5 & 0 & 0 \\ 0 & 0 & 0 & 0 & v_5 & -v_6 & -v_7 \\ 0 & 0 & v_3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -v_5 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -v_7 \end{array} = \begin{array}{c|ccccccc} & R_1 & R_2 & R_3 & R_4 & R_5 & R_6 & R_7 \\ \hline A & -1 & 0 & 0 & 0 & 0 & 0 & 1 \\ B & 1 & -1 & 0 & 0 & 0 & 1 & 0 \\ C & 0 & 1 & -1 & -1 & 0 & 0 & 0 \\ D & 0 & 0 & 0 & 1 & -1 & 0 & 0 \\ E & 0 & 0 & 0 & 0 & 1 & -1 & -1 \\ F & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ G & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ H & 0 & 0 & 0 & 0 & 0 & 0 & -1 \end{array} \begin{bmatrix} \boldsymbol{V_1} \\ \boldsymbol{V_2} \\ \boldsymbol{V_3} \\ \boldsymbol{V_4} \\ \boldsymbol{V_5} \\ \boldsymbol{V_6} \\ \boldsymbol{V_7} \end{bmatrix} = \begin{bmatrix} \mathbf{0} \\ \mathbf{0} \\ \mathbf{0} \\ \mathbf{0} \\ \mathbf{0} \\ \mathbf{0} \\ \mathbf{0} \\ \mathbf{0} \end{bmatrix}$$

In general terms, the representation of the system to solve is:

$$S \cdot \overrightarrow{v} = 0 \qquad (3.51)$$

where S is the stoichiometric matrix m x n, normally being $m > n$ and therefore an indeterminate system. Conversion to a given ($m = n$) or supradetermined ($m < n$) system is achieved by incorporating thermodynamic and/or biological restrictions. Restrictions can be divided into two groups: those that group metabolite intake and excretion and those that limit flow through metabolic reactions in the system.

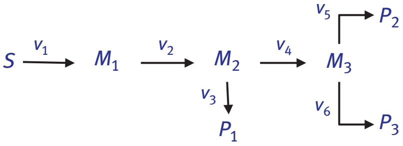
The incorporation of these restrictions allows transforming the system defined by eq. (3.51) into a certain system ($m = n$) called *metabolic balance equation*, which could be expressed as follows:

$$S \cdot \overrightarrow{v} = B \qquad (3.52)$$

where B is the matrix (1 x n) that includes both the reaction rates of measurable fluxes and those corresponding to the metabolites in steady state. The positive values of r correspond to production and the negative values to consumption:

$$B = \begin{pmatrix} r \\ 0 \end{pmatrix}$$

Example 3.14: Calculate the reaction rates or metabolic fluxes of the following metabolic pathway, taking into account that $r_s = -1$ mmol/L min, $r_{p1} = 0.3$, $r_{p2} = 0.5$.



Solution:

The reactions that define the metabolic pathway are as follows:

$$\begin{array}{ll} R_1: S \longrightarrow M_1 & R_4: M_2 \longrightarrow M_3 \\ R_2: M_1 \longrightarrow M_2 & R_5: M_3 \longrightarrow P_2 \\ R_3: M_2 \longrightarrow P_1 & R_6: M_3 \longrightarrow P_3 \end{array}$$

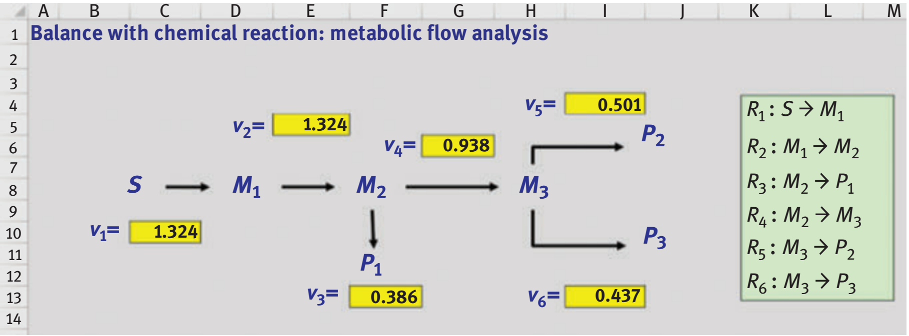
The matrix equation that defines the metabolic path implies a system of seven equations with six unknowns (v_1, v_2, v_3, v_4, v_5, v_6), where three of the metabolites are M_1, M_2 and M_3 and the steady-state condition applies to them.

$$\begin{bmatrix} \boldsymbol{d[S]/dt} \\ \boldsymbol{d[M_1]/dt} \\ \boldsymbol{d[M_2]/dt} \\ \boldsymbol{d[M_3]/dt} \\ \boldsymbol{d[P_1]/dt} \\ \boldsymbol{d[P_2]/dt} \\ \boldsymbol{d[P_3]/dt} \end{bmatrix} = \begin{array}{cccccc} \mathbf{R_1} & \mathbf{R_2} & \mathbf{R_3} & \mathbf{R_4} & \mathbf{R_5} & \mathbf{R_6} \\ -v_1 & 0 & 0 & 0 & 0 & 0 \\ v_1 & -v_2 & 0 & 0 & 0 & 0 \\ 0 & v_2 & -v_3 & -v_4 & 0 & 0 \\ 0 & 0 & 0 & v_4 & -v_5 & -v_6 \\ 0 & 0 & v_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & v_5 & 0 \\ 0 & 0 & 0 & 0 & 0 & v_6 \end{array} = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 & -1 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{-1} \end{pmatrix} \begin{bmatrix} \boldsymbol{v_1} \\ \boldsymbol{v_2} \\ \boldsymbol{v_3} \\ \boldsymbol{v_4} \\ \boldsymbol{v_5} \\ \boldsymbol{v_6} \end{bmatrix} = \begin{bmatrix} \boldsymbol{r_S} \\ \mathbf{0} \\ \mathbf{0} \\ \mathbf{0} \\ \boldsymbol{r_{P1}} \\ \boldsymbol{r_{P2}} \\ \boldsymbol{r_{P3}} \end{bmatrix}$$

The system has three degrees of freedom and therefore three restrictions need to be known. In this case, the experimental data correspond to the consumption of substrate, S, and the production of two products: P_1 and P_2. Thus, the metabolic balance equation (3.48) would be formed by the following determined system of six equations with six unknowns:

$$\begin{bmatrix} \boldsymbol{d[S]/dt} \\ \boldsymbol{d[M_1]/dt} \\ \boldsymbol{d[M_2]/dt} \\ \boldsymbol{d[M_3]/dt} \\ \boldsymbol{d[P_1]/dt} \\ \boldsymbol{d[P_2]/dt} \end{bmatrix} = \begin{array}{cccccc} \mathbf{R_1} & \mathbf{R_2} & \mathbf{R_3} & \mathbf{R_4} & \mathbf{R_5} & \mathbf{R_6} \\ -v_1 & 0 & 0 & 0 & 0 & 0 \\ v_1 & -v_2 & 0 & 0 & 0 & 0 \\ 0 & v_2 & -v_3 & -v_4 & 0 & 0 \\ 0 & 0 & 0 & v_4 & -v_5 & -v_6 \\ 0 & 0 & v_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & v_5 & 0 \end{array} = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 & -1 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \begin{bmatrix} \boldsymbol{v_1} \\ \boldsymbol{v_2} \\ \boldsymbol{v_3} \\ \boldsymbol{v_4} \\ \boldsymbol{v_5} \\ \boldsymbol{v_6} \end{bmatrix} = \begin{bmatrix} \mathbf{1.324} \\ \mathbf{0} \\ \mathbf{0} \\ \mathbf{0} \\ \mathbf{0.386} \\ \mathbf{0.501} \end{bmatrix}$$

Applying the inverse matrix method (Appendix D), the result of all metabolic flows can be obtained (Figure 3.25).



Balance with chemical reaction: metabolic flow analysis

v_1= 1.324

v_2= 1.324

v_3= 0.386

v_4= 0.938

v_5= 0.501

v_6= 0.437

$R_1: S \rightarrow M_1$

$R_2: M_1 \rightarrow M_2$

$R_3: M_2 \rightarrow P_1$

$R_4: M_2 \rightarrow M_3$

$R_5: M_3 \rightarrow P_2$

$R_6: M_3 \rightarrow P_3$

Figure 3.25: Result of metabolic flow analysis for the route considered in Example 3.14.

3.4 Proposed problems

3.4.1 Stoichiometry

One reaction

3.1 A process industry discharges 800 m^3/d of wastewater consisting of 1,600 ppm benzene, 2,500 ppm phenol and 3 g/L ethanol. Calculate the number of equivalent inhabitants of a city discharging urban wastewater with the same organic load. If you choose to install an advanced oxidation system that removes 90% of benzene and 95% of phenol, what would the equivalent number of inhabitants be now?

Solution: (a) 228.552 h-eq; (b) 94.014 h-eq.

3.2 In a combustion process ammonia is burned to form nitric oxide with 90% efficiency. Calculate:
(a) Composition of dry-basis combustion gas.
(b) NO moles produced per mole of oxygen consumed.
(c) If the boiler were properly maintained at 92% efficiency, what would be the new composition of dry-base combustion gases?

Solution: (a) 1.72% NH_3, 2.15% O_2, 80.69% N_2 and 15.44% NO; (b) 0.8; (c) 1.38% NH_3, 1.72% O_2, 81.04% N_2 and 15.86% NO.

3.3 Chlorine is the most commonly used conventional disinfectant in wastewater treatment. For economic reasons as well as for reasons of safety in the storage of chlorine gas, a system for producing chlorine gas from hydrochloric acid and oxygen on site has been installed in an urban waste water treatment plant. Calculate the composition of the reactor product stream if it is designed to operate with 22% excess air and 72% efficiency:

Solution: 12.32% HCl, 5.50% O_2, 50.49% N_2, 15.84% Cl_2 and 15.84% H_2O.

3.4 The saponification reaction for obtaining soap from glycerin can be represented by the following reaction:

$$3NaOH + (C_{17}H_{35}COO)_3C_3H_5 \rightarrow 3C_{17}H_{35}COONa + C_3H_5(OH)_3$$

If the initial mixture consists of a solution of NaOH (10 kmol/m^3) and glyceryl stearate (2.5 kmol/m^3), what value will the concentration of glycerin, sodium hydroxide, sodium stearate and glyceryl stearate have when the conversion rate, referred to NaOH, is 22%? What would happen if the conversion rate were 90%?

Solution: 7.80, 1.77, 2.20 and 0.73 kmol/m^3 of NaOH, glycerin, soap and stearate, respectively; with the composition of the initial mixture it is not possible to achieve this degree of conversion, since a negative value of the concentration in the output stream would be obtained.

3.5 To obtain barium in solution, the natural sulfate, barite, is melted with sodium carbonate. For this purpose, a quantity of barite (barium sulfate and inert) is melted with an excess of pure anhydrous sodium carbonate. The analysis of the resulting mass is as follows: 11.3% $BaSO_4$, 21.35% Na_2CO_3 and 26.70% Na_2SO_4. Calculate:

(a) The degree of conversion of barium sulfate.
(b) The composition of the initial barite.
(c) The percentage of excess sodium carbonate.

Solution: (a) 79.52%; (b) 93.94% of $BaSO_4$ and 6.06% of Inert; (c) 64.74%.

3.6 In a thermal power station, 5,000 tons/day of coal with a sulfur content of 1.2% are burned. Its combustion generates SO_2 (complete conversion), which is removed 85% effectively by a dry gas cleaning system using $CaCO_3$ to give rise to $CaSO_4$ and CO_2. Calculate:

(a) The quantity of $CaCO_3$ expressed as kg/Tm of coal.
(b) The daily emission of sulfur dioxide which is finally emitted into the atmosphere (mt/d).
(c) If, as an environmental improvement action, it is decided to change the raw material to a lignite containing 1.03% S, what would be the daily emission of SO_2?

Solution: (a) 31.90 kg $CaCO_3$/Tm of coal; (b) 18.0 mt/d; (c) 15.5 mt/d.

3.7 The fresh feed of an ammonia synthesis reactor almost always contains small quantities of nonreactive substances, such as Ar or CH_4. These inert materials do not condense and are therefore recirculated together with N_2 and H_2, which are not consumed in the reaction. In order to avoid the concentration of inert materials in the system, a continuous purge of the recirculation stream is carried out according to the flow diagram:

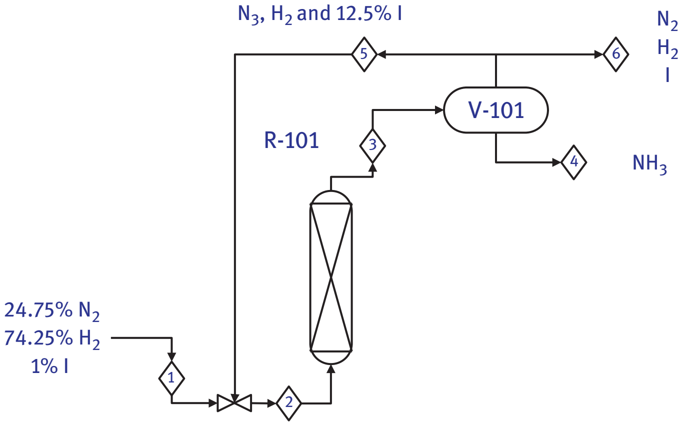


Figure P3.7

If the step conversion of N_2 in the reactor is 25%, calculate:
(a) Global conversion.
(b) Ratio of purged moles per mole of fresh feed.
(c) Ratio of moles entering the reactor per mole of feed.

Solution: (a) 92.92%; (b) 0.08; (c) 4.07.

3.8 Ethylene and oxygen react in a multitubular reactor in the presence of an Ag-based catalyst. The ethylene oxide corresponds to the only product of the main reaction that is characterized by its easy dissolution in water, which allows it to be separated effectively in an absorption column. The ethylene/air ratio in the fresh feed is 1/10 and the conversion per step in the reactor is 50%.

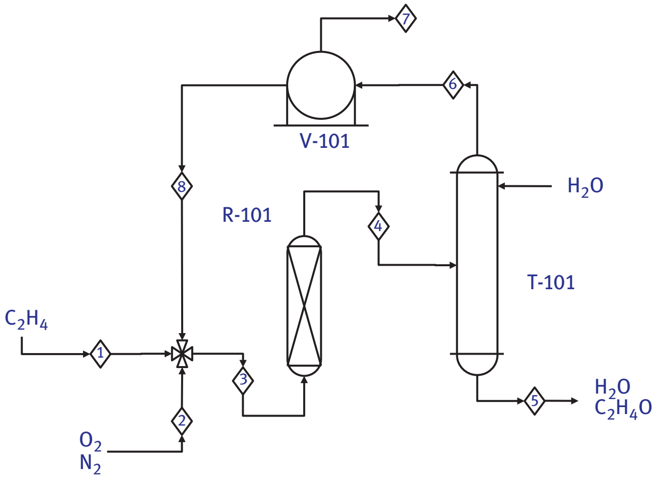


Figure P3.8

Calculate:

(a) The overall conversion of the system if 60% of the gases leaving the absorption column are recirculated.

(b) The composition of the flue gases.

(c) If the catalyst is changed so that the conversion per step is 55%, what would be the overall conversion?

(d) In addition, if it were decided to increase recirculation to 65% of the gases leaving the absorption column, what would be the overall conversion?

Solution: (a) 71.4%; (b) C_2H_4 2.88%, O_2 17.55%, N_2 79.57%; (c) 75.3%; (d) 77.7%.

3.9 The basic process unit for methanol synthesis (see Example 3.5) works with a stoichiometric feed of CO and H_2 to achieve an overall conversion of 95.2% CO. All the methanol formed comes out of the system as a product. No more than 1.95% CO and 0.45% H_2 leaving the reactor continues in the product stream, the rest is recycled. Calculate:

(a) Step-by-step conversion.

(b) The recirculation ratio.

(c) The composition of the products.

Solution: (a) 27.89%; (b) 7.88; (c) 4.38% CO, 8.76% H_2 and 86.86% methanol.

3.10 Nylon is one of the most common polymers used as a fiber, which belongs to the polyamide group. Nylon 6 is obtained from the monomer, caprolactam, which is generated from the transposition of the cyclohexanone oxime. This oxime ($C_6H_{10} = NOH$) is synthesized by the photochemical reaction of cyclohexane (C_6H_{12}) and nitrosyl chloride (NOCl):

$$C_6H_{12} + NOCl \rightarrow C_6H_{10} = NOH + HCl$$

For each mole of cyclohexane, 0.75 moles of NOCl and 0.15 moles of N_2 enter the system. The reactor conversion is 28% (based on the NOCl entering the reactor). The mole fraction of N_2 in the recirculation stream must not exceed 0.38, as this would cause process problems.

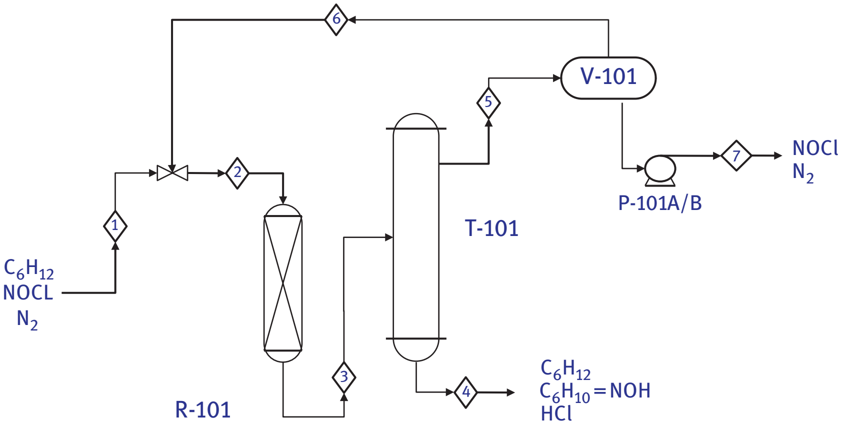


Figure P3.10

Calculate:

(a) The recirculation, purge and product flows per mole of cyclohexane fed.
(b) The molar composition of the product obtained.
(c) The overall conversion of the process to cyclohexane.
(d) Recirculation ratio: n_6/n_1.
(e) If due to temperature control problems in the reactor the step conversion in the reactor were reduced to 22%, what would be the overall conversion and recirculation ratio?

Solution: (a) 1.701, 0.395 and 1.505 mol/h, respectively; (b) C_6H_{12} 33.33%, $C_6H_{10} = NOH$ 33.6%, HCl 33.6%; (c) 50.5%; (d) 0.9; (e) 50.5% and 1.31.

Multiple reactions

3.11 The composition (in volume) of a commercial propane (according to the technical specifications indicated in the legislation – BOE of the year 2006) is the following: 1% CH_4, 82% C_3H_8, 15% C_4H_{10} and 2% CO_2. The above-mentioned propane (with a flow of 100 mol/h) is used to produce energy by combustion in a boiler, with 30% excess air. Assuming combustion is complete, calculate:
(a) The amount of air used.
(b) The composition of the flue gases on a wet basis.

Solution: (a) 3,154 mol/h; (b) 4.55% O_2, 74.19% N_2, 9.20% CO_2 and 12.06% H_2O.

3.12 About 5,000 m^3/h, measured under normal conditions, of a dry gas of the following composition (by volume) are burned in an oven: 50% CH_4, 8% C_2H_6, 12% H_2, 10% CO, 5% O_2, 10% N_2 and 5% CO_2. Combustion is carried out with 25% excess enriched air of composition (in volume): 35% O_2 and 65% N_2. The air is fed at 1 atm pressure and 112 °C. The combustion products leave the furnace at 1 atm and 1,200 °C, with a CO_2 and CO content at a molar ratio of 8/1. Knowing that there is no H_2, CH_4 or C_2H_6 in the flue gas, calculate:
(a) The flow rate of enriched air fed m^3/h.
(b) The flow rate of combustion gases produced in m^3/h and their composition on a wet basis.
(c) If the excess enriched air is increased to 40%, the molar ratio of CO_2 and CO is 20/1. What is the conversion value of the initial CO?

Solution: (a) 33,745 m^3/h; (b) 153,704 m^3/h, 6.61% O_2, 56.35% N_2; 11.70% CO_2, 1.46% CO and 23.87% H_2O; (c) 64.3%.

3.13 The combustion of a lignite (elemental analysis: 90% C and 1.5% S) generates SO_2 in the combustion gases (complete conversion). Sulfur dioxide is removed (95% efficiency) by the addition of magnesite (85% purity in $MgCO_3$) 25% in excess of that required for stoichiometric conditions. Calculate the kg of magnesite required per ton of coal.

Solution: 58.13 kg/Tm.

3.14 The elimination of hydrogen sulfide from natural gas or biogas is very important, since this flammable and colorless gas is highly toxic and corrosive, which is a great disadvantage, as it makes it difficult to move the gas through pipes, its storage in tanks and other metallic structures.

One of the possible elimination strategies consists of chemical oxidation by means of oxygen using various catalysts, which allows the transformation of sulfur into insoluble elemental sulfur that is separated in the liquid phase:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

A biogas containing 3.5% (by weight) of S as H_2S needs to be treated prior to use in a boiler. For this purpose, 0.056 m^3 of air (measured under normal conditions) is consumed per m^3 of biogas gas in the oxidation process. The average density of biogas is 0.97 g/L under normal conditions. Consider that in the first reaction 88% of O_2 is converted and in the second 100% of SO_2. Calculate:

(a) Quantity of elemental sulfur that can be obtained per m^3 of treated gas.
(b) The quantity of H_2S that the biogas expressed in mg/m^3 will continue to possess.
(c) If a state-of-the-art catalyst were to be used to obtain a 90.5% conversion in the first reaction, what would be the concentration of hydrogen sulfide in the treated biogas?

Solution: (a) 29.57 g S per m^3/h; (b) 934.7 mg/m^3; (c) 42.2 mg/m^3.

3.15 A furnace is fed with pure sulfur and transforms 90% of the charge into oxides (SO_2 and SO_3). After oxidation, the gas is introduced to a washing tower where all the sulfur that did not react, 90% of SO_3 and 40% of SO_2, is absorbed in water. An analysis of sulfur in the washing water leads to the conclusion that 10 kg/h of sulfur is separated. If the gases leaving the scrubber have the following composition: 83% N_2, 4% SO_2, 1% SO_3 and 12% O_2; calculate:

(a) Kilograms of sulfur per hour entering the furnace.
(b) Excess air used necessary to obtain complete combustion of all sulfur charged into the furnace.

Solution: (a) 13.70 kg/h; (b) 21.2%.

3.16 Formaldehyde (HCHO) is one of the key components in the formulation of adhesives. Most of the formaldehyde currently on the market is obtained from the oxidation of methanol, but there are numerous lines of work to obtain a cost-effective route by direct oxidation from methane using a new generation of catalysts:

$$CH_4 + O_2 \rightarrow HCHO + H_2O$$

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

A number of experiments have been carried out in a pilot installation; the data for which are given below:

(a) The reactor feed contains equimolar amounts of methane and oxygen, resulting in a global fractional methane conversion of 96%, and a fractional formaldehyde yield of 92.5%. Calculate the molar composition of the flow at the outlet of the reactor and the selectivity of formaldehyde production with respect to carbon dioxide production.

(b) The outflow from the reactor contains (% molar): 46.0% HCHO, 1.5% CO_2, 4% CH_4 and the rest oxygen and water. To calculate the fractional conversion of methane, the fractional yield of formaldehyde and the selectivity of formaldehyde production with respect to carbon dioxide production.

Solution: (a) $y_{CH4} = 0.0200$, $y_{O2} = 0.0025$; $y_{HCHO} = 0.4625$, $y_{H2O} = 0.4975$, $y_{CO2} = 0.0175$, $S_{HCHO/CO2} = 26.4$ mol HCHO/mol CO_2; (b) 93.14% methane conversion, 90.2% formaldehyde yield and a selectivity of 30.7 mol HCHO/mol CO_2.

3.17 Phosphorus is prepared by heating in an oven a perfectly mixed mass of $Ca_3(PO_4)_2$, sand (SiO_2) and coal. The amount of SiO_2 used is 19.5% in excess of what is theoretically necessary for the combination with Ca to give silicate and the carbon is 55.0% in excess of what is theoretically necessary for the complete reaction of all the P_2O_5 generated in the obtaining of silicate. Calculate:

(a) The percentage of composition of the initial load.

(b) The kilograms of P obtained per 100 kg load, assuming that the decomposition of phosphate by silica is 92% and that the reduction of phosphorus oxide released by carbon is completed by 75%.

Solution: (a) 50.7% $Ca_3(PO_4)_2$, 35.3% SiO_2 and 14.0% C; (b) 7.0 kg P per 100 kg load.

3.18 A fuel derived from waste (RDF) has the following elemental composition (% by weight): 87% C, 11% H, 1.4% S and the rest of non-combustible materials. Calculate:

(a) The composition of the emission gas if the RDF is burned with 20% excess air. Suppose complete combustion.

(b) The composition of the emission gas if the oil is burned with 20% excess air and 5% of the carbon forms CO.

Solution:

Complete combustion and 20% excess air	
Compound	**% Wet base**
O_2	3.34
CO_2	12.03
H_2O	9.13
SO_3	0.07
N_2	75.42

Partial combustion and 20% excess air	
Compound	**% Wet base**
O_2	3.63
CO_2	11.40
H_2O	9.10
SO_3	0.072
N_2	75.20
CO	0.60

3.19 The elemental analysis of a biodiesel provides the following results: 5% H, 4% S, 65% C, 10% O, 16% inert. Assuming that all biodiesel is burned, calculate:

(a) The composition of the combustion gas if this occurs completely by adding 20% excess air.

(b) The composition of the combustion gas for 20% excess air, if only 80% of C is oxidized to CO_2, with 15% transformed into CO and 5% transformed into black smoke.

Solution:

Complete combustion and 20% excess air	
Compound	**% Wet base**
O_2	4.14
CO_2	13.32
H_2O	6.15
SO_3	0.31
N_2	76.09

Partial combustion and 20% excess air	
Compound	**% Wet base**
O_2	5.75
CO_2	10.55
H_2O	6.09
SO_3	0.30
N_2	75.33
CO	1.98

3.4.2 Systems in equilibrium

Gas phase chemical equilibrium: a reaction

3.20 The following reversible reaction takes place in a stirred tank reactor:

$$2A + B \rightleftarrows C$$

which is characterized by the following equilibrium relationship

$$K = \frac{c_C}{c_A^2 \cdot c_B}$$

Calculate the intensive conversion under the following conditions: $K = 0.021$, $c_{A\text{o}} = 45$ mol/L, $c_{B\text{o}} = 28.5$ mol/L and $c_{C\text{o}} = 3$ mol/L.

Solution: $\xi = 17.717$.

3.21 The decomposition of 2-propanol results in acetone and hydrogen by the following reversible reaction:

$$(CH_3)_2CHOH_{(g)} \rightleftarrows (CH_3)_2CO_{(g)} + H_{2(g)}$$

The change in free Gibbs energy under standard conditions is 3.05 10^3 J/mol. Calculate the equilibrium conversion to 452 K and 0.5 atm pressure if the inlet is 1 mol/h of 2-propanol.

Solution: 68.6%.

3.22 In the hydrogen economy, the water gas shift reaction (WGS), which allows additional hydrogen to be obtained from gases from biomass energy recovery processes such as gasification, has gained much interest. The reaction is reversible and exothermic:

$$CO_{(g)} + H_2O_{(g)} \rightleftarrows H_{2(g)} + CO_{2(g)}$$

Callaghan (2006)[13] has defined the expression of the equilibrium constant as a function of temperature for a range of 600–2,000 K:

$$\log_{10} K_{eq} = -2.4198 + 0.0003855 \cdot T + \frac{2,180.6}{T}$$

A gas enrichment system from a biomass gasifier consists of a fixed bed reactor with a Fe/Cr catalyst where the WGS reaction takes place (at 350 °C and 1 atm pressure) and an adsorption column (PSA) where all the CO_2 and a majority of the CO are separated to obtain a stream with high H_2 and CH_4 concentrations that can be used as a substitute for natural gas (Figure P3.22). The reactor feed stream is 20 Nm^3/h wet gas with a dry to wet gas fraction of 0.4. Calculate:
(a) The equilibrium conversion of the WGS reaction.
(b) The CO recovery fraction in R-101.
(c) The dry base concentration of H_2 and CH_4 in stream 4.

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[13] https://web.wpi.edu/Pubs/ETD/Available/etd-050406-023806/unrestricted/ccallaghan.pdf

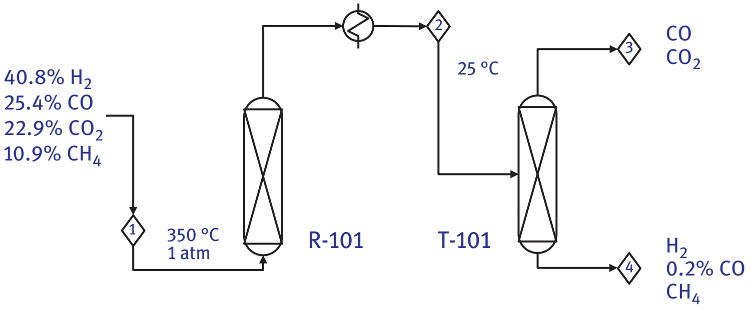

Figure P3.22: (The compositions are expressed in % volume on a dry basis.).

Solution: (a) 86.6; (b) 87.0% y (c) 85.5% H_2 and 14.3% CH_4.

Gas phase chemical equilibrium: multiple reactions

3.23 In high-temperature systems (e.g., volcanoes), there is a balance between the amount of carbon dioxide and carbon monoxide, as well as the formation of nitric oxide from oxygen and nitrogen. Calculate the composition of the equilibrium mixture at 3,000 K and 1 atm if initially the system is composed of 1 kmol of CO_2, 0.8 kmol of O_2 and 0.5 kmol of N_2. Data: $K_{CO_2/CO} = 0.3273$ and $K_{O_2/NO} = 0.1222$.

Solution: 0.2675 CO_2, 0.1448 CO, 0.3655 O_2, 0.1900 N_2, 0.0322 NO.

3.24 The following reversible reactions take place in an agitated tank reactor:

$$R_1: 2A + B \rightleftarrows C$$

$$R_2: A + D \rightleftarrows C$$

They are characterized by the following equilibrium relationships:

$$K_1 = \frac{c_C}{c_A^2 \cdot c_B} K_2 = \frac{c_C}{c_A \cdot c_D}$$

Calculate the intensive conversion under the following conditions: $K_1 = 3{\cdot}10^{-4}$, $K_2 = 3.7{\cdot}10^{-2}$, $c_{Ao} = 50$ mol/L, $c_{Bo} = 20$ mol/L, $c_{Co} = 5$ mol/L and $c_{Do} = 10$ mol/L.

Solution: $\xi_1 = 3.337$ and $\xi_2 = 2.677$.

3.25 Ethylene and acetylene can be obtained from the catalytic dehydrogenation of ethane:

$$R_1{:}C_2H_6 \rightleftarrows C_2H_4 + H_2$$

$$R_2{:}C_2H_6 \rightleftarrows C_2H_2 + 2H_2$$

The reactions develop at 1.160 K and 1 atm, reaching the equilibrium of the compositions in gas phases:

Equilibrium constants[14]			
$C_2H_6 \rightleftarrows C_2H_4 + H_2$		$C_2H_6 \rightleftarrows C_2H_2 + 2H_2$	
T (K)	K (atm)	T (K)	K (atm^2)
1.000	0.349	1.100	0.0253
1.100	1.70	1.150	0.110
1.200	6.34	1.200	0.507
1.300	19.2	1.300	6.40
1.400	49.9	1.400	56.0
1.500	114.0	1.500	290.0

In order to achieve a higher overall ethane conversion, the unreacted ethane is recirculated after a separation system where a 95% ethane recovery fraction is achieved.

For a reactor load of 100 mol/h, calculate:

(a) Conversion in each of the reactions.
(b) Composition at reactor output.

Solution: (a) ξ_1 = 82.87 and ξ_2 = 6.622; (b) C_2H_6:0.0536; C_2H_4: 0.4226; C_2H_2: 0.0338; H_2: 0.4901.

Acid–base reactions

3.26 If ammonia, in the form of NH_3 and NH_4^+, has a total concentration of $7.1{\cdot}10^{-4}$ M in a wastewater treatment plant. Calculate:

(a) Does it determine whether the nitrogen portion is in the form of ammonia (and therefore potentially separable by a stripping process) as a function of pH?
(b) If the pH of the wastewater rises to 10 and the partial pressure of ammonia in the air is approximately $5{\cdot}10^{-10}$ atm, what would be the equilibrium concentration of total nitrogen in the wastewater after the stripping process?
(c) The effectiveness of the stripping process.

Data: Henry's constant value: log Ha = 0.22.

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[14] Brickwedde et al. (1946). Journal of Research 37:263–279.

Solution: (a) Ammoniacal proportion = 1/(1+10^(pKa-pH)); (b) $3.61 \cdot 10^{-8}$ mol/L; (c) 99.995%.

3.27 Hydrogen sulfide (H_2S) can be separated by stripping by maintaining an adequate pH in the process stream. Calculate which portion of hydrogen sulfide in the form of H_2S at pH 4.5 and 7.5.

Solution: 99.68 and 23.61%, respectively.

3.28 Calculate the *pH* of rainwater, assuming that the only one that affects it is the absorption of atmospheric CO_2. Assume that the CO_2 concentration is 350 ppm, and the temperature and pressure are 25 °C and 1 atm. Data: Henry's law constant for CO_2 at 25 °C is 0.033363 mol/L atm.

Solution: 5.64.

3.29 One of the important aspects in the operation of anaerobic digesters, like most processes that have biological reactions, is the *pH*. Thus, the acidification of an anaerobic digester is one of the most common problems due to the accumulation of volatile fatty acids generated in the process due to inhibition of the methanogenic stage (methane formation). For this purpose, it is generally recommended to maintain an alkalinity value of at least 1.5 g/L $CaCO_3$.

Alkalinity is a measure of the buffer capacity of the system, that is, a measure of the ability to absorb hydrogen ions produced by an acidification of the system. This is defined by:

$$\text{Alk}(\text{mol/L}) = \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[OH^-\right] - \left[H^+\right]$$

An anaerobic digester is operated under the following parameters: (i) $pH = 7.5$; (ii) $T = 25$ °C; (iii) total inorganic carbon of 20 mmol/L. Determine whether or not it is necessary to add bicarbonate to maintain the appropriate safety threshold in alkalinity.

Solution: If bicarbonate needs to be added as the alkalinity is 0.94 mg $CaCO_3$/L.

Solubility product

3.30 A dissolution of 0.15 M in NaCl, 0.10 M in NaBr and 0.22 M in NaI. To selectively separate the different anions, add $AgNO_3$. Determine:

(a) Which anion will precipitate first? Which second and which third?
(b) How much of the anion that precipitates first will remain in solution when the second begins to precipitate and how much of the second will remain when the third begins to precipitate?

Solution: (a) $I^- > Br^- > Cl^-$; (b) I^-: $1.46\ 10^{-5}$ M; Br^-: $4.58\ 10^{-4}$ M

3.31 The chemical analysis of a certain water sample determines that each liter contains among other species: 398 mg of calcium ion and 72.4 mg of sulfate ion. It justifies why no calcium sulfate precipitate was observed in the water sample. If 350 cm^3 of a solution of 0.025 M sodium sulfate were added to 1 L of the previous solution, would precipitate be observed?

Solution: Yes, precipitation of calcium sulfate would occur.

3.4.3 Kinetic controlled systems

3.32 The concentration of contaminating bacteria c in a lake decreases according to the equation:

$$[\text{Bacterias}]_t = 75 \cdot e^{-1.5 \cdot t} + 20 \cdot e^{-0.075 \cdot t}$$

Determine the time required for the concentration of bacteria to be reduced to 15 using a graphical method and a numerical method.

Solution: (a) 4 h and (b) 4.016 h

3.33 We wish to know the metabolic flows of the network described in Figure P3.33[15], knowing that the consumption of substrates are: $r_{S1} = 2.153$ and $r_{S2} = 2.961$.

Solution: $v_1 = 2.153$; $v_2 = 2.961$; $v_3 = 2.961$; $v_4 = 2.153$; $v_5 = 0.404$; $v_6 = 2.557$; $v_7 = 0.404$.

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[15] "Co-factor pairs (e.g. ATP/ADP or NADH/NAD^+) has coefficients with opposite and identical signs in the stoichiometric equations. Therefore, only one of the two is included (always the same for all reactions), to discard linearly dependent columns"

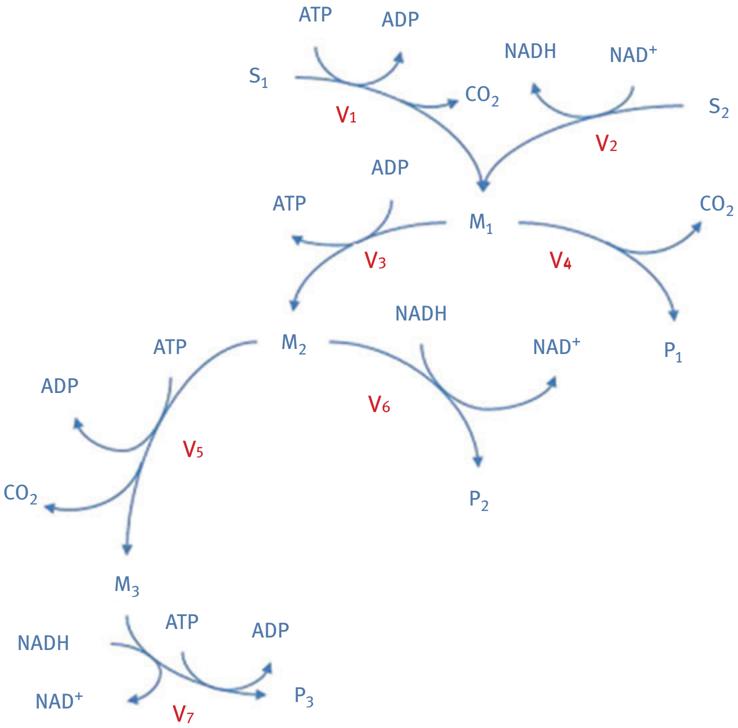


Figure P3.33: Metabolic network.

4 Balances in multiple systems

4.1 Analysis of degrees of freedom

4.1.1 Specification of a system

In multiple systems and/or processes, with many variables and equations, the correct specification of the problem to be solved is very important, that is, the correct identification of the number of unknowns (N_x) and the definition of the number of independent equations (N_{ec}) that represent the same. This specification can lead to three situations:

A. $N_x > N_{\text{ec}}$ Subspecified
B. $N_x = N_{\text{ec}}$ Specified
C. $N_x < N_{\text{ec}}$ Overspecified

The difference between the number of unknowns and the number of independent equations constitutes the number of degrees of freedom of a system and/or process:

$$GL = N_x - N_{\text{ec}} = \left\{ \begin{array}{c} \text{number} \\ \text{of} \\ \text{unknowns} \end{array} \right\} - \left\{ \begin{array}{c} \text{number of} \\ \text{independent} \\ \text{equations} \end{array} \right\} \tag{4.1}$$

A subspecified problem ($GL > 0$) is essentially a design problem; therefore, it will be necessary to determine a number of variables (equal to the number of degrees of freedom) in a set of independent equations to which to assign values to solve the equations. Depending on the set chosen, the different design methods for the process units are defined.

A specified problem ($GL = 0$), all values are fixed only by the conditions specified in the problem statement, being able to obtain the solution (unique in most cases) by solving the equations.

An overspecified problem ($GL < 0$) is sometimes caused by the redundancy of correct information, but is usually the result of an error that has gone unnoticed. In these cases, it is important to check the validity of each equation by extracting the invalid equations. If all independent equations of an overspecified problem are validated, then the set that produces the most efficient or precise solution can be chosen.

4.1.2 Calculation of the number of degrees of freedom

The number of unknowns for a control volume is given by the difference between the number of variables and the number of data:

https://doi.org/10.1515/9783110624304-004

$$N_x = N_{\text{variables}} - N_{\text{data}} \tag{4.2}$$

Among the most common variables in mass balances for steady-state systems, it is worth highlighting:

i. the mass or molar flow rate for each component of the different streams, or the concentration of each component plus the total flow rate;
ii. the degree of advancement or conversion of each of the chemical reactions;
iii. the recirculation and/or purge ratio.

In a process with "*S*" streams, "*J*" components and "*I*" independent chemical reactions, the number of variables will be given by eq. (4.3):

$$N_{\text{variables}} = N_S \cdot N_J + N_I \tag{4.3}$$

The most frequent independent equations to use are as follows:

i. Mass balances (with or without chemical reaction) of each of the components. For a system of *J* components and *U* units, the units refer to the volumes of control on which to draw up the balances; therefore, the points of mixing and division of streams are considered as units:

$$N_{\text{balances}} = N_J \cdot N_U \tag{4.4}$$

ii. Phase equilibrium relationships.
iii. Implicit relationships, for example, the concentration or quantity of a component is zero in a given stream.
iv. Explicit relationships, such as a recovery fraction in a "separator."

The number of independent equations will be given by the sum of the number of balances and the other relationships or conditions of the system:

$$N_{\text{ec}} = N_{\text{balances}} + N_{\text{relationships}} = N_J \cdot N_U + N_{\text{relationships}} \tag{4.5}$$

If eqs. (4.2), (4.3) and (4.5) are combined in eq. (4.1) to define the number of degrees of freedom, the following general expression is obtained:

$$GL = N_x - N_{\text{eq}} = \left[N_S \cdot N_J + N_I - N_{\text{data}}\right] - \left[N_J \cdot N_U + N_{\text{relationships}}\right] \tag{4.6}$$

Example 4.1: Calculate the number of degrees of freedom of the steady-state process indicated in Figure 4.1, as well as that of the R-101 reactor.

Solution:

Reactor R-101

The R-101 reactor is characterized by three process streams (two inputs and one output) where an independent chemical reaction takes place; therefore, the number of variables will be given by eq. (4.3):

$$N_{\text{variables}} = N_S \cdot N_J + N_I = 3 \cdot 3 + 1 = 10$$

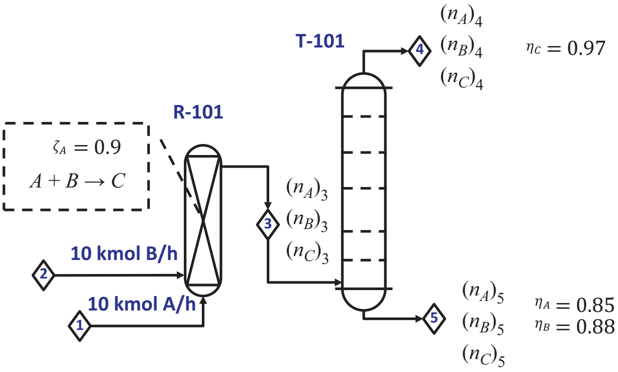


Figure 4.1: Flow diagram of a stationary-state process consisting of two units: reactor and distillation tower.

Corresponding to the molar flow rates of each of the streams and the degree of advancement of the reaction: $(n_A)_1$, $(n_B)_1$, $(n_C)_1$, $(n_A)_2$, $(n_B)_2$, $(n_C)_2$, $(n_A)_3$, $(n_B)_3$, $(n_C)_3$, ζ_A.

Three data are provided: molar flow of A in stream 1 $(n_A)_1$, molar flow of B in stream 2 $(n_B)_2$ and the degree of advancement of the reaction, ζ_A. Consequently, the number of unknowns:

$$N_x = N_{\text{variables}} - N_{\text{data}} = 10 - 3 = 7$$

The independent equations for reactor R-101 (single unit) correspond to the following:

- Balances: $N_{\text{balances}} = N_J \cdot N_U = 3 \cdot 1 = 3$
- Implicit relationships: the molar flow of B and C in stream 1 is zero and the molar flow of A and C in stream 2 is zero.
- Independent equations: $N_{\text{ec}} = N_{\text{balances}} + N_{\text{relationships}} = 3 + 4 = 7$.

Finally, the number of degrees of freedom of the reactor will be zero, that is, a specified system, where when solving the balances, a unique solution will be obtained:

$$GL = N_x - N_{\text{ec}} = 7 - 7 = 0$$

Overall process

Unknown:

Variables: – 5 streams – 3 components (A, B, C) – 1 chemical reaction	$\Rightarrow$ $N_{\text{variables}} = N_S \cdot N_J + N_I = 5 \cdot 3 + 1 = 16$
Data: – 2 molar flow rates – Degree of advancement of the reaction	$\Rightarrow$ $N_{\text{data}} = 3$
Unknowns:	$\Rightarrow$ $N_x = N_{\text{variables}} - N_{\text{data}} = 16 - 3 = 13$

Independent equations:

Balances: – 3 components – 2 units (R-101 y T-101)	⇒ $N_{\text{balances}} = N_J \cdot N_U = 3 \cdot 2 = 6$
Implicit relationships: – Stream 1 [2]: molar flow rates of B and C are zero – Stream 2 [2]: molar flow rates of A and C are zero	⇒ $N_{\text{implicit relationships}} = 4$
Explicit relationships: – Recovery fraction of C (in head), A and B (in bottom)	⇒ $N_{\text{explicit relationships}} = 3$
Independent equations:	⇒ $N_{\text{eq}} = N_{\text{balances}} + N_{\text{relationships}} = 6 + 7 = 13$

Number of degrees of freedom:

Degrees of freedom	⇒ $GL = N_x - N_{\text{ec}} = 13 - 13 = 0$

It is a perfectly specified problem that can proceed to the resolution of the system of independent equations that will allow to obtain a unique solution.

4.2 Solution strategies

There are two calculation strategies for solving mass balances in multiple systems:

- *Simultaneous solution method*: The equations that represent the whole system and/or process are defined, and then proceed to their simultaneous resolution. It is also called an *equation-based* or *equation-oriented method*. Most of the examples and problems proposed in Chapters 2 and 3 have been solved using this method.
- *Sequential modular method*: In this case, the independent equations (balances and any other equation that defines process specifications or physical considerations) of each control unit/volume that constitutes each of the modules into which the system and/or process can be divided are solved sequentially. Most simulators use this method because it is easier to apply in multiple systems, being able to detect calculation errors more quickly. If there are no recirculation streams, the calculation goes from one unit to the next until all of them are covered. In systems with recirculation streams, an iterative calculation will be required until an acceptable convergence in the closing of the matter balance is obtained.

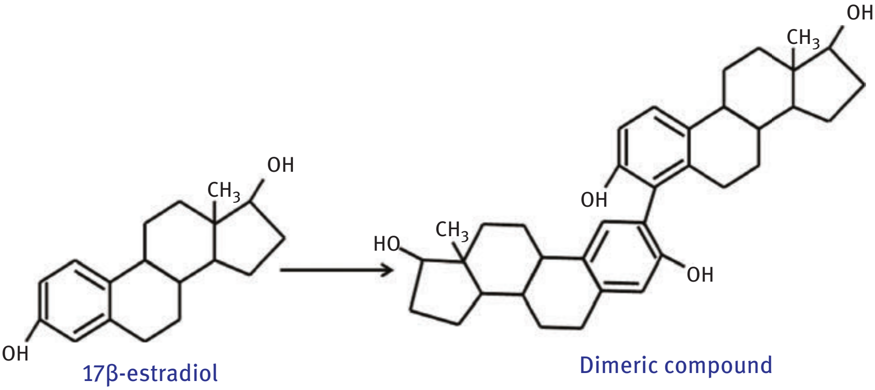
The closing of the mass balance (ε_M) is defined as the relationship between the velocity of material flow at the inlet and outlet of a system:

$$\varepsilon_M(\%) = \frac{\left(\sum_i m_i\right)_{\text{output}}}{\left(\sum_i m_i\right)_{\text{input}}} \cdot 100 \tag{4.7}$$

The acceptable value of ε_M depends on the type and purpose of the mass balance. For simulation/modeling calculations, the seal must be 100.0%, but with data measured in real processes, a seal between 90 and 110% may be acceptable. For chemical process design calculations, the closure of the mass balance is generally set above 99.9%. The closure of the mass balance is an important issue in the application of the sequential modular method.

Example 4.2: One of the removal alternatives for 17β-estradiol in urban wastewater is oxidation catalyzed by the enzyme laccase in membrane reactors. One of the mechanisms described corresponds to the formation of the C–C-dimer of estrogen:

2



The design of a process is proposed (Figure 4.2) with a conversion per step in the reactor of 36%, which is introduced in a nanofilter (F-101) that retains 12% of the 17-estradiol and 85% of the dimer; the rest is recirculated at the entrance of the reactor. If the feed stream has a flow of 15 mmol/h of the estrogen, calculate the overall conversion and recirculation ratio. Apply both the simultaneous solution method and the modular sequential method.

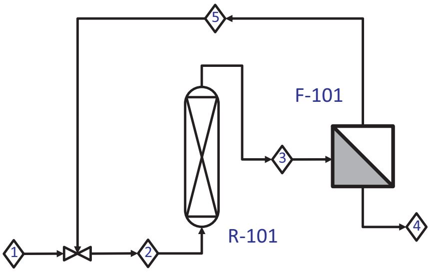


Figure 4.2: Flowchart of a process for the elimination of 17β-estradiol by laccase.

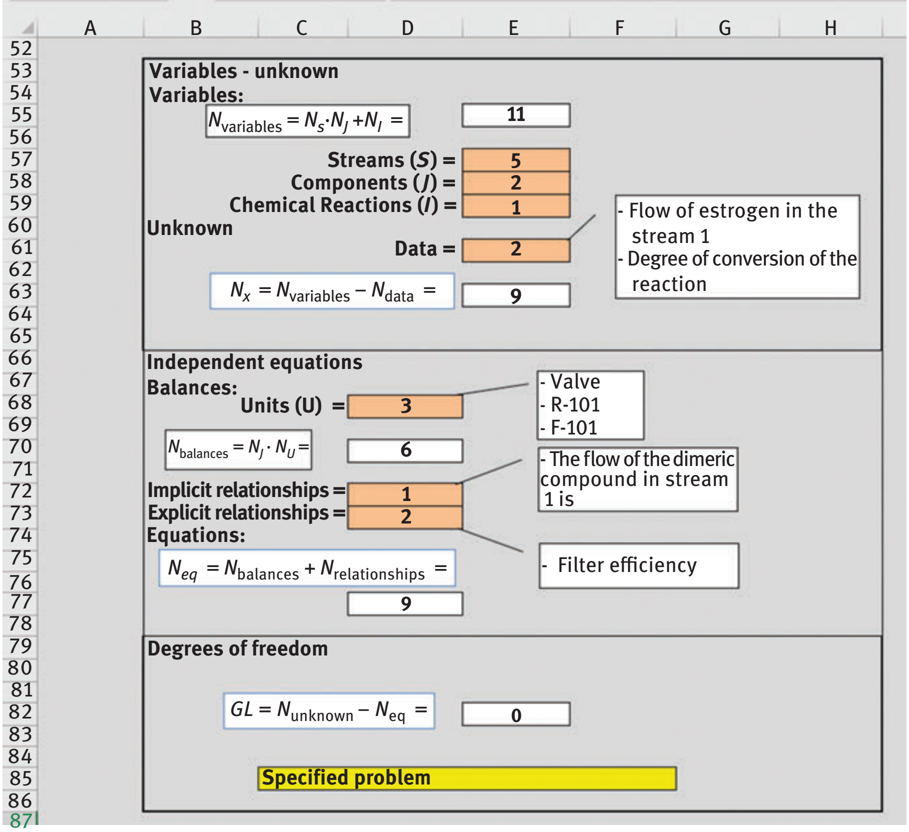
Solution:

A. Number of degrees of freedom

The necessary data for the calculation of the number of degrees of freedom are as follows:

Variables: – 5 streams – 2 components – 1 chemical reaction	Data: – Molar flow rate of 17β-estradiol in the feed – Degree of advancement of the reaction
Balances: – 2 components – 3 units (valve, R-101, F-101)	Implicit relationships: – Flow of dimeric compound in stream 1 is zero Explicit relationships: – Filter efficiency

Figure 4.3 shows the calculation of the number of degrees of freedom by applying eqs. (4.1)–(4.5). Depending on the number of degrees of freedom, cell C85 automatically displays the type of problem from the point of view of the specification:



Variables - unknown

Variables:

$N_{\text{variables}} = N_S \cdot N_J + N_I =$ 11

Streams (S) = 5

Components (J) = 2

Chemical Reactions (I) = 1

Unknown

Data = 2

- Flow of estrogen in the stream 1
- Degree of conversion of the reaction

$N_x = N_{\text{variables}} - N_{\text{data}} =$ 9

Independent equations

Balances:

Units (U) = 3

- Valve
- R-101
- F-101

$N_{\text{balances}} = N_J \cdot N_U =$ 6

Implicit relationships = 1

- The flow of the dimeric compound in stream 1 is

Explicit relationships = 2

- Filter efficiency

Equations:

$N_{eq} = N_{\text{balances}} + N_{\text{relationships}} =$ 9

Degrees of freedom

$GL = N_{\text{unknown}} - N_{eq} =$ 0

Specified problem

Figure 4.3: Degrees of freedom in Example 4.2.

C85: = IF(E89 = 0; “Specified problem”; IF(E89 < 0; “Over-specified, check for errors”; “Degrees of freedom”))

In this example, the problem is perfectly specified and therefore the solution to the problem can be obtained by solving the equations independent of the process.

B. Simultaneous solution method

Step 1: Flowchart with identification and enumeration of streams

Reaction data: If we call $A_1 \equiv C_{18}H_{24}O_2$ (17β-estradiol) and $A_2 \equiv C_{36}H_{46}O_4$ (C–C dimer) the reaction can be expressed as follows:

$$A_2 - 2A_1 = 0$$

Being $C_{18}H_{24}O_2$ the limiting reactant and, therefore, $k = 1$ and a degree of conversion of 0.36.

Process data: Filter efficiencies, $\eta_1 = 0.12$ and $\eta_2 = 0.85$:

$$(n_1)_4 = \eta_1 \cdot (n_1)_3$$

$$(n_2)_4 = \eta_2 \cdot (n_2)_3$$

Step 2: Basis of calculations

The feed flow rate of $C_{18}H_{24}O_2$ shall be considered as the calculation basis: $(n_1)_1 = 15$ mmol/h.

Step 3: Definition of control volumes and formulation of the mass balances

To calculate the molar flow of the components in each stream, the component balances with and without chemical reaction will be applied:

- Mass balance without chemical reaction:
  - Any component: $$\Sigma(n_j)_{\text{input}} = \Sigma(n_j)_{\text{output}} \quad (4.8)$$
- Mass balance with chemical reaction:
  - Limiting reactant (k): $$n_k = n_{ko}\left(1 - \sum_{i=1}^{h} \zeta_{ki}\right) \quad (4.9)$$
  - Other reactants and products (j): $$n_j = n_{jo} - \sum_{i=1}^{h}\left(n_{k_0 i} \cdot \zeta_{ki} \cdot \frac{\alpha_{ji}}{\alpha_{ki}}\right) \quad (4.10)$$

– Volume control to the mixing point of the feed and recirculation	
Balance for $C_{18}H_{24}O_2$	$(n_1)_1 + (n_1)_5 = (n_1)_2$
Balance for $C_{36}H_{46}O_4$	$(n_2)_1 + (n_2)_5 = (n_2)_2$
– Control volume corresponding to reactor R-101	
Balance for $C_{18}H_{24}O_2$ (limiting reactant)	$(n_1)_3 = (n_1)_2 \cdot (1 - \zeta_1)$
Balance for $C_{36}H_{46}O_4$	$(n_2)_3 = (n_2)_2 - (n_1)_2 \cdot \zeta_1 \cdot \frac{\alpha_2}{\alpha_1}$

– Control volume corresponding to filter F-101		
Balance for $C_{18}H_{24}O_2$ and filter efficiency	$(n_1)_3 = (n_1)_4 + (n_1)_5$ $(n_1)_4 = \eta_1 \cdot (n_1)_3$	$(n_1)_5 = (1-\eta_1)(n_1)_3$
Balance for $C_{36}H_{46}O_4$ and filter efficiency	$(n_2)_3 = (n_2)_4 + (n_2)_5$ $(n_2)_4 = \eta_2 \cdot (n_2)_3$	$(n_2)_5 = (1-\eta_2)(n_2)_3$

Step 4: Solving the system of equations
From the above equations, the system is defined by six linearly independent equations:

Equations	**Unknowns**	**Coded equations**
[1] $(n_1)_1 + (n_1)_5 = (n_1)_2$	$x_1 = (n_1)_2$	[1] $x_1 - x_5 = (n_1)_1$
[2] $(n_2)_1 + (n_2)_5 = (n_2)_2$	$x_2 = (n_2)_2$	[2] $x_2 - x_6 = (n_2)_1$
[3] $(n_1)_3 = (n_1)_2 \cdot (1-\zeta_1)$	$x_3 = (n_1)_3$	[3] $(1-\zeta_1)x_1 - x_3 = 0$
[4] $(n_2)_3 = (n_2)_2 - (n_1)_2 \cdot \zeta_1 \cdot \dfrac{\alpha_2}{\alpha_1}$	$x_4 = (n_2)_3$	[4] $-\left(\zeta_1 \cdot \dfrac{\alpha_2}{\alpha_1}\right)x_1 + x_2 - x_4 = 0$
[5] $(n_1)_5 = (1-\eta_1)(n_1)_3$	$x_5 = (n_1)_5$	[5] $(1-\eta_1)x_3 - x_5 = 0$
[6] $(n_2)_5 = (1-\eta_2)(n_2)_3$	$x_6 = (n_2)_5$	[6] $(1-\eta_2)x_4 - x_6 = 0$

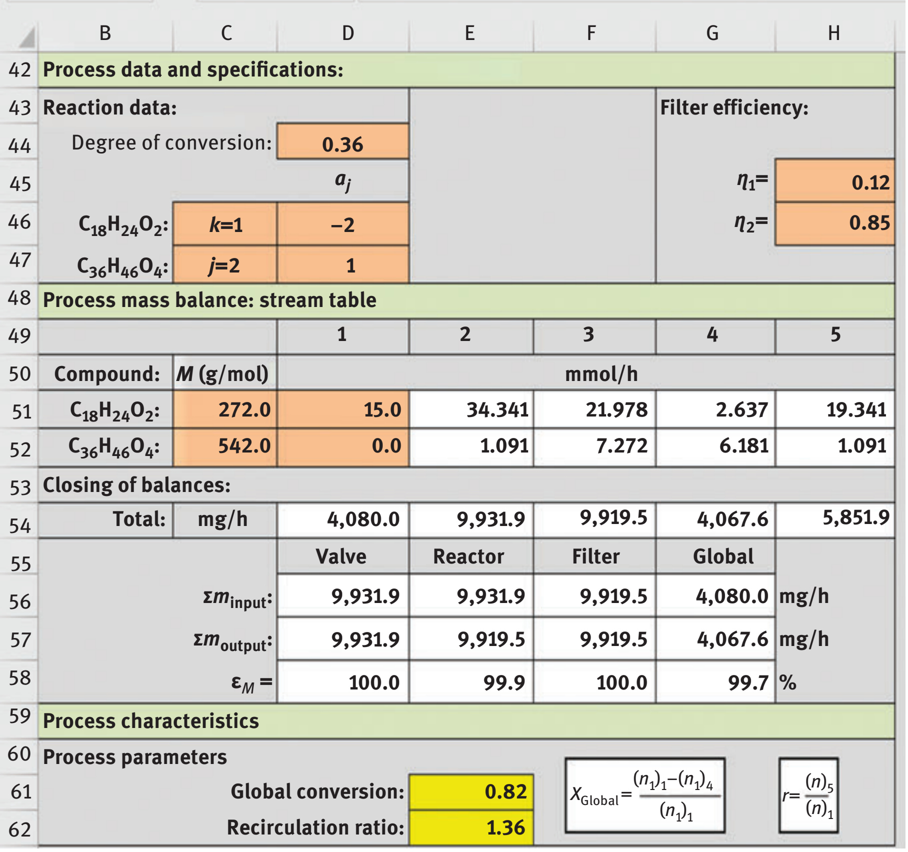
First, a copy of the “6 variables” sheet from the “Appendix D_Matrix Inversion” file (see Appendix D) to the book where the solution to the problem is being elaborated. Both sheets are then “interconnected” with the introduction of the coefficients of the linear equations as data or as a formula, as appropriate, when related to the spreadsheet of the problem. When you finish entering the coefficients, you will automatically obtain the calculation of the solution of the system of linear equations that we can, in turn, transfer to the corresponding cells in the main spreadsheet of the problem (Figure 4.4).

Applying eq. (4.7) you can obtain the closing of balances for each of the units and the overall process, where you get a closing of 99.7% for the overall process. With the molar flows of all streams both the overall conversion and the recirculation ratio can be calculated:
- Global conversion of 82%: G54: = ((F51–I51)/F51)
- Recirculation ratio of 1.36: G55: = ((J51 + J52)/(F51 + F52))

C. Sequential modular method
Steps 1 and 2: Flowchart with identification of streams and choice of calculation basis
Both steps are common to the simultaneous solution method, since the difference lies in the strategy for solving the equations independent of the process.

Steps 3 and 4: Formulation and resolution of the mass balances
The modular sequential method is based on the solution of the balances for each of the units (modules) consecutively.

Valve	**Reactor (R-101)**	**Filter (F-101)**
$(n_1)_2 = (n_1)_1 + (n_1)_5$ $(n_2)_2 = (n_2)_1 + (n_2)_5$	$(n_1)_3 = (n_1)_2 \cdot (1-\zeta_1)$ $(n_2)_3 = (n_2)_2 - (n_1)_2 \cdot \zeta_1 \cdot \dfrac{\alpha_2}{\alpha_1}$	$(n_1)_4 = \eta_1 \cdot (n_1)_3$ $(n_2)_4 = \eta_2 \cdot (n_2)_3$ $(n_1)_5 = (n_1)_3 - (n_1)_4$ $(n_2)_5 = (n_2)_3 - (n_2)_4$

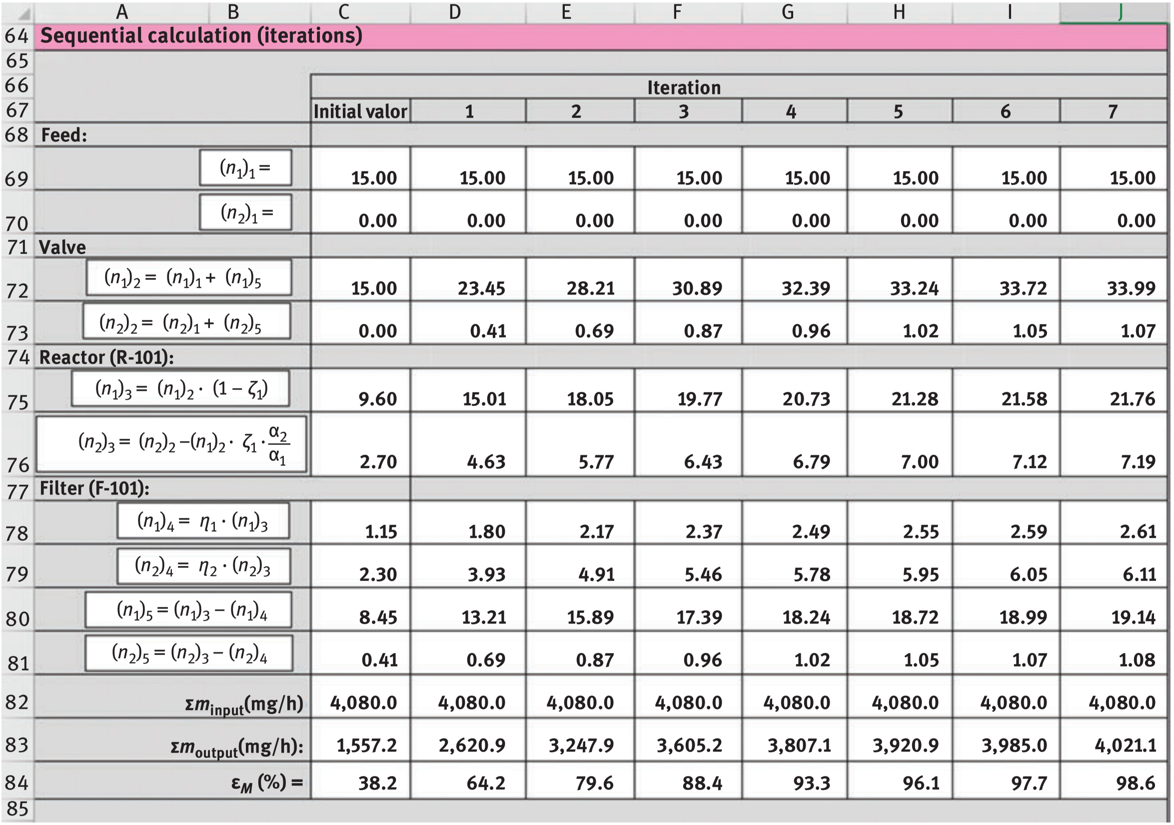


	B	C	D	E	F	G	H
42	**Process data and specifications:**						
43	**Reaction data:**					**Filter efficiency:**	
44	Degree of conversion:		**0.36**				
45			a_j			η_1=	**0.12**
46	$C_{18}H_{24}O_2$:	k=1	−2			η_2=	**0.85**
47	$C_{36}H_{46}O_4$:	j=2	1				
48	**Process mass balance: stream table**						
49			**1**	**2**	**3**	**4**	**5**
50	**Compound:**	**M (g/mol)**	**mmol/h**				
51	$C_{18}H_{24}O_2$:	272.0	15.0	34.341	21.978	2.637	19.341
52	$C_{36}H_{46}O_4$:	542.0	0.0	1.091	7.272	6.181	1.091
53	**Closing of balances:**						
54	**Total:**	**mg/h**	4,080.0	9,931.9	9,919.5	4,067.6	5,851.9
55			**Valve**	**Reactor**	**Filter**	**Global**	
56		Σm_{input}:	9,931.9	9,931.9	9,919.5	4,080.0	mg/h
57		Σm_{output}:	9,931.9	9,919.5	9,919.5	4,067.6	mg/h
58		ε_M =	100.0	99.9	100.0	99.7	%
59	**Process characteristics**						
60	**Process parameters**						
61		**Global conversion:**		**0.82**	$X_{Global}=\frac{(n_1)_1-(n_1)_4}{(n_1)_1}$		$r=\frac{(n)_5}{(n)_1}$
62		**Recirculation ratio:**		**1.36**			

Figure 4.4: Spreadsheet with mass balance data.

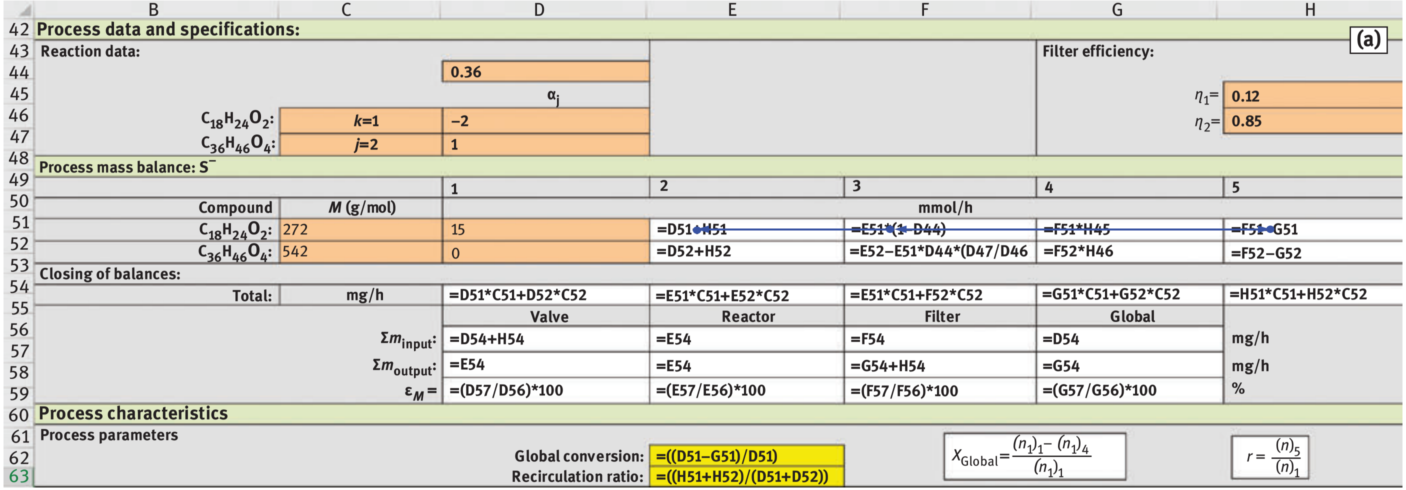
In the case of recirculation streams, as in this case, the calculation must be iterative until the desired convergence is reached (Figure 4.5). The initial value considered at the feed and recirculation mixing point for the molar flow velocities of the recirculation streams $(n_1)_5$ and $(n_2)_5$ was zero. After seven iterations the balance closes with 98.6% (cell J84), obtaining a global conversion of 83% and a recirculation ratio of 1.35.

The use of spreadsheet allows a simpler application of the modular sequential method, starting from the application of the “circular reference” tool for iterative calculation. Thus, the equations can be entered directly into the corresponding cells of the molar flow velocities (Figure 4.6a), so that when writing the flow velocities of the filter recirculation stream (stream 5) the program will issue a note about the existence of a circular reference. Enabling this calculation (see Appendix C) will show the calculation that is obtained either after 100 iterations or that calculation that reaches a convergence between the flow velocities of stream 5 such that the difference in values of the molar flow velocity is less than 0.00001 (Figure 4.6b). The result is, in this case, identical to that obtained with the simultaneous solution method: global conversion of 82% and recirculation ratio of 1.36.



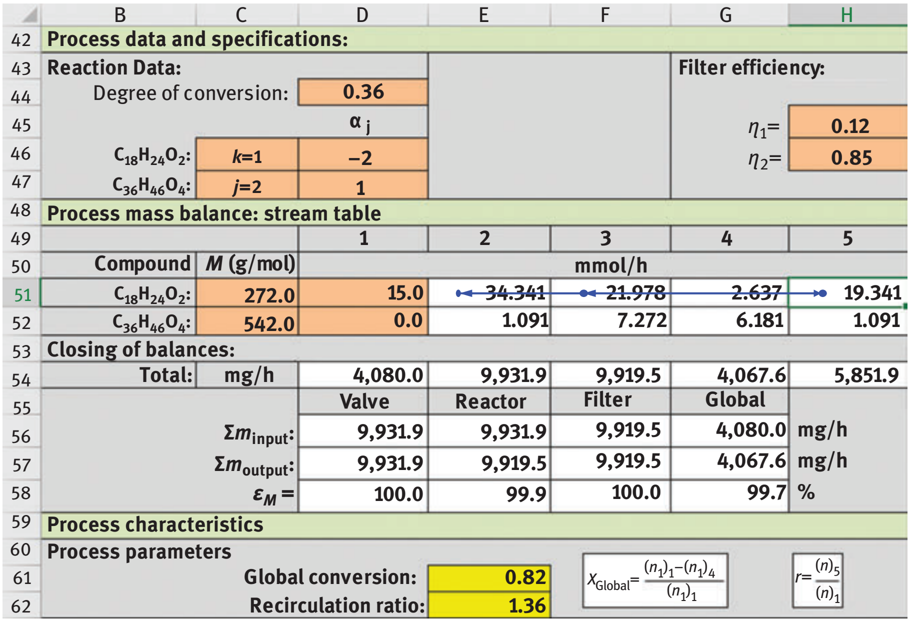
	A	B	C	D	E	F	G	H	I	J
64	**Sequential calculation (iterations)**									
65										
66			**Iteration**							
67			**Initial valor**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
68	**Feed:**									
69		$(n_1)_1 =$	15.00	15.00	15.00	15.00	15.00	15.00	15.00	15.00
70		$(n_2)_1 =$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
71	**Valve**									
72	$(n_1)_2 = (n_1)_1 + (n_1)_5$		15.00	23.45	28.21	30.89	32.39	33.24	33.72	33.99
73	$(n_2)_2 = (n_2)_1 + (n_2)_5$		0.00	0.41	0.69	0.87	0.96	1.02	1.05	1.07
74	**Reactor (R-101):**									
75	$(n_1)_3 = (n_1)_2 \cdot (1 - \zeta_1)$		9.60	15.01	18.05	19.77	20.73	21.28	21.58	21.76
76	$(n_2)_3 = (n_2)_2 - (n_1)_2 \cdot \zeta_1 \cdot \frac{\alpha_2}{\alpha_1}$		2.70	4.63	5.77	6.43	6.79	7.00	7.12	7.19
77	**Filter (F-101):**									
78	$(n_1)_4 = \eta_1 \cdot (n_1)_3$		1.15	1.80	2.17	2.37	2.49	2.55	2.59	2.61
79	$(n_2)_4 = \eta_2 \cdot (n_2)_3$		2.30	3.93	4.91	5.46	5.78	5.95	6.05	6.11
80	$(n_1)_5 = (n_1)_3 - (n_1)_4$		8.45	13.21	15.89	17.39	18.24	18.72	18.99	19.14
81	$(n_2)_5 = (n_2)_3 - (n_2)_4$		0.41	0.69	0.87	0.96	1.02	1.05	1.07	1.08
82		Σm_{input}(mg/h)	4,080.0	4,080.0	4,080.0	4,080.0	4,080.0	4,080.0	4,080.0	4,080.0
83		Σm_{output}(mg/h):	1,557.2	2,620.9	3,247.9	3,605.2	3,807.1	3,920.9	3,985.0	4,021.1
84		ε_M (%) =	38.2	64.2	79.6	88.4	93.3	96.1	97.7	98.6
85										

Figure 4.5: Iterative calculation when applying the sequential solution method to Example 4.2.



	B	C	D	E	F	G	H
42	**Process data and specifications:**						**(a)**
43	**Reaction data:**					**Filter efficiency:**	
44			**0.36**				
45			α_j			$\eta_1=$	**0.12**
46	$C_{18}H_{24}O_2$:	$k=1$	**−2**			$\eta_2=$	**0.85**
47	$C_{36}H_{46}O_4$:	$j=2$	**1**				
48	**Process mass balance: S^-**						
49			**1**	**2**	**3**	**4**	**5**
50	**Compound**	**M (g/mol)**			**mmol/h**		
51	$C_{18}H_{24}O_2$:	272	15	**=D51+H51**	**=E51*(1−D44)**	**=F51*H45**	**=F51−G51**
52	$C_{36}H_{46}O_4$:	542	0	**=D52+H52**	**=E52−E51*D44*(D47/D46**	**=F52*H46**	**=F52−G52**
53	**Closing of balances:**						
54	**Total:**	**mg/h**	**=D51*C51+D52*C52**	**=E51*C51+E52*C52**	**=E51*C51+F52*C52**	**=G51*C51+G52*C52**	**=H51*C51+H52*C52**
55			**Valve**	**Reactor**	**Filter**	**Global**	
56		Σm_{input}:	**=D54+H54**	**=E54**	**=F54**	**=D54**	**mg/h**
57		Σm_{output}:	**=E54**	**=E54**	**=G54+H54**	**=G54**	**mg/h**
58		$\varepsilon_M=$	**=(D57/D56)*100**	**=(E57/E56)*100**	**=(F57/F56)*100**	**=(G57/G56)*100**	**%**
59							
60	**Process characteristics**						
61	**Process parameters**						
62			**Global conversion:**	**=((D51−G51)/D51)**	$X_{Global}=\frac{(n_1)_1-(n_1)_4}{(n_1)_1}$		$r=\frac{(n)_5}{(n)_1}$
63			**Recirculation ratio:**	**=((H51+H52)/(D51+D52))**			

Figure 4.6: (a) Cells with the formulas to apply the modular sequential method by circular reference in Example 4.2 and (b) result after enabling the calculation with circular reference.
Press CTRL + ` (grave accent): Switch between displaying formulas and their results.



	B	C	D	E	F	G	H
42	**Process data and specifications:**						
43	**Reaction Data:**					**Filter efficiency:**	
44	Degree of conversion:		0.36				
45			α j			η_1=	0.12
46	$C_{18}H_{24}O_2$:	k=1	−2			η_2=	0.85
47	$C_{36}H_{46}O_4$:	j=2	1				
48	**Process mass balance: stream table**						
49			1	2	3	4	5
50	Compound	M (g/mol)	mmol/h				
51	$C_{18}H_{24}O_2$:	272.0	15.0	34.341	21.978	2.637	19.341
52	$C_{36}H_{46}O_4$:	542.0	0.0	1.091	7.272	6.181	1.091
53	**Closing of balances:**						
54	Total:	mg/h	4,080.0	9,931.9	9,919.5	4,067.6	5,851.9
55			Valve	Reactor	Filter	Global	
56		Σm_{input}:	9,931.9	9,931.9	9,919.5	4,080.0	mg/h
57		Σm_{output}:	9,931.9	9,919.5	9,919.5	4,067.6	mg/h
58		ε_M =	100.0	99.9	100.0	99.7	%
59	**Process characteristics**						
60	**Process parameters**						
61		Global conversion:		0.82	$X_{Global}=\frac{(n_1)_1-(n_1)_4}{(n_1)_1}$		$r=\frac{(n)_5}{(n)_1}$
62		Recirculation ratio:		1.36			

Figure 4.6 (continued)

4.3 Synthesis of methanol

Methanol (CH_3OH) is the most significant representative of the group of organic compounds of a carbon atom (group C_1), which under normal conditions of pressure and temperature is presented as a colorless, flammable and toxic liquid that is used as antifreeze, solvent and fuel.

It is used as a raw material in the synthesis of other compounds of group C_1 such as formaldehyde (a key element in the manufacture of adhesives) and of group C_2 such as acetic acid (whose esters, vinyl acetate or cellulose acetate are the basis for the manufacture of nylon, cellophane and other polymers; Figure 4.7).

Methanol is produced primarily from synthesis gas from natural gas by catalytic reaction of hydrogen with CO_2 (Figure 4.8).

Natural gas desulfurized with 1.2% (% molar) N_2 (stream 1) undergoes catalytic reforming (cracking or methane rupture) in a multitubular furnace (H-101) where the synthesis gas is obtained by reacting with H_2O vapor at high temperatures:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad \text{Main reaction}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

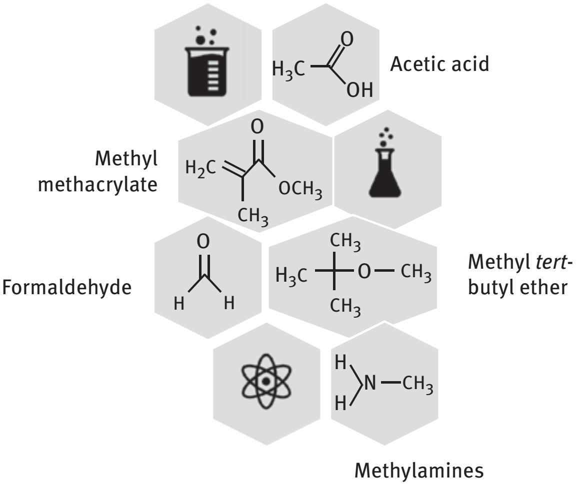


Figure 4.7: Different chemical compounds obtained from methanol, which in turn are the basis for different polymers.

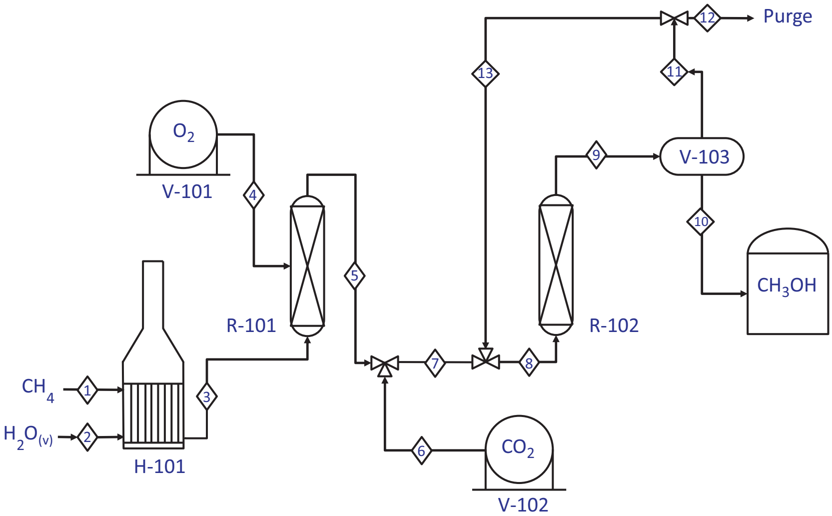


Figure 4.8: Simplified flowchart for methanol synthesis.

In order to favor a global conversion of methane, an excess of 12% is used in the water vapor (stream 2), with a yield of 88% CO_2 (H-101). A complete conversion of CO to CO_2 takes place by reaction with O_2 in stoichiometric quantities (R-101):

$$2CO + O_2 \longrightarrow 2CO_2$$

To the resulting synthesis gas a CO_2 stream is added that feeds the methanol synthesis reactor (R-102) along with the recirculation gas maintaining an H_2/CO_2 ratio of 3/1 at the reactor inlet (stream 8):

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

The degree of advancement of the CO_2 reaction is 52%. The output of the R-102 reactor cools and condenses methanol and water, recirculating the noncondensable gases, where a ratio of 3/1 H_2/CO_2 is maintained (stream 13). To avoid an increase in the concentration of inert materials, a purge is carried out in the synthesis circuit (contains 4% N_2).

On the basis of these data, a simulation of the process will be carried out based on the mass balances, which will make it possible to estimate the flow and composition of the expected raw methanol flow, as well as other operational characteristics of the process, for example, the relationship between the flow of the recirculation and purge flows.

4.3.1 Degrees of freedom

For the calculation of the number of degrees of freedom of the global process, it is necessary to determine the unknowns in function of the number of variables and process data, as well as the number of independent equations obtained by the sum of the number of matter balances and the number of implicit and explicit relations of the process:

- Variables:
  - The molar flows of the eight components (CH_4, H_2O, CO_2, H_2, N_2, CO, O_2 and CH_3OH) in each of the 13 streams: $(n_1)_1$, $(n_2)_1$, $(n_3)_1$, $(n_4)_1$, [..], $(n_6)_{13}$, $(n_7)_{13}$ and $(n_8)_{13}$,
  - The degrees of advancement of the four chemical reactions: ζ_1, ζ_2, ζ_3 and ζ_4
- Data:
  - Flows:
    - Concentration of N_2 in the streams 1 and 12
    - Excess H_2O in the stream 2
    - O_2 stoichiometric in the stream 4
  - Reactions:
    - Global conversion of CH_4 into H-101
    - Conversion of CO in R-101
    - Conversion of CO_2 in R-102
- Independent equations:
  - Balances:

  - Mass balances with or without chemical reaction in each of the process units: H-101, R-101, R-102 and V-103. As noted earlier in this chapter, the mixing and flow separation points are also control volumes where balances are made and, therefore, computed within the term "units": $\text{Valve}_{5/6\to7}$, $\text{Valve}_{7/13\to8}$ and $\text{Valve}_{11\to12/13}$
- Implicit relationships:
  - Stream 1: the flow rate of H_2O, CO_2, H_2, CO, O_2 and CH_3OH is zero
  - Stream 2: the flow rate of CH_4, CO_2, H_2, N_2, CO, O_2 and CH_3OH is zero
  - Stream 4: the flow rate of CH_4, H_2O, CO_2, H_2, N_2, CO and CH_3OH is zero
  - Stream 6: the flow rate of CH_4, H_2O, H_2, N_2, CO, O_2 and CH_3OH is zero
  - Streams 7 and 8: the flow rate of CH_3OH is zero
  - Streams 7, 8 and 9: the flow rate of H_2/CO_2 is 3/1
  - Streams 7 and 12: the flow rate of N_2 is the same
  - Stream 10: the flow rate of CO_2, H_2, N_2 is zero
  - Streams 11, 12 and 13:
    - The flow rate of H_2O and CH_3OH is zero
    - The concentration of N_2 in the three streams is the same
- Explicit relationships:
  - Mole ratio of H_2/CO_2 in the streams 8 and 13
  - CO_2 performance in H-101

Figure 4.9 shows the calculation of the number of degrees of freedom by applying eqs. (4.1)–(4.5). Depending on the number of degrees of freedom, cell B76 automatically shows the type of problem from the point of view of the specification.

In this example, the problem has a degree of freedom, being the one corresponding to the calculation base that is chosen for the solution of the problem.

4.3.2 Simulation based on mass balances: sequential modular method

To obtain the simulation (based on mass balances) of the process, proceed in the same way as described in the preceding chapters for the solution of mass balances.
Step 1: Flowchart with identification and enumeration of streams

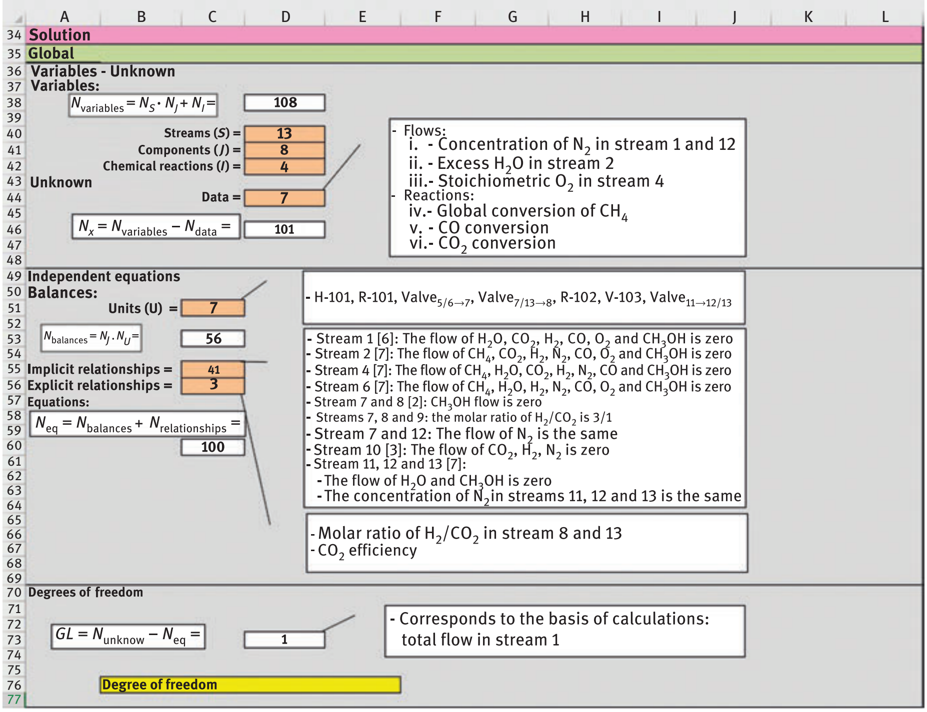
- Reaction data (Figure 4.10)
  - If we call $A_1 \equiv CH_4$, $A_2 \equiv H_2O$, $A_3 \equiv CO_2$, $A_4 \equiv H_2$, $A_5 \equiv N_2$, $A_6 \equiv CO$, $A_7 \equiv O_2$ and $A_8 \equiv CH_3OH$, the reactions can be expressed:

$$\text{R1:}\quad 4A_4 + A_3 - 2A_2 - A_1 = 0$$

$$\text{R2:}\quad A_6 + 3A_4 - A_2 - A_1 = 0$$

$$\text{R3:}\quad -A_7 - 2A_6 + 2A_3 = 0$$

$$\text{R4:}\quad A_8 - 3A_4 - A_3 + A_2 = 0$$



Solution

Global

Variables - Unknown

Variables:

$N_{variables} = N_S \cdot N_J + N_I =$ 108

Streams (S) = 13

Components (J) = 8

Chemical reactions (I) = 4

Unknown

Data = 7

- Flows:
  - i. - Concentration of N_2 in stream 1 and 12
  - ii. - Excess H_2O in stream 2
  - iii.- Stoichiometric O_2 in stream 4
- Reactions:
  - iv.- Global conversion of CH_4
  - v. - CO conversion
  - vi.- CO_2 conversion

$N_x = N_{variables} - N_{data} =$ 101

Independent equations

Balances:

Units (U) = 7

- H-101, R-101, $Valve_{5/6\rightarrow 7}$, $Valve_{7/13\rightarrow 8}$, R-102, V-103, $Valve_{11\rightarrow 12/13}$

$N_{balances} = N_J \cdot N_U =$ 56

Implicit relationships = 41

- Stream 1 [6]: The flow of H_2O, CO_2, H_2, CO, O_2 and CH_3OH is zero
- Stream 2 [7]: The flow of CH_4, CO_2, H_2, N_2, CO, O_2 and CH_3OH is zero
- Stream 4 [7]: The flow of CH_4, H_2O, CO_2, H_2, N_2, CO and CH_3OH is zero
- Stream 6 [7]: The flow of CH_4, H_2O, H_2, N_2, CO, O_2 and CH_3OH is zero
- Stream 7 and 8 [2]: CH_3OH flow is zero
- Streams 7, 8 and 9: the molar ratio of H_2/CO_2 is 3/1
- Stream 7 and 12: The flow of N_2 is the same
- Stream 10 [3]: The flow of CO_2, H_2, N_2 is zero
- Stream 11, 12 and 13 [7]:
  - The flow of H_2O and CH_3OH is zero
  - The concentration of N_2 in streams 11, 12 and 13 is the same

Explicit relationships = 3

- Molar ratio of H_2/CO_2 in stream 8 and 13
- CO_2 efficiency

Equations:

$N_{eq} = N_{balances} + N_{relationships} =$ 100

Degrees of freedom

$GL = N_{unknow} - N_{eq} =$ 1

- Corresponds to the basis of calculations: total flow in stream 1

Degree of freedom

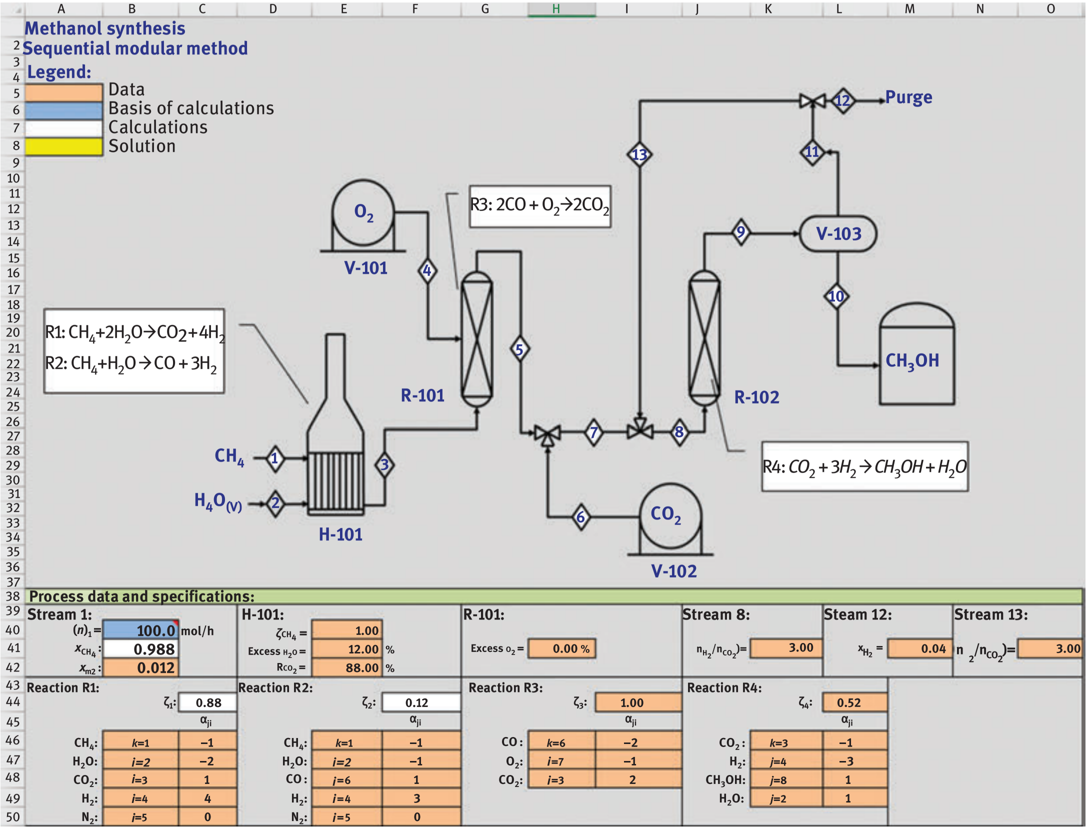
Figure 4.9: Calculation of the number of degrees of freedom in methanol synthesis.

- R1 and R2: CH_4 is the limiting reactant and therefore k = 1. The degree of advancement of each of these two reactions is unknown, but the overall conversion (i.e., the sum of the two) is 100%.
- R3: Since oxygen enters in stoichiometric quantities, any of the reactants can be considered a limiting factor. CO shall be considered as the limiting reactant, k = 6. The conversion is 100%.
- R4: The H_2/CO_2 input ratio in the R-102 reactor is 3/1 (stoichiometric conditions). The limiting reactant will be CO_2, that is, k = 3 for this reaction. The conversion is 52% CO_2.

- Process data and specifications:
  - Concentration of N_2 in streams 1 and 12:
    - Stream 1: The concentration of N_2 is 1.2% and, therefore, the molar fraction of CH_4

$$\left(x_{CH_4}\right)_1 = 1 - \left(x_{N_2}\right)_1 = 1 - 0.012 = 0.988$$

    - Stream 12: (x_{N2}) = 0.04.
  - Excess H_2O in the stream 2: 12%.



Methanol synthesis

Sequential modular method

Legend:

- 🟧 Data
- 🟦 Basis of calculations
- ⬜ Calculations
- 🟨 Solution

Process data and specifications:

Stream 1:

$(n)_1$ = 100.0 mol/h

x_{CH_4}: 0.988

x_{m2}: 0.012

H-101:

ζ_{CH_4} = 1.00

Excess H_2O = 12.00 %

R_{CO_2} = 88.00 %

R-101:

Excess O_2 = 0.00 %

Stream 8:

n_{H_2}/n_{CO_2})= 3.00

Steam 12:

x_{H_2} = 0.04

Stream 13:

n $_2/n_{CO_2}$)= 3.00

Reaction R1: ζ_1: 0.88

		α_{ji}
CH_4:	k=1	−1
H_2O:	i=2	−2
CO_2:	i=3	1
H_2:	i=4	4
N_2:	i=5	0

Reaction R2: ζ_2: 0.12

		α_{ji}
CH_4:	k=1	−1
H_2O:	i=2	−1
CO:	i=6	1
H_2:	i=4	3
N_2:	i=5	0

Reaction R3: ζ_3: 1.00

		α_{ji}
CO:	k=6	−2
O_2:	i=7	−1
CO_2:	i=3	2

Reaction R4: ζ_4: 0.52

		α_{ji}
CO_2:	k=3	−1
H_2:	j=4	−3
CH_3OH:	j=8	1
H_2O:	j=2	1

Figure 4.10: Data and specifications for the simulation of methanol synthesis.

- Stream 4 (inlet to R-101) containing O_2 has such a flow that the ratio is stoichiometric, that is, an excess of 0% (Cell H41).
- There are two additional data that refer to two explicit process relationships:
  - The CO_2 yield in reaction R1 is 88%.
  - The molar ratio in H_2/CO_2 in streams 8 and 13 is 3/1.

Step 2: Basis of calculations
The natural gas supply flow $(n)_1 = 100$ mol/h shall be considered as the calculation basis. Cell B40 is shown in Figure 4.10.

Step 3: Definition of the volume of control and formulation and resolution of the mass balances
The modular sequential method is based on the solution of the balances for each of the control units or volumes consecutively. The following equations shall be used for this purpose:

- Mass balance without chemical reaction:
  - Any component:

$$\Sigma(n_j)_{\text{input}} = \Sigma(n_j)_{\text{output}} \tag{4.11}$$

- Mass balance with chemical reaction:
  - Limiting reactant(k):

$$n_k = n_{ko}\left(1 - \sum_{i=1}^{h} \zeta_{ki}\right) \tag{4.12}$$

  - Other reactants and products(j):

$$n_j = n_{jo} - \sum_{i=1}^{h}\left(n_{k_0 i} \cdot \zeta_{ki} \cdot \frac{\alpha_{ji}}{\alpha_{ki}}\right) \tag{4.13}$$

  - Component in excess(j):

$$\%A_j = \frac{{n_{jo}}/{\alpha_j} - {n_{ko}}/{\alpha_k}}{{n_{ko}}/{\alpha_k}} \cdot 100 \tag{4.14}$$

  - Performance of a component(j):

$$R_j = \frac{n_{jo} - n_j}{n_{ko}} \cdot \frac{\alpha_k}{\alpha_j} \tag{4.15}$$

Feed streams

From the total molar flow of stream 1 (calculation basis) and the composition of each component the molar flow of each component can be calculated:

$$(n_1)_1 = (n)_1 \cdot (x_1)_1$$

$$(n_5)_1 = (n)_1 \cdot (x_5)_1$$

They are introduced into cells C54 and C58 (Figure 4.11) to obtain values of 98.80 and 1.20 mol/h, respectively:

C54: = $B$40*B41
C58: = $B$40*B42

The molar flow rate for all other components in stream 1 is zero (implicit ratio). In stream 2, the molar flow of H_2O is obtained by clearing the value of $(n_2)_2$ from eq. (4.14):

$$(n_2)_2 = \frac{\alpha_{21}}{\alpha_{11}} (n_1)_1 \left[1 + \left(\frac{\%\ A_{21}}{100}\right)\right]$$

This equation is introduced in cell D55 that reflects a value of 221.31 mol/h. The molar flow rate for the rest of the components in stream 2 is zero.

D55: = (C47/C46)*C54*(1 +(E41/100))

Furnace H-101

First, it will be necessary to calculate the degree of progress for each of the reactions that occur in the furnace. For this purpose, from the CO_2 yield (eq. (4.11)) the molar flow of CO_2 at the exit of the furnace can be calculated to then obtain the degree of progress of the first reaction when considering the CO_2 balance (eq. 4.10) since only the first of the reactions is involved in its formation:

$$R_3 = \frac{(n_3)_{[1-2]} - (n_3)_3}{(n_1)_1} \cdot \frac{\alpha_{11}}{\alpha_{31}} \quad \Rightarrow \quad (n_3)_3 = (n_3)_{[1-2]} - \left((n_1)_1 \cdot R_3 \cdot \frac{\alpha_{31}}{\alpha_{11}}\right)$$

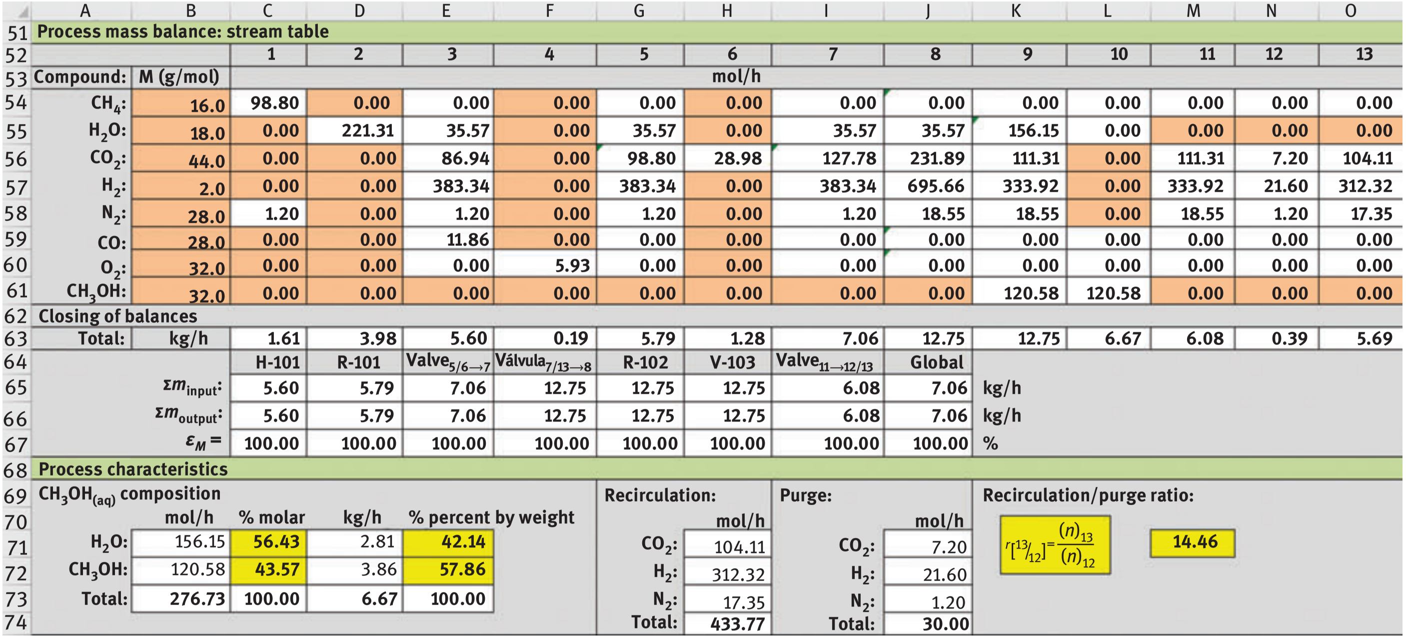
$$(n_3)_3 = (n_3)_{[1-2]} - (n_1)_1 \cdot \zeta_1 \cdot \frac{\alpha_{31}}{\alpha_{11}} \quad \Rightarrow \quad \zeta_1 = \frac{(n_3)_{[1-2]} - (n_3)_3}{(n_1)_1} \cdot \frac{\alpha_{11}}{\alpha_{31}}$$

Since the overall methane conversion is the sum of the conversions that are achieved in the two reactions, the degree of advancement of the second reaction can be obtained:

$$\zeta_{CH_4} = \zeta_1 + \zeta_2 \quad \Rightarrow \quad \zeta_2 = \zeta_{CH_4} - \zeta_1$$

These equations are introduced in cells E56 (Figure 4.10), C44 and F44 (Figure 4.11), respectively:

E56: = (C56 + D56)-(C54*(E42/100)*(C48/C46))
C44: = (((C56 + D56)–E56)/C54)*(C46/C48)
F44: = E40-C44



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
51	Process mass balance: stream table														
52			1	2	3	4	5	6	7	8	9	10	11	12	13
53	Compound:	M (g/mol)						mol/h							
54	CH_4:	16.0	98.80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
55	H_2O:	18.0	0.00	221.31	35.57	0.00	35.57	0.00	35.57	35.57	156.15	0.00	0.00	0.00	0.00
56	CO_2:	44.0	0.00	0.00	86.94	0.00	98.80	28.98	127.78	231.89	111.31	0.00	111.31	7.20	104.11
57	H_2:	2.0	0.00	0.00	383.34	0.00	383.34	0.00	383.34	695.66	333.92	0.00	333.92	21.60	312.32
58	N_2:	28.0	1.20	0.00	1.20	0.00	1.20	0.00	1.20	18.55	18.55	0.00	18.55	1.20	17.35
59	CO:	28.0	0.00	0.00	11.86	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
60	O_2:	32.0	0.00	0.00	0.00	5.93	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
61	CH_3OH:	32.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	120.58	120.58	0.00	0.00	0.00
62	Closing of balances														
63	Total:	kg/h	1.61	3.98	5.60	0.19	5.79	1.28	7.06	12.75	12.75	6.67	6.08	0.39	5.69
64			H-101	R-101	$Valve_{5/6\to7}$	$Válvula_{7/13\to8}$	R-102	V-103	$Valve_{11\to12/13}$	Global					
65		Σm_{input}:	5.60	5.79	7.06	12.75	12.75	12.75	6.08	7.06	kg/h				
66		Σm_{output}:	5.60	5.79	7.06	12.75	12.75	12.75	6.08	7.06	kg/h				
67		$\varepsilon_M =$	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	%				
68	Process characteristics														
69	$CH_3OH_{(aq)}$ composition						Recirculation:		Purge:		Recirculation/purge ratio:				
70		mol/h	% molar	kg/h	% percent by weight			mol/h		mol/h					
71	H_2O:	156.15	56.43	2.81	42.14		CO_2:	104.11	CO_2:	7.20	$r[^{13}/_{12}] = \frac{(n)_{13}}{(n)_{12}}$		14.46		
72	CH_3OH:	120.58	43.57	3.86	57.86		H_2:	312.32	H_2:	21.60					
73	Total:	276.73	100.00	6.67	100.00		N_2:	17.35	N_2:	1.20					
74							Total:	433.77	Total:	30.00					

Figure 4.11: Mass balances and process characteristics in the simulation of methanol synthesis.

The remaining molar flows of stream 3 for each of the components involved in the reaction are obtained by means of the corresponding balances with chemical reaction (eq. (4.9) and (4.10)), bearing in mind that the limiting reactant is CH_4:

Methane balance $\Rightarrow$ $(n_1)_3 = (n_1)_3 \cdot (1 - \zeta_1 - \zeta_2)$

Water balance $\Rightarrow$ $(n_2)_3 = (n_2)_2 - (n_1)_1 \cdot \zeta_1 \cdot \dfrac{\alpha_{21}}{\alpha_{11}} - (n_1)_1 \cdot \zeta_2 \cdot \dfrac{\alpha_{22}}{\alpha_{12}}$

Hydrogen balance $\Rightarrow$ $(n_4)_3 = (n_4)_1 - (n_1)_1 \cdot \zeta_1 \cdot \dfrac{\alpha_{41}}{\alpha_{11}} - (n_1)_1 \cdot \zeta_2 \cdot \dfrac{\alpha_{42}}{\alpha_{12}}$

Carbon monoxide balance $\Rightarrow$ $(n_6)_3 = (n_6)_1 - (n_1)_1 \cdot \zeta_2 \cdot \dfrac{\alpha_{62}}{\alpha_{12}}$

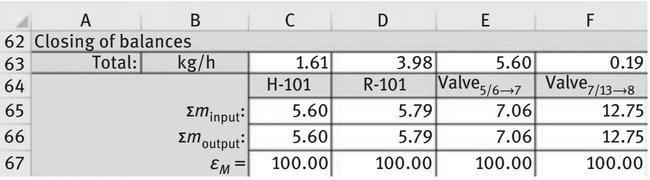
The molar nitrogen flow at the outlet of H-101 will be the same as at the inlet as it is an inert component (eq. (4.8)):

$$(n_5)_3 = (n_5)_1 + (n_5)_2$$

All these equations are entered into cells E54, E55, E57, E58, E59 and E60 (Figure 4.11). Stream 3 is fully characterized because the molar flow of oxygen and methanol is zero:

E54: = C54*(1-C44–F44)
E55: = D55–C54*C44*(C47/C46)–C54*F44*(F47/F46)
E57: = C57–C54*C44*(C49/C46)–C54*F44*(F49/F46)
E58: = (C58 + D58)
E59: = C59–C54*F44*(F48/F46)

The closing of balances for this unit is obtained with eq. (4.7), previously calculating the mass flow in streams 1, 2 and 3. This mass flow is obtained by multiplying the molar flow by the molecular weight of the components. As an example, the equation for the stream 1 in cell C63 is described (units of kg/h), being obtained in an analogous way for the rest of streams (Figure 4.12):



	A	B	C	D	E	F
62	Closing of balances					
63	Total:	kg/h	1.61	3.98	5.60	0.19
64			H-101	R-101	Valve$_{5/6\to7}$	Valve$_{7/13\to8}$
65		Σm_{input}:	5.60	5.79	7.06	12.75
66		Σm_{output}:	5.60	5.79	7.06	12.75
67		ε_M =	100.00	100.00	100.00	100.00

Figure 4.12: Closing balances for H-101.

C63: = (C54*$B$54 + C55*$B$55 + C56*$B$56 + C57*$B$57 + C58*$B$58 + C59*$B$59 + C60*$B$60 + C61*$B$61)/1000

Therefore, the incoming, outgoing and closing balance mass flow for the H-101 unit are presented in cells C65, C66 and C67, respectively:

C65: = C63 + D63
C66: = E63
C67: = (C66/C65)*100

The mass balance is closed with a value of 100%.

Reactor R-101

The input streams to the reactor are number 3 (fully characterized) and number 4, which corresponds to a flow of oxygen in stoichiometric conditions, that is, clearing the value of $(n_7)_4$ in eq. (4.14) for an excess value of zero (in this way it will be possible to simulate various situations later regarding the flow of oxygen):

$$(n_7)_2 = \frac{\alpha_{73}}{\alpha_{63}}(n_6)_3\left[1+\left(\frac{\%\ A_{73}}{100}\right)\right]$$

This equation is written in cell F60. All other values for stream 4 are zero (implicit ratio):

F60: = (I47/I46)*E59*(1 +(H41/100))

Analogously with eqs. (4.9) and (4.10) the molar flow at the reactor output (stream 5) can be obtained for the components involved in the reaction:

$$\text{Carbon dioxide balance} \quad \Rightarrow \quad (n_3)_5 = (n_3)_3 - (n_6)_3 \cdot \zeta_3 \cdot \frac{\alpha_{33}}{\alpha_{63}}$$

$$\text{Carbon monoxide balance} \quad \Rightarrow \quad (n_6)_5 = (n_6)_3 \cdot (1-\zeta_3)$$

$$\text{Oxygen balance} \quad \Rightarrow \quad (n_7)_5 = (n_7)_4 - (n_6)_3 \cdot \zeta_3 \cdot \frac{\alpha_{73}}{\alpha_{63}}$$

For the inert ones in the reaction (CH_4, H_2O, H_2, N_2) the balance corresponds to the eq. (4.8):

$$(n_j)_5 = (n_j)_3 + (n_j)_4$$

Therefore, these equations are introduced in cells G54 to G60 (Figure 4.10). In stream 5 the methanol value is zero, cell G61:

G54: = E54 + F54
G55: = E55 + F55
G56: = E56-E59*I44*(I48/I46)
G57: = E57 + F57
G58: = E58 + F58
G59: = E59*(1–I44)
G60: = F60-E59*I44*(I47/I46)

Control volume corresponding to valve$_{5/6\to 7}$

This control volume corresponds to the mixing point of stream 5 with stream 6 (CO_2) such that a stream 7 is obtained, which must have a ratio 3/1 of H_2/CO_2 because at the input of the reactor (stream 8) this ratio must be obtained. For the rest of the components, it is verified that the molar flow in stream 7 is identical to that of stream 5 (eq. (4.8)):

$$(n_j)_7 = (n_j)_5$$

The value of CO_2 in the streams 6 and 7 [$(n_3)_7$, $(n_3)_7$,] is obtained from the explicit relationship of the molar flows of H_2/CO_2 and the balance of CO_2 to the valve:

$$\left[r_{[4/3]_7}\right] = \left[r_{[4/3]_8}\right] = \left[r_{[4/3]_{13}}\right] \quad \Rightarrow \left[r_{[4/3]_7}\right] = \frac{(n_4)_7}{(n_3)_7} \quad \Rightarrow \quad (n_3)_7 = \frac{(n_4)_7}{\left[r_{[4/3]_7}\right]}$$

$$(n_3)_6 = (n_3)_7 - (n_3)_5$$

The rest of the molar flows in stream 6 are zero (implicit relation). These equations are introduced into the corresponding cells (Figure 4.10).

Control volume corresponding to valve$_{7/13\to 8}$

This control volume corresponds to the mixing point with the recirculation stream (stream 13) containing CO_2, H_2 and N_2. Therefore, when applying eq. (4.8):

$$\begin{array}{lll} CO_2, H_2 \text{ and } N_2\text{:} & \Rightarrow & (n_j)_8 = (n_j)_7 + (n_j)_{13} \\ \text{Other components:} & \Rightarrow & (n_j)_8 = (n_j)_7 \end{array}$$

Reactor R-102

Equations (4.9) and (4.10) allow to obtain the molar flow at the output of the reactor (stream 9) for the components involved in the reaction:

$$\text{Water vapor balance} \quad \Rightarrow \quad (n_2)_9 = (n_2)_8 - (n_3)_8 \cdot \zeta_4 \cdot \frac{\alpha_{24}}{\alpha_{34}}$$

$$\text{Carbon dioxide balance} \quad \Rightarrow \quad (n_3)_9 = (n_3)_8 \cdot (1 - \zeta_4)$$

$$\text{Hydrogen balance} \quad \Rightarrow \quad (n_4)_9 = (n_4)_8 - (n_3)_8 \cdot \zeta_4 \cdot \frac{\alpha_{44}}{\alpha_{34}}$$

$$\text{Methanol balance} \quad \Rightarrow \quad (n_8)_9 = (n_8)_8 - (n_3)_8 \cdot \zeta_4 \cdot \frac{\alpha_{84}}{\alpha_{34}}$$

For the inert ones in the reaction (in this case only N_2 enters the unit) the balance is given by the eq. (4.8):

$$(n_5)_9 = (n_5)_8$$

Condenser V-103

In the V-103 unit there is complete condensation of methanol and water (stream 10) while the gases CO_2, H_2 and N_2 come out through the stream 11. The balances (eq. (4.8)) are as follows:

$$\begin{array}{lcl} CH_3OH \text{ and } H_2O: & \Rightarrow & (n_j)_{10} = (n_j)_9 \\ CO_2, H_2 \text{ and } N_2: & \Rightarrow & (n_j)_{11} = (n_j)_9 \end{array}$$

Purge stream (12)

The main purpose of the purge stream is to avoid the accumulation of N_2 in the system, so the molar flow in stream 7 must be the same as in stream 12 (implicit relation):

$$(n_5)_{12} = (n_5)_7$$

Since the concentration of nitrogen in stream 12 is available (problem data) and the molar ratio of H_2/CO_2 in the same stream (separating streams have the same composition), it is possible to calculate the flows of CO_2 and H_2 in stream 12:

$$\begin{array}{c} (x_5)_{12} = \frac{(n_5)_{12}}{(n_3)_{12} + (n_4)_{12} + (n_5)_{12}} \\ \left[r_{[4/3]_{12}}\right] = \left[r_{[4/3]_{13}}\right] = \frac{(n_4)_{12}}{(n_3)_{12}} \end{array} \Rightarrow \begin{array}{c} (n_3)_{12} = \frac{(n_3)_{12} \cdot [1 - (x_5)_{12}]}{(x_5)_{12} \cdot \left(1 + \left[r_{[4/3]_{12}}\right]\right)} \\ (n_4)_{12} = (n_3)_{12} \cdot \left[r_{[4/3]_{12}}\right] \end{array}$$

Control volume corresponding to valve$_{11 \rightarrow 12/13}$

Stream 11 is subdivided into stream 12 (purge) and 13 (recirculation), being the balances for CO_2 and H_2 (eq. (4.8)):

$$(n_j)_{13} = (n_j)_{11} - (n_j)_{12}$$

By entering these equations in cells O56 and O57, the program will activate a “circular reference” message that must be enabled (see Appendix C) in order for the iterative calculation to be performed.

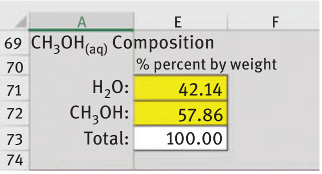
To calculate the molar flow of nitrogen in stream 13 it must be taken into account that the composition of N_2 in the same stream as in purge (dividing streams have the same composition):

$$(x_5)_{13} = (x_5)_{12} = \frac{(n_5)_{13}}{(n_3)_{13} + (n_4)_{13} + (n_5)_{13}} \qquad \Rightarrow \qquad (n_5)_{12} = \frac{(x_5)_{12} \cdot \left[(n_3)_{13} + (n_4)_{13}\right]}{1 - (x_5)_{13}}$$

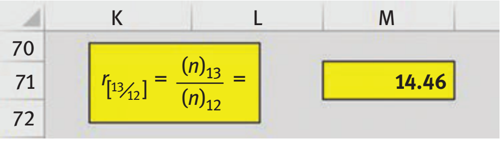
Step 4: Process characteristics

All the streams have been characterized and, therefore, the main characteristics of the process can be evaluated: composition of the product and relationship between the recirculation and purge stream.

Product composition:	**Relationship between recirculation and purge:**



	A	E	F
69	$CH_3OH_{(aq)}$ Composition		
70		% percent by weight	
71	H_2O:	42.14	
72	CH_3OH:	57.86	
73	Total:	100.00	
74			

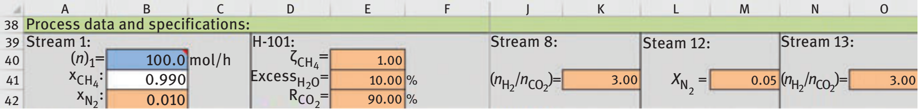


	K	L	M
70			
71	$r_{[13/12]} = \frac{(n)_{13}}{(n)_{12}} =$		14.46
72			

Questions/simulations:

i. *Effect of the calculation basis*: The calculation basis has no influence on the composition or relationship of the recirculation/purge ratio, although it does influence the molar flows. If, for example, the value of 250 mol/h is entered in the B40, the result will not change.

ii. *Scenario simulation*: Simulation makes it possible to evaluate the situation of the process in different scenarios by estimating the new characteristics of the process. If the data were considered as described in Figure 4.13, the methanol composition would increase to 58.92%.



	A	B	C	D	E	F	J	K	L	M	N	O
38	Process data and specifications:											
39	Stream 1:			H-101:			Stream 8:		Steam 12:		Stream 13:	
40	$(n)_1$=	100.0	mol/h	ζ_{CH_4}=	1.00							
41	x_{CH_4}:	0.990		$Excess_{H_2O}$=	10.00	%	(n_{H_2}/n_{CO_2})=	3.00	X_{N_2} =	0.05	(n_{H_2}/n_{CO_2})=	3.00
42	x_{N_2}:	0.010		R_{CO_2}=	90.00	%						

Figure 4.13: Process data and specifications for the new evaluated scenario.

4.4 Circular economy: obtaining sodium alginate from marine algae

Although the term *circular economy* was coined in the 1980s, it was not until the 2010s that it became widely used in all productive sectors. The circular economy is the intersection of environmental and economic aspects. The linear system of our economy (extraction, manufacture, use and disposal) has reached its limits. The technical feasibility of a production process is not synonymous of sustainability. The protection of existing resources must be ensured by taking into account the minimization of both resource consumption and, consequently, waste production, as well as the implementation of strategies for the recovery of waste. The production process is proposed under the premise that waste is a resource that is not used properly. Therefore, the circular economy proposes a new model of society that uses and optimizes stocks and flows of materials, energy and waste and aims to be efficient in the use of resources. It is based on a multi-R system (Figure 4.14): the waste of some

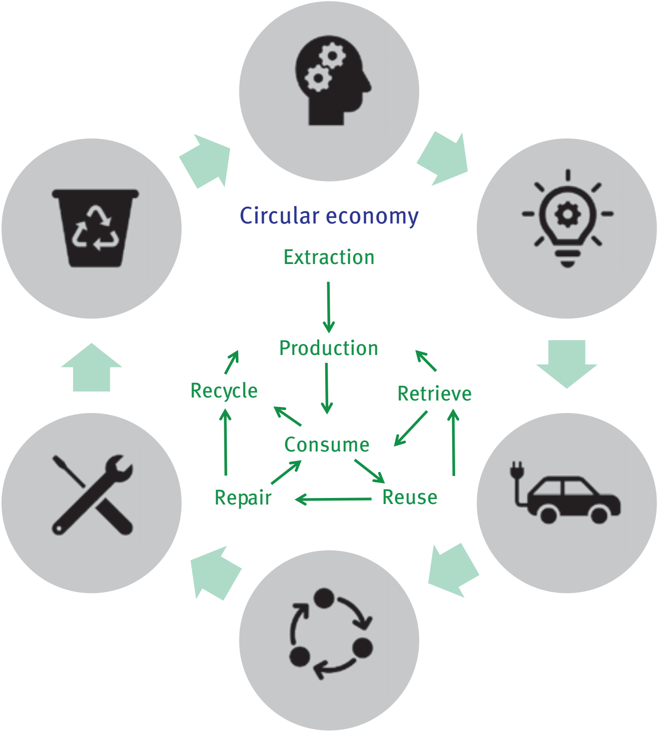


Figure 4.14: Multi-R system of the circular economy.

processes becomes a resource for others; the product must be designed to be deconstructed and repair and reuse are other elements in this new productive paradigm.

The application of circular economy strategies has reconfigured both production processes and defined new production or business models (Figure 4.15). One of these is based on obtaining energy and resources from waste, recovering the value of a product at the end of its life cycle for use in a new cycle and allowing waste to

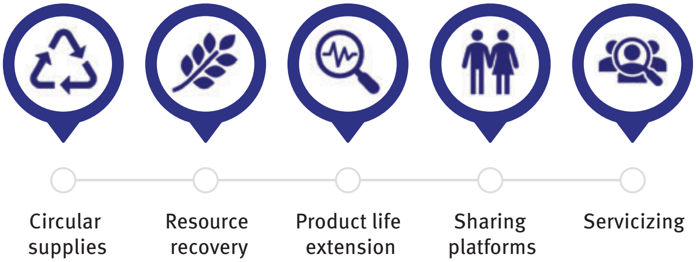


Figure 4.15: Business models arising from the perspective of the circular economy.

be transformed into value through innovative valorization systems. The solutions range from industrial symbiosis to integrated recycling in closed cycles or "Cradle to Cradle" systems. This model is ideal for companies that produce large volumes of waste or that can recover and reprocess waste in a profitable way.

Marine biotechnology (also called *blue biotechnology*) is an emerging sector for which annual growth is estimated at 10%, with a global market value of around 2.4 billion euros (year 2015). In recent decades, it has been possible to obtain a wide variety of high value-added products from marine organisms, with applications in the pharmaceutical, cosmetic or agri-food sectors, among others.

One of the most interesting raw materials is algae, from which high added-value products such as sodium alginate can be obtained. Pérez et al. (2014)[16] evaluated from an environmental perspective the use of *Sargassum muticum* (invasive species in the Galician coast) as a source for a biorefinery process where sodium alginate is one of the products obtained (Figure 4.16).

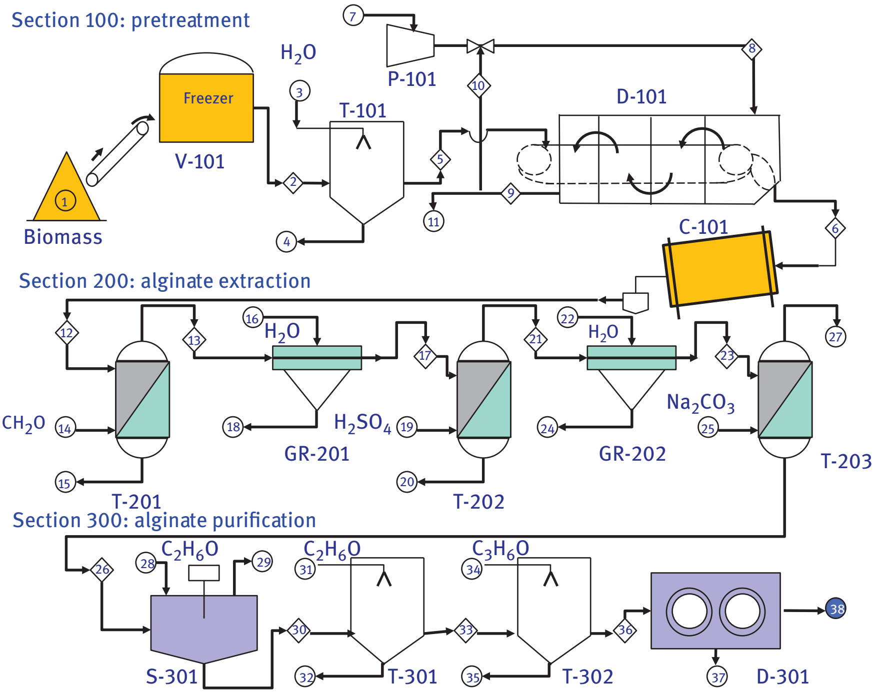


Figure 4.16: Flow diagram for obtaining sodium alginate from the algae *Sargassum muticum*.

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[16] Pérez-López et al. (2014). Comparative environmental assessment of valorization strategies of the invasive macroalgae *Sargassum muticum*. Bioresource Technology 161:137–148.

Biomass, once extracted from the sea, washed and transported to industrial facilities, contains (% by weight on a dry basis): 11.39% alginate, 20.61% extracts, 24.21% other components, 26.40% fines and 17.39% solid waste. The moisture content of the biomass is 85.5% (by weight). The algae are frozen for one week to facilitate the subsequent stages of alginate extraction and purification. The biomass is washed (T-101) with water (ratio of 54 L kg dry biomass) and then dried (D-101) in an air recirculation system under the following conditions:

- 97.8% water removal efficiency;
- humidity of fresh inlet air (stream 7): 0.002 kg H_2O/kg dry air;
- humidity of the air inlet to the dryer (stream 8): 0.006 kg H_2O/kg dry air;
- exhaust air humidity (stream 11): 0.016 kg H_2O/kg dry air.

The dried algae are then ground (C-101) prior to the units of the extraction section, which consists of the following stages:

i. Extraction with formaldehyde (T-201; ρ = 815 kg/m^3) to eliminate the fraction "other components" with an efficiency of 82.6% and a recovery of 92.8% of CH_2O. The extraction requires 565 mL of pure formaldehyde per kg of dry seaweed, for which a solution of 1% (volume) of CH_2O is used.
ii. Washing with H_2O (169.3 L/kg dry seaweed) and filtration (GR-201) that removes the remains of the formaldehyde solution, together with 97.6% of the washing water.
iii. Extraction with sulfuric acid (T-202; ρ = 1,800 kg/m^3) to remove heavy metals. A solution (0.2 N) is used in a ratio of 56.4 L/kg dry seaweed. 92.8% of the sulfuric acid is recovered in stream 20.
iv. Washing with H_2O (169.3 L/kg dry seaweed) and filtration (GR-202) that eliminates the remains of sulfuric acid with a recovery of 100% of the washing water in the stream 24.
v. This section ends with an extraction with a solution of Na_2CO_3 (56.4 L/kg dry seaweed) of a concentration of 1% that solubilizes the sodium alginate that is separated by stream 26, while the rest of the compounds are separated by stream 27 to feed other biorefinery processes. About 92.8% of Na_2CO_3 is recovered in stream 26.

The purification section has the following stages:

i. Precipitation (S-303) of sodium alginate (stream 30) and separation of the entire Na_2CO_3 (stream 29), by the addition of 95% ethanol (stream 28) with a flow of 200 L/kg Na_2CO_3. In stream 29, 100% of the ethanol and 95% of the incoming water are recovered.
ii. Washed with pure ethanol (T-301), 54.5 L/kg alginate, which separates all water by the stream 32 and with a 95% recovery of ethanol. The rest of the ethanol along with the sodium alginate is incorporated into stream 33.

iii. Washed with acetone (T-302), 74.3 L/kg alginate, which eliminates impurities, recovering 95% of the acetone in stream 35. Stream 36 contains alginate, ethanol and the rest of acetone.
iv. Finally, with a vacuum drying, ethanol and acetone are eliminated, obtaining pure sodium alginate in stream 38.

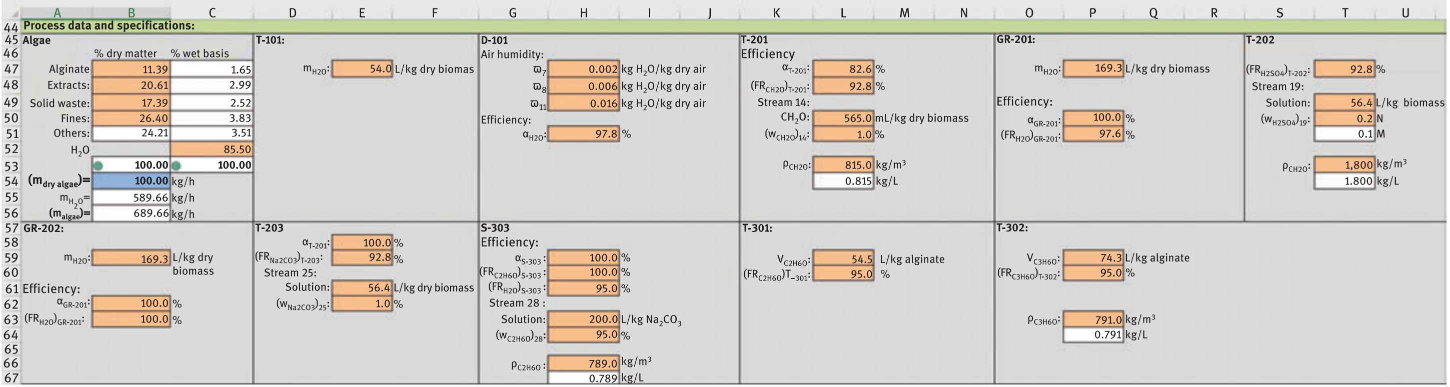
Calculate the daily production of sodium alginate for a feed stream of 100 kg/h of dry seaweed. In addition, determine the production yield (kg alginate/kg dry seaweed) and the air recirculation ratio in the D-101 dryer.

4.4.1 Simulation based on mass balances

To obtain the simulation (based on mass balances) of the process, proceed in the same way as described in the preceding chapters for the solution of mass balances.

Step 1: Flowchart with identification and enumeration of streams
Figure 4.16 corresponds to the flowchart of alginate production, which allows identification of the nomenclature and correlation of the starting data (Figure 4.17).

Step 2: Basis of calculations
The flow of dry algae is considered as the basis of calculation: 100 kg/h (cell B54 in Figure 4.18).



Process data and specifications:

Algae

	% dry matter	% wet basis
Alginate	11.39	1.65
Extracts:	20.61	2.99
Solid waste:	17.39	2.52
Fines:	26.40	3.83
Others:	24.21	3.51
H_2O		85.50
	100.00	100.00

$(m_{dry\ algae})=$ 100.00 kg/h

$m_{H_2O}=$ 589.66 kg/h

$(m_{algae})=$ 689.66 kg/h

T-101:

m_{H2O}: 54.0 L/kg dry biomas

D-101

Air humidity:

ϖ_7 0.002 kg H_2O/kg dry air

ϖ_8 0.006 kg H_2O/kg dry air

ϖ_{11} 0.016 kg H_2O/kg dry air

Efficiency:

α_{H2O}: 97.8 %

T-201

Efficiency

$\alpha_{T\text{-}201}$: 82.6 %

$(FR_{CH2O})_{T\text{-}201}$: 92.8 %

Stream 14:

CH_2O: 565.0 mL/kg dry biomass

$(w_{CH2O})_{14}$: 1.0 %

ρ_{CH2O}: 815.0 kg/m³

0.815 kg/L

GR-201:

m_{H2O}: 169.3 L/kg dry biomass

Efficiency:

$\alpha_{GR\text{-}201}$: 100.0 %

$(FR_{H2O})_{GR\text{-}201}$: 97.6 %

T-202

$(FR_{H2SO4})_{T\text{-}202}$: 92.8 %

Stream 19:

Solution: 56.4 L/kg biomass

$(w_{H2SO4})_{19}$: 0.2 N

0.1 M

ρ_{CH2O}: 1,800 kg/m³

1.800 kg/L

GR-202:

m_{H2O}: 169.3 L/kg dry biomass

Efficiency:

$\alpha_{GR\text{-}201}$: 100.0 %

$(FR_{H2O})_{GR\text{-}201}$: 100.0 %

T-203

$\alpha_{T\text{-}201}$: 100.0 %

$(FR_{Na2CO3})_{T\text{-}203}$: 92.8 %

Stream 25:

Solution: 56.4 L/kg dry biomass

$(w_{Na2CO3})_{25}$: 1.0 %

S-303

Efficiency:

$\alpha_{S\text{-}303}$: 100.0 %

$(FR_{C2H6O})_{S\text{-}303}$: 100.0 %

$(FR_{H2O})_{S\text{-}303}$: 95.0 %

Stream 28 :

Solution: 200.0 L/kg Na_2CO_3

$(w_{C2H6O})_{28}$: 95.0 %

ρ_{C2H6O} : 789.0 kg/m³

0.789 kg/L

T-301:

V_{C2H6O}: 54.5 L/kg alginate

$(FR_{C2H6O})T_{-301}$: 95.0 %

T-302:

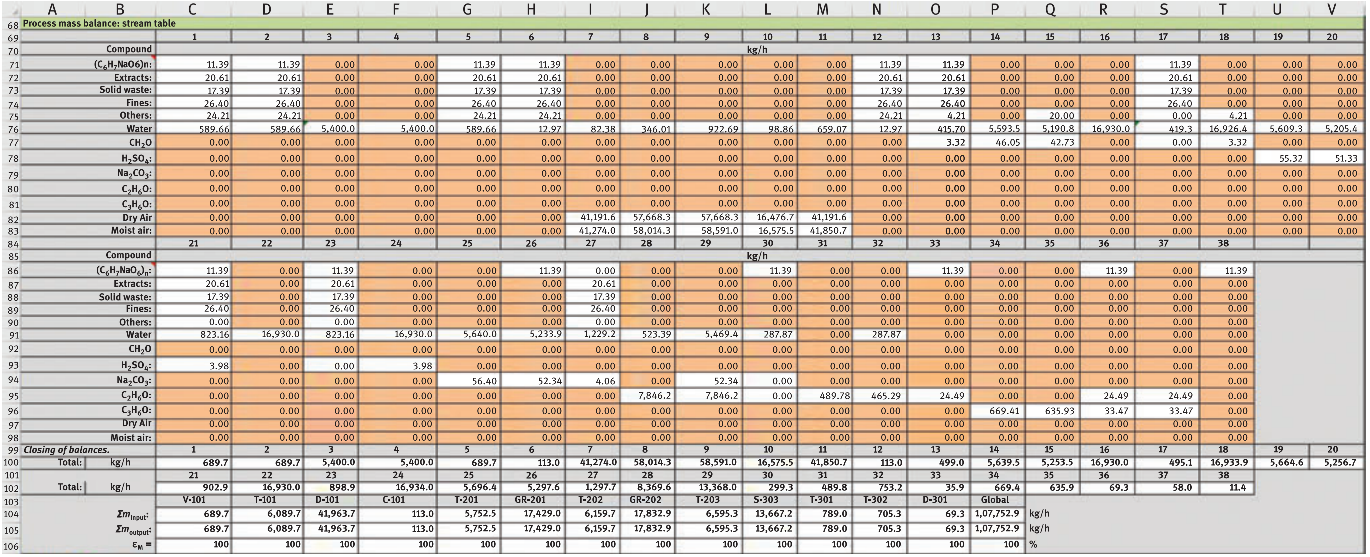
V_{C3H6O}: 74.3 L/kg alginate

$(FR_{C3H6O})_{T\text{-}302}$: 95.0 %

ρ_{C3H6O}: 791.0 kg/m³

0.791 kg/L

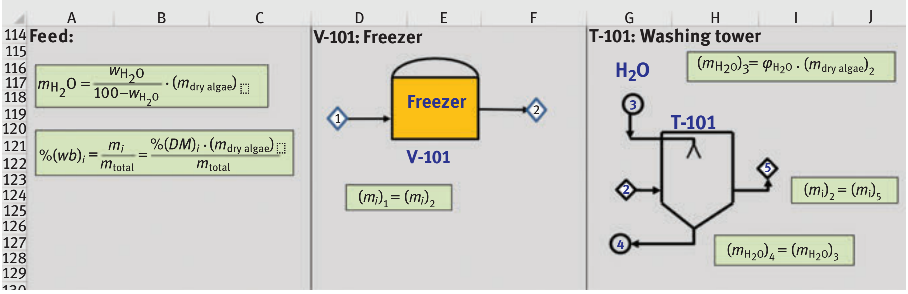
Figure 4.17: Data for the production of sodium alginate.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V
68	Process mass balance: stream table																					
69			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
70		Compound										kg/h										
71		$(C_6H_7NaO6)n$:	11.39	11.39	0.00	0.00	11.39	11.39	0.00	0.00	0.00	0.00	0.00	11.39	11.39	0.00	0.00	0.00	11.39	0.00	0.00	0.00
72		Extracts:	20.61	20.61	0.00	0.00	20.61	20.61	0.00	0.00	0.00	0.00	0.00	20.61	20.61	0.00	0.00	0.00	20.61	0.00	0.00	0.00
73		Solid waste:	17.39	17.39	0.00	0.00	17.39	17.39	0.00	0.00	0.00	0.00	0.00	17.39	17.39	0.00	0.00	0.00	17.39	0.00	0.00	0.00
74		Fines:	26.40	26.40	0.00	0.00	26.40	26.40	0.00	0.00	0.00	0.00	0.00	26.40	26.40	0.00	0.00	0.00	26.40	0.00	0.00	0.00
75		Others:	24.21	24.21	0.00	0.00	24.21	24.21	0.00	0.00	0.00	0.00	0.00	24.21	4.21	0.00	20.00	0.00	0.00	4.21	0.00	0.00
76		Water	589.66	589.66	5,400.0	5,400.0	589.66	12.97	82.38	346.01	922.69	98.86	659.07	12.97	415.70	5,593.5	5,190.8	16,930.0	419.3	16,926.4	5,609.3	5,205.4
77		CH_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.32	46.05	42.73	0.00	0.00	3.32	0.00	0.00
78		H_2SO_4:	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	55.32	51.33
79		Na_2CO_3:	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80		C_2H_6O:	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
81		C_3H_6O:	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
82		Dry Air	0.00	0.00	0.00	0.00	0.00	0.00	41,191.6	57,668.3	57,668.3	16,476.7	41,191.6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
83		Moist air:	0.00	0.00	0.00	0.00	0.00	0.00	41,274.0	58,014.3	58,591.0	16,575.5	41,850.7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84			21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38		
85		Compound										kg/h										
86		$(C_6H_7NaO_6)_n$:	11.39	0.00	11.39	0.00	0.00	11.39	0.00	0.00	0.00	11.39	0.00	0.00	11.39	0.00	0.00	11.39	0.00	11.39		
87		Extracts:	20.61	0.00	20.61	0.00	0.00	0.00	20.61	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
88		Solid waste:	17.39	0.00	17.39	0.00	0.00	0.00	17.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
89		Fines:	26.40	0.00	26.40	0.00	0.00	0.00	26.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
90		Others:	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
91		Water	823.16	16,930.0	823.16	16,930.0	5,640.0	5,233.9	1,229.2	523.39	5,469.4	287.87	0.00	287.87	0.00	0.00	0.00	0.00	0.00	0.00		
92		CH_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
93		H_2SO_4:	3.98	0.00	0.00	3.98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
94		Na_2CO_3:	0.00	0.00	0.00	0.00	56.40	52.34	4.06	0.00	52.34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
95		C_2H_6O:	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7,846.2	7,846.2	0.00	489.78	465.29	24.49	0.00	0.00	24.49	24.49	0.00		
96		C_3H_6O:	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	669.41	635.93	33.47	33.47	0.00		
97		Dry Air	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
98		Moist air:	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
99	*Closing of balances.*		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
100	Total:	kg/h	689.7	689.7	5,400.0	5,400.0	689.7	113.0	41,274.0	58,014.3	58,591.0	16,575.5	41,850.7	113.0	499.0	5,639.5	5,253.5	16,930.0	495.1	16,933.9	5,664.6	5,256.7
101			21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38		
102	Total:	kg/h	902.9	16,930.0	898.9	16,934.0	5,696.4	5,297.6	1,297.7	8,369.6	13,368.0	299.3	489.8	753.2	35.9	669.4	635.9	69.3	58.0	11.4		
103			V-101	T-101	D-101	C-101	T-201	GR-201	T-202	GR-202	T-203	S-303	T-301	T-302	D-301	Global						
104		Σm_{input}:	689.7	6,089.7	41,963.7	113.0	5,752.5	17,429.0	6,159.7	17,832.9	6,595.3	13,667.2	789.0	705.3	69.3	1,07,752.9	kg/h					
105		Σm_{output}:	689.7	6,089.7	41,963.7	113.0	5,752.5	17,429.0	6,159.7	17,832.9	6,595.3	13,667.2	789.0	705.3	69.3	1,07,752.9	kg/h					
106		ε_M =	100	100	100	100	100	100	100	100	100	100	100	100	100	100	%					

Figure 4.18: Stream table.

Step 3: Definition of the volume of control and formulation and resolution of the mass balances.



Feed:

$$m_{H_2O} = \frac{w_{H_2O}}{100 - w_{H_2O}} \cdot (m_{\text{dry algae}})$$

$$\%(wb)_i = \frac{m_i}{m_{\text{total}}} = \frac{\%(DM)_i \cdot (m_{\text{dry algae}})}{m_{\text{total}}}$$

V-101: Freezer

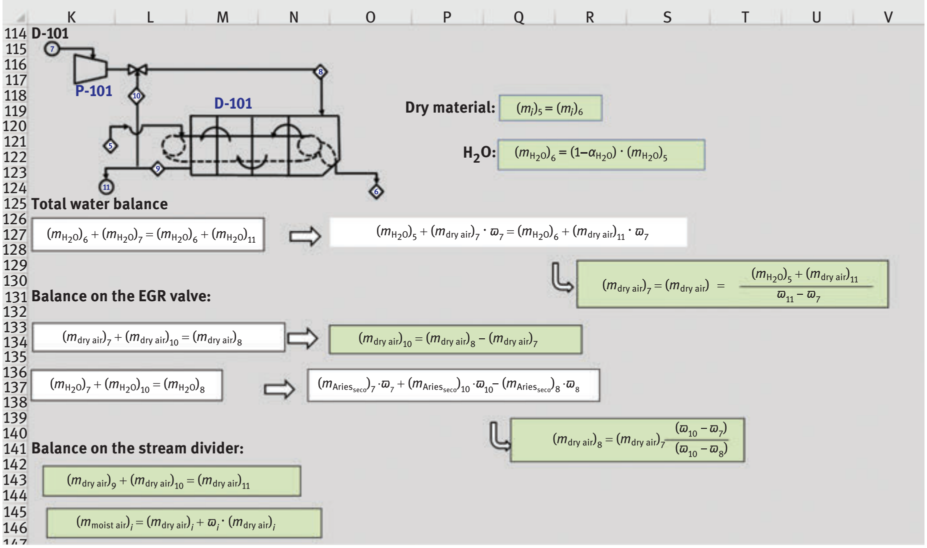
$$(m_i)_1 = (m_i)_2$$

T-101: Washing tower

$$(m_{H_2O})_3 = \varphi_{H_2O} \cdot (m_{\text{dry algae}})_2$$

$$(m_i)_2 = (m_i)_5$$

$$(m_{H_2O})_4 = (m_{H_2O})_3$$



D-101

Dry material: $(m_i)_5 = (m_i)_6$

H₂O: $(m_{H_2O})_6 = (1 - \alpha_{H_2O}) \cdot (m_{H_2O})_5$

Total water balance

$$(m_{H_2O})_6 + (m_{H_2O})_7 = (m_{H_2O})_6 + (m_{H_2O})_{11} \Rightarrow (m_{H_2O})_5 + (m_{\text{dry air}})_7 \cdot \varpi_7 = (m_{H_2O})_6 + (m_{\text{dry air}})_{11} \cdot \varpi_7$$

$$(m_{\text{dry air}})_7 = (m_{\text{dry air}}) = \frac{(m_{H_2O})_5 + (m_{\text{dry air}})_{11}}{\varpi_{11} - \varpi_7}$$

Balance on the EGR valve:

$$(m_{\text{dry air}})_7 + (m_{\text{dry air}})_{10} = (m_{\text{dry air}})_8 \Rightarrow (m_{\text{dry air}})_{10} = (m_{\text{dry air}})_8 - (m_{\text{dry air}})_7$$

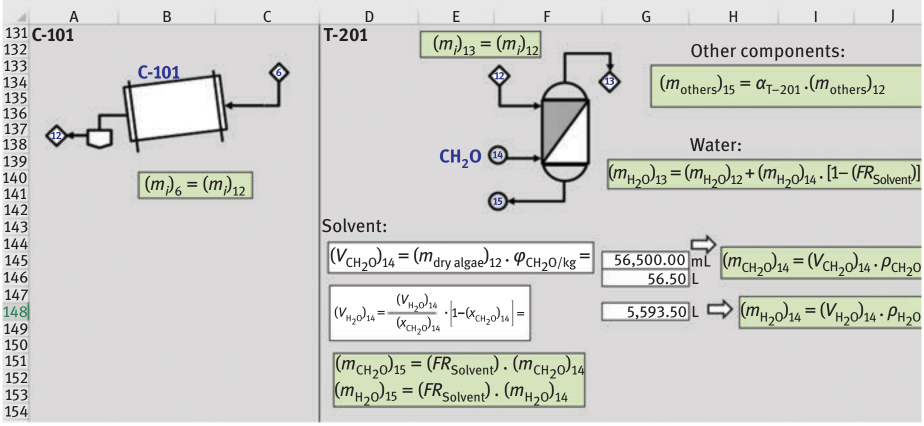
$$(m_{H_2O})_7 + (m_{H_2O})_{10} = (m_{H_2O})_8 \Rightarrow (m_{\text{Aries}_{\text{seco}}})_7 \cdot \varpi_7 + (m_{\text{Aries}_{\text{seco}}})_{10} \cdot \varpi_{10} - (m_{\text{Aries}_{\text{seco}}})_8 \cdot \varpi_8$$

$$(m_{\text{dry air}})_8 = (m_{\text{dry air}})_7 \frac{(\varpi_{10} - \varpi_7)}{(\varpi_{10} - \varpi_8)}$$

Balance on the stream divider:

$$(m_{\text{dry air}})_9 + (m_{\text{dry air}})_{10} = (m_{\text{dry air}})_{11}$$

$$(m_{\text{moist air}})_i = (m_{\text{dry air}})_i + \varpi_i \cdot (m_{\text{dry air}})_i$$



C-101

$$(m_i)_6 = (m_i)_{12}$$

T-201

$$(m_i)_{13} = (m_i)_{12}$$

Other components:

$$(m_{\text{others}})_{15} = \alpha_{T-201} \cdot (m_{\text{others}})_{12}$$

Water:

$$(m_{H_2O})_{13} = (m_{H_2O})_{12} + (m_{H_2O})_{14} \cdot [1 - (FR_{\text{Solvent}})]$$

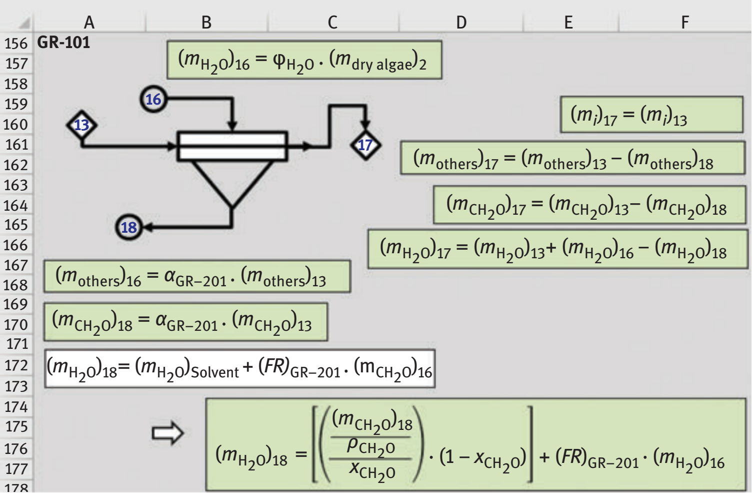
Solvent:

$$(V_{CH_2O})_{14} = (m_{\text{dry algae}})_{12} \cdot \varphi_{CH_2O/kg} = 56{,}500.00 \text{ mL} = 56.50 \text{ L} \Rightarrow (m_{CH_2O})_{14} = (V_{CH_2O})_{14} \cdot \rho_{CH_2O}$$

$$(V_{H_2O})_{14} = \frac{(V_{H_2O})_{14}}{(x_{CH_2O})_{14}} \cdot \left|1 - (x_{CH_2O})_{14}\right| = 5{,}593.50 \text{ L} \Rightarrow (m_{H_2O})_{14} = (V_{H_2O})_{14} \cdot \rho_{H_2O}$$

$$(m_{CH_2O})_{15} = (FR_{\text{Solvent}}) \cdot (m_{CH_2O})_{14}$$

$$(m_{H_2O})_{15} = (FR_{\text{Solvent}}) \cdot (m_{H_2O})_{14}$$



GR-101

$(m_{H_2O})_{16} = \varphi_{H_2O} \cdot (m_{dry\ algae})_2$

$(m_i)_{17} = (m_i)_{13}$

$(m_{others})_{17} = (m_{others})_{13} - (m_{others})_{18}$

$(m_{CH_2O})_{17} = (m_{CH_2O})_{13} - (m_{CH_2O})_{18}$

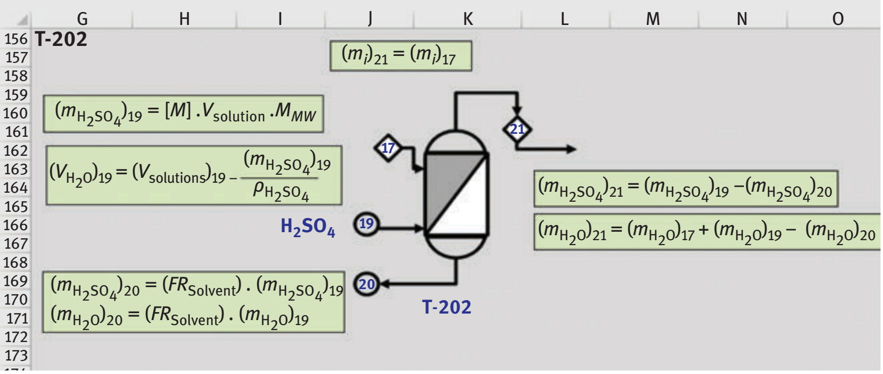
$(m_{H_2O})_{17} = (m_{H_2O})_{13} + (m_{H_2O})_{16} - (m_{H_2O})_{18}$

$(m_{others})_{16} = \alpha_{GR-201} \cdot (m_{others})_{13}$

$(m_{CH_2O})_{18} = \alpha_{GR-201} \cdot (m_{CH_2O})_{13}$

$(m_{H_2O})_{18} = (m_{H_2O})_{Solvent} + (FR)_{GR-201} \cdot (m_{CH_2O})_{16}$

$$\Rightarrow \quad (m_{H_2O})_{18} = \left[\left(\frac{\frac{(m_{CH_2O})_{18}}{\rho_{CH_2O}}}{x_{CH_2O}}\right) \cdot (1 - x_{CH_2O})\right] + (FR)_{GR-201} \cdot (m_{H_2O})_{16}$$



T-202

$(m_i)_{21} = (m_i)_{17}$

$(m_{H_2SO_4})_{19} = [M] \cdot V_{solution} \cdot M_{MW}$

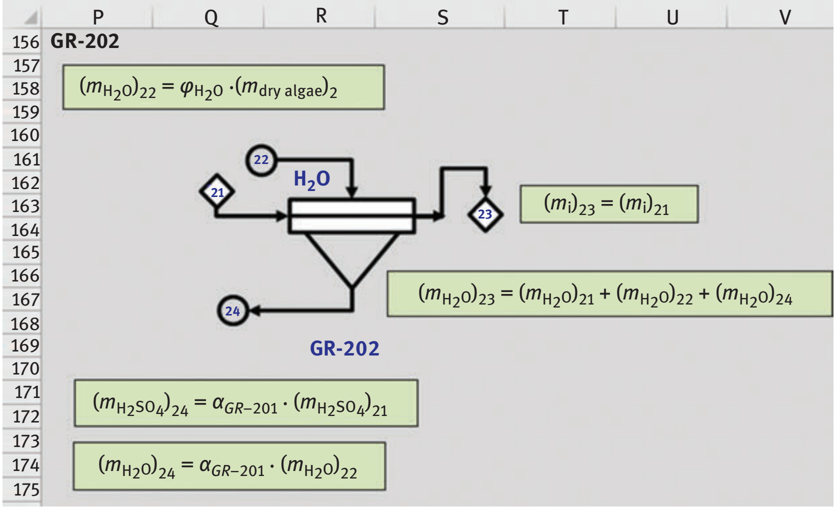
$(V_{H_2O})_{19} = (V_{solutions})_{19} - \frac{(m_{H_2SO_4})_{19}}{\rho_{H_2SO_4}}$

$(m_{H_2SO_4})_{21} = (m_{H_2SO_4})_{19} - (m_{H_2SO_4})_{20}$

$(m_{H_2O})_{21} = (m_{H_2O})_{17} + (m_{H_2O})_{19} - (m_{H_2O})_{20}$

$(m_{H_2SO_4})_{20} = (FR_{Solvent}) \cdot (m_{H_2SO_4})_{19}$

$(m_{H_2O})_{20} = (FR_{Solvent}) \cdot (m_{H_2O})_{19}$



GR-202

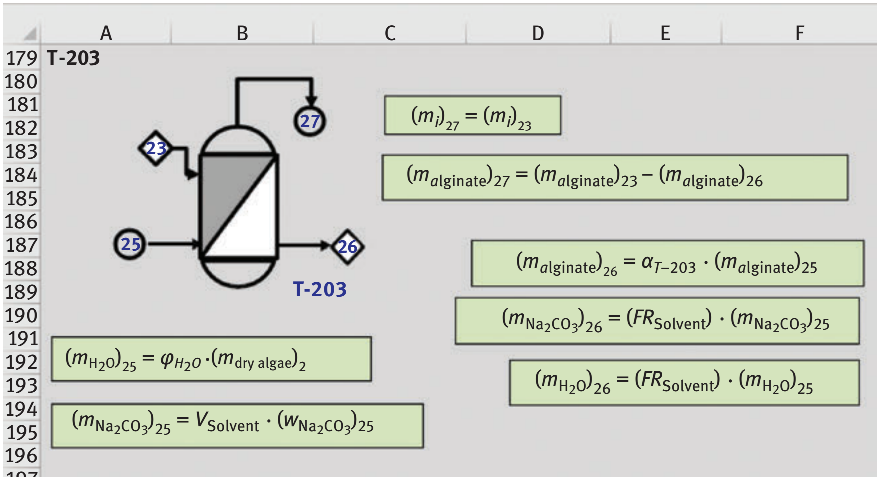
$(m_{H_2O})_{22} = \varphi_{H_2O} \cdot (m_{dry\ algae})_2$

$(m_i)_{23} = (m_i)_{21}$

$(m_{H_2O})_{23} = (m_{H_2O})_{21} + (m_{H_2O})_{22} + (m_{H_2O})_{24}$

$(m_{H_2SO_4})_{24} = \alpha_{GR-201} \cdot (m_{H_2SO_4})_{21}$

$(m_{H_2O})_{24} = \alpha_{GR-201} \cdot (m_{H_2O})_{22}$



$$(m_i)_{27} = (m_i)_{23}$$

$$(m_{\text{alginate}})_{27} = (m_{\text{alginate}})_{23} - (m_{\text{alginate}})_{26}$$

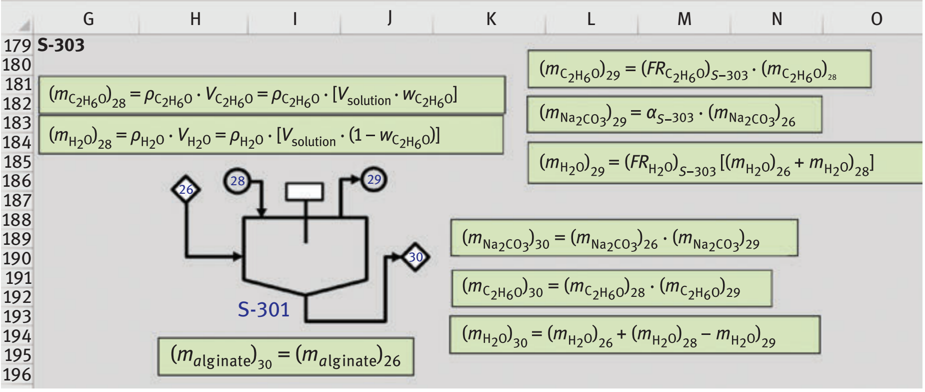
$$(m_{\text{alginate}})_{26} = \alpha_{T-203} \cdot (m_{\text{alginate}})_{25}$$

$$(m_{Na_2CO_3})_{26} = (FR_{\text{Solvent}}) \cdot (m_{Na_2CO_3})_{25}$$

$$(m_{H_2O})_{26} = (FR_{\text{Solvent}}) \cdot (m_{H_2O})_{25}$$

$$(m_{H_2O})_{25} = \varphi_{H_2O} \cdot (m_{\text{dry algae}})_2$$

$$(m_{Na_2CO_3})_{25} = V_{\text{Solvent}} \cdot (w_{Na_2CO_3})_{25}$$



$$(m_{C_2H_6O})_{28} = \rho_{C_2H_6O} \cdot V_{C_2H_6O} = \rho_{C_2H_6O} \cdot [V_{\text{solution}} \cdot w_{C_2H_6O}]$$

$$(m_{H_2O})_{28} = \rho_{H_2O} \cdot V_{H_2O} = \rho_{H_2O} \cdot [V_{\text{solution}} \cdot (1 - w_{C_2H_6O})]$$

$$(m_{C_2H_6O})_{29} = (FR_{C_2H_6O})_{S-303} \cdot (m_{C_2H_6O})_{28}$$

$$(m_{Na_2CO_3})_{29} = \alpha_{S-303} \cdot (m_{Na_2CO_3})_{26}$$

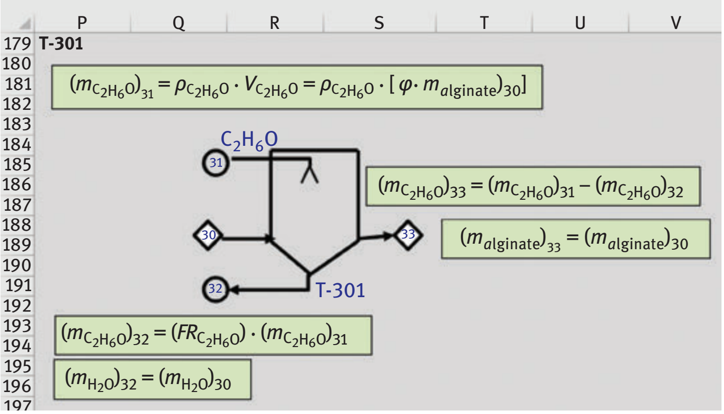
$$(m_{H_2O})_{29} = (FR_{H_2O})_{S-303} [(m_{H_2O})_{26} + m_{H_2O})_{28}]$$

$$(m_{Na_2CO_3})_{30} = (m_{Na_2CO_3})_{26} \cdot (m_{Na_2CO_3})_{29}$$

$$(m_{C_2H_6O})_{30} = (m_{C_2H_6O})_{28} \cdot (m_{C_2H_6O})_{29}$$

$$(m_{H_2O})_{30} = (m_{H_2O})_{26} + (m_{H_2O})_{28} - m_{H_2O})_{29}$$

$$(m_{\text{alginate}})_{30} = (m_{\text{alginate}})_{26}$$



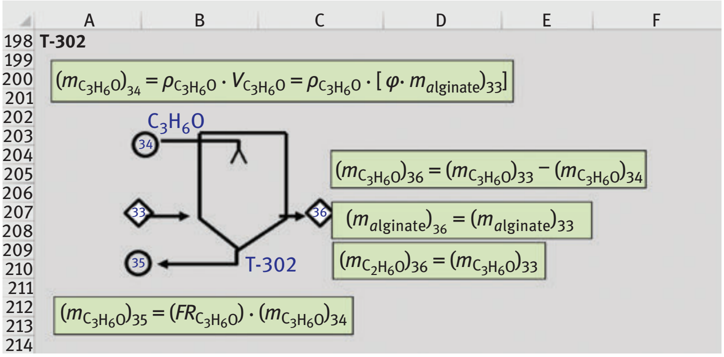
$$(m_{C_2H_6O})_{31} = \rho_{C_2H_6O} \cdot V_{C_2H_6O} = \rho_{C_2H_6O} \cdot [\varphi \cdot m_{\text{alginate}})_{30}]$$

$$(m_{C_2H_6O})_{33} = (m_{C_2H_6O})_{31} - (m_{C_2H_6O})_{32}$$

$$(m_{\text{alginate}})_{33} = (m_{\text{alginate}})_{30}$$

$$(m_{C_2H_6O})_{32} = (FR_{C_2H_6O}) \cdot (m_{C_2H_6O})_{31}$$

$$(m_{H_2O})_{32} = (m_{H_2O})_{30}$$



T-302

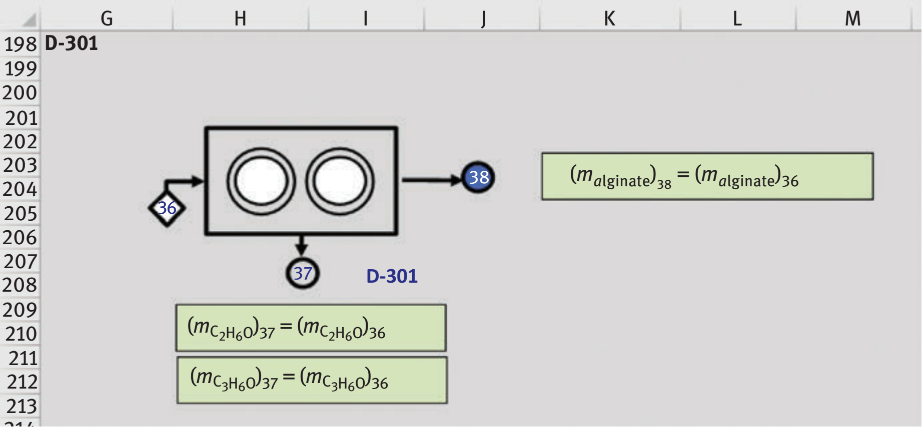
$(m_{C_3H_6O})_{34} = \rho_{C_3H_6O} \cdot V_{C_3H_6O} = \rho_{C_3H_6O} \cdot [\varphi \cdot m_{alginate})_{33}]$

$(m_{C_3H_6O})_{36} = (m_{C_3H_6O})_{33} - (m_{C_3H_6O})_{34}$

$(m_{alginate})_{36} = (m_{alginate})_{33}$

$(m_{C_2H_6O})_{36} = (m_{C_3H_6O})_{33}$

$(m_{C_3H_6O})_{35} = (FR_{C_3H_6O}) \cdot (m_{C_3H_6O})_{34}$



D-301

$(m_{alginate})_{38} = (m_{alginate})_{36}$

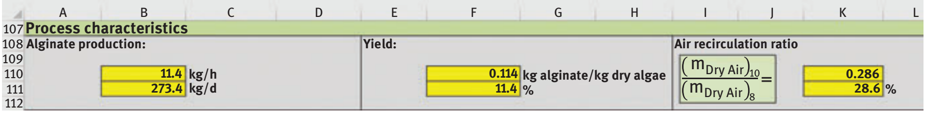
$(m_{C_2H_6O})_{37} = (m_{C_2H_6O})_{36}$

$(m_{C_3H_6O})_{37} = (m_{C_3H_6O})_{36}$

The application of these balances allows to obtain the stream table (Figure 4.18).

Step 4: Process characteristics

All the streams have been characterized and, therefore, the main characteristics of the process can be evaluated (Figure 4.19).



Process characteristics

Alginate production:		Yield:		Air recirculation ratio	
11.4	kg/h	0.114	kg alginate/kg dry algae	$\frac{(m_{\text{Dry Air}})_{10}}{(m_{\text{Dry Air}})_{8}} =$	0.286
273.4	kg/d	11.4	%		28.6 %

Figure 4.19: Process characteristics.

B110: = T86
B111: = B110*24
F110: = B110/B54
F111: = F110*100
K110: = L82/J82
K111: = K110*100

4.5 Proposed case studies

4.5.1 Production of iodine (I_2)

One of the conventional processes for obtaining iodine (I_2) is through the reduction of sodium iodide (NaI) contained in algae with manganese oxide (MnO_2) in the presence of sulfuric acid (H_2SO_4) (Figure 4.20):

$$2NaI + MnO_2 + 2H_2SO_4 \rightarrow Na_2SO_4 + I_2 + 2H_2O + MnSO_4$$

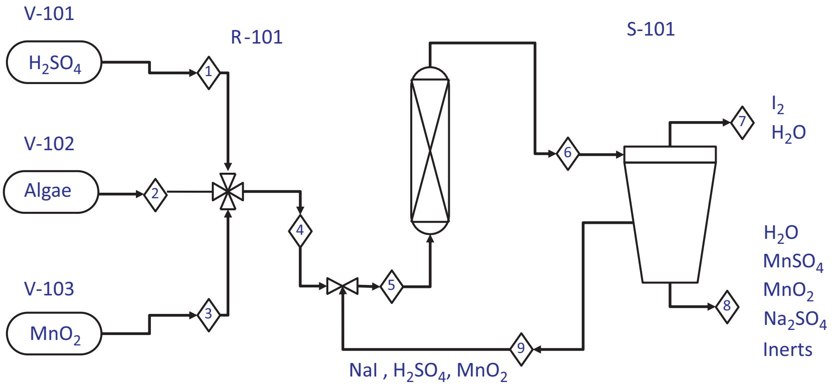


Figure 4.20: Simplified flow diagram for obtaining iodine from seaweeds.

Thus, a given flow of algae (6.5% NaI, 35% H_2O and rest inert) is treated in stoichiometric quantities with MnO_2 and H_2SO_4 in a reactor with a conversion of 82%. Part of the reactor output stream is recirculated and mixed with the fresh feed (Figure 4.20). The rest of the reactor outflow is fed into a separation unit where it is obtained:

i. Product: 55% I_2 and 45% H_2O.
ii. Waste stream with residual content of H_2O, $MnSO_4$, Na_2SO_4 and inert.
iii. Recirculation: 25% of MnO_2.

All percentages are expressed as % by weight. Calculate:

a. Kilograms of I_2 per ton of fresh feed seaweed.
b. Stream composition 8.

Solution: (a) 55.03 kg I_2/t algae; (b) 32.54% H_2O, 3.20% Na_2SO_4, 3.40% $MnSO_4$, 60.86% inerts.

4.5.2 Biomass gasification

Forest biomass is one of the major raw materials that must be valued in order to seek or close processes based on the circular economy. Various pilot and industrial-scale initiatives are being developed under the auspices of European research programs. One of the different strategies consists of coupling to a conventional wood chip gasification process several reaction and separation units that make it possible to valorize the gas phase and obtain an H_2/CH_4 mixture that can be used as an alternative fuel to natural gas (Figure 4.21).

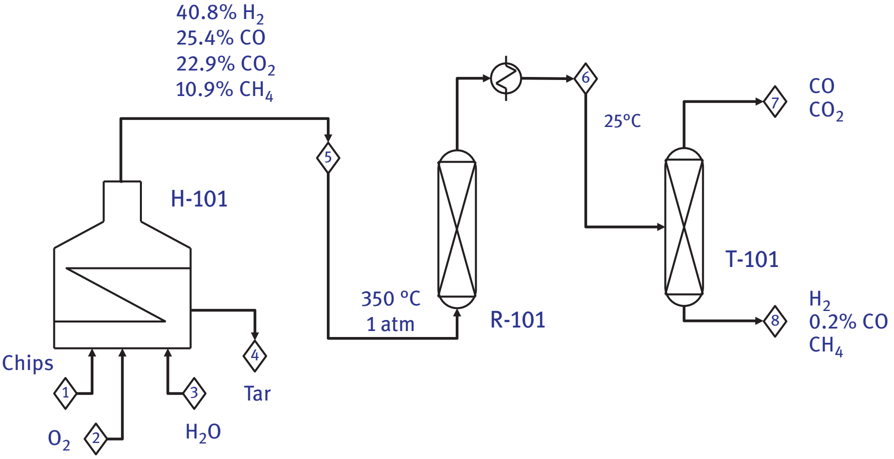


Figure 4.21: Simplified flow diagram for obtaining a fuel mixture of H_2/CH_4 from biomass.

In the gasifier (H-101) a thermochemical process takes place in which biomass is transformed into a combustible gas by the addition of oxygen (under limiting conditions) and water vapor. The biomass used (6 Tm/d) contains 48.5% C, which is transformed into H_2 and CH_4 according to the following reactions:

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$$

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$$

$$2CO_{(g)} + 2H_{2(g)} \rightarrow CH_{4(g)} + CO_{2(g)}$$

The noncarbon fraction of biomass such as carbonate that does not react is converted to tar (stream 4). The degree of conversion of the oxidation reaction from CO to CO_2 is 100%. The gas produced (stream 5) has a flow of 20 Nm^3/h of wet gas with a dry to wet gas fraction of 0.4, which is introduced into a fixed bed reactor with a Fe/Cr catalyst where the water gas shift reaction takes place at 350 °C and 1 atm pressure, which allows additional hydrogen to be obtained. This reaction is reversible and exothermic:

$$CO_{(g)} + H_2O_{(g)} \rightleftarrows H_{2(g)} + CO_{2(g)}$$

Callaghan (2006)[17] has defined the expression of the equilibrium constant as a function of temperature for a range of 600–2,000 K:

$$\log_{10} K_{eq} = -2.4198 + 0.0003855 \cdot T + \frac{2,180.6}{T}$$

Finally, the gases produced are introduced into an adsorption column (T-101) where all the CO_2 and a majority of the CO are separated to obtain a stream with a high H_2 and CH_4 content that can be used as a substitute for natural gas.

Calculate:

a. Conversion of the carbonate fraction.
b. The vapor fraction, expressed as kg vapor/kg biomass, fed to the gasifier.
c. The CO recovery fraction in R-101.
d. The dry base concentration of H_2 in the stream 8.

Solution: (a) 92.2%; (b) 2.28; (c) 87.0%; (d) 85.5%.

4.5.3 Alkylation: iso-octane synthesis

Alkylation is a catalytic process in which an isoparaffin (iso-butane) and an olefin (butylene) are combined to produce a higher molecular weight compound (iso-octane) called *alkylate*:

$$iC_4H_{10} + C_4H_8 \rightarrow iC_8H_{18}$$

The fresh feed stream has a mass flow rate of 50,000 kg/h with a concentration of 25% iso-butane, 25% butylene and 50% *n*-butane (all expressed as molar percentage). The *n*-butane is an inert in this process. The fresh feed is combined with three recirculation streams (Figure 4.22) prior to entry into the reactor. Virtually all of the butylene fed into the reactor is consumed. The output stream from the reactor is partially recirculated to the reactor, and the remaining flow is fed into a decanter where the aqueous phase (sulfuric acid) and the organic phase are separated. The aqueous phase is recirculated to the reactor, and the organic phase with the hydrocarbons is fed to a distillation column. At the head of the column is separated iso-octane and *n*-butane, and the background stream (only contains iso-butane) is recirculated to the reactor inlet.

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[17] https://web.wpi.edu/Pubs/ETD/Available/etd-050406-023806/unrestricted/ccallaghan.pdf.

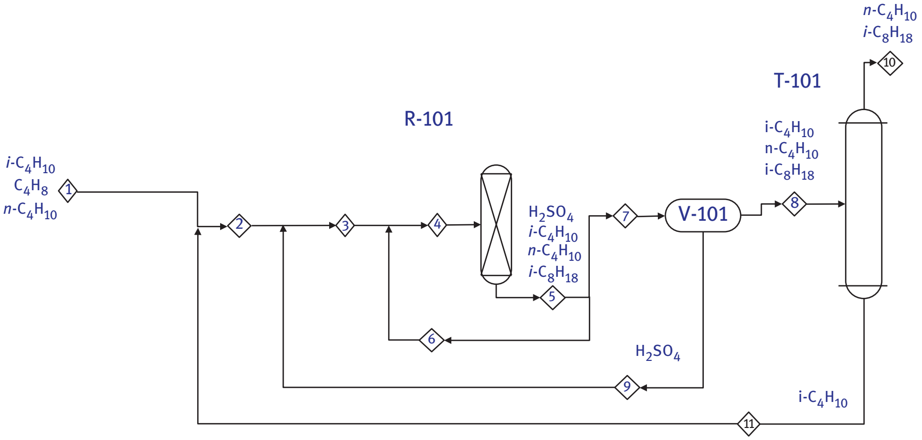

Figure 4.22: Simplified flow diagram for isooctane synthesis.

Data

i. Stream 4 contains 190 moles of iso-butane per mole of butylene and 2 kg of sulfuric acid (91% by weight) per kg of hydrocarbons.

ii. Stream 2 contains 4.5 moles of iso-butane per mole of butylene.

Solution: 217.4 kmol/h of i-C_8H_{18} in stream 10 and 760.9 kmol/h of i-C_4H_{10} in stream 11.

4.5.4 Catalytic desalkylation of toluene for benzene production

Desalkylation is a chemical process by which the alkyl radical (methyl group, $-CH_3$) of a molecule is suppressed. This type of reaction is of great importance in the petrochemical and pharmaceutical industries.

One of the industrial processes for the production of benzene consists of the catalytic desalkylation of toluene in the gaseous phase with hydrogen (Figure 4.23):

$$C_7H_8 + H_2 \longrightarrow C_6H_6 + CH_4$$

A step conversion of 24.5% of toluene is achieved in the reactor, but there is also a secondary reaction, the generation of biphenyl (diphenyl, phenylbenzene or 1,1-biphenyl) from benzene:

$$2C_6H_6 \longrightarrow C_{12}H_{10} + H_2$$

Data

i. The reactor input (stream 2) has a molar ratio of H_2/C_7H_8 of 5.

ii. The molar ratio of H_2/CH_4 in stream 10 is 1.

iii. C_6H_6/C_7H_8 efficiency is 97.5%.

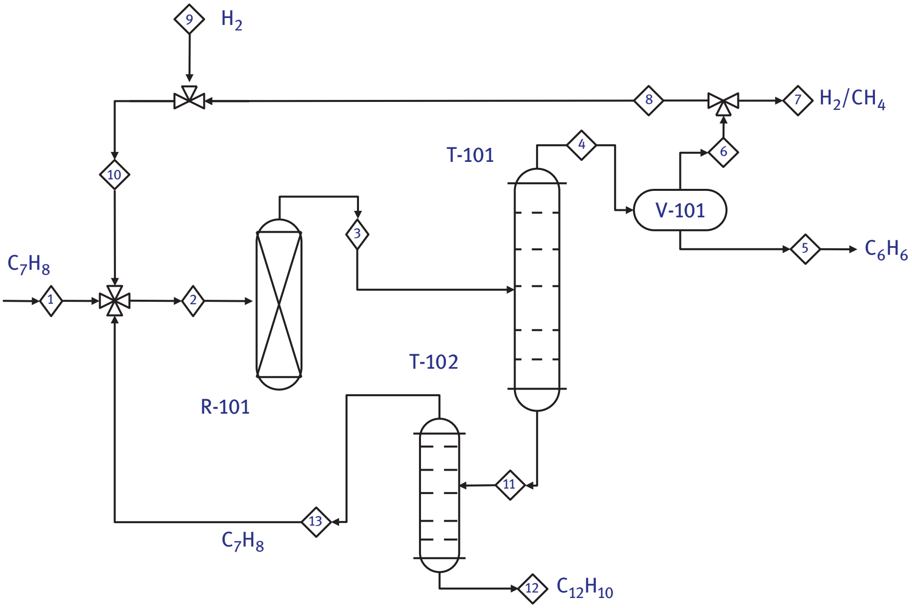

Figure 4.23: Simplified flow diagram for obtaining benzene by catalytic desalkylation of toluene in gaseous phase with hydrogen.

Calculate for a load of 2,500 mol/h of C_7H_8 at the input of the reactor (stream 2):

(a) The production of benzene and biphenyl.
(b) The recirculation/purge ratio for the line with H_2 and CH_4.
(c) The degree of conversion of the secondary reaction.

Solution: (a) 46.58 kg/h benzene and 1.18 kg/h biphenyl; (b) 20.41; (c) 2.5%.

4.5.5 Synthesis of sulfuric acid

The contact method for the production of sulfuric acid is based on the use of a catalyst (platinum or vanadium pentaoxide) to convert SO_2 into SO_3, which is subsequently transformed into H_2SO_4. (Figure 4.24). In a furnace (H-101) SO_2 is obtained by combustion of pure S (1.25 Tm/h) reaching a conversion of 100%:

$$S_{(s)} + O_2 \rightarrow SO_2$$

The combustion products are fed into a converter (R-101) where a part of the SO_2 is converted to SO_3 at high rate due to the high temperature of the gas. Subsequently, the gas is cooled and in a second converter (with an addition of air) allows a higher conversion of SO_2 to be achieved:

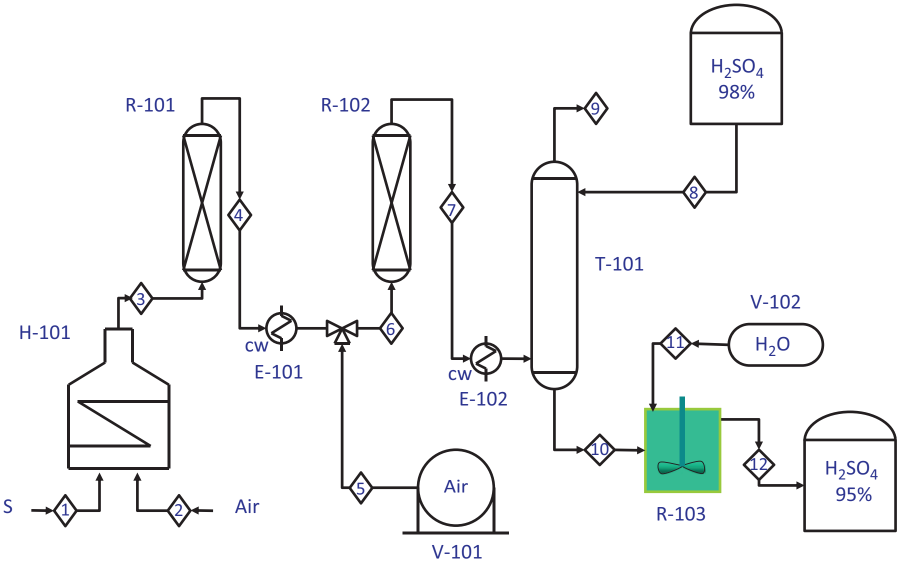

Figure 4.24: Synthesis of sulfuric acid by the contact method.

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$

It is not convenient to directly hydrate SO_3 to obtain sulfuric acid because the reaction releases a lot of energy and is potentially dangerous. This SO_3 is passed through an absorption tower where it is combined with concentrated sulfuric acid to form pyrosulfuric acid (oleum), which is then broken down by hydration into sulfuric acid:

$$HSO_4 + SO_3 \rightarrow H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \rightarrow H_2SO_4$$

The data of the installation are as follows:

- About 45% excess enriched air in the furnace (23% O_2).
- The concentration (% by volume) of SO_2 at the output of R-101 (stream 4) is 3.75%.
- Standard air in flow 5.
- About 90% conversion of SO_2 to R-102.
- The concentration of SO_3 at the output of R-102 (stream 7) is 8.75% (% by volume).
- In the absorption column, the SO_3 conversion is 100%. All SO_2, O_2 and N_2 are coming out of stream 9.
- About 5% in excess of H_2SO_4 in stream 8.

Solution: 95% sulfuric acid production is 336.6 kg/h (stream 12).

4.5.6 Second-generation bioethanol production

The term *bioethanol* refers to ethanol produced by fermentation of cellulosic, sugar or starchy raw materials. The engines of most vehicles can directly use ethanol–gasoline blends in percentages of 5–10%. For mixtures with percentages from 10 to 85%, flexible fuel vehicles are required, which are equipped with a fuel sensor that detects the proportion of ethanol and gasoline, adapting the injection and ignition systems to the characteristics of the mixture.

There are different technologies for obtaining ethanol (C_2H_5OH) from lignocellulosic biomass (also known as *second-generation bioethanol*),[18] the separate hydrolysis fermentation technology being one of them (Figure 4.25). The hemp biomass (25% moisture) undergoes acid hydrolysis in the processing unit (TK-101) to convert cellulose into hexose and hemicellulose into pentose with the following yields (9.9% and 90%, respectively). The composition of the biomass is 37.14% cellulose –$C_6H_{10}O_5$–, 32.38% hemicellulose –$C_5H_8O_4$– and 30.48% lignin and the H_2SO_4 requirement (93%)

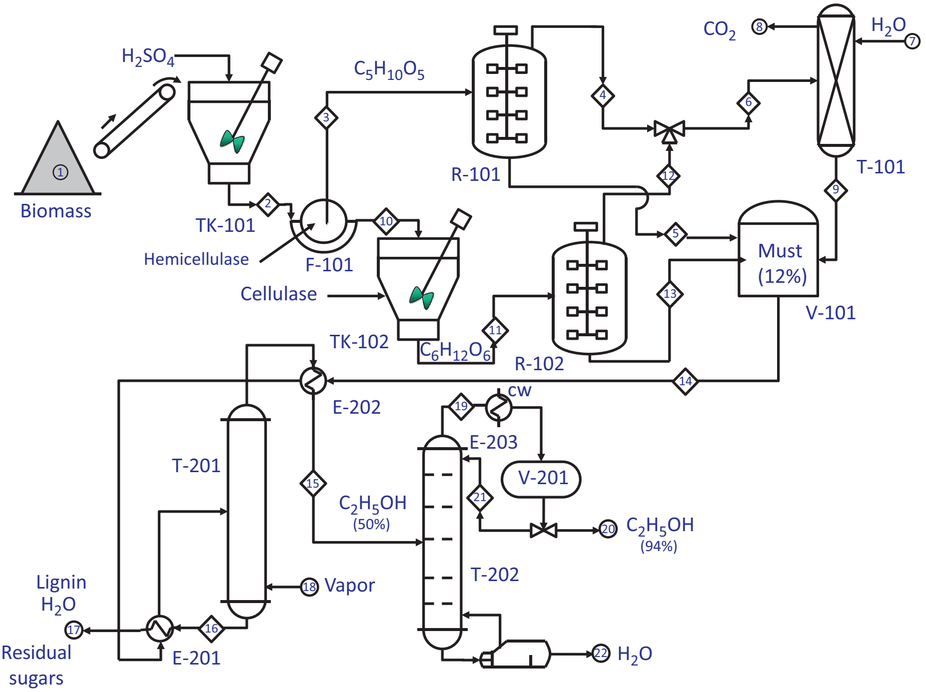

Figure 4.25: Simplified flow diagram for the production of ethanol from lignocellulosic biomass.

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[18] González-García et al. (2010). Renewable and Sustainable Energy Reviews 14: 2077–2085

is 20 kg/ton of dry biomass. (percentage by weight). Stream 2 is introduced in a solid–liquid separator (F-101), to which a cocktail of hemicellulases (20 U/g biomass) is added. This allows a conversion of 100% of hemicellulose to pentoses that are separated (100% recovery) in a liquid stream (stream 3) with 75% of the input water. The solid cake with cellulose and the rest of the components come out of the stream 10.

The pentoses (stream 3) are fermented (R-101) with a recombinant *Zymomonas mobilis* bacterium to obtain ethanol with a conversion of 85%:

$$3C_5H_{10}O_5 \rightarrow 5C_2H_5OH + 2CO_2$$

Stream 4 carries all the CO_2 produced and 1% of the ethanol generated, while stream 5 carries the must stored in tank V-101 (where the concentration of ethanol is 12%). Ethanol from streams 4 and 5 is recovered in Tower 101 by dragging with water.

The cellulose of stream 10 is combined with cellulases (TK-102), which allows a conversion of 90% into hexose. Hexoses are fermented (R-102) with a recombinant *Saccharomyces cerevisiae* yeast (95% conversion):

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

As in the R-101 reactor, the gas stream contains all of the CO_2 produced and 1% of the ethanol generated. The must is poured into the V-101 tank.

The must (stream 14) is purified in a first distillation column (T-201) by steam entrainment, which allows all the ethanol to be recovered at a concentration of 50%, which is fed to a dish distillation column where a concentration of 94% is achieved. The flow rate used is 20%.

If the installation allows to feed 30 tons of dry biomass per hour, calculate:

i. Bioethanol production (kg/d).
ii. Biomass yield (kg ethanol/t dry biomass).
iii. The carbon footprint generated by the CO_2 produced during fermentation (kg CO_2/kg bioethanol).

Note: Consider as density of ethanol and water 789 and 1,000 kg/m^3, respectively.

Solution: (i) 5,356 kg/d; (ii) 7.44 kg/t; (iii) 0.95 kg/kg.

4.5.7 Synthesis of β-galactosidase

β-Galactosidase is an intestinal enzyme capable of hydrolyzing lactose in the monosaccharides that form it, glucose and galactose, which are easily absorbed into the bloodstream. Lactose is found in milk and other dairy products, which play a key role in the development and growth of the human being, providing elements such as calcium, phosphorus or magnesium. However, many consumers are unable to take advantage of this type of benefit due to intolerance or allergy to it, that is, they are unable to digest this disaccharide due to a genetic deficiency of the enzyme β-Galactosidase in the digestive tract. For this reason, products labeled "lactose-free" are increasingly in demand, which means breaking down this disaccharide through the action of β-galactosidase, which must be produced in industrial quantities.

Accordingly, aerobic fermentation is proposed in complete mix reactors operated in discontinuous (Figure 4.26) from cheese whey (50 g/L lactose – $C_{12}H_{22}O_{11}$, and 25% in excess) with recombinant *Saccharomyces cerevisiae*.[19] As a source of nitrogen (TK-102) urea is used (CH_4N_2O: 2.5 g/L) complemented by various salts: 2.5 g/L de $(NH_4)_2SO_4$, 5/L de KH_2PO_4 and 0.4 g/L de $MgSO_4{\cdot}7H_2O$.

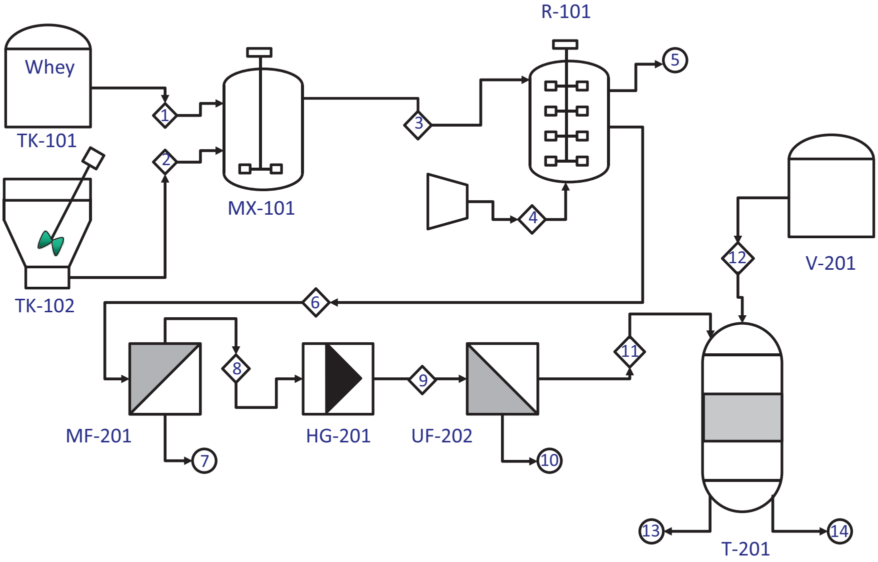

Figure 4.26: Simplified flowchart for the production of β-Galactosidase from whey cheese.

At the end of the fermentation reaction, the amount of biomass would be obtained from the following stoichiometric ratio:

$$C_{12}H_{12}O_{11} + 1.2512NH_3 + 5.4311O_2 \rightarrow 6.2561CH_{1,8}O_{0,5}N_{0,2} + 5.7439CO_2 + 7.2463H_2O$$

The conversion is 100% with respect to ammonium and an excess of 500% air is used. In order to extract the intracellular enzyme β-galactosidase from the biomass and other reaction residues, the product has to be separated and purified through various techniques. First, a hollow fiber microfiltration unit (MF-201) allows for the

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[19] Feijoo et al. (2017). Journal of Cleaner Production 165:204–212.

reduction of broth volume and the elimination of extracellular impurities, as well as reaching a concentration of 30 g/L of biomass in the broth. Homogenization then takes place, where host cells are broken down and intracellular products are released. This cell rupture occurs due to the combination of large pressure drops and high turbulence flows with strong shear forces. As a result, biomass is broken down into amino acids (21%), β-galactosidase (4%), proteins (40%) and cellular waste (35%, all representing percentages by weight). The biomass fraction that can be broken is 85% (by weight). An ultrafiltration stage (UF-202) is then required to remove all remaining waste and biomass, which achieves a β-galactosidase recovery fraction of 97.25% and a (stream 10) concentration of 2.1 g/L. This is followed by an ultrafiltration stage (UF-202) to remove all remaining waste and biomass, which achieves a β-galactosidase recovery fraction of 97.25% and a (stream 10) concentration of 2.1 g/L. Finally, the -galactosidase is purified in an ion-exchange column (T-201), where the solution passes in two cycles through a fixed bed column containing diethylaminoethyl cellulose resins, a positively charged resin to which β-galactosidase binds due to electrostatic forces. Once bonding occurs, the product is eluted with a sodium chloride solution (2 m^3/kg purified β-galactosidase and a concentration of 6.0 g/L). The column is then subjected to stages of equilibrium, washing and regeneration, while the eluted product is obtained (with a composition of 52.0 kg/m^3 of β-galactosidase). The recovery fraction in the column is 98%.

Calculate the volume of the cheese whey stream (stream 1), volume of the stream containing the nitrogen source (stream 2) and volume of air (stream 4) to obtain 30 kg of the enzyme β-galactosidase.

Solution: $V_1 = 51.4\ m^3$; V_2: 62.1 m^3 and $V_4 = 20.9\ m^3$.

4.5.8 Biogas conditioning for a cogeneration system

One of the principles of circular economy is the conversion of waste into raw material for the production of products and/or energy. One of the most widely used technologies today for the treatment of wastewater or waste consists of anaerobic digestion that allows biogas to be obtained (mainly a mixture of methane and carbon dioxide). This biogas must be conditioned, that is, maximize the concentration of methane for subsequent use as fuel in a cogeneration unit (Figure 4.27).

Thus, 158.5 kmol/h containing 72.5% CH_4 and 27.5% CO_2 (percentages by volume) is fed to a system of two absorption columns between which there is a recirculation of methanol as an extractive separating agent (consider that for the purposes of the process it is nonvolatile; therefore, it is not found in any of the gas streams of the process units). In the absorption column T-102 a molar nitrogen flow (stream 6) of 2.5 times, the biogas flow is fed. In the cogeneration unit (H-101), complete combustion to CO_2 and H_2O is produced with 25% excess air.

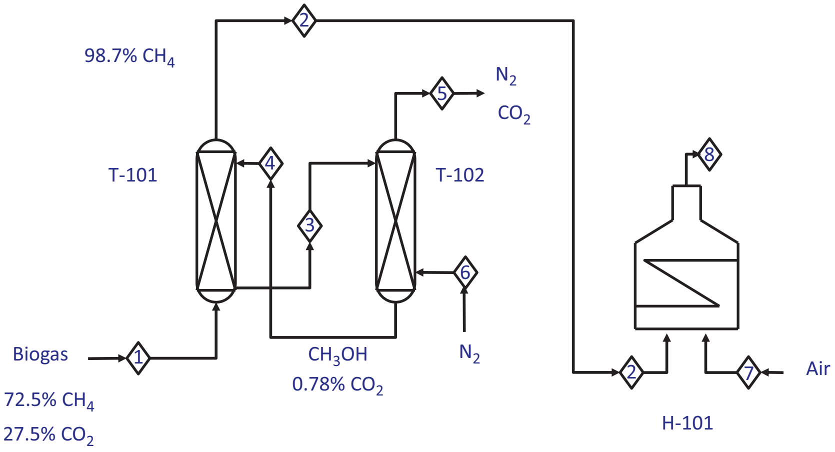

Figure 4.27: Flow diagram for biogas conditioning and subsequent methane cogeneration.

In addition to the value inherent in the benefit of obtaining energy obtained in the unit, it is necessary to assess the reduction in global warming potential, since the characterization factors defined by the IPPC[20] for methane and carbon dioxide are 25 $CO_{2eq}/kgCH_4$ and 1 kg $CO_{2eq}/kgCO_2$. The two emission scenarios are: (a) stream 1 or (b) streams 5 and 8.

Calculate:

i. Recirculation flow rate (stream 4).
ii. Flow rate of the stream 3 and mole fraction of CO_2.
iii. Fractional CO_2 extraction expressed as absorbed moles/moles in the feed.
iv. Variation of CO_{2eq} in the two emission scenarios.
v. For emission scenario (b), what would be the annual emission cost if the CO_2 market price had a value of 5.00 €/Tm?

Solution: (i) 595.1 kmol/h; 637.1 kmol/h and 7.3% CO_2; (iii) 96.5%; (iv) 40,910 kg CO_{2eq}; (v) 305,398 €/year.

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[20] Acronym for the Intergovernmental Panel on Climate Change: http://www.ipcc.ch/.

Nomenclature

A	Notation in the algebraic formulation of a reagent and/or product
a	Activity
c	Concentration (kg/m^3)
E_a	Energy of activation
f_i^{α}	Fugacity of component i in phase α
F	Degrees of freedom
g	Generation rate in molar units (mol/m^3 s)
G	Generation rate in mass units (kg/m^3 s)
G^{o}	Standard Gibbs free energy
GL	Number of degrees of freedom
K	Kinetic coefficient
K	Equilibrium constant
$K_{a/b}$	Acidity or basicity constant
K_{PS}	Solubility product
K_i	Equilibrium concentration ratio in the vapor and liquid phase
K_{Hi}	Henry's constant of the chemical species i
L	Moles of liquid in equilibrium
m	Mass flow rate (kg/s)
m_a	Mass of dry air (kg)
m_v	Mass of water vapor (kg)
M	Mass (kg)
n	Molar flow rate (mol/s)
N	System mass in molar units
N_{ec}	Number of independent equations
N_I	Number of streams
N_J	Number of components
N_K	Number of units
N_S	Number of independent chemical reactions
N_x	Number of unknown variables
p	Partial pressure (N/m^2)
P_i^{sat}	Saturation pressure of component i (N/m^2)
P	Pressure (N/m^2)
q	Volumetric flow rate (m^3/s)
R	Ideal gas constant
R_j	Product yield/performance A_j
S_j	Product selectivity $\mathrm{A_j}$
T	Temperature (K)
t	Time (s)
V	Volume (m^3), or vapor moles
v	Rate (m/s)
$\langle v \rangle$	Average/mean rate (m/s)
w_i	mass fraction (kg A_i/kg total mass)
x	Mole fraction (mole A_i/total mol)
X	Molar conversion
y	Mole fraction of the vapor phase

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Subscripts

i	Reaction: 1,2 … S
j	Species or compound: 1,2 … w
k	Limiting reagent

Greek letters

α	Stoichiometric coefficient
α_{ik}	Relative volatility of two chemical species i and k
$\alpha_{a/b}$	Degree of ionization or dissociation of an acid or base
ρ	Density (kg/m^3)
ϕ_i^V	Fugacity coefficient of component i in the vapor phase
η	Yield, performance or efficiency
γ_i^L	Fugacity coefficient of component i in the liquid phase
ξ_k	Intensive conversion (mol/m^3)
ζ_k	Degree of conversion with respect to the limiting reagent
ε_M	Closing the material balance
ϖ	Specific humidity (kg H_2O/kg dry air)
ϖ_r	Relative specific humidity
Δ	Difference between input and output flows; it also denotes increments

Glossary

Accumulation Corresponds to the amount of property within the system after a time *t*, so it can be both positive and negative.

Acid Any substance that tends to give up protons (hydrogen ions) (definition according to the Brönsted–Lorry theory[21]).

Base Any substance that tends to accept protons (hydrogen ions) (definition according to the Brönsted–Lorry theory).

Basis of calculation Unit (global quantity of a flow or of one of its components) on which all unknowns in a balance of matter and/or energy are referred.

Catalyst Substance that modify the rate of a chemical reaction without being consumed during it.

Circular Economy It is a new production and consumption model based on the optimal use of raw materials and energy, based on a multi-R system: redesign, rethinking, reduction, retrieve, reuse, repair and recycling.

Combustion A chemical process in which substances mix with oxygen in the air to produce heat.

Conversion Number of moles that have reacted of that component for each mole of reactant present in the initial mixture.

Degrees of freedom Degree of freedom of a system is the difference between the number of unknowns and the number of independent equations.

Derivation or bypass A stream that avoids the physical and/or chemical transformation of a unit to be reintegrated later into the system.

Furnace A structure or an apparatus in which heat may be generated.

Input/output This corresponds to the flow of property (mass and/or energy) that crosses the limits of the system in a given time.

Limiting reactant It is the reactant found in the lowest stoichiometric proportion.

Linear equation It is any equation that can be written in the form: $ax+b=0$, where *a* and *b* are real numbers and *x* is a variable. A system of linear equations is a collection of two or more linear equations.

Mass fraction Ratio of mass of a component to the total mass of a mixture.

Mole fraction Ratio of moles of a component to the total moles of a mixture.

Most air Mixture of dry air and water vapor in which dry air is treated as if it were a pure component.

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[21] Johannes Nicolaus Bronsted: Danish chemist and physicist (1879–1947); Thomas Martin Lowry: English physicist and chemist (1874–1936).

https://doi.org/10.1515/9783110624304-006

Nonlinear equation Equation in which one or more independent variables are multiplied by other variables and/or are arguments in algebraic functions. A system of nonlinear equations is a system of two or more equations in two or more variables containing at least one equation that is not linear.

Packed bed column It is a chemical unit consisting of an hollow tube, pipe or other vessel that is filled with a packing material.

Phase A homogeneous region of matter. A gas or gas mixture, a liquid or liquid solution and a crystalline solid are examples of phases. Several phases may coexist, but they must be in equilibrium in order to apply the rule of phases.

Pressure It is the action of a force that acts perpendicularly to a surface. It is called *absolute* (used in most thermodynamic relationships) when measured against a perfect vacuum. The gauge pressure is the difference between absolute pressure and atmospheric pressure.

Process flow diagram It is a diagram widely used in chemical engineering to indicate the flow of chemical plant processes and equipment.

Property Any magnitude used to describe a system. They are classified in: (i) *intensive*, those that do not depend on the mass of the system (temperature, pressure, density, etc.) and (ii) *extensive*, those that depend on the mass of the system (volume, amount of movement, etc.).

Purge Output stream of a recirculation or unit in order to avoid unwanted accumulations.

Recirculation A discharge stream from a unit that is reintroduced back into the system.

Saturated air Mixture of dry air and saturated water vapor. The amount of water vapor in humid air varies from zero in dry air to a maximum, depending on pressure and temperature, when the mixture is saturated.

Solubility The maximum amount that can be dissolved from a solute in a given amount of solvent or dissolution at a given temperature. Usually expressed in g/L or mol/L.

Stoichiometry Quantitative relation between substances consumed and generated in chemical reaction.

Stream table Tabular quantitative summary of a mass balance on an open system.

Tray column Chemical equipment used to carry out basic operations (e.g., distillation and absorption) in which it is necessary to transfer mass between a liquid phase and a vapor or gaseous phase To facilitate the transfer of matter, a series of plates (or tray) are arranged along the column to facilitate contact between the two phases.

Valve A device that regulates flow by opening, closing or partially blocking a pipe or process unit.

Vapor pressure It is the pressure exerted by a pure component in the equilibrium at any temperature, when the liquid and vapor phases coexist.

Yield Fraction of reactant converted to a product.

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Appendices

Appendix A Systems of units: Excel CONVERT function

A.1 Absolute systems: international system of units

A magnitude is any quality relating to a natural process or a body that can be measured, either by direct or by indirect methods, and therefore expressed as a numerical value. When we measure a certain magnitude, we need to express its measurement with a unit, that is, a value next to the known pattern with which we have compared the magnitude. Length, mass, volume, the quantity of a substance, voltage, and so on are magnitudes. Units allow to express a magnitude quantitatively, for example, grams for mass or centimeters for length.

Since the physical properties of bodies are related by the laws of physics, the definition of a system of magnitudes and units requires a number of basic or fundamental magnitudes, deducing the remaining, called *derived magnitudes*, by means of these laws.

Although the choice of the basic magnitudes is arbitrary, in the usual systems there are always two: length, L, and time, t. To express the quantity of mass, a third basic magnitude is required: mass, M, or weight, that is, the force of attraction that the Earth exerts on a system, F. Based on the use of M and/or F, the systems of magnitudes can be as follows:

- *Absolute systems*: They consider mass as a basic magnitude. The International System, SI, belongs to this type of systems and kg is the unit for mass. Prior to the SI, the absolute centimeter–gram–second system considered these basic mechanical units for distance, mass and time. Similarly, the British system considered foot–pound–second as the ternary of units. Table A.1 lists the main characteristic units.
- *Technical systems*: They use force as a basic magnitude and, therefore, mass is a derived magnitude.
- *Engineering systems*: They use mass and force as basic magnitudes.

A.1.1 Temperature

The concept of temperature originates in the perception of our senses, from the notion of “heat” or “cold” that a body transmits. For its quantification, temperature scales are used that are defined by numerical values assigned to the triple point of water (state of equilibrium between steam, ice and liquid water). Thermodynamic or absolute temperature scales are also used, where the assignment of temperature values does not depend on the properties of a particular substance or type of substance (Figure A.1).

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Table A.1: Absolute unit systems.

Magnitude	Centimeter–gram–second (CGS)	British (FPS)	International (SI)
Basic			
Length, *L*	centimeter (cm)	foot (ft)	meter (m)
Mass, *M*	gram (g)	pound (lb)	kilogram (kg)
Time, *t*	second (s)	second (s)	second (s)
Temperature, *T*	degree Celsius (°C)	degree Fahrenheit (°F)	Kelvin (K)
Derived			
Force, $M{\cdot}L{\cdot}t^{-2}$	dyne (dyn)	poundal	Newton (N)
Pressure, $M{\cdot}L^{-1}{\cdot}t^{-2}$	bar (Ba)	poundal/ft^2	Pascal (Pa)
Energy, $M{\cdot}L^{2}{\cdot}t^{-2}$	erg (erg)	poundal ft	Joule (J)
Viscosity, $M{\cdot}L^{-1}{\cdot}t^{-1}$	poise (P)	lb/ft s	kg/m s

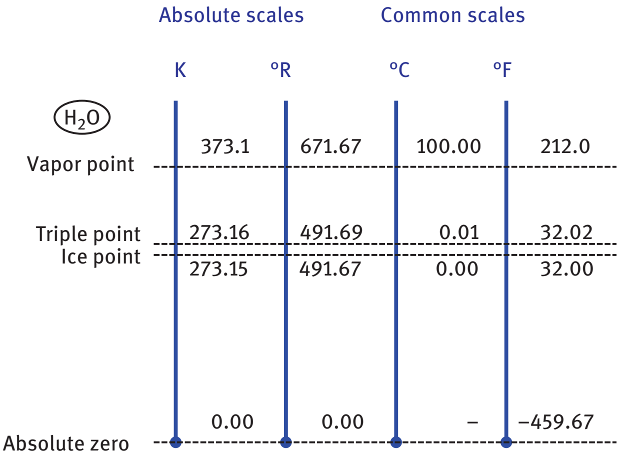

Figure A.1: Comparison between the different temperature scales: Kelvin scale,[22] Rankine scale,[23] Celsius scale,[24] Fahrenheit scale[25].

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[22] **William Thomson** (1824–1907): British physicist, mathematician and inventor. He proposed that a new scale be used to measure the temperature of bodies that would begin to count at the so-called absolute zero, a temperature limit below which it is impossible to go below. In 1892 they decided to name him Lord, being Thomson himself the one who proposed to be granted it as Lord Kelvin, in honor to the small river on whose shore is settled the University of Glasgow where he developed his professional career as professor and scientist.

[23] **William John Macquorn Rankine** (1820–1872): Scottish engineer who stood out for his work on the thermodynamics of steam engines.

[24] **Anders Celsius** (1701–1744): Swedish astronomer.

[25] **Daniel Gabriel Fahrenheit** (1686–1736): German physicist who invented various meteorological instruments, such as an aerometer (measures air density), the alcohol thermometer and the mercury thermometer.

Equations (A.1), (A.2), (A.3) and (A.4) show the conversions between the different scales:

$$T(\mathrm{K}) = T(^\circ\mathrm{C}) + 273.15 \tag{A.1}$$

$$T(^\circ\mathrm{R}) = 1.8 \cdot T(\mathrm{K}) \tag{A.2}$$

$$T(^\circ\mathrm{R}) = T(^\circ\mathrm{F}) + 459.67 \tag{A.3}$$

$$T(^\circ\mathrm{F}) = 1.8 \cdot T(^\circ\mathrm{C}) + 32.0 \tag{A.4}$$

A.1.2 International system

The General Conference on Weights and Measures defined the International System of Units (SI) in 1960 with the aim of establishing a standard and homogeneous system throughout the world (Table A.2).

Table A.2: SI basic units.

Magnitude	Unit	SI base unit
Length	meter	m
Mass	kilogram	kg
Time, duration	second	s
Electric current	Ampere	A
Thermodynamic temperature	Kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

Decimal multiples and submultiples of SI units are formed by prefixes designating the numerical decimal factors by which the unit is multiplied and which are listed in the “factor” column (Table A.3).

Table A.3: SI multiples and submultiples.

Factor	Prefix	Symbol	Factor	Prefix	Symbol
10^1	deca	da	10^{-1}	deci	d
10^2	hecto	h	10^{-2}	centi	c
10^3	kilo	k	10^{-3}	milli	m
10^6	mega	M	10^{-6}	micro	µ
10^9	giga	G	10^{-9}	nano	n
10^{12}	tera	T	10^{-12}	pico	p
10^{15}	peta	P	10^{-15}	femto	f
10^{18}	exa	E	10^{-18}	atto	a
10^{21}	zetta	Z	10^{-21}	zepto	z
10^{24}	yotta	Y	10^{-24}	yocto	y

A.2 Engineering systems

These systems are characterized by considering mass and force as basic magnitudes (Table A.4).

Table A.4: Basic magnitudes for engineering systems.

Magnitude	Metric system	British system
Length, *L*	meter (m)	feet (ft)
Mass, *M*	kilogram-mass (kg or kg_m)	pound-mass (lb or lb_m)
Force, *F*	kilogram-force (kg_f)	pound-force (lb_f)
Time, *t*	second (s)	second (s)
Temperature, *T*	degree Celsius (°C)	degree Fahrenheit (°F)

When considering M and F as basic quantities it is necessary to explicitly introduce the constant of proportionality into Newton's second law, as indicated in eq. (A.5):

$$F = \frac{1}{g_c} m \cdot a \tag{A.5}$$

where g_c is a fundamental physical constant that expresses the proportionality between the force and the product of mass by acceleration. From this point of view, the pound-force is the force with which 1 pound-mass is attracted to the Earth at a location where the acceleration of gravity is the standard value, 32.1740 ft/s^2. Therefore, eq. (A.5) would be expressed as

$$1\mathrm{lb_f} = \frac{(1\mathrm{lb}) \cdot 32.1740\ \frac{ft}{\mathrm{s}^2}}{g_c} \tag{A.6}$$

From eq. (A.6), the definition of g_c can be obtained:

$$g_c = 32.1740 \frac{\mathrm{lb} \cdot \mathrm{ft}}{\mathrm{lb_f} \cdot \mathrm{s}^2} \tag{A.7}$$

Equivalently in the engineering metric system, kg and kg_f, the value of g_c can be calculated:

$$g_c = 9.81 \frac{\mathrm{kg} \cdot \mathrm{m}}{\mathrm{kg_f} \cdot \mathrm{s}^2} \tag{A.8}$$

A.3 Conversion factors

Table A.5 lists the conversion factors between different units for some magnitudes.

Table A.5: Equivalences between units.

Length			
meter (m)	inches (in.)	foot (ft)	mille – U.S.- (mi)
1	39.37	3.2808	$6.214\cdot10^{-4}$
$2.54\cdot10^{-2}$	1	$8.333\cdot10^{-2}$	$1.58\cdot10^{-5}$
0.3048	12	1	$1.8939\cdot10^{-4}$
1,609.3	$6.336\cdot10^{4}$	5.280	1
Mass			
pound (lb)	kilogram (kg)		
1	0.4536		
2.20	1		
Pressure			
mmHg	bar	atm	Pa (N/m^2)
1	$1.333\cdot10^{-3}$	$1.316\cdot10^{-3}$	$1.333\cdot10^{2}$
750.06	1	0.9869	$1.000\cdot10^{5}$
760	1.013	1	$1.013\cdot10^{5}$
$7.502\cdot10^{-2}$	$1.000\cdot10^{-5}$	$9.872\cdot10^{-6}$	1
Energy, heat or work			
Joules (J)	calorie (cal)	British thermal unit (Btu)	
1	0.2390	$9.478\cdot10^{-4}$	
4.184	1	$3.97\cdot10^{-3}$	
$1.055\cdot10^{3}$	252.16	1	
Power			
Horse power (HP)	kW	Btu/s	Watt (W = J/s)
1	0.7457	0.7068	$7.457\cdot10^{2}$
1.341	1	0.9478	$1.000\cdot10^{3}$
1.415	1.055	1	$1.055\cdot10^{3}$
$1.341\cdot10^{-3}$	$1.000\cdot10^{-3}$	$9.478\cdot10^{-4}$	1

A.4 Excel CONVERT function

The CONVERT function interprets or converts data from one measuring system to another:
=CONVERT (number, from_unit, to_unit)

- Number: the numeric value to convert.
- From_unit: the starting units for number.
- To unit: the ending units for the result.

Table A.6 lists the nomenclature used by the CONVERT function for some of the most commonly used units. The Excel help function allows you to obtain a detailed description of them.

Table A.6: Nomenclature of the units in the CONVERT function.

Unit	Change of unit	Unit	Change of unit
Mass		Force	
Gram	"g"	Newton	"N"
Pound-mass	"lbm"	pound-force	"lbf"
Length		Pressure	
Metro	"m"	Pascal	"Pa"
Inch	"in"	Atmosphere	"atm"
Time		Energy	
Day	"day"	July	"J"
Time	"hr"	Erg	"erg"
Second	"s"	Calorie (4.184 J)	"c"
Temperature		Btu	"BTU"
Degree Celsius	"C"	Power	
Degree Fahrenheit	"F"	Horse-Power	"HP"
Kelvin	"K"	Watt	"W"

Appendix B Graphic symbols for process flow diagrams

B.1 Process flow diagrams

The process flow diagram represents the operating mode, configuration and operation of a process plant or a section of plant. The representation must be clear, comprehensive, accurate and complete. There are several types of flow diagrams:

- Block diagram:[26] This is the simplest form of representation and contains the basic information with the stages and units of the process.
- Process diagram:[27] It represents a process or a process plant by means of graphic symbols linked by lines.
- Piping and instrumentation diagram:[28] Based on the process diagram, it represents the technical realization of a process with the help of graphic symbols for the equipment and the piping together with the graphic symbols representing the measurement and control functions of the process.

Each part or unit shown in the process diagram (Figure B.1) must be identified with a code number and a name. The identification number consists of a combination of letters and digits with a general format XX-YZZ A/B, where

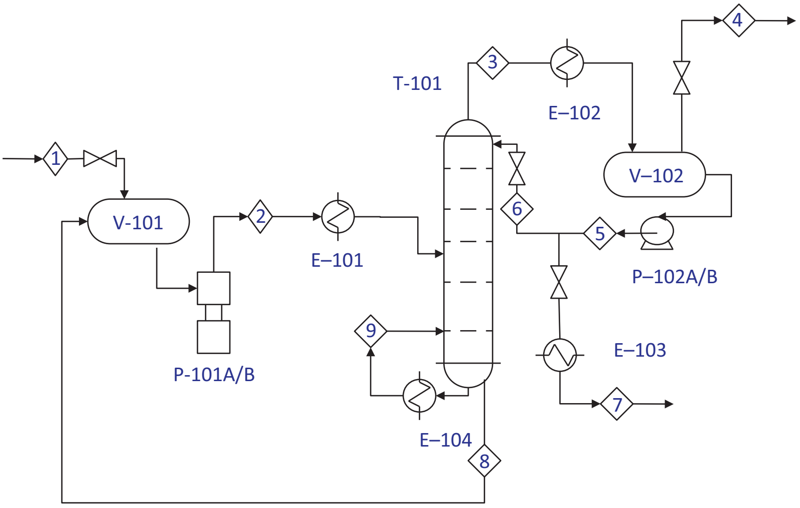

Figure B.1: Process flow diagram for a distillation unit with reflux and output recirculation.

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[26] Blocks flux diagram

[27] Process flux diagram – PFD

[28] Pipping and instrumentation diagram – P&I D

- XX: it identifies the equipment (Table B.1);
- Y: it indicates the sector number of the plant where it is;
- ZZ: it is the number designated to each item for each class of equipment;
- A/B: it identifies units in parallel or in backup (generally, they are not duplicated in the process diagram).

Table B.1: Letter code used in the flowchart.

Symbol	English
C	Compressor/turbine
E	Heat exchanger
H	Fired heater
P	Pump
R	Reactor
T	Tower
TK	Storage tank
V	Vessel

The piping and instrumentation diagram show the engineering details of the equipment, instrumentation, piping, valves and fittings, as well as their arrangement. Table B.2 lists the letter code for the different symbols used in the piping and instrumentation diagram. Figure B.2 also shows the basic piping and instrumentation diagram for a distillation column.

Table B.2: Most common symbols used in the piping and instrumentation diagram.

Location of instrumentation	
	Instrument located in the plant.
	Instrument located on the front panel of the control room
	Instrument located on the back of the control room panel

Table B.2 (continued)

Letter code – XYY		
First letter (X)		Second or third letter (Y)
C	Conductivity	Control
F	Flow rate	
I		Indicate
L	Level	Light or low
P	Pressure or vacuum	Point
R	Radioactivity	Record
T	Temperature	Transmit

Type of line or connection			
—//——//—	Pneumatic	—///——///—	Electrical
——	Supply to instrument or process connection	—○——○—	Internal system link (program or data link)

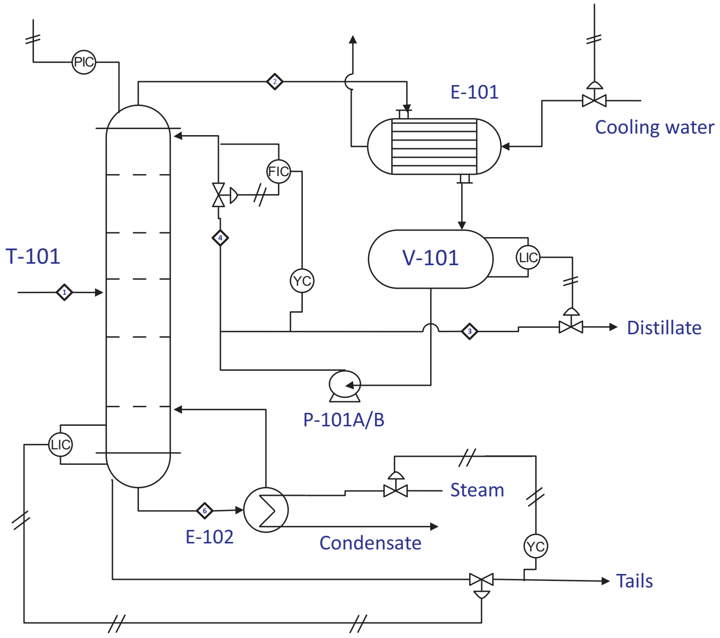
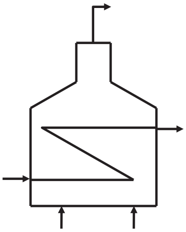


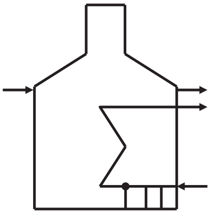
Figure B.2: Piping and instrumentation diagram defining the basic control on a reflux distillation column.

B.2 Graphical symbols

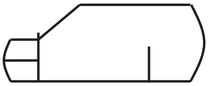
Heat Transmission Equipment



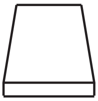
Heater/Furnace



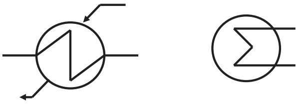
Fired Heater/Furnace



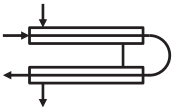
Reboiler Heat Exchanger



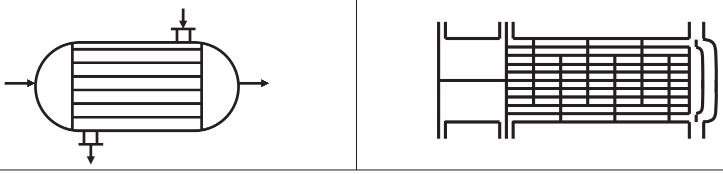
Cooling Tower



Heat Exchangers (basic symbols)



Double pipe heat exchanger



Shell and tube heat exchanger

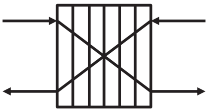
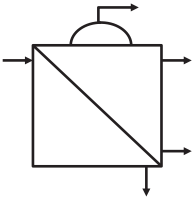
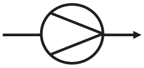


Plate & frame heat exchanger

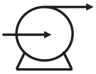


Evaporator (basic symbol)

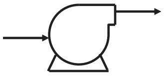
Fluid Transport Equipment



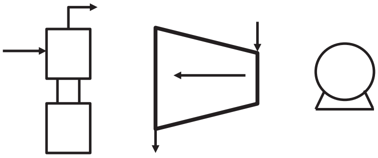
Pump



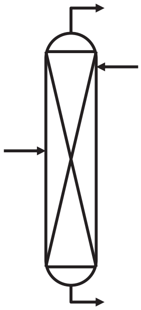
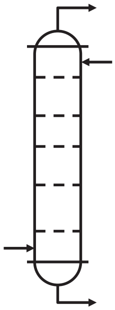
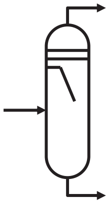
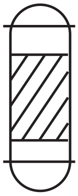
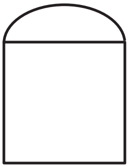
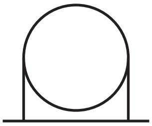
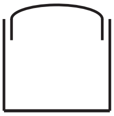
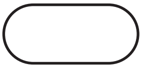
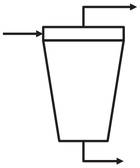
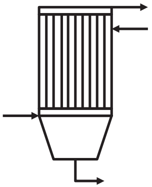
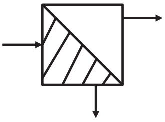
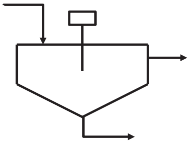
Centrifugal pump

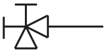


Centrifugal Fan



Compressor/Turbine/Pump

Material Transfer Equipment	
 Packed column/Tower	 Tray column/Tower
 Flash drum	 Reactor or absorber
Vessels	
 Storage tank	 Storage sphere
 Gas Tank or Gasometer	 Storage drum/vessel
Separators	
 Cyclone	 Electrostatic precipitator or bag filter
 Filter	 Clarifier/Thickener

Valves	
 In-line valve	 Diaphragm control valve
 3-way plug valve	 4-way valve
 Hand operated valve	 Ball valve
 Needle valve	 Butterfly valve
 Intermittent blowdown	 Plug valve

B.3 ISO standards

International Standard Organization – www.iso.ch

ISO 10628:1997. Flow diagrams for process plants – General Rules

ISO 14617-2:2002. Graphical symbols for diagrams – Part 2: Symbols having general application

ISO 14617-3:2002. Graphical symbols for diagrams – Part 3: Connections and related devices

ISO 14617-4:2002. Graphical symbols for diagrams – Part 4: Actuators and related devices.

ISO 14617-5:2002. Graphical symbols for diagrams – Part 5: Measurement and control devices

ISO 14617-6:2002. Graphical symbols for diagrams – Part 6: Measurement and control functions

ISO 14617-7:2002. Graphical symbols for diagrams – Part 7: Basic mechanical components

ISO 14617-8:2002. Graphical symbols for diagrams – Part 8: Valves and dampers

ISO 14617-9:2002. Graphical symbols for diagrams – Part 9: Pumps, compressors and fans

ISO 14617-10:2002. Graphical symbols for diagrams – Part 10: Fluid power converters

ISO 14617-11:2002. Graphical symbols for diagrams – Part 11: Devices for heat transfer and heat engines

Appendix C Solving nonlinear equations

C.1 Newton–Raphson method

For a single equation (y variable), $f(x)=0$, Newton[29]–Raphson's[30] method is one of the most widely used formulas. The method is based on the expansion of the function in a Taylor series around a reference point (an initial estimate for the solution) x_0:

$$f(x) \simeq f(x_0) + \frac{df(x_0)}{dx}(x - x_0) \tag{C.1}$$

If $f(x)$ is equal to zero, the resulting equation can be solved for $(x-x_0)$:

$$(x - x_0) = -\frac{f(x_0)}{df(x_0)/dx}$$

$$x = x_0 - \frac{f(x_0)}{df(x_0)/dx} \tag{C.2}$$

For an iteration k, x_k will be obtained analogous to that expressed in eq. (C.2) from the previous value x_{k-1} (Figure C.1):

$$x_k = x_{k-1} - \frac{f(x_{k-1})}{df(x_{k-1})/dx} \tag{C.3}$$

The application of Newton–Raphson involves the following:

- Knowing the derivative of the function either analytically or numerically:

$$\frac{df(x_{k-1})}{dx} = \frac{f(x_{k-1} + \Delta x) - f(x_{k-1})}{\Delta x} \tag{C.4}$$

- The initial value of the iteration must be close enough to the solution to ensure convergence. Excel is an excellent tool to obtain a good initial value by graphically representing the function.

---

[29] **Isaac Newton** (1642–1727): One of the greatest scientists of all time, together with Gottfried Leibniz, is the creator of differential and integral calculus. He is the author of the “Philosophiae naturalis principia mathematica,” in which he described the law of universal gravitation and established the basis of classical mechanics. Among his other scientific discoveries are works on the nature of light and optics.

[30] **Joseph Raphson** (1648–1715): English mathematician, contemporary of Isaac Newton. His work “Analysis aequationum universalis” contains a discussion of Newton's method for approximating the roots of an equation.

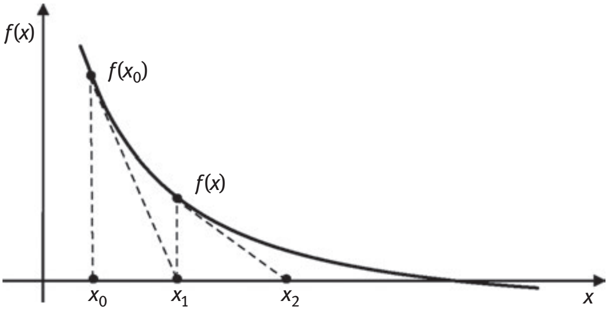


Figure C.1: Graphical representation of the Newton–Raphson method.

One of the challenges faced by numerical methods is to determine estimates of error in the absence of knowledge of true values. For example, in Newton–Raphson's method an approximation is made considering the previous approximation. This process is carried out several times, or in an iterative way, to calculate in a successive way, waiting each time for better approximations. In such cases, the error is often calculated as the difference between the previous approximation and the current one. Therefore, the relative percentage error is given as follows:

$$\varepsilon_a = \frac{\text{current approximation} - \text{previous approximation}}{\text{current approximation}} 100\% \tag{C.5}$$

If a percentage tolerance is set, ε_s, the calculations are repeated until the result obtained is within the acceptable level set previously:

$$|\varepsilon_a| < \varepsilon_s \tag{C.6}$$

These errors should also be related to the number of significant figures in the approximation (eq. (C.7)). Thus, if the criterion defined in eq. (B.6) is met, the result is certain to be correct in at least *n* significant figures:

$$\varepsilon_s = \left(0.5 \cdot 10^{2-n}\right)\% \tag{C.7}$$

In the file "Newton–Raphson Method" the spreadsheets showing the application of the different solution strategies using Excel are attached.

Example C.1: Resolution of a nonlinear equation by applying Newton–Raphson method

a) Solving the equation: $1.12x^5 - 30.78x^3 = 55.98$

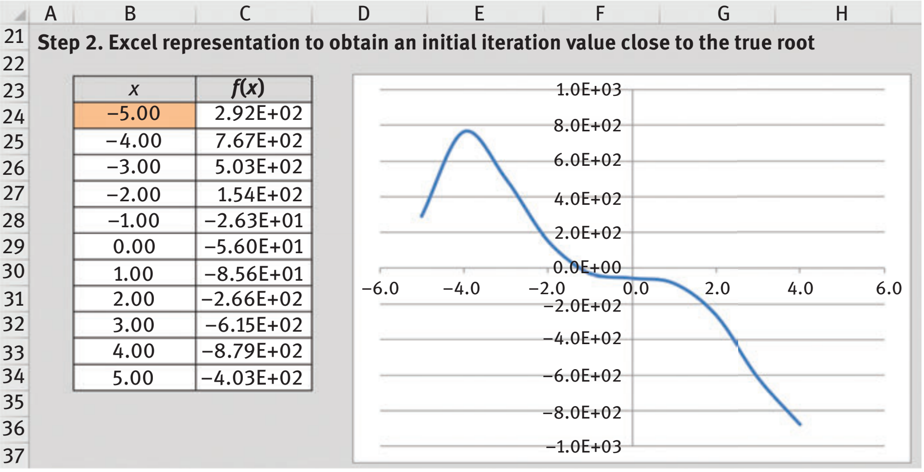
b) Solving the equation: $e^{\ln\left(x^2+0,3\right)} = \ln\left(\frac{x^2}{3} + 5.18\right)$

a) Analytical calculation of the derivative

Step 1: Calculate the derivative of the function

$$\frac{df(x)}{dx} = 5.60x^4 - 92.34x^2$$

Step 2: Excel representation to obtain an initial iteration value close to the true root (Figure C.2).



Step 2. Excel representation to obtain an initial iteration value close to the true root

x	$f(x)$
−5.00	2.92E+02
−4.00	7.67E+02
−3.00	5.03E+02
−2.00	1.54E+02
−1.00	−2.63E+01
0.00	−5.60E+01
1.00	−8.56E+01
2.00	−2.66E+02
3.00	−6.15E+02
4.00	−8.79E+02
5.00	−4.03E+02

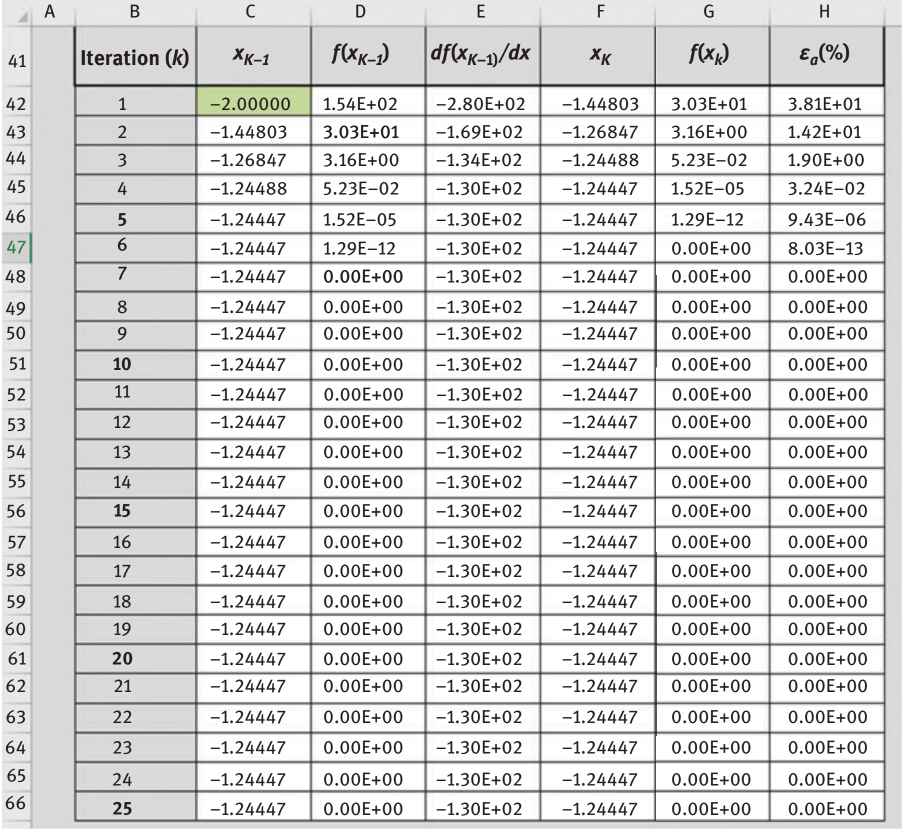
Figure C.2: Graphical representation of the target function.

As can be seen from the graph, an $x = -2$ value would be a good starting point for the iteration.

Step 3: Using the Newton–Raphson formula (Figure C.3).
C42: -2.0 (initial iteration value)
D42: =1.12*C42^5-30.78*C42^3-55.98 (function)
E42: =5.60*C42^4-92.34*C42^2 (derivative)
F42: =C42-(D42/E42) (value of x_k)
G42: =1.12*F42^5-30.78*F42^3-55.98 (function value in x_k)
H42: =(ABS((F42-C42)/F42)*100 (relative percentage error)
C43: =F42

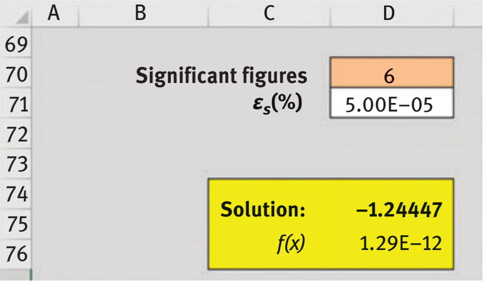
The other cells are obtained with the "copy" and "paste" commands.
The data for the first 25 iterations are presented in the spreadsheet.

Step 4: Calculation of the solution based on the relative percentage error, $|\varepsilon_a| < \varepsilon_s$.
Depending on the number of significant figures desired in the solution, the relative percentage error tolerated can be calculated, ε_s (Figure C.4). To determine which point in the iteration meets the desired error, the Excel IF function can be used:
=IF(logical_test;[value_if_true];[value_if_false])
In this case a search is made on the results obtained after iteration 5, 10, 15, 20 and 25 (Figure C.2) by means of an interconnection of successive SI functions:
D75: =IF(H46<D71;F46;(IF(H51<D71;F51;(IF(H56<D71;F56;(IF(H61<D71;F61;(IF(H66<D71;F66;” keep iterating”))))))))



	A	B	C	D	E	F	G	H
41		**Iteration (k)**	x_{K-1}	$f(x_{K-1})$	$df(x_{K-1})/dx$	x_K	$f(x_k)$	$\varepsilon_a(\%)$
42		1	−2.00000	1.54E+02	−2.80E+02	−1.44803	3.03E+01	3.81E+01
43		2	−1.44803	3.03E+01	−1.69E+02	−1.26847	3.16E+00	1.42E+01
44		3	−1.26847	3.16E+00	−1.34E+02	−1.24488	5.23E−02	1.90E+00
45		4	−1.24488	5.23E−02	−1.30E+02	−1.24447	1.52E−05	3.24E−02
46		**5**	−1.24447	1.52E−05	−1.30E+02	−1.24447	1.29E−12	9.43E−06
47		6	−1.24447	1.29E−12	−1.30E+02	−1.24447	0.00E+00	8.03E−13
48		7	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
49		8	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
50		9	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
51		**10**	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
52		11	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
53		12	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
54		13	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
55		14	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
56		**15**	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
57		16	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
58		17	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
59		18	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
60		19	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
61		**20**	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
62		21	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
63		22	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
64		23	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
65		24	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00
66		**25**	−1.24447	0.00E+00	−1.30E+02	−1.24447	0.00E+00	0.00E+00

Figure C.3: Newton–Raphson calculation.



	A	B	C	D
69				
70		**Significant figures**		6
71		$\varepsilon_s(\%)$		5.00E−05
72				
73				
74				
75			**Solution:**	**−1.24447**
76			$f(x)$	1.29E−12

Figure C.4: Solution according to the percentage tolerance set.

If the condition is not finally met, the message would be “keep iterating,” as greater convergence to the real solution would be needed. It is also noted that by substituting the solution obtained the result is close to zero. This test ensures certainty about the solution, since in some cases small values can be obtained from ε_a as a result of slow or oscillatory convergence.

b) Numerical calculation of the derivative

Step 1: Define the value of Δx for the derivative calculation.

Step 2: Excel representation to obtain an initial iteration value close to the true root (Figure C.5). As you can see from the graph, a value of $x = 2$ would be a good starting value to start the iteration.

Step 3: Using the Newton–Raphson formula (Figure C.6).

C41: 2,0 (initial iteration value)

D41: =((EXP(LN(C41^2+0.3)))/LN((C41^2/3)+5.18))-1 (function)

E41: =C41+$C$18 (value of $x_{k-1}+\Delta x$). The command $ implies that the cell $C$18 has been entered as an absolute reference, that is, the cell has been locked in a formula so that it will not change when copied.

F41: =((EXP(LN(E41^2+0.3)))/LN((E41^2/3)+5.18))-1 (function value for $x_{k-1}+\Delta x$)

G41: = (F41-D41)/$C$18 (numerical value of the derivative)

H41: =C41-(D41/G41) (value of x_k)

I41: =((EXP(LN(H41^2+0.3)))/LN((H41^2/3)+5.18))-1 (function value for x_k)

J41: =(ABS((H41-C41)/H41))*100 (relative percentage error)

C42: =H41

The other cells are obtained with the “copy” and “paste” commands. The data for the first 25 iterations are presented in the spreadsheet.

Step 4: Calculation of the solution based on the relative percentage error, $|\varepsilon_a| < \varepsilon_s$.

Similar to the procedure followed in the previous section for the analytical calculation of the derivative, the SI function is used to define the solution based on the relative percentage error tolerated (Figure C.7):

D74: =IF(J45<D70;H45;(IF(J50<D70;H50;(IF(J55<D70;H55;(IF(J60<D70;H60;(IF(J65<D70;H65;”keep iterating”)))))))))

Note: This equation has two roots (Figure C.5) to obtain the second root just change the initial value of the iteration to -2.0 in cell C41.

C.2 Using the Excel circular reference application for iterative calculation

When a formula refers to its own cell, directly or indirectly, it is called a *circular reference*. In the case of iterative calculations this application simplifies the spreadsheet.

Thus, for step 3 of Example C.1 (Newton–Raphson method), the circular reference to force iterative calculation would mean that in cell C41 it would be connected to H41 (Figure C.8):

C41: =H41 (value of x_{k-1})

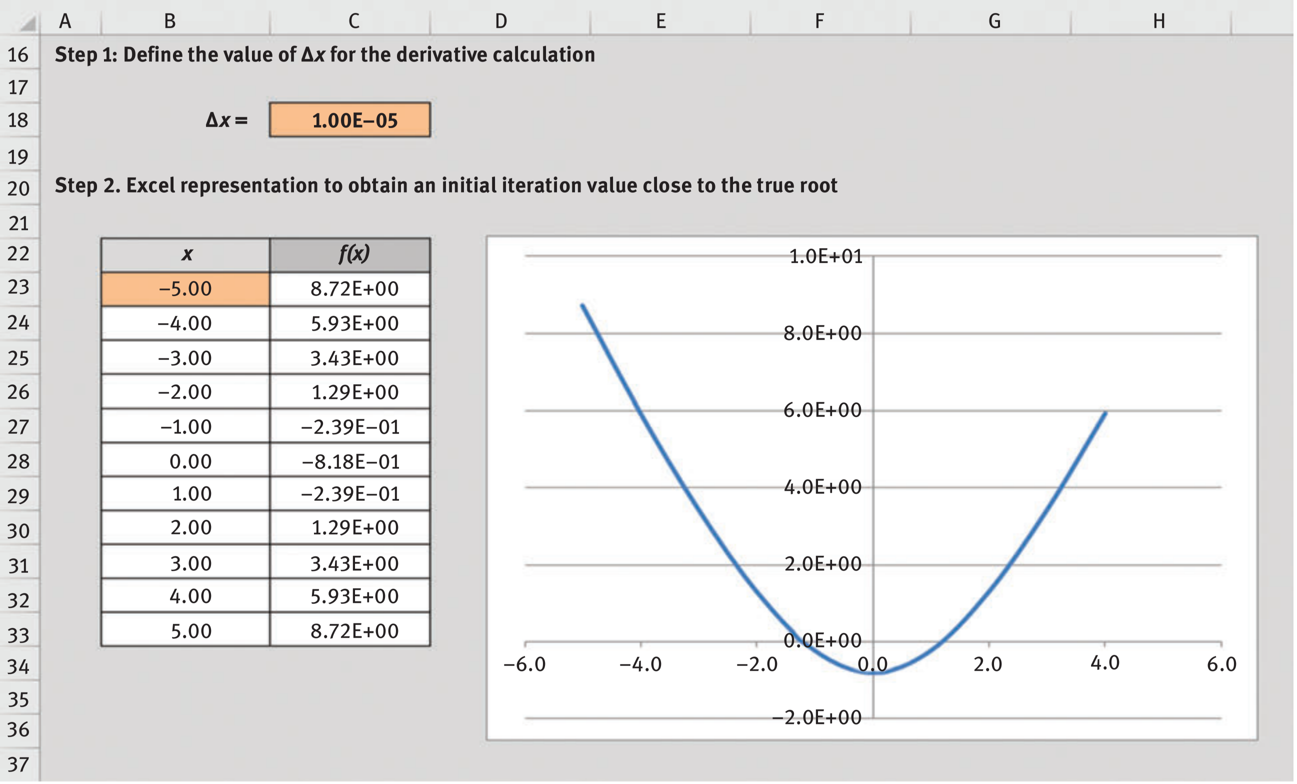
D41: =((EXP(LN(C41^2+0.3)))/LN((C41^2/3)+5.18))-1 (function value for x_{k-1})

E41: =C41+$C$18 (value of $x_{k-1}+\Delta x$).

F41: =((EXP(LN(E41^2+0.3)))/LN((E41^2/3)+5.18))-1 (function value for $x_{k-1}+\Delta x$)

G41: = (F41-D41)/$C$18 (numerical value of the derivative)

H41: =C41-(D41/G41) (value of x_k)



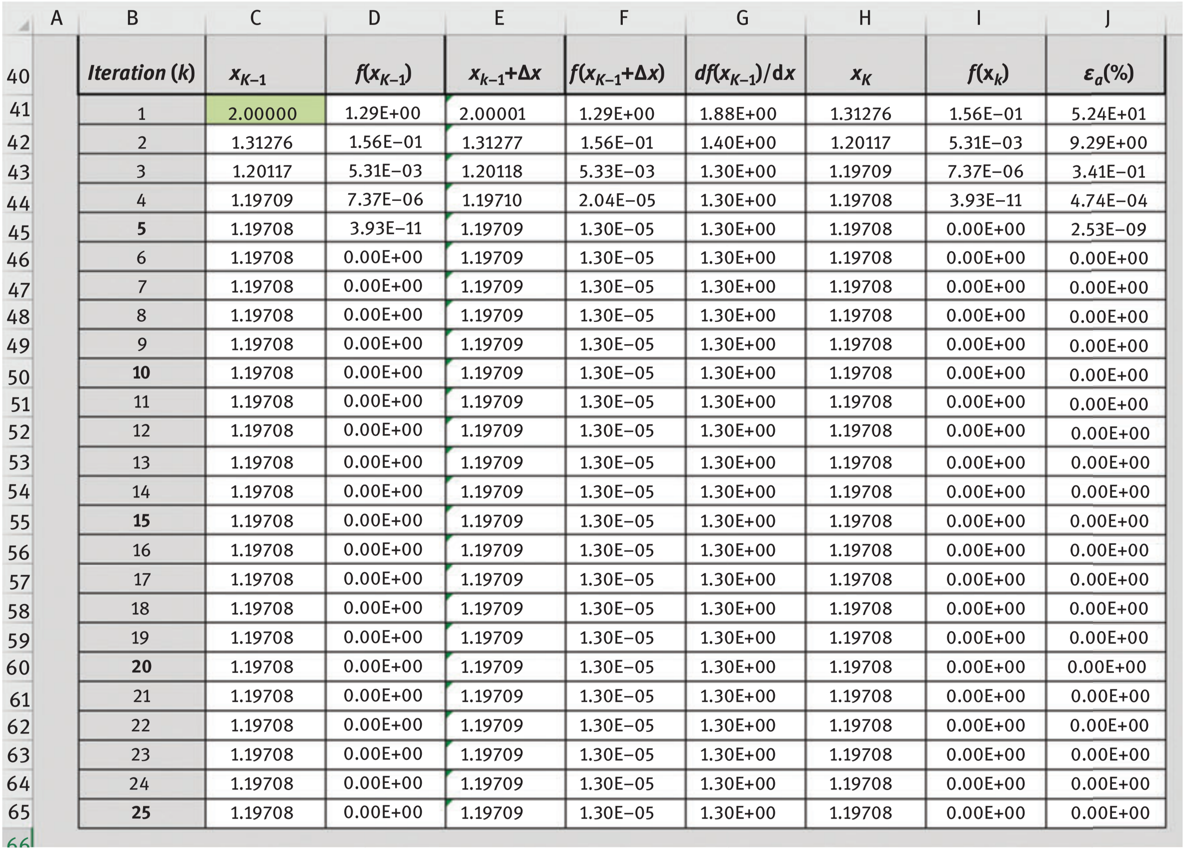
Step 1: Define the value of Δ*x* for the derivative calculation

Δ*x* = **1.00E−05**

Step 2. Excel representation to obtain an initial iteration value close to the true root

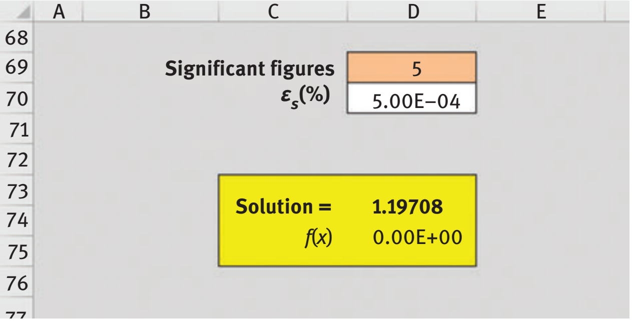
x	***f(x)***
−5.00	8.72E+00
−4.00	5.93E+00
−3.00	3.43E+00
−2.00	1.29E+00
−1.00	−2.39E−01
0.00	−8.18E−01
1.00	−2.39E−01
2.00	1.29E+00
3.00	3.43E+00
4.00	5.93E+00
5.00	8.72E+00

Figure C.5: Graphical representation of the target function.



	A	B	C	D	E	F	G	H	I	J
40		**Iteration (k)**	x_{K-1}	$f(x_{K-1})$	$x_{k-1}+\Delta x$	$f(x_{K-1}+\Delta x)$	$df(x_{K-1})/dx$	x_K	$f(x_k)$	$\varepsilon_a(\%)$
41		1	2.00000	1.29E+00	2.00001	1.29E+00	1.88E+00	1.31276	1.56E−01	5.24E+01
42		2	1.31276	1.56E−01	1.31277	1.56E−01	1.40E+00	1.20117	5.31E−03	9.29E+00
43		3	1.20117	5.31E−03	1.20118	5.33E−03	1.30E+00	1.19709	7.37E−06	3.41E−01
44		4	1.19709	7.37E−06	1.19710	2.04E−05	1.30E+00	1.19708	3.93E−11	4.74E−04
45		**5**	1.19708	3.93E−11	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	2.53E−09
46		6	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
47		7	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
48		8	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
49		9	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
50		**10**	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
51		11	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
52		12	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
53		13	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
54		14	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
55		**15**	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
56		16	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
57		17	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
58		18	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
59		19	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
60		**20**	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
61		21	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
62		22	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
63		23	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
64		24	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00
65		**25**	1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00

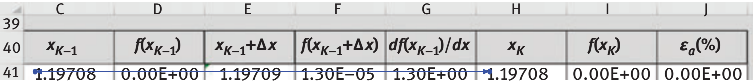
Figure C.6: Newton–Raphson calculation.



Significant figures	5
$\varepsilon_s(\%)$	5.00E−04

Solution =	**1.19708**
$f(x)$	0.00E+00

Figure C.7: Solution according to the percentage tolerance set.



x_{K-1}	$f(x_{K-1})$	$x_{K-1}+\Delta x$	$f(x_{K-1}+\Delta x)$	$df(x_{K-1})/dx$	x_K	$f(x_K)$	$\varepsilon_a(\%)$
1.19708	0.00E+00	1.19709	1.30E−05	1.30E+00	1.19708	0.00E+00	0.00E+00

Figure C.8: Circular reference warning for Newton-Raphson calculation.

I41: =((EXP(LN(H41^2+0.3)))/LN((H41^2/3)+5.18))-1 (function value for x_k)
J41: =(ABS((H41-C41)/H41))*100 (relative percentage error)

Microsoft Office Excel would display a warning message about the existence of a circular reference.

To operate the circular reference:

1. Click on the Microsoft Office button, Excel Options and then on the Formulas menu.
2. In the Calculation options section, select the Enable iterative calculation check box. If you do not change the default value of the iteration, Excel will stop calculations after 100 iterations or after all values in the circular reference change less than 0.001 between iterations, whichever comes first.

C.3 Successive iterations method using Excel "Goal Seek" application

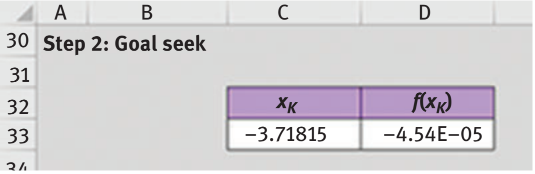
A spreadsheet such as Excel can be used to locate the root through successive iterations or trial and error. You can vary the value of x in a given cell until the cell of $f(x)$ approaches zero. Excel has two tools "Find Target" and "Solver" to systematically adjust the initial values. Find Target is used expressly to bring the equation to a value (in this case, zero) by varying a single parameter.

Example C.2: Solving a nonlinear equation using the “Find Target” application:

$$0.88x^3 + 3.38x^2 - 0.58x = 3.65$$

Step 1: Representation in Excel to obtain a value of the initial iteration interval close to the true root.

Step 2: Application of the “Goal Seek” option. First you must create a cell that has the value of the function to be solved and then make the value dependent on another cell (Figure C.9).
The Goal Seek option exists by default in the different versions of Excel, although the configuration in the menu may be different.



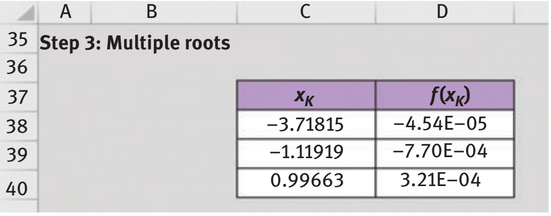
Step 2: Goal seek

x_K	$f(x_K)$
−3.71815	−4.54E−05

Figure C.9: Value of *x* and *f*(*x*).

In the subsequent dialog box one can specify the cell to adjust (i.e., the value of the function) D33, with the default value for a value when another cell (*x*-value) is changed, C33.

Step 3: Multiple roots: To obtain the different solutions of the function, it is enough to vary the initial value of the iteration with values close to the true root (Figure C.10) and to apply for each case the option seek objective.



Step 3: Multiple roots

x_K	$f(x_K)$
−3.71815	−4.54E−05
−1.11919	−7.70E−04
0.99663	3.21E−04

Figure C.10: Initial iteration and result values after applying the “Goal Seek” option.

C.4 Iteration method by “Solver”

Solver is an excellent option for solving nonlinear equations system as a systematic adjustment of the initial values in successive iterations. To load the Solver application (it is not by default in Excel):

1. Click on Excel Options.
2. Click on Add-ins, select Solver and then click on go.
3. In the Available Add-ins box, check the box for Solver and then click on OK.

Example C.3: Solving a system of nonlinear equations using the “Solver” application:

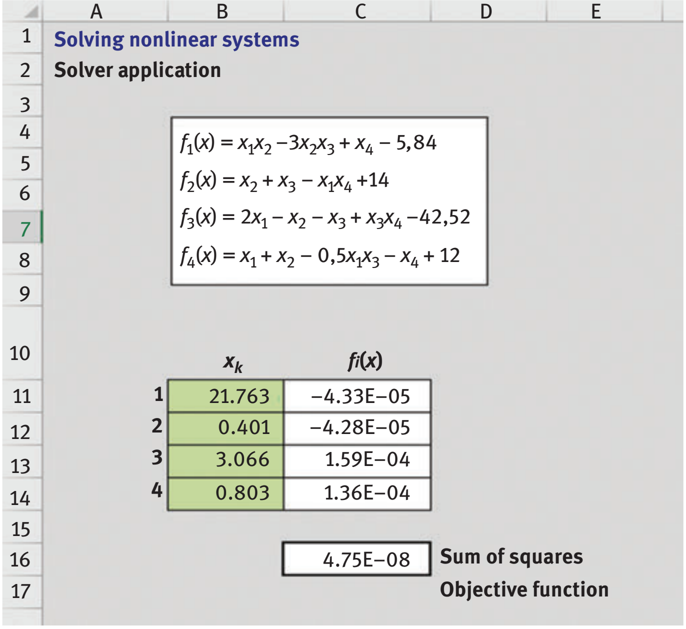
$$f_1(x) = x_1x_2 - 3x_2x_3 + x_4 - 5.84$$

$$f_2(x) = x_2 + x_3 - x_1x_4 + 14$$

$$f_3(x) = 2x_1 - x_2 - x_3 - x_3x_4 - 42.52$$

$$f_4(x) = x_1 + x_2 - 0.5x_1x_3 - x_4 + 12$$

Step 1: Preparation of the spreadsheet. Figure C.11 shows the sheet for a system of four nonlinear equations, where zero has been entered as the initial value of the iteration. Cell C16 corresponds to the sum of squares of the function values. If it is met for all functions it should also be zero, so it will be the target function.



Solving nonlinear systems

Solver application

$$f_1(x) = x_1x_2 - 3x_2x_3 + x_4 - 5{,}84$$

$$f_2(x) = x_2 + x_3 - x_1x_4 + 14$$

$$f_3(x) = 2x_1 - x_2 - x_3 + x_3x_4 - 42{,}52$$

$$f_4(x) = x_1 + x_2 - 0{,}5x_1x_3 - x_4 + 12$$

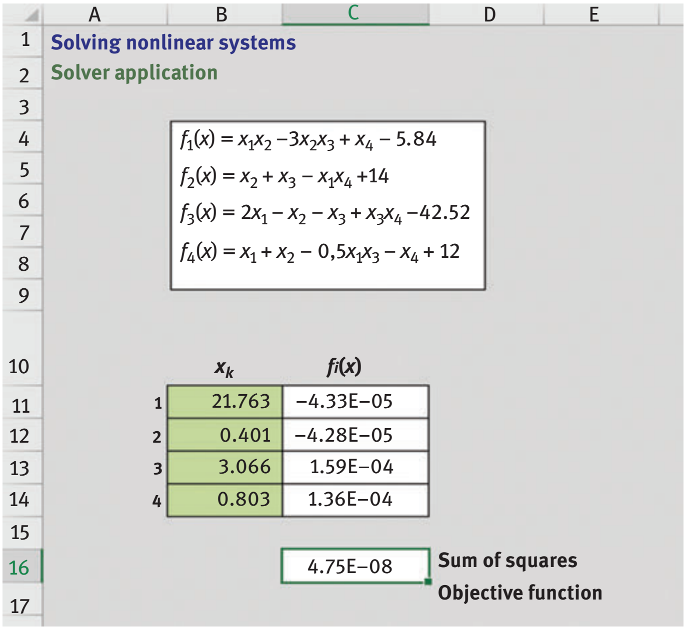
	x_k	$fi(x)$
1	21.763	−4.33E−05
2	0.401	−4.28E−05
3	3.066	1.59E−04
4	0.803	1.36E−04

4.75E−08 **Sum of squares**

Objective function

Figure C.11: Spreadsheet for Solver application for a system of 4 non-linear equations.

Step 2: Application of Solver. On the Data, click Solver. In the subsequent dialog box, specify the cell you want to set, C16, to 0 for a range of cells B11:B14. The solution obtained by Solver is shown in Figure C.12.



Solving nonlinear systems

Solver application

$$f_1(x) = x_1x_2 - 3x_2x_3 + x_4 - 5.84$$

$$f_2(x) = x_2 + x_3 - x_1x_4 + 14$$

$$f_3(x) = 2x_1 - x_2 - x_3 + x_3x_4 - 42.52$$

$$f_4(x) = x_1 + x_2 - 0,5x_1x_3 - x_4 + 12$$

	x_k	$f_i(x)$
1	21.763	−4.33E−05
2	0.401	−4.28E−05
3	3.066	1.59E−04
4	0.803	1.36E−04

4.75E−08 Sum of squares

Objective function

Figure C.12: Solution obtained by Solver.

Appendix D Solving a system of linear equations

D.1 Matrix inversion method

For a system of linear equation,

$$\begin{aligned}
E_1 &: a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n = b_1 \\
E_2 &: a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n = b_2 \\
&\quad \vdots \qquad \vdots \qquad\qquad \vdots \qquad \vdots \\
E_n &: a_{n1}x_1 + a_{n2}x_2 + \cdots + a_{nn}x_n = b_n
\end{aligned}$$

Simultaneous equations can be represented in matrix notation as follows:

$$AX = B \tag{D.1}$$

$$A = \begin{bmatrix} a_{11}a_{12}\cdots a_{1n} \\ a_{21}a_{22}\cdots a_{2n} \\ \vdots \quad \vdots \quad\quad \vdots \\ a_{n1}a_{n2}\cdots a_{nn} \end{bmatrix}, \; X = \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{bmatrix}, \; B = \begin{bmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{bmatrix}$$

where A is the matrix of coefficients, X the matrix of unknowns and B the matrix of constants.

If A is a nonsingular square matrix of order n x n (the determinant of A is not zero), then there exists a unique matrix A^{-1} such that

$$A^{-1}A = I \tag{D.2}$$

The matrix A^{-1} is said to be the inverse of matrix A. Multiplying both sides of eq. (D.1) by A^{-1} yields:

$$X = A^{-1}B \tag{D.3}$$

The solution matrix is obtained by multiplying the matrix of constants by the inverse matrix of the coefficients.

The related functions in Excel are as follows:

- {=MDETERM(array)}: it allows to calculate the determinant of a matrix.
- {=MINVERSE(array)}: it calculates the inverse matrix of a matrix with the same number of rows and columns.
- {=MMULT(array;array)}: it calculates the matrix product of two matrices.

When operating with matrix functions, the calculation of each term is obtained by specifying it as a “matrix formula,” since the “copy” and “paste” commands do not apply in these cases. In the file “Appendix D_Matrix Inversion” you will find the predefined spreadsheets for systems of linear equations with 2, 3, 4, 5 and 6 variables.

Example D.1: Solving a system of five linear equations by matrix inversion

$$E_1:\ -x_1+x_2+x_3=1$$

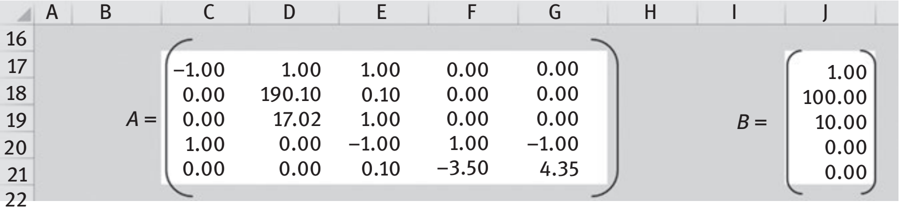
$$E_2:\ 190,1\cdot x_2+0,1\cdot x_3=100$$

$$E_3:\ 17,02\cdot x_2+x_3=10$$

$$E_4:\ x_1-x_3+x_4-x_5=0$$

$$E_5:\ 0,1\cdot x_3-3,5\cdot x_4+4,35\cdot x_4=0$$

Step 1: Matrix of coefficients and matrix of constants (Figure D.1)

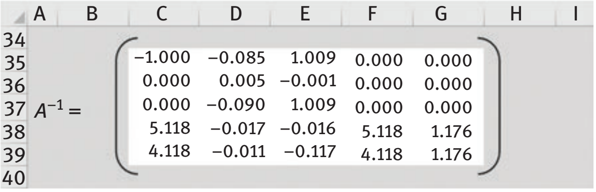


$$A=\begin{pmatrix}-1.00 & 1.00 & 1.00 & 0.00 & 0.00\\ 0.00 & 190.10 & 0.10 & 0.00 & 0.00\\ 0.00 & 17.02 & 1.00 & 0.00 & 0.00\\ 1.00 & 0.00 & -1.00 & 1.00 & -1.00\\ 0.00 & 0.00 & 0.10 & -3.50 & 4.35\end{pmatrix}\qquad B=\begin{pmatrix}1.00\\ 100.00\\ 10.00\\ 0.00\\ 0.00\end{pmatrix}$$

Figure D.1: Matrix of coefficients and matrix of constants.

Step 2: Calculation of the determinant of *A*. As the determinant {I27=MDETERM(C25:G29)} is not zero, the inverse matrix of *A* can be calculated and therefore this method can be applied to solve the system of linear equations

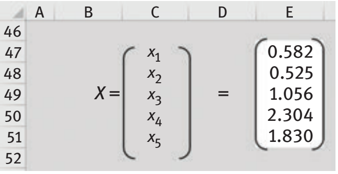
Step 3: Inverse matrix
To obtain the inverse matrix of each of the terms, it is necessary to specify it as a matrix formula. In the cell C35, enter the function you want to apply, {=MINVERSE(C17:G21)}, then select the range C35:G39, press the F2 key and then CTRL+SHIFT+ENTER (Figure D.2).



$$A^{-1}=\begin{pmatrix}-1.000 & -0.085 & 1.009 & 0.000 & 0.000\\ 0.000 & 0.005 & -0.001 & 0.000 & 0.000\\ 0.000 & -0.090 & 1.009 & 0.000 & 0.000\\ 5.118 & -0.017 & -0.016 & 5.118 & 1.176\\ 4.118 & -0.011 & -0.117 & 4.118 & 1.176\end{pmatrix}$$

Figure D.2: Inverse matrix calculation.

Step 4: The solution is obtained by the matrix multiplication of A^{-1} and B
To obtain the solution, the matrix product of the inverse matrix and the matrix of constants is made. In the cell E47, enter the function to be applied, {=MMULT(array; array)}, then select the range E47: E51, press the F2 key and then CTRL+SHIFT+ENTER (Figure D.3).



$$X = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \end{pmatrix} = \begin{pmatrix} 0.582 \\ 0.525 \\ 1.056 \\ 2.304 \\ 1.830 \end{pmatrix}$$

Figure D.3: Calculation of the solution.

D.2 Gauss–Seidel method

For a system of linear equation,

$$\begin{aligned} E_1 &: a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n = b_1 \\ E_2 &: a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n = b_2 \\ &\quad \vdots \qquad \vdots \qquad\qquad \vdots \qquad \vdots \\ E_n &: a_{n1}x_1 + a_{n2}x_2 + \cdots + a_{nn}x_n = b_n \end{aligned}$$

If the elements of the diagonal (a_{ii}) are not zero, a classic eighteenth-century iterative method can be used, such as that of Gauss[31]–Seidel[32], which for the k iteration the solution would be given as follows:

$$x_i^{(k)} = \frac{-\sum_{j=1}^{i-1}\left(a_{ij}x_j^{(k)}\right) - \sum_{j=i+1}^{n}\left(a_{ij}x_j^{(k-1)}\right) + b_i}{a_{ii}} \tag{D.4}$$

One of the challenges of numerical methods is the calculation of error in the absence of knowledge of true values. For example, in the Gauss–Seidel method, an approximation is made considering the previous approximation. This process is carried out several times, or in an iterative way, to calculate in a successive way, waiting each time for better approximations. In such cases, the error is often calculated as the

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[31] **Johann Carl Friedrich Gauss** (1777–1855): German mathematician, astronomer and physicist considered "the prince of mathematics."

[32] **Philipp Ludwig von Seidel** (1821–1896): German astronomer and mathematician.

difference between the previous approximation and the current one. Therefore, the relative percentage error is given by

$$\varepsilon_a = \frac{\text{current approximation} - \text{previous approximation}}{\text{current approximation}} 100\% \tag{D.5}$$

If a percentage tolerance is set, ε_s, the calculations are repeated until the result obtained is within the acceptable level set previously:

$$|\varepsilon_a| < \varepsilon_s \tag{D.6}$$

These errors should also be related to the number of significant figures in the approximation. Thus, if the criterion defined in D.7 is met, it will be certain that the result is correct in at least n significant figures:

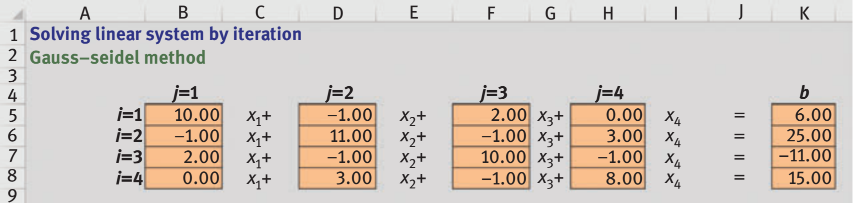
$$\varepsilon_s = \left(0.5 \cdot 10^{2-n}\right)\% \tag{D.7}$$

In the file "Appendix D_Gauss-Seidel" you will find the predefined spreadsheets for systems of linear equations with 3, 4, 5 and 6 variables.

Example D.2: Solving a system of four linear equations using the iterative Gaussian–Seidel method (Figure D.4):

$$E_1 : 10x_1 - x_2 + 2x_3 = 6$$
$$E_2 : -x_1 + 11x_2 - x_3 + 3x_4 = 25$$
$$E_3 : 2x_1 - x_2 + 10x_3 - x_4 = -11$$
$$E_4 : 3x_2 - x_3 + 8x_4 = 15$$

First you enter the coefficients of the unknowns in Excel.

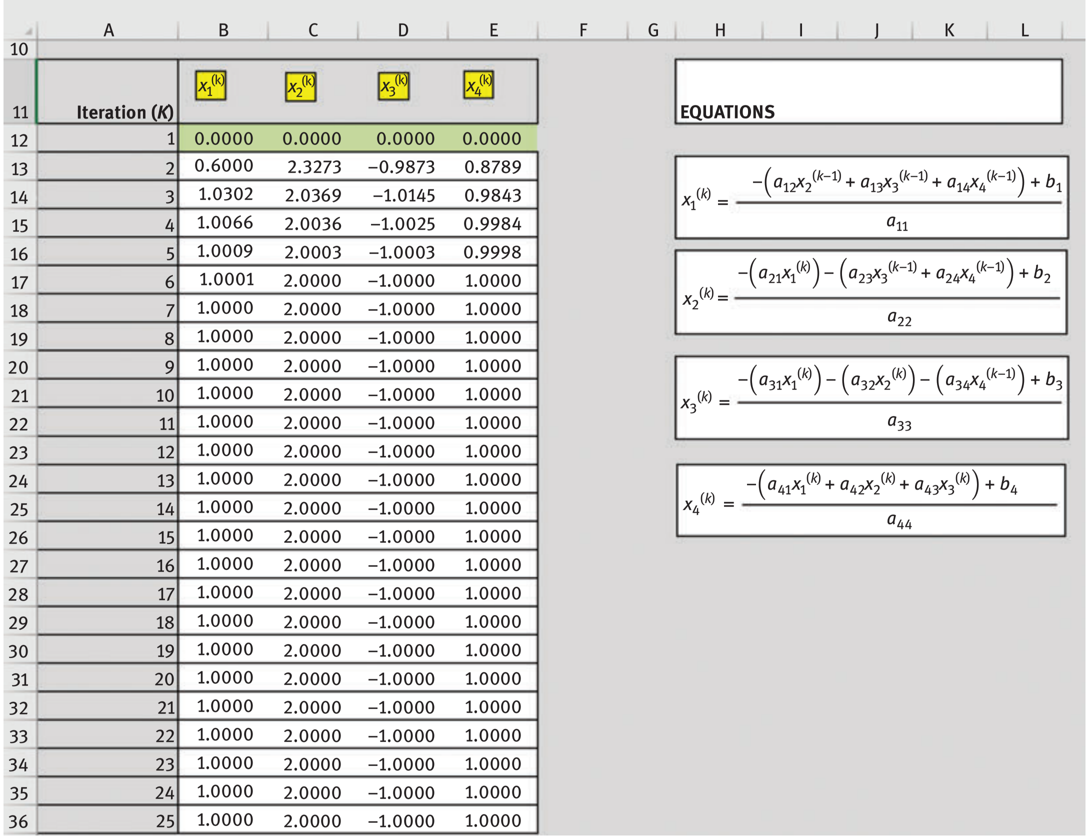


	A	B	C	D	E	F	G	H	I	J	K
1	**Solving linear system by iteration**										
2	**Gauss–seidel method**										
3											
4		***j*=1**		***j*=2**		***j*=3**		***j*=4**			***b***
5	***i*=1**	10.00	x_1+	−1.00	x_2+	2.00	x_3+	0.00	x_4	=	6.00
6	***i*=2**	−1.00	x_1+	11.00	x_2+	−1.00	x_3+	3.00	x_4	=	25.00
7	***i*=3**	2.00	x_1+	−1.00	x_2+	10.00	x_3+	−1.00	x_4	=	−11.00
8	***i*=4**	0.00	x_1+	3.00	x_2+	−1.00	x_3+	8.00	x_4	=	15.00
9											

Figure D.4: Systems of linear equations with 4 variables.

Equation (D.4) displayed for a four-variable system leads us to the equations that must be implemented in Excel (Figure D.5). In addition, the zero value in each of the variables has been considered as the initial value.

> B13: =((−1)*($D$5*C12+$F$5*D12+$H$5*E12)+$K$5)/$B$5 (equation of the variable x_1) The command $ implies that the cell $D$5 has been entered as an absolute reference, that is, the cell has been locked in a formula so that it does not change when you copy and paste.



	A	B	C	D	E
10					
11	Iteration (K)	$x_1^{(k)}$	$x_2^{(k)}$	$x_3^{(k)}$	$x_4^{(k)}$
12	1	0.0000	0.0000	0.0000	0.0000
13	2	0.6000	2.3273	−0.9873	0.8789
14	3	1.0302	2.0369	−1.0145	0.9843
15	4	1.0066	2.0036	−1.0025	0.9984
16	5	1.0009	2.0003	−1.0003	0.9998
17	6	1.0001	2.0000	−1.0000	1.0000
18	7	1.0000	2.0000	−1.0000	1.0000
19	8	1.0000	2.0000	−1.0000	1.0000
20	9	1.0000	2.0000	−1.0000	1.0000
21	10	1.0000	2.0000	−1.0000	1.0000
22	11	1.0000	2.0000	−1.0000	1.0000
23	12	1.0000	2.0000	−1.0000	1.0000
24	13	1.0000	2.0000	−1.0000	1.0000
25	14	1.0000	2.0000	−1.0000	1.0000
26	15	1.0000	2.0000	−1.0000	1.0000
27	16	1.0000	2.0000	−1.0000	1.0000
28	17	1.0000	2.0000	−1.0000	1.0000
29	18	1.0000	2.0000	−1.0000	1.0000
30	19	1.0000	2.0000	−1.0000	1.0000
31	20	1.0000	2.0000	−1.0000	1.0000
32	21	1.0000	2.0000	−1.0000	1.0000
33	22	1.0000	2.0000	−1.0000	1.0000
34	23	1.0000	2.0000	−1.0000	1.0000
35	24	1.0000	2.0000	−1.0000	1.0000
36	25	1.0000	2.0000	−1.0000	1.0000

EQUATIONS

$$x_1^{(k)} = \frac{-\left(a_{12}x_2^{(k-1)} + a_{13}x_3^{(k-1)} + a_{14}x_4^{(k-1)}\right) + b_1}{a_{11}}$$

$$x_2^{(k)} = \frac{-\left(a_{21}x_1^{(k)}\right) - \left(a_{23}x_3^{(k-1)} + a_{24}x_4^{(k-1)}\right) + b_2}{a_{22}}$$

$$x_3^{(k)} = \frac{-\left(a_{31}x_1^{(k)}\right) - \left(a_{32}x_2^{(k)}\right) - \left(a_{34}x_4^{(k-1)}\right) + b_3}{a_{33}}$$

$$x_4^{(k)} = \frac{-\left(a_{41}x_1^{(k)} + a_{42}x_2^{(k)} + a_{43}x_3^{(k)}\right) + b_4}{a_{44}}$$

Figure D.5: Application of the Gauss–Seidel method for a four-variable system.

C13: =((−1)*($B$6*B13)+((-1)*($F$6*D12+$H$6*E12))+$K$6)/$D$6 (equation of the variable x_2).
D13:=((−1)*($B$7*B13+$D$7*C13)+((-1)*(+$H$7*E12))+$K$7)/$F$7 (equation of the variable x_3).
E13: =((−1)*($B$8*B13+$D$8*C13+$F$8*D13)+$K$8)/$H$8 (equation of the variable x_4).

Then you "copy" and "paste" these cells into as many rows as you want. The result for the first 25 iterations is shown on the sheet.

Depending on the number of significant figures desired in the solution, the relative percentage error tolerated can be calculated, ε_s (D.7), and compared with the error obtained in the iterations:

P17: =(ABS((B16-B15)/B16))*100 (relative percentage error obtained in iteration five for variable x_1)

To determine which number of the iteration fulfils the desired error, the IF function (=IF(logic_test; [true_yes_value]; [false_yes_value]) of Excel can be used, through a successive interconnection of it:

=IF(P17<P14;B16;SI(P20<P14;B21;SI(P23<P14;B26;SI(P26<P14;B31;SI(P29<P14;B36;"please keep iterating"))))) (condition for variable x_1)

If the condition is not finally verified, the message that would be displayed would be "please keep iterating," as greater convergence to the true solution would be needed.

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