Materials and Energy Balance

Methodology for Analysis of Metallurgical Processes

Metallurgical and chemical processes are classified as batch, continuous and semibatch

1. Batch processes

   The feed is charged into a vessel at the beginning of the process and the contents of the vessel are removed later. No mass enters the system boundaries between the time of the feed and the time the product is removed. Example: cupola furnace, induction furnace

2. Continuous processes

   The inputs and outputs flow continuously throughout the duration of the process. Example: Calcination kiln, basic oxygen furnace

3. Semibatch processes

   Any process that is neither batch nor continuous. Example: Bessemer furnace

Suppose CH_4 fuel is a component of both the input and output streams of a continuous furnace and the measured mass flow rates in both streams are found to be different

$$\dot{m}_{in} \neq \dot{m}_{out}$$

There are several possible explanations for the observed difference between the measured flow rates:

a. Methane is being consumed as a reactant or generated as a product within the furnace
b. Methane is accumulating in the furnace
c. Methane is leaking from the furnace
d. The measurements are wrong

Generation or consumption in a reaction and accumulation within the furnace are usually the only reasons for the difference between the input and output flow rates

A balance on a conserved quantity in a system may be written in the following general way

Input (enters through the system boundaries) + generation (produced within the system) – output (leaves through system boundaries) – consumption (consumed within system) = accumulation (buildup within system)

Two types of balances may be written:

1. Differential balances

   Balances that indicate what is happening in a system at an instant in time

   Each term of the balance equation is a rate (unit of the balanced quantity divided by a time unit). This type of balance is usually applied in a continuous process

2. Integral balances

   Balances that describe what happens between two instants of time

   Each term of the equation is an amount of the balanced quantity and its unit

   Usually applied to a batch process with the two instants of time being the moment after the input takes place and the moment before the product is withdrawn

The following rules simplify the material balance equation:

- If the balanced quantity is total mass, set generation = 0 and consumption = 0
- If the balanced substance is a nonreactive species, set generation = 0 and consumption = 0
- If a system is at steady-state (all variables in the system constant), for any balanced quantity set accumulation = 0

For continuous processes at steady-state, the accumulation term equals zero and the balance equation simplifies to

Input + generation = output + consumption

If the balance is on a nonreactive species or total mass, the equation reduces to the following form

Input = output

For nonsteady-state batch processes, no product enters or leaves the system between the feed charge time and the product withdrawal time. So the balance equation reduces to

Generation = accumulation

More generally for any reactant or product in the system,

Generation – consumption = accumulation

The following broad integral balance is also correct:

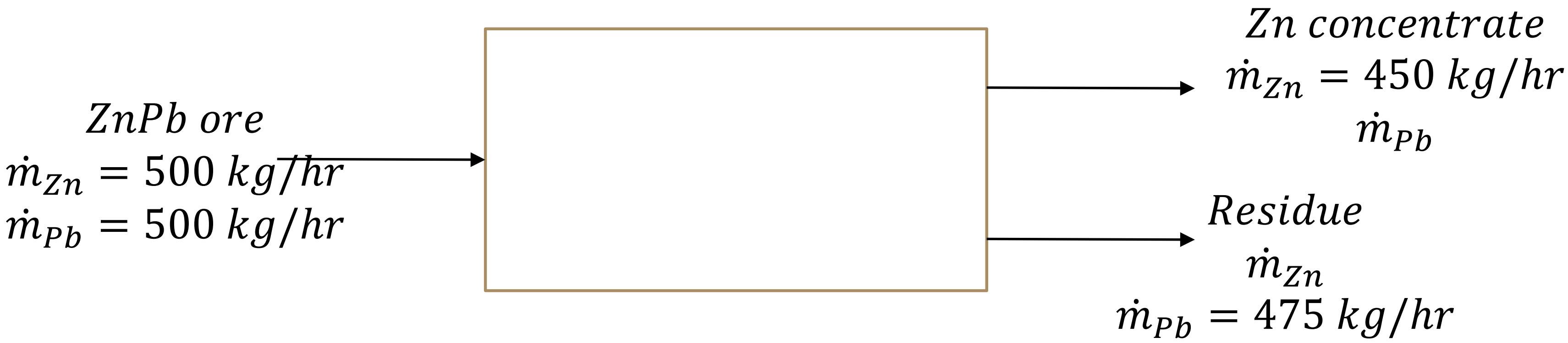
Accumulation = Final output – initial input

Thus for a batch process the material balance equation is

Initial input + generation = final output + consumption

Example – Material balances on a continuous Zn condenser

One ton of a ZnPb ore is separated by evaporation and condensation of Zn. Some Pb is mixed to the Zn product and some Zn remains in the ore residue. The mass flow rate of Zn is 450 kg/h and that of Pb is 475 kg/h. The operation is a steady-state, continuous process. Write balances on Zn and Pb to calculate the unknown component rates in the output streams.



$ZnPb\ ore$

$\dot{m}_{Zn} = 500\ kg/hr$

$\dot{m}_{Pb} = 500\ kg/hr$

$Zn\ concentrate$

$\dot{m}_{Zn} = 450\ kg/hr$

$\dot{m}_{Pb}$

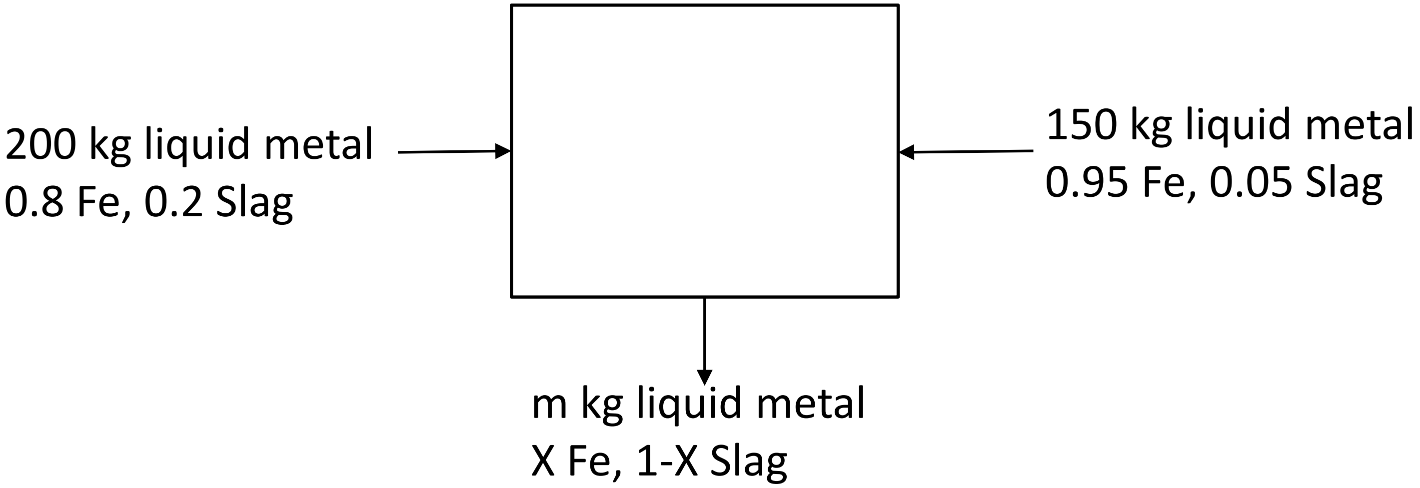
$Residue$

$\dot{m}_{Zn}$

$\dot{m}_{Pb} = 475\ kg/hr$

Example – Material balances on a batch mixing process

Pure liquid iron and slag mixtures are contained in separate furnaces. The first mixture contains 80% pure iron and the second contains 95% pure iron. If 200 kg of the first metal is combined with 150 kg of the second, what are the mass and composition of the product?



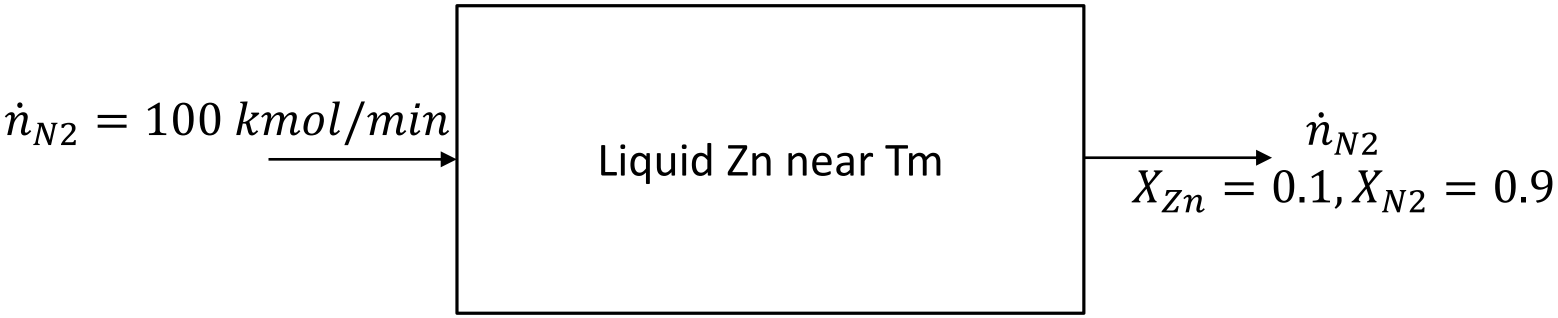
200 kg liquid metal
0.8 Fe, 0.2 Slag

150 kg liquid metal
0.95 Fe, 0.05 Slag

m kg liquid metal
X Fe, 1-X Slag

Example – Material balances on a semibatch and continuous Zn evaporator

Nitrogen is bubbled through a furnace containing liquid zinc near the boiling point of Zn, at a rate of 100 kmol/min. The gas mixture leaving the furnace contains 10 mole% Zn vapor. Use an integral balance to estimate the time required to vaporize 1000 m^3 of the liquid Zn. Density Zn= 7140kg/m^3, MW_{Zn}= 65.4



$\dot{n}_{N2} = 100\ kmol/min$

Liquid Zn near Tm

$\dot{n}_{N2}$

$X_{Zn} = 0.1, X_{N2} = 0.9$

Solving metallurgical material balance problems

In general all problems give values of some input and output stream variables, and ask to derive and solve equations for others

Deriving them from a description of a process and a collection of process data is more difficult than the algebraic solution step

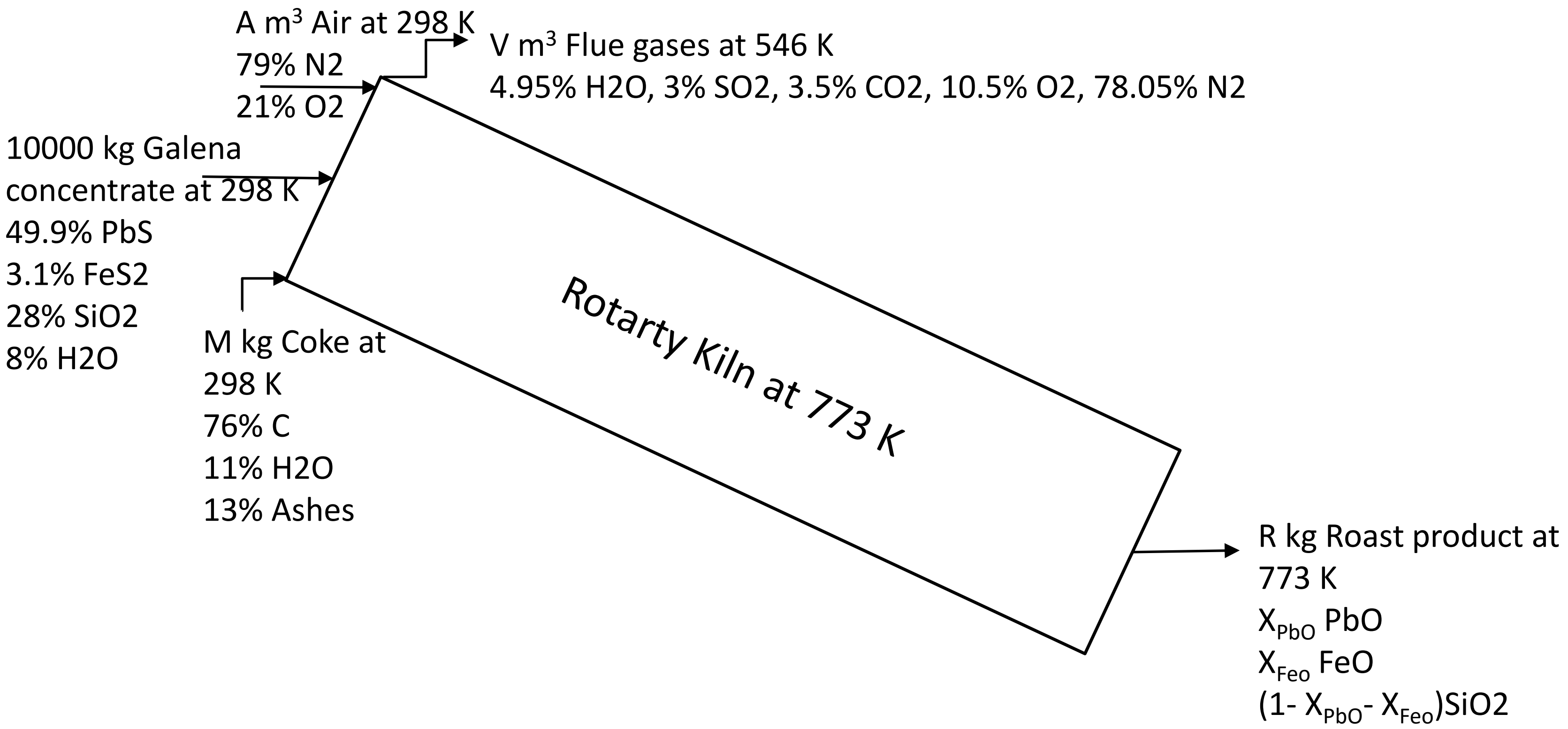
What is known and what is required may not be obvious from the problem statement

A procedure is given here for simplifying a description of a process to a set of equations that can be solved for unknown variables

Example: A galena concentrate consisting of 49.9% PbS, 3.1% FeS_2, 28% SiO_2 and 8% H_2O is roasted in a rotary kiln until 2% S remained in the product. Roast product contains FeS, PbO and SiO_2. Coke is used as the fuel with composition of 76% C, 11% H_2O and 13% ashes. Neglect heat content in the ash. Dry analysis of flue gases is given as 4.95% H2O, 3% SO2, 3.5% CO2, 10.5% O2, 78.05% N2. Flue gases leave at 546 K, and roast product at 773 K while the input materials enter at 298 K.

It is essential to organize the information in a way that is convenient for calculations

Example: 10 tons of a galena concentrate consisting of 49.9% PbS, 3.1% FeS_2, 28% SiO_2 and 8% H_2O is roasted in a rotary kiln until 2% S remained in the product. Roast product contains FeS, PbO and SiO_2. Coke is used as the fuel with composition of 76% C, 11% H_2O and 13% ashes. Neglect heat content in the ash. Dry analysis of flue gases is given as 4.95% H2O, 3% SO2, 3.5% CO2, 10.5% O2, 78.05% N2. Flue gases leave at 546 K, and roast product at 773 K while the input materials enter at 298 K.



A m^3 Air at 298 K
79% N2
21% O2

V m^3 Flue gases at 546 K
4.95% H2O, 3% SO2, 3.5% CO2, 10.5% O2, 78.05% N2

10000 kg Galena concentrate at 298 K
49.9% PbS
3.1% FeS2
28% SiO2
8% H2O

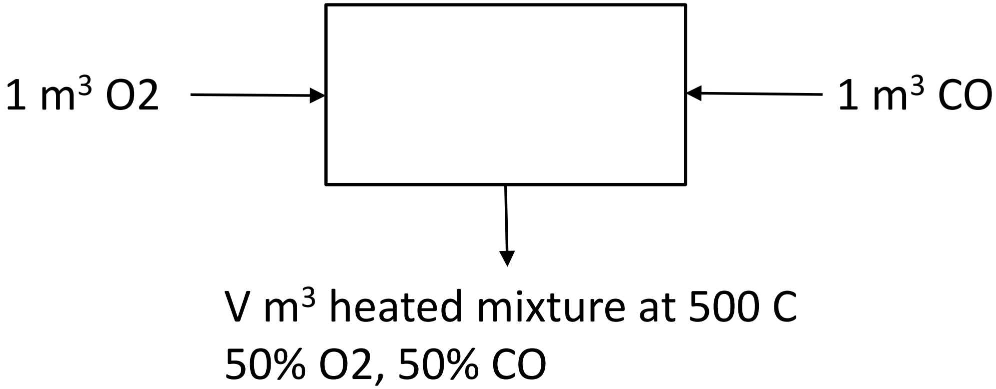
M kg Coke at 298 K
76% C
11% H2O
13% Ashes

Rotarty Kiln at 773 K

R kg Roast product at 773 K
X_{PbO} PbO
X_{Feo} FeO
(1- X_{PbO}- X_{Feo})SiO2

Flowchart scaling and basis of calculation

Consider a simple balance process in which 1 m^3 O_2 is mixed with 1 m^3 CO in a furnace



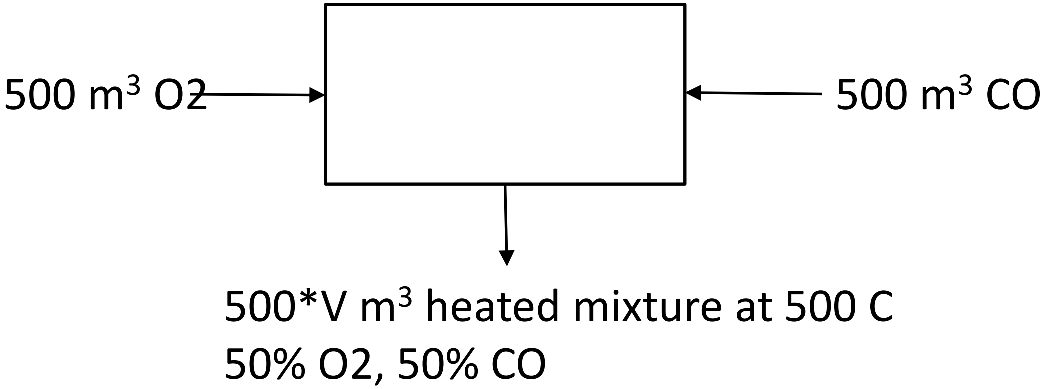
1 m^3 O2

1 m^3 CO

V m^3 heated mixture at 500 C
50% O2, 50% CO

Observe that the masses of all streams can be multiplied by a common factor and the process remains balanced.

The procedure of changing the values of all stream amounts or flow rates by a proportional amount while leaving the stream compositions unchanged is referred to as scaling: up if the final stream quantities are larger than the original.



500 m^3 O2

500 m^3 CO

500*V m^3 heated mixture at 500 C
50% O2, 50% CO

Flowchart scaling and basis of calculation

If we have a balanced process and the amount or flow rate of one of the streams is n_1, we can scale the flowchart to make the amount n_2 by multiplying all stream amounts or flow rates by n_2/n_1

A basis of calculation is an amount or flow rate of one stream or a stream component that we take into account as n_1.

Hint: If a stream amount is given in a problem statement, it is best to use it as a basis of calculation

If no stream amounts or flow rates are known, assume one of a stream with a known composition.

Balancing a process

Consider a simple continuous process of mixing $3 m^3/min$ O_2 and $1 m^3/min$ CO

$3 m^3/min$ O_2

$1 m^3/min$ CO

$\dot{V}$ m^3/min gas mixture

X_{O2}, $X_{CO}=1- X_{O2}$

There are two unknown quantities ($\dot{V}$ and X), so two equations are needed to calculate them

Material balance equation for this nonreactive continuous process has the simple form

input = output

Three possible balances can be written on total mass balance, O_2 balance and CO balance

Two of these provide the equations needed to determine the unknown variables.

These general rules apply to nonreactive processes:

- The maximum number of independent equations that can be derived by writing balances on a nonreactive system equals the number of chemical species in the input and output streams
- Write balances first that involve the fewest unknown variables

Apply to the above example

Equations are independent if you cannot derive one by adding and subtracting combinations of others

Example – consider $x=3$, $y=2$, $x+y=5$ or $x+2y=4$ and $3X+6y=12$

When we make molecular species balances to analyze a reactive system, the analysis must account for the number of independent chemical reactions among the chemical species.

Chemical reactions are independent if the stoichiometric equation of any one of them cannot be obtained by adding and subtracting multiples of the stoichiometric equations of the others

Example – consider the reactions

$A = 2B$

$B = C$

$A = 2C$

See that any two of them are independent

Example - a steady-state continuous process involves the following reaction

$CH_4 + 2O_2 = CO_2 + 2H_2O$

One hundred kmol/min of methane and 200 kmol/min of air is fed to the furnace at 500 C. Methane burns partially during the process to produce CO_2 and H_2O. Its flow rate out is 20 kmol/min

How many independent molecular species are involved in the process?

Write the stoichiometric equations for the combustion of methane with oxygen to CO and CO_2. How many independent reactions are there in the system?

Degree of Freedom Analysis

Metallurgical material balance problems have multiple input and output streams and many variables. If the problem description is not complete with all the relevant independent equations, it will not be possible to solve it.

Degree of Freedom Analysis is the method that helps us decide if the problem is described completely and it is solvable.

Degree of Freedom Analysis is done by counting the unknown variables on the chart, counting the independent equations relating them and subtracting the second from the first. The result is the degree of freedom of the process:

$n_{df} = n_{unknowns} - n_{independenteqns}$

The possibilities are:

1. $n_{df} = 0$, there are n independent equations in n unkowns and the problem can be solved
2. $n_{nd} > 0$, there are more unknowns than independent equations relating them. At least n_{df} additional variable values must be specified in the problem, or the relations have infinitely many solutions
3. $n_{df} < 0$, there are more independent equations than unknowns.
   In this case either the flowchart is incompletely labeled or the problem is overspecified with redundant relations

The sources of equations relating unknown process stream variables may be:

- Material balances

  No more than n_{ms} independent material balances can be written for a nonreactive system where n_{ms} is the number of molecular species in the system
- Energy balances

  The energy balance provides a relationship between inlet and outlet material flows and temperatures if the amount of energy exchanged between the system and its surroundings is specified or is an unknown process variable
- Process specifications

  The problem statement may specify how several process variables are related. For example it may state that CO fuel entering a furnace is present in the off-gases by 40%

  $\dot{V_{in}} = 0.4 * \dot{V_{out}}$
- Physical properties and law

  Two of the unknown variables may be the mass and volume of a stream material. In this case a tabulated density value or an ideal gas equation of state would provide an equation relating them.
- Physical constraints

  The mole fractions of three components of a stream X_a, X_b, X_c are related as $X_a+X_b+X_c = 1$. So X_c is actually $1-X_a-X_b$
- Stoichiometric relations (if chemical reactions occur in the system)

  The stoichiometric numbers of the reaction provide relationships between reactants consumed and products generated

General procedure for the Degree of Freedom Analysis

1. Choose as a basis of calculation an amount or flow rate of one of the process streams
2. Draw a flowchart and fill in all known variable values. Then label unknown stream variables on the chart

The flowchart is completely labeled if you can express the mass or mass flow rate of each component of each stream in terms of labeled quantities. (or mole and mole flow rates)

3. Express what the problem statement asks you to determine in terms of the labeled variables.
4. If you are given mixed mass and mole units for a stream, convert all quantities to one basis
5. Do the Degree of Freedom analysis

Count unknowns and identify equations that relate them. If you count more unknown variables than the equations or vice versa, find what's wrong. There is no point to go further and try to solve the problem.

6. If the system has zero degrees of freedom, write the equations in an efficient order, minimizing simultaneous equations. Highlight the variables in the equations for which you will solve for.
7. Solve the equations and fill the missing values in the flowchart
8. Calculate the quantities requested in the problem statement
9. Scale the process if necessary

Balances on reactive processes

Consider a steady-state continuous process that involves the following reaction

$CH_4 + 2O_2 = CO_2 + 2H_2O$

One hundred kmol/min of methane and 200 kmol/min of air is fed to the furnace at 500 C. Methane burns partially during the process. Its flow rate out is 20 kmol/min.

A number of different balances can be written for this process:

Total mass : input = output

CH_4: input = output + consumption

O_2: input = consumption

CO_2: generation = output

H_2O: generation = output

N_2: input = output

Balance equations may also be written for atomic carbon, hydrogen, oxygen and nitrogen regardless of the molecular species in which the they are found. Balances on atomic species are always in the form input = output

In general, systems that involve chemical reactions may be analyzed using three types of balances:

1. Molecular species balances (always used in nonreactive systems)
2. Atomic species balances
3. Extents of reaction

All three give the same result with varying difficulties

Degree of Freedom analyses for each approach involve different terms

DOF analysis involving molecular species balances in reactive systems

The balances on reactive molecular species must be in the form

Input + generation = output + consumption

Once a generation or consumption term has been calculated for a species in a reaction, those for all other species in that reaction can be determined directly from the stoichiometric equation.

A generation or consumption term must therefore be available for each independent reaction

DOF analysis:

Number of unknown labeled variables

+ Number of independent chemical reactions

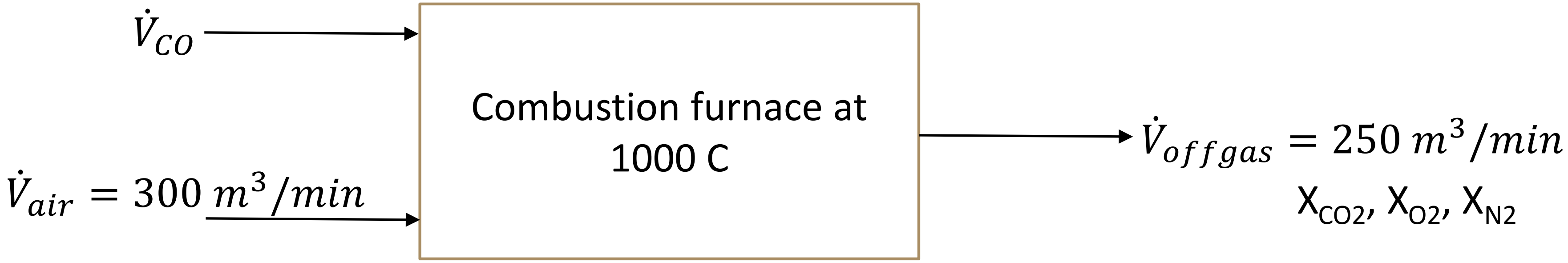
- Number of independent molecular species balances

- Number of other equations relating unknown variables

= Number of degrees of freedom

Example

A stream of CO and a stream of air (0.79% N_2, 0.21% O_2) at 120 m^3/min enter a combustion furnace. CO is fully combusted to CO_2. The flow rate of the off-gas is measured and found as 141 m_3/min. Calculate the flow rates of inlet streams and the concentration of the outlet stream.



$\dot{V}_{CO}$

$\dot{V}_{air} = 300\, m^3/min$

Combustion furnace at 1000 C

$\dot{V}_{offgas} = 250\, m^3/min$

X_{CO2}, X_{O2}, X_{N2}

DOF analysis

4 unknown labeled variables ($\dot{V}_{CO}$, X_{CO2}, X_{O2}, X_{N2})

+ 1 independent chemical reactions

- 4 independent molecular species balances (CO, CO_2, O_2, N_2)

- 1 other equation relating unknown variables ($X_{CO2} + X_{O2} + X_{N2} = 1$)

= 0 degrees of freedom

DOF analysis involving atomic species balances in reactive systems

As all balances on atomic species are in the form input = output, no additional degrees of freedom are contributed by the reactions

DOF analysis:

Number of unknown labeled variables

- Number of independent molecular species balances

- Number of molecular balances on independent nonreactive species

- Number of other equations relating unknown variables

= Number of degrees of freedom

In the CO combustion process, the 4 unknowns will be determined from balances on atomic carbon, and oxygen:

4 unknown labeled variables ($\dot{V}_{CO}$, X_{CO2}, X_{O2}, X_{N2})

- 2 independent atomic species balances that are involved in the reactions (C, O)

- 1 molecular balances on independent nonreactive species (N_2)

- 1 other equation relating unknown variables ($X_{CO2} + X_{O2} + X_{N2} = 1$)

= 0 degrees of freedom

DOF analysis involving extents of reactions in reactive systems

Each product species flow rate is expressed in terms of reaction extents

The extents of reactions and the flow rates for the remaining reactive species are found from known feed and product flow rates

DOF analysis:

Number of unknown labeled variables

+ Number of independent reactions (one extent of reaction for each)

- Number of independent reactive species (one equation for each species in terms of extents of reaction)

- Number of independent nonreactive species (one balance equation for each)

- Number of other equations relating unknown variables

= Number of degrees of freedom

For the CO combustion process:

4 unknown labeled variables ($\dot{V}_{CO}$, X_{CO2}, X_{O2}, X_{N2})

+ 1 independent reaction

- 3 independent reactive species (CO, O_2, CO_2)

- 1 independent nonreactive species (N_2)

- 1 other equations relating unknown variables ($X_{CO2} + X_{O2} + X_{N2} = 1$)

= 0 Number of degrees of freedom