Chapter 1

Process analysis – The importance of mass and energy balances

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Concepts of Chemical Engineering for Chemists

Chapter 1

Process analysis - The importance of mass and energy balances

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1.1 Introduction

Process engineering includes the generation, study and analysis of process designs. All processes must obey some fundamental laws of conservation.

We can group these into conservation of matter and conservation of energy.[1] Mass and energy balances are fundamental operations in the analysis of any process. This chapter describes some of their basic principles.

1.1.1 Nomenclature and units of measurement

In carrying out any analysis, it is important to ensure that all units of measurement used are consistent. For example, mass may be given in kg (kilogrammes), in lb (pounds) or in many other units. If two quantities are given in different units, one quantity must be converted to the same units as the other quantity. Any book on chemical engineering (or physics and chemistry) will have conversion tables for standard units.

There are 7 fundamental quantities which are typically used to describe chemical processes, mass, length, volume, force, pressure, energy and power, although some of these can be described in terms of others in the list. For example, volume is length raised to the power 3; power is energy per unit time, pressure is force per area or force per length squared, and so on.

Chemical engineering uses some standard notation for many of the quantities we will encounter in process analysis. These are summarized in Table 1.1, where the dimensional terms are T for time, M for mass and L for length.

In describing processes, the variables that describe the condition of a process

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[1]These two laws are separate in non-nuclear processes. For nuclear processes, we of course have the well known equation, $E = mc^2$, which relates mass and energy. For this lecture, we will consider only non-nuclear processes, but the same fundamental principles apply to all processes.

Table 1.1:   Some of the quantities encountered in process analysis with typical notation and units of measurement.

Quantity	Notation	Dimension	Units
Time	t	T	s
Mass	m	M	kg
Mass Flow	$\dot{m}$	MT^{-1}	kg s^{-1}
Mole	n	M	mol
Molar Flow	$\dot{n}$	MT^{-1}	mol s^{-1}
Pressure	P	$MT^{-2}L^{-2}$	bar
Energy	H, Q, W	ML^2T^{-2}	Joule

fall into two categories:

extensive variables, which depend on (are proportional to) the size of the system, such as mass and volume, and

intensive variables, which do not depend on the size of the system, such as temperature, pressure, density and specific volume, and mass and mole fractions of individual system components.

The number of intensive variables that can be specified independently for a system at equilibrium is known as the **degrees of freedom** of the system.

1.2   Mass balances

Chemical processes may be classified as batch, continuous or semibatch and as either steady-state or transient. Although the procedure required for performing mass, or material, balances depends on the type of process, most of the concepts translate directly to all types.

The general rule for the mass balance in a *system box* (a box drawn around the complete process or the part of the process of interest) is

$$\text{input} + \text{generation} - \text{output} - \text{consumption} = \text{accumulation} \qquad (1.1)$$

where

input: the material entering through the system box. This will include feed and makeup streams.

generation: material produced within the system, such as the reaction products in a reactor.

output: the material which leaves through the system boundaries. These will typically be the product streams of the process.

consumption: material consumed within the system, such as the reactants in a reactor.

accumulation: the amount of material that builds up within the system.

In a steady-state continuous process, the accumulation should always be zero, which leads to a more simple mass balance equation:

$$\text{input} + \text{generation} = \text{output} + \text{consumption} \qquad (1.2)$$

In the case of systems with no reaction, where mass is neither generated nor

consumed, the result is even simpler:

$$\text{input} = \text{output} \tag{1.3}$$

1.2.1 Process analysis procedure

The analysis of the mass balance of a process typically follows a number of steps:

1. Draw and label a diagram for the process, clearly indicating the information given by the problem definition and the values that have been requested.

2. Choose a basis of calculation, if required. If no extensive variables (e.g. amount or flow rate of a stream) have been defined, a basis of calculation is required and this must be an extensive variable.

3. Write down appropriate equations until the number of equations equals the number of unknown variables and such that all the desired unknown variables are referred to in the equations. Possible sources of equations include the following:

    (a) Mass balances. For a system with n species, n mass balance equations may be written down. These mass balance equations may be drawn from a total mass balance and from individual species mass balances. The only exception is where the system box contains solely a splitter, where all the streams have the same

composition and differ only in extensive variables. In this case, only one mass balance equation can be included.

(b) Process specifications and conditions, such as, for example, the separation achieved by a distillation unit or the conversion in a reactor.

(c) Definitions, such as the relationship between density, mass and volume or the relationship between mole fraction and total mass.

4. Identify the order in which the equations should be solved.

5. Solve the equations for the unknown values.

These steps are illustrated by the following example.

Example 1. Mass balance on a continuous distillation process

Suppose that 1000 kmol h^{-1} of a feed stream, consisting of 30.0% by mole n-pentane and the remainder n-hexane, is to be separated into 95.0 molar% pentane and 95.0 molar% hexane streams using a distillation column. Determine the flow rates of the output streams through the use of mass balances, assuming steady state operation. We will assume three digits of signficance for this example.

Solution:

The first step is to draw and label a flowsheet diagram, indicating the process steps and all the streams. Figure 1.1 shows the layout of the distillation unit labelled with both the known variables and the variables we wish to determine. The system box for this example is the whole process, i.e. the distillation unit. The streams we wish to consider are those that intersect this system box and consist of the feed stream and the two output streams. All other streams can be ignored in solving this example.
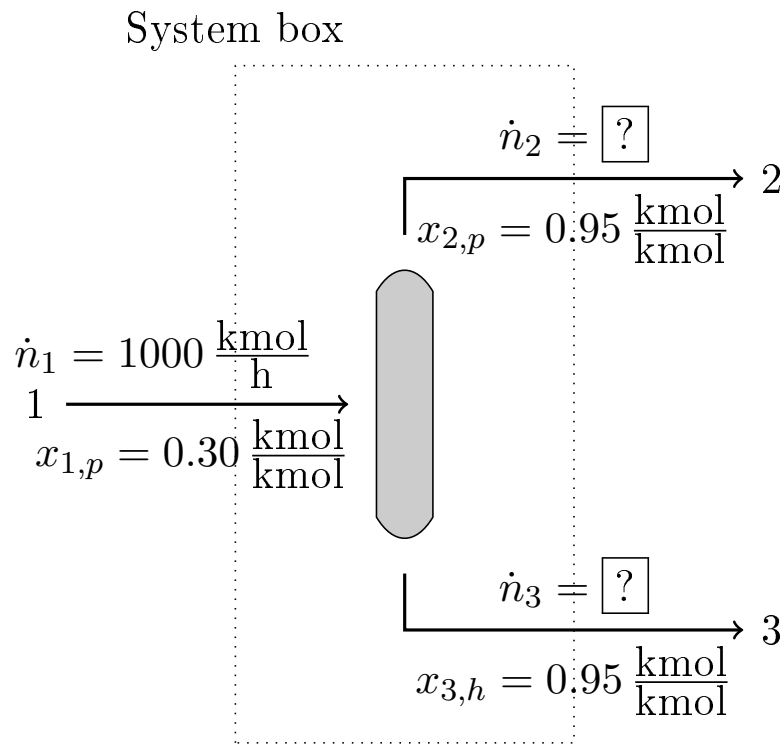

Figure 1.1: Distillation process diagram for Example 1, showing the system box and the streams that intersect this system box.

Each of the three streams has been numbered and subscripts are used on every variable associated with streams. $\dot{n}$ is a molar flowrate and x is a mole fraction. We know one flow rate, that of the feed, and wish to determine the flow rates of the two product or output streams, $\dot{n}_2$ and $\dot{n}_3$. The p subscript refers to pentane and h to hexane.

There are two unknowns and, as there are two species involved, we can write down two mass balance equations. We should be able to solve this problem.

As this is the simplest case described above (steady state, continuous and no reaction), we can use the simplest mass balance equation:

$$\text{input} = \text{output}$$

As indicated above, we have two unknowns. Therefore, we need to generate two independent equations that will allow us to solve for these unknowns. For mass balance problems, the general rule is that we can define n_c equations if there are n_c components in the streams involved in the mass balance problem defined by the system box chosen. The one exception is that if the system box includes only a splitter, there is only one independent equation that can be defined. This is because the splitter does not change the compositions of the streams involved, only the amounts or flows.

For this example, we have two components, so we can define two mass balance equations. The choice of equations is a total mass balance and two individual

component balances:

$$\dot{n}_1 = \dot{n}_2 + \dot{n}_3 \tag{1.4}$$

$$x_{1,p}\dot{n}_1 = x_{2,p}\dot{n}_2 + x_{3,p}\dot{n}_3 \tag{1.5}$$

$$x_{1,h}\dot{n}_1 = x_{2,h}\dot{n}_2 + x_{3,h}\dot{n}_3 \tag{1.6}$$

We can choose any two of these three equations to solve our problem. For this example, we will choose the total mass balance, eq. (1.4), and the pentane mass balance, eq. (1.5). Together with the mole fraction values already labelled on the diagram, we are left with 0 degrees of freedom. The number of degrees of freedom is defined as the difference between the number of unknowns and the number of equations relating these unknowns.

Although it would appear that we have more than 2 unknowns, we implicitly know the value of $x_{3,p}$ as mole fractions must add up to 1. We can either consider that we know the value of $x_{3,p}$ or we can explictly add the equation

$$x_{3,p} + x_{3,h} = 1$$

Either way, we end up with 0 degrees of freedom.

We can solve the two equations, 1.4 and 1.5, by rearranging the first equation to have $\dot{n}_2$ alone on one side and then replace $\dot{n}_2$ in the second equation with

the expression on the other side. The second equation can be solved for $\dot{n}_3$. This value can then be used to solve the first equation for $\dot{n}_2$.

$$(1.4) \Rightarrow \qquad\qquad \dot{n}_2 = \dot{n}_1 - \dot{n}_3 \qquad\qquad (1.7)$$

$$(1.5) \Rightarrow \qquad\qquad x_{1,p}\dot{n}_1 = x_{2,p}\left(\dot{n}_1 - \dot{n}_3\right) + x_{3,p}\dot{n}_3$$

$$\Rightarrow \qquad \left(x_{3,p} - x_{2,p}\right)\dot{n}_3 = x_{1,p}\dot{n}_1 - x_{2,p}\dot{n}_1$$

$$\Rightarrow \qquad\qquad \dot{n}_3 = \frac{x_{1,p} - x_{2,p}}{x_{3,p} - x_{2,p}}\dot{n}_1$$

$$= \frac{x_{1,p} - x_{2,p}}{\left(1 - x_{3,h}\right) - x_{2,p}}\dot{n}_1$$

$$= \frac{0.3 - 0.95}{\left(1 - 0.95\right) - 0.95} \times 1000\,\frac{\text{kmol}}{\text{h}}$$

$$= 722\,\frac{\text{kmol}}{\text{h}}$$

$$(1.7) \Rightarrow \qquad\qquad \dot{n}_2 = 1000\,\frac{\text{kmol}}{\text{h}} - 722\,\frac{\text{kmol}}{\text{h}} = 278\,\frac{\text{kmol}}{\text{h}}$$

The example has been solved. We can now use the unused mass balance equation, in this case being the hexane component mass balance, eq. (1.6), to provide a check for consistency:

$$x_{1,h}\dot{n}_1 = x_{2,h}\dot{n}_2 + x_{3,h}\dot{n}_3$$

$$\therefore \qquad (1 - x_{1,p})\dot{n}_1 = (1 - x_{2,p})\dot{n}_2 + x_{3,h}\dot{n}_3$$

$$\therefore \qquad 0.7 \times 1000 \, \frac{\text{kmol}}{\text{h}} = 0.05 \times 278 \, \frac{\text{kmol}}{\text{h}} + 0.95 \times 722 \, \frac{\text{kmol}}{\text{h}}$$

$$\checkmark \qquad 700 \, \frac{\text{kmol}}{\text{h}} = 700 \, \frac{\text{kmol}}{\text{h}}$$

(assuming three significant digits in the calculations) so the results are at least consistent which gives some confidence in their correctness.

1.2.2 Processes with reactions

For processes involving reactions, the mass balance equation, eq. (1.3), used in the first example, is not sufficient. Equations (1.1) or (1.2) must be used. The presence of reactions means that the *generation* and *consumption* terms in these equations are non-zero. The first key difference between a simple separation process and a process involving reactions is the need to define these extra terms in terms of the amounts of the components in the system. Extra equations are required to satisfy the extra degrees of freedom introduced by having these extra terms present. There is another key difference: each reaction has associated with it a degree of freedom, one which essentially describes the extent to which the reaction takes place. Therefore, the analysis of a process involving a reaction will require extra equations to satisfy degrees of freedom introduced by the reactions taking place.

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Two concepts are often used to describe the behaviour of a process involving reactions: *conversion* and *selectivity*. Conversion is defined with respect to a particular reactant and describes the extent of the reaction that takes place relative to the amount that could take place. If we consider the *limiting reactant*, the reactant that would be consumed first based on the stoichiometry of the reaction, the definition of conversion is straightforward:

$$\text{conversion} \equiv \frac{\text{amount of reactant consumed}}{\text{amount of reactant fed}}$$

Selectivity is a concept that applies to processes with multiple simultaneous reactions. It is used to quantify the relative rates of the individual reactions. However, any discussion about multiple reactions and the analysis of these is beyond the scope of this chapter. Refer to the further reading material identified at the end of this chapter for more information. In any case, the specification of conversion and/or selectivity will often provide the extra information required to satisfy those extra degrees of freedom introduced by having reactions present in the process.

Example 2: Mass balance on a process with reaction.

Suppose that an initially empty tank is filled with 1000 mol of Ethane (C_2H_6) and the remainder air. A spark is used to ignite this mixture and the following combustion reaction takes place:

$$2\,C_2H_6 + 7\,O_2 \longrightarrow 4\,CO_2 + 6\,H_2O \qquad (1.8)$$
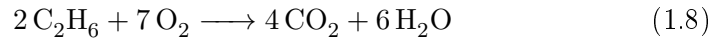
Assume that the amount of air provides twice the stoichiometric requirement of oxygen for this reaction and that air is composed of 79% nitrogen and the remainder oxygen. Suppose that the reaction reaches a 90% conversion. What is the composition of the mixture in the tank at the end?

Solution

As in the first example, the first step is to draw and label a diagram, as shown in Figure 1.2. This example is a batch problem, so arrows indicate material flow in the sense of loading and discharging the reactor. The subscripts for mass amounts are the stream index (1 for the original contents of the tank and 2 for the final contents after combustion) and the species involved. The key is E for ethane, O for oxygen, N for nitrogen, C for carbon dioxide and W for water.

As in the first example, the boxed question marks highlight the variables which need to be determined. As there are five highlighted variables, we will require at least five equations. As there are five species involved, five mass balance equations can be defined. In this case, we should use eq. (1.1), but with *accumulation* set to zero to indicate that the tank is empty to start with and also empty at the end. This means that the mass balance equation we should use is identical in form to eq. (1.2):
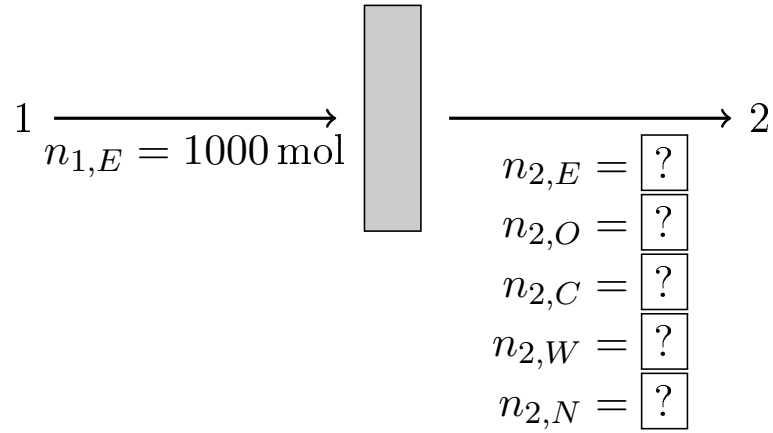
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key: $\boxed{2\,\mathrm{E} + 7\,\mathrm{O} \longrightarrow 4\,\mathrm{C} + 6\,\mathrm{W}}$

$$1 \xrightarrow{\quad\quad\quad\quad} \qquad\qquad \xrightarrow{\quad\quad\quad} 2$$

$n_{1,E} = 1000\,\mathrm{mol}$

$n_{2,E} = \boxed{?}$

$n_{2,O} = \boxed{?}$

$n_{2,C} = \boxed{?}$

$n_{2,W} = \boxed{?}$

$n_{2,N} = \boxed{?}$
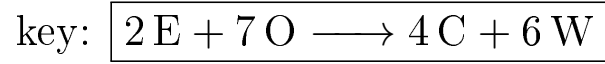
Figure 1.2:   Diagram for the reaction mass balance problem for the combustion of ethane.

$$\mathrm{input} + \mathrm{generation} = \mathrm{output} + \mathrm{consumption}$$

However, as there is one reaction taking place, we will need another equation to satisfy our degrees of freedom. We will use the specification of conversion to provide this extra equation.

The result is 6 equations:

$$
\left.
\begin{aligned}
n_{1,E} + n_{g,E} &= n_{2,E} + n_{c,E} && \text{(ethane balance)} \\
n_{1,O} + n_{g,O} &= n_{2,O} + n_{c,O} && \text{(oxygen balance)} \\
n_{1,N} + n_{g,N} &= n_{2,N} + n_{c,N} && \text{(nitrogen balance)} \\
n_{1,C} + n_{g,C} &= n_{2,C} + n_{c,C} && \text{(carbon dioxide balance)} \\
n_{1,W} + n_{g,W} &= n_{2,W} + n_{c,W} && \text{(water balance)} \\
\text{conversion} &= \frac{n_{1,E} - n_{2E}}{n_{1,E}} && \text{(specification)}
\end{aligned}
\right\} \quad (1.9)
$$

where the subscript g is used to indicate an amount generated and the subscript c indicates an amount consumed. At this point, all the variables except for $n_{1,E}$ are unknown. We have 19 unknown variables. As we have just defined 6 equations, we have 13 degrees of freedom remaining.

To solve this problem, therefore, it would seem that we need to define at least 13 more equations. We can write down new equations relating the unknown and known variables by making use of the stoichiometric coefficients given by eq. (1.8). It is helpful to write all of these in terms of one of the consumption or generation terms. In this case, given that the key process specification is the conversion of ethane, it helps to write the equations in terms of the amount of ethane consumed:

$$
\left.
\begin{aligned}
n_{g,E} &= 0 & \text{(no ethane is generated)} \\[6pt]
n_{g,O} &= 0 & \text{(no oxygen is generated)} \\[6pt]
n_{c,O} &= \frac{7}{2} n_{c,E} & \\[6pt]
n_{g,N} &= 0 & \text{(no nitrogen is generated)} \\[6pt]
n_{c,N} &= 0 & \text{(no nitrogen is consumed)} \\[6pt]
n_{g,C} &= \frac{4}{2} n_{c,E} & \\[6pt]
n_{c,C} &= 0 & \text{(no carbon dioxide is consumed)} \\[6pt]
n_{g,W} &= \frac{6}{2} n_{c,E} & \\[6pt]
n_{c,W} &= 0 & \text{(no water is consumed)}
\end{aligned}
\right\} \quad (1.10)
$$

This set of 9 equations reduces the degrees of freedom to 4 as no new variables have been introduced.

Further equations can be defined based on the specifications of the feed:

$$
\left.
\begin{aligned}
n_{1,O} &= 2 \times \frac{7}{2} n_{1,E} & \text{(twice as much as required)} \\[6pt]
n_{1,N} &= 0.79 \times \frac{n_{1,O}}{0.21} & \text{(nitrogen is remainder of air)} \\[6pt]
n_{1,C} &= 0 & \text{(no carbon dioxide in the feed)} \\[6pt]
n_{1,W} &= 0 & \text{(no water in the feed)}
\end{aligned}
\right\} \quad (1.11)
$$

This set of 4 equations also introduces no new unknown variables. The result is that we have 19 equations, comprising the three sets of equations above, (1.9), (1.10) and (1.11). These can now be solved as follows. Given

$n_{1,E} = 1000\,\text{mol}$, the initial amount of ethane, we evaluate the equations in set (1.11):

$$
\begin{aligned}
n_{1,O} &= 2 \times \frac{7}{2} n_{1,E} = 7 \times 1000 \text{ mol} = 7000 \text{ mol} \\
n_{1,N} &= 0.79 \times \frac{n_{1,O}}{0.21} = 0.79 \frac{7000 \text{ mol}}{0.21} \approx 26333 \text{ mol} \\
n_{c,E} &= 0.90 \times n_{1,E} = 0.90 \times 1000 \text{ mol} = 900 \text{ mol}
\end{aligned}
$$

Now determine the amounts generated and consumed for each species using the set of equations (1.10):

$$
\begin{aligned}
n_{c,O} &= \frac{7}{2} n_{c,E} = \frac{7}{2} \times 900 \text{ mol} = 3150 \text{ mol} \\
n_{g,C} &= \frac{4}{2} n_{c,E} = \frac{4}{2} \times 900 \text{ mol} = 1800 \text{ mol} \\
n_{g,W} &= \frac{6}{2} n_{c,E} = \frac{6}{2} \times 900 \text{ mol} = 2700 \text{ mol}
\end{aligned}
$$

Finally, we use the mass balance equations, (1.9), to determine the amount of each species in the output:

$$
\begin{aligned}
n_{2,E} &= n_{1,E} + n_{g,E} - n_{c,E} = 1000 \text{ mol} + 0 - 900 \text{ mol} = 100 \text{ mol} \\[6pt]
n_{2,O} &= n_{1,O} + n_{g,O} - n_{c,O} = 7000 \text{ mol} + 0 - 3150 \text{ mol} = 3850 \text{ mol} \\[6pt]
n_{2,N} &= n_{1,N} + n_{g,N} - n_{c,N} = 26333 \text{ mol} + 0 - 0 = 26333 \text{ mol} \\[6pt]
n_{2,C} &= n_{1,C} + n_{g,C} - n_{c,C} = 0 + 1800 \text{ mol} - 0 = 1800 \text{ mol} \\[6pt]
n_{2,W} &= n_{1,W} + n_{g,W} - n_{c,W} = 0 + 2700 \text{ mol} - 0 = 2700 \text{ mol}
\end{aligned}
$$

1.2.3   More complex process configurations

The two examples above consist of a single processing unit or step. More realistic problems will consist of multiple steps. When there are multiple steps, connected to each other, we have not only input and output streams, but also internal streams. In such a case, we have alternative system boxes and we often need to consider more than one such box to solve a problem. The key concept is that the input and output streams in the mass balance equations are only those streams that enter or leave the particular system box. Streams internal to the system box are not involved at all.

Example 3: Process with recycle

Consider the production of cyclohexane from 1-hexene, both C_6H_{12}, but with different configurations of the atoms:

C

C   C

C   C   C

C   C   C   C   C

1-hexene   C

cyclohexane
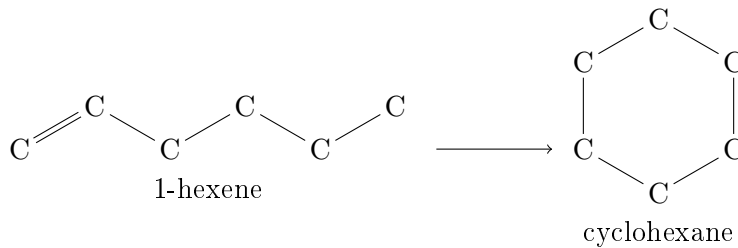
This reaction does not achieve 100% conversion, so the *effluent* (the output) from the reactor needs to be processed to separate the reactant from the product. This is undertaken using a distillation unit. Any unused reactant is then recycled back to the reactor.

The feed to the continuous process, which should operate at steady state, is 10 mol s^{-1} pure 1-hexene. The product is to be cyclohexane at 95 molar% purity. The reactor effluent will be fed to a distillation unit that has two outputs: a distillate stream and a bottoms stream. The distillate product is to contain 90 mol% 1-hexene and the bottoms product should meet the process requirements. The distillate is combined with the feed to the process before the mixture is sent to the reactor. This mixture will be 95 molar% 1-hexene.

We want to find the composition of all streams in the process and the conversion that is achieved in the reactor.

Solution

We start by drawing and labelling the process diagram, including all the information we have about the process. This is shown in Figure 1.3. There
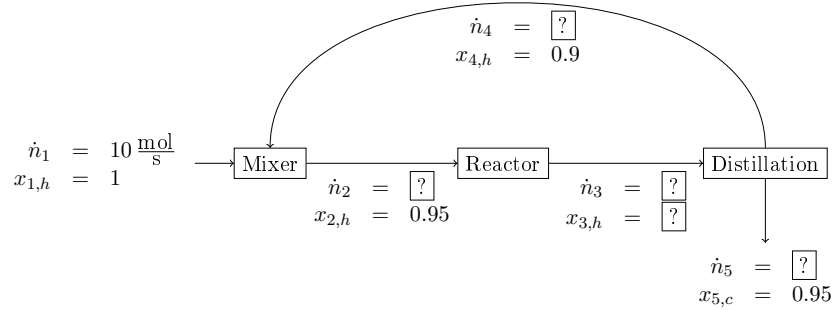
are 5 streams involved at this level of view.

Figure 1.3: Process diagram for Example 3. h as a subscript refers to 1-hexene and c as a subscript refers to cyclohexane.

If we take the whole process as the system box, we have one input stream, the feed, and one output stream, the bottoms product of the distillation unit. There are two unknowns: the amount of the output and the extent of the reaction overall. We can write two equations, one for each species using eq. 1.2:

$$x_{1,h}\dot{n}_1 = (1 - x_{5,c})\dot{n}_5 + \dot{n}_{c,h} \quad \text{(1-hexene mass balance)} \quad (1.12)$$

$$(1 - x_{1,h})\dot{n}_1 + \dot{n}_{g,c} = x_{5,c}\dot{n}_5 \qquad \text{(cyclohexane mass balance)}$$

$$(1.13)$$

where $\dot{n}_{c,h}$ is the rate at which 1-hexene is consumed and $\dot{n}_{g,c}$ the rate at which cyclohexane is generated. These two equations have three unknowns, so we need at least another equation to be able to solve them. This equation

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comes from the stoichiometry, which tells us that for each mole of 1-hexene consumed, 1 mole of cyclohexane is generated:

$$\dot{n}_{c,h} = \dot{n}_{g,c} \tag{1.14}$$

Solving this set of three equations, given the input flow rate and the mole fractions of 1-hexene in the feed stream and cyclohexane in the output stream, we find that $\dot{n}_5 = 10$ mol s^{-1}. The rate at which 1-hexene is consumed and cyclohexane is generated are both 9.5 mol s^{-1}.

To determine the flows and compositions of the other streams in the process, we have to consider different system boxes. For instance, we can use a system box that contains only the mixer, as shown in figure 1.4. Given the specification on the inlet to the reactor, that the composition is 95% 1-hexene, we have two unknowns and we can write two mass balance equations for this system box:

$$
\begin{aligned}
\dot{n}_4 &= \boxed{?} \\
x_{4,h} &= 0.9
\end{aligned}
$$

$$
\begin{aligned}
\dot{n}_1 &= 10\,\frac{\text{mol}}{\text{s}} \\
x_{1,h} &= 1
\end{aligned}
\quad\longrightarrow\ \boxed{\text{Mixer}}\longrightarrow\quad
\begin{aligned}
\dot{n}_2 &= \boxed{?} \\
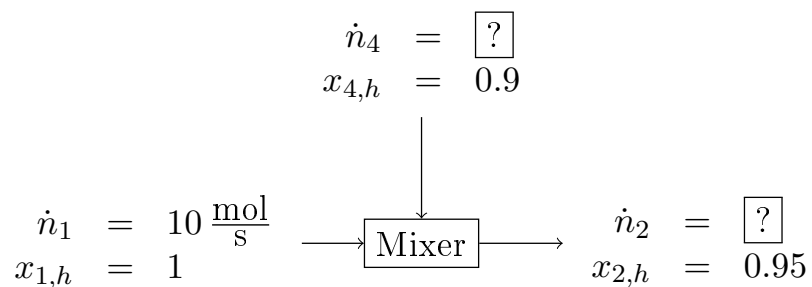x_{2,h} &= 0.95
\end{aligned}
$$

Figure 1.4: System box containing only the mixer for the process in example 3.

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$$\dot{n}_1 + \dot{n}_4 = \dot{n}_2 \qquad \text{(total mass balance)} \qquad (1.15)$$

$$x_{1,h}\dot{n}_1 + x_{4,h}\dot{n}_4 = x_{2,h}\dot{n}_2 \qquad \text{(1-hexene mass balance)} \qquad (1.16)$$

We can solve these two equations to get $\dot{n}_2 = 20$ mol s^{-1} and $\dot{n}_4 = 10$ mol s^{-1}.

With stream 4 known, we can now determine stream 3 by considering a system box around the distillation unit, as shown in Figure 1.5. We again have two unknowns, $\dot{n}_3$ and $x_{3,h}$, and we can write two mass balance equations:

$$\dot{n}_3 = \dot{n}_4 + \dot{n}_5 \qquad \text{(total mass balance)} \qquad (1.17)$$

$$x_{3,h}\dot{n}_3 = x_{4,h}\dot{n}_4 + (1 - x_{5,c})\dot{n}_5 \qquad \text{(1-hexene mass balance)} \qquad (1.18)$$

which yields $\dot{n}_3 = 20$ mol s^{-1} and $x_{3,h} = 0.475$.

We now have determined all the stream compositions and can therefore cal-

$$
\dot{n}_4 = 10\,\frac{\text{mol}}{\text{s}}
$$
$$
x_{4,h} = 0.9
$$

$$
\dot{n}_3 = \boxed{?}
$$
$$
x_{3,h} = \boxed{?}
$$

Distillation

$$
\dot{n}_5 = 10\,\frac{\text{mol}}{\text{s}}
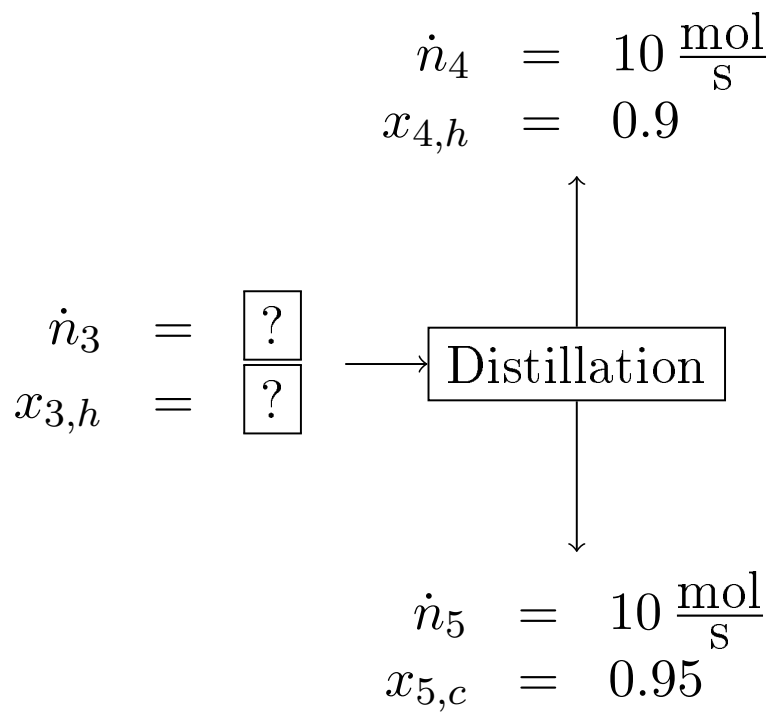$$
$$
x_{5,c} = 0.95
$$

Figure 1.5: System box containing only the distillation unit for the process in example 3.

culate the single pass conversion of the reactor:

$$\text{conversion} = \frac{\text{reactant consumed}}{\text{reactant fed}} \tag{1.19}$$

$$= \frac{x_{2,h}\dot{n}_2 - x_{3,h}\dot{n}_3}{x_{2,h}\dot{n}_2} \tag{1.20}$$

$$= \frac{0.95 \times 20\,\frac{\text{mol}}{\text{s}} - 0.475 \times 20\,\frac{\text{mol}}{\text{s}}}{0.95 \times 20\,\frac{\text{mol}}{\text{s}}} \tag{1.21}$$

$$= 0.5 \tag{1.22}$$

which is 50%.

1.3 Energy balances

Energy balances can be treated in much the same way as material balances. The only fundamental difference is that there are three types of energy (for non-nuclear processes):

kinetic: Energy due to the translational motion of the system as a whole, relative to some frame of reference (the earth's surface, for instance) or to the rotation of the system about some axis.

potential: Energy due to the position of the system in a potential field. In chemical engineering, the potential field will typically be gravitational.

internal: All energy possessed by the system other than kinetic or potential. For example, the energy due to the motion of molecules relative to the

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centre of mass of the system and to the motion and interactions of the atomic and subatomic constituents of the molecules.

Energy may be transferred between a system and its surroundings in two ways:

1. As <u>heat</u>, or energy that flows as a result of a temperature difference between a system and its surroundings. The direction of flow is always from the higher temperature to the lower. Heat is defined as *positive* when it is transferred to the system from its surroundings.

2. As <u>work</u>, or energy that flows in response to any driving force other than a temperature difference. For example, if a gas in a cylinder expands and moves a piston against a restraining force, the gas does work on the piston. Energy is transferred as work from the gas to its surroundings, including the piston. Positive work means work done by the system on its surroundings, although this convention is sometimes not followed and one should be careful to note the convention used by other people.

In this chapter, we will deal solely with heat.

Energy and work have units of force times distance, such as a Joule (J), which is a Newton-metre (N m). Energy is sometimes measured as the amount of heat that must be transferred to a specified mass of water to raise the temperature of the water a specified temperature interval at a specified

pressure (e.g. 1 kcal corresponds to raising 1 kilogramme of water from 15 °C to 16 °C).

As in material balances, energy must be conserved.[2] We have two energy balance equations: one for *closed* systems and one for *open* systems. A closed system is one in which no mass comes in or goes out of the process during its operation. An example of this would be a batch process with an initial state and a final state. An open system has mass coming in and/or going out during the operation. A continuous process is an example of an open system. In either case, the energy balance equations are based on the first law of thermodynamics.

The full energy balance equation for a *closed* system is

$$\Delta U + \Delta E_k + \Delta E_p = Q - W \tag{1.23}$$

where ΔU is the difference in internal energy of all the streams at the end of the process in relation to those streams at the start of the process, ΔE_k the change in kinetic energy of the system, ΔE_p the change in potential energy of the system, Q the amount of heat put into the system and W the amount of work done by the system.

For continuous processes, we wish to consider rates of energy, so the equivalent equation is

$$\Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p = \dot{Q} - \dot{W}$$

---

[2]Noting again that we are refering only to non-nuclear processes.

where H is the *enthalpy* of the inlet and outlet streams and the changes in kinetic and potential energies refer to the streams coming out of the process and the streams coming into the process. Specific enthalpy (enthalpy per unit mass), denoted by $\hat{H}$, is defined as the combination of internal energy and *flow work*, the work that is required to move material into and out of a process:

$$\hat{H} = \hat{U} - P\hat{V}$$

where P is the system pressure and $\hat{V}$ the specific volume of the material. The actual rate of enthalpy for a stream, $\dot{H}$, will be calculated by $\dot{n}\hat{H}$.[3] In working with changes of enthalpy, we will use a reference state, a combination of temperature and pressure for which the enthalpy is assumed to be zero. Enthalpy data in property tables is typically given with reference to a specified reference state.

In this chapter we will introduce some of the basic properties required to perform energy balances on a process. Specifically, we will describe how to estimate changes in the rate of enthalpy due to changes in temperature and phase for streams. We will consider open systems and will ignore changes in kinetic and potential energies. For systems in which kinetic and potential energies are assumed to not change or where the changes in these energies

---

[3]This calculation assumes that the specific enthalpy is given in units of energy per mole. However, many tables will have units of energy per unit mass, so a unit conversion using molecular weights may be required.

are assumed to be negligible, the energy balance equation can be reduced to

$$\Delta \dot{H} = \dot{Q} - \dot{W}$$

for an open system.

In working with materials, there are two types of heat:

sensible heat, which signifies heat that must be transferred to raise or lower the temperature of a substance, assuming no change in phase (solid, liquid, gas), and

latent heat, which is the heat necessary to change from one phase to another.

The calculation of sensible heat is based on the *heat capacity* (at constant pressure) of the substance, $C_p(T)$, which is in units of heat (energy) per unit mass. Heat capacity information is typically in the form of coefficients for a polynomial expression:

$$C_p(T) = a + bT + cT^2 + dT^3$$

The values of the coefficients are given in physical property tables found in most chemical engineering reference books. To determine the change in enthalpy in heating a substance from one temperature, T_1, to another temperature, T_2, without a phase change, we integrate the polynomial over

the temperature range:

$$\int_{T_1}^{T_2} C_p(T)\, dT = \left[aT + b\frac{T^2}{2} + c\frac{T^3}{3} + d\frac{T^4}{4} \right]_{T_1}^{T_2} \qquad (1.24)$$

We evaluate the right hand side of this equation as the difference of the polynomial evaluated at T_2 and at T_1. The relation between the heat capacity (integrated over a temperature interval) and the change in enthalpy is exact for ideal gases, exact for nonideal gases only if the pressure is indeed constant, and a close approximation for solids and liquids.

For latent heat, we look up the corresponding entry in the tables for either the *latent heat of vapourization* (or simply the heat of vapourization) or the *heat of fusion*, depending on the type of phase change encountered: liquid to vapour and solid to liquid, respectively. These quantities are in units of energy per unit mass and are given for a specific reference state, often the 1 atm boiling point or melting point of the substance.

The calculation of the change in enthalpy from one temperature to another for a given substance will often be a multi-step process. The main principle is to identify a path of pressure and temperature changes that goes from the initial state to the final state, passing through states at which we have reference data (e.g. the heat of vapourization) available. Any sections of the path that do not involve phase changes will simply require the calculation of sensible heat using the heat capacity equation given above. Phase changes will then require the use of the appropriate latent heat quantity.

For process analysis including energy balances, the same procedure defined for mass balances is followed. The only change is that the source of equations, described in step 3 of the procedure, now includes the energy balance equation, as well as the definition of the different energy terms. Again, this procedure will be illustrated by an example.

1.3.1 Example 3. Energy balance on distillation column:

We again consider the distillation unit introduced in Example 1, updated with temperature information for each of the streams, and now including detail about the inner workings on the unit. Specifically, the process now includes the total condenser, which cools the vapour coming out of the top of the column into liquid, and the reboiler, which boils up the liquid from the bottom of the column into vapour (see Figure 1.6). These two processing steps were previously considered to be internal to the system box used in solving the mass balance problem.

The temperatures noted on the diagram have been estimated using a physical property estimation system. There are a number of computer based tools for estimating physical properties and most simulation software systems will include appropriate methods. Figure 1.6 shows these temperatures, as well as the results obtained earlier. As more streams have been included in this diagram, we have new unknowns. Specifically, we now have the vapour stream, V, from the top of the column to the condenser and the liquid reflux stream, L, from the condenser back into the column. Both of these streams have the

$$
\begin{aligned}
V \\
T_V \quad &= 312.2\,^\circ\mathrm{C} \qquad \dot{Q}_c = \boxed{?} \\
& \qquad\qquad\qquad \text{Condenser}
\end{aligned}
$$

$$
\begin{aligned}
\dot{n}_1 \quad &= 1000\,\tfrac{\text{kmol}}{\text{h}} & \dot{n}_2 \quad &= 278\,\tfrac{\text{kmol}}{\text{h}} \\
x_{1,p} \quad &= 0.30\,\tfrac{\text{kmol}}{\text{kmol}} & T_2 \quad &= 310.2\,^\circ\mathrm{C} \\
T_1 \quad &= 328.1\,^\circ\mathrm{C}
\end{aligned}
$$

L

Reboiler $\qquad \dot{Q}_r = \boxed{?}$

$$
\begin{aligned}
\dot{n}_3 \quad &= 722\,\tfrac{\text{kmol}}{\text{h}} \\
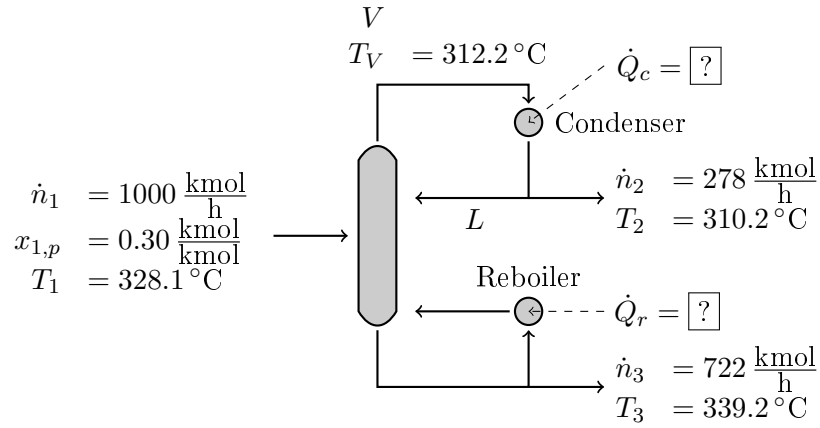T_3 \quad &= 339.2\,^\circ\mathrm{C}
\end{aligned}
$$

Figure 1.6: Distillation unit including a total condenser and a partial reboiler with streams annotated with temperatures.

same composition as the distillate product, stream 2, and their flow rates will be denoted by $\dot{n}_V$ and $\dot{n}_L$, respectively. The relationship between the liquid reflux stream back into the column and the actual distillate product stream ($\dot{n}_2$) is given by the *reflux ratio*:

$$
R = \frac{\dot{n}_L}{\dot{n}_2} \tag{1.25}
$$

For this particular configuration, the reflux ratio required to achieve the separation is $R = 1.6$.

Neglecting the effect of pressure on enthalpy, we wish to estimate the rate at which heat must be supplied to the reboiler.

1.3.2   Solution

Figure 1.6 is the flowsheet diagram for this problem with all the streams labelled, both with known quantities and with an indication of what we require to estimate to solve this problem. The specific answer to the question posed is the value of $\dot{Q}_r$, the rate of heat supplied to the reboiler. To determine this amount, we will need to determine the change in enthalpy of the output streams relative to the feed stream and the amount of cooling done in the condenser, $\dot{Q}_c$. We will consider two system boxes: one around the whole unit, essentially the same system box as was used in solving Example 1, and one around the condenser section of the unit, shown in Figure 1.7. The latter system box will be useful for determining $\dot{Q}_c$ and will be the first we consider.

$$
\begin{aligned}
\dot{n}_V &= \boxed{?} \\
x_{V,p} &= 0.95\,\tfrac{\text{kmol}}{\text{kmol}} \\
T_V &= 312.2\,°\text{C}
\end{aligned}
$$

$$
\begin{aligned}
\dot{n}_2 &= 278\,\tfrac{\text{kmol}}{\text{h}} \\
x_{2,p} &= 0.95\,\tfrac{\text{kmol}}{\text{kmol}} \\
T_2 &= 310.2\,°\text{C}
\end{aligned}
$$

$$
\dot{Q}_c = \boxed{?}
$$

$$
\begin{aligned}
\dot{n}_L &= \boxed{?} \\
x_{L,p} &= 0.95\,\tfrac{\text{kmol}}{\text{kmol}} \\
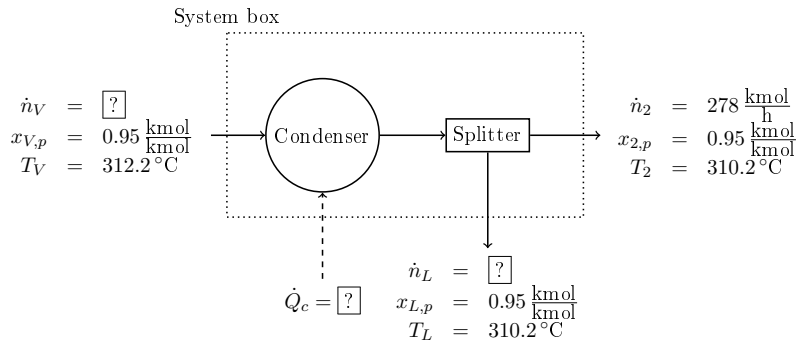T_L &= 310.2\,°\text{C}
\end{aligned}
$$

Figure 1.7:   System box containing the condenser of the distillation unit with a splitter. The input stream is vapour from the top of the distillation column. The output streams are the distillate product (indicated by subscript 2) and the liquid reflux. There is also a heat input, $\dot{Q}_c$, for the condenser.

For this system box, there are three streams: an input vapour stream, which

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originates in the top of the column and two output streams, the distillate product of the unit and the liquid reflux going back into the column. The system box includes a splitter and a condenser. There are three unknowns indicated in the figure: the amount of cooling required, $\dot{Q}_c$ and the flow rates of the vapour, $\dot{n}_V$, and liquid streams, $\dot{n}_L$. Material and energy balances must be addressed simultaneously. As the only step that changes stream amounts is a splitter, we will only be able to write down one mass balance equation for this system box. Together with the appropriate energy balance equation, we have

$$\dot{n}_V = \dot{n}_2 + \dot{n}_L \qquad (1.26)$$

$$\Delta \dot{H} = \dot{Q}_c \qquad (1.27)$$

As there are three unknowns in the diagram, we will need at least one more equation. We will use eq. (1.25), which relates the flows of the liquid reflux and the distillate product stream. We also need to calculate the change enthalpy, which we do by estimating the sensible and latent heats for each of the streams involved, relative to a reference temperature. For this problem, we will use 0 °C = 273.15 K as the reference temperature.

The estimate of the specific enthalpy of each stream requires data, available from a number of sources as discussed above, for the heat capacity equation and the latent heat of vapourisation. For each stream, we will have a

contribution for each compound present. For instance, the enthalpy of the distillate stream will be composed of the enthalpy contribution of pentane and of hexane:

$$\dot{H}_2 = x_{2,p}\dot{n}_2\hat{H}_{2,p} + x_{2,h}\dot{n}_2\hat{H}_{2,h} \tag{1.28}$$

where the subscripts $2, p$, for instance, indicate the pentane component in the distillate stream.

The results of these calculations, using equation (1.24) and data from Felder & Rousseau (2000) (see further reading section below), are shown in Table 1.2. The table presents the specific enthalpies for the two species before and after the condenser. The specific enthalpies for the species in the liquid reflux stream will be the same as in the distillate output stream. The difference between the enthalpies in the vapour stream and the distillate stream is primarily due to the heats of vapourisation, but there is a small contribution from the drop in temperature across the condenser.

Table 1.2: Specific enthalpies for species before and after the condenser. Note that the specific enthalpy $\hat{H}_{L,i}$ is the same as $\hat{H}_{2,i}$, where i is either p for pentane or h for hexane.

Species	$\hat{H}_{V,i}$ (J mol^{-1})	$\hat{H}_{2,i}$ (J mol^{-1})
Pentane	38521	7377
Hexane	38601	8013

Using the specific enthalpies in Table 1.2 to get the actual stream enthalpies allows us to then solve for the remaining 3 unknowns, with the following

results: $\dot{n}_V = 722$ kmol h^{-1}, $\dot{n}_L = 444$ kmol h^{-1} and $\dot{Q}_c = -2.25 \times 10^7$ kJ h^{-1}. The negative sign on $\dot{Q}_c$ indicates that the condenser is removing heat from the process, as expected.

To determine the amount of heating required in the reboiler, we now look at the first system box, the box that includes the whole distillation unit: the column, the condenser and the reboiler. This box also has three streams, the feed stream and the two output streams, and two heat inputs, $\dot{Q}_c$ and $\dot{Q}_r$. All mass flow rates are known and we also know the condenser requirements, so we have one unknown, the reboiler heat duty. We have only one equation, the energy balance around the column

$$\Delta \dot{H} = \dot{Q}_c + \dot{Q}_r \qquad (1.29)$$

We again need to calculate the enthalpies of the stream, noting that we have already calculated the enthalpy of the distillate product stream. If we calculate the enthalpies of the feed and bottom product streams and solve eq. 1.29, we get $\dot{Q}_r = 2.20 \times 10^7$ kJ h^{-1}, a positive value indicating that heat is being added to the process, again as expected.

1.4   Summary

This chapter has introduced the concepts of mass and energy balances. These are essential steps in the analysis of any process. Simple examples have been

used to illustrate the different steps, including not only mass and energy balances, but also simultaneously solving mass and energy balances together.

The key to doing process analysis is the identification of the extra equations that it may be necessary to solve for the unknown variables. These equations will come from a number of sources, including the balance equations themselves (eq. (1.1) and eq. (1.23)), process specifications (such as the purity of output streams and the reflux ratio), physical relations (such as the definition of enthalpy for liquid and vapour streams) and other constraints imposed by the problem. Once a full set of equations has been developed, the equations can be solved, usually with little difficulty, and the desired results obtained.

1.5   Further reading

1. J. Coulson, J. F. Richardson, J. R. Backhurst & J. H. Harker, "Coulson & Richardson's Chemical Engineering Volume 1: Fluid Flow, Heat Transfer and Mass Transfer," $5th$ Edition, Butterworth-Heinemann, 1997.

2. R M Felder & R W Rousseau, "Elementary principles of chemical processes," $3rd$ Edition, John Wiley & Sons (New York), 2000.

3. C. A. Heaton (Editor), "An Introduction to Industrial Chemistry," Leonard Hill (Glasgow), 1984.

4. R. H. Perry, D. W. Green & J. O. Maloney, "Perry's Chemical Engineers' Handbook," 7*th* Edition, McGraw-Hill, 1997.