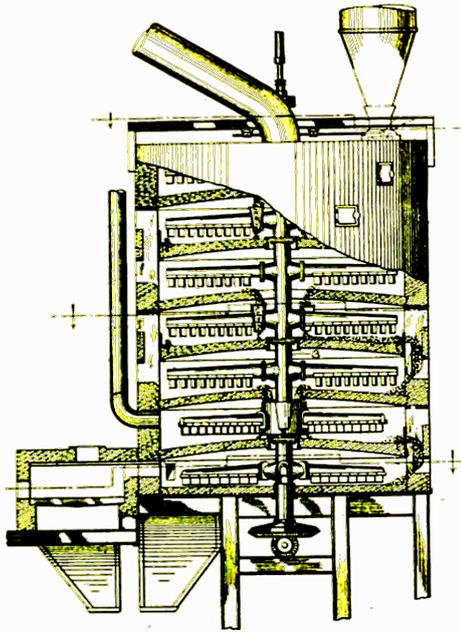
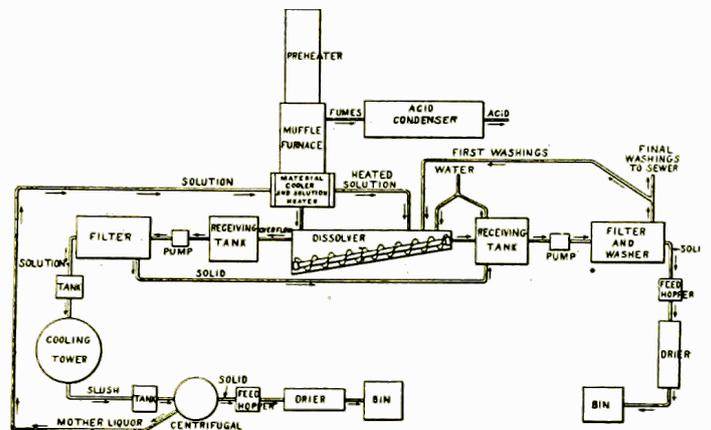
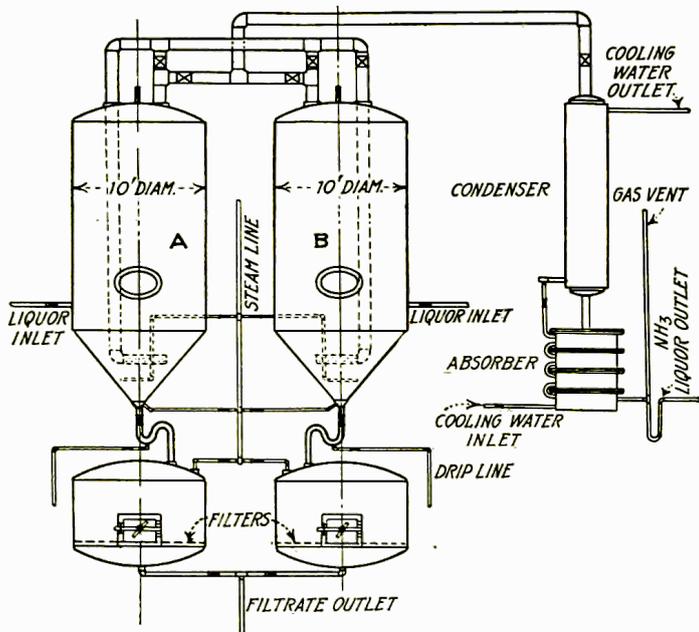
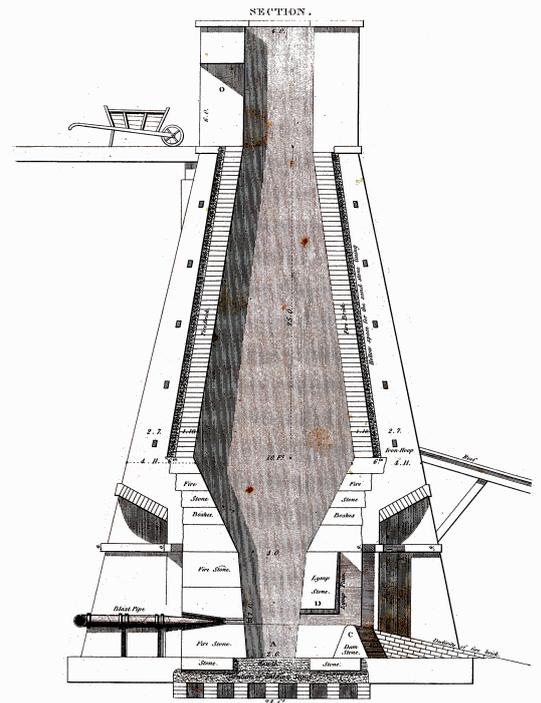


Chemical Engineering Design



2019



Thomas Rodgers

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Nomenclature

Roman

C	Concentration	mol m^{-3}
c	Speed of light	$3 \times 10^8 \text{ m s}^{-1}$
C_p	Specific heat capacity	$\text{J kg}^{-1} \text{ }^\circ\text{C}^{-1}$
E	Energy	J
G	Generation	mol s^{-1}
h	Specific enthalpy	kJ kg^{-1}
k	Rate constant	<i>varies</i>
\dot{m}	Mass flow rate	kg s^{-1}
m	Mass	kg
M_w	Molecular weight	—
\dot{n}	Molar flow rate	$\text{mol m}^{-3} \text{ s}^{-1}$
N	Moles	mol
P	Pressure	Pa
Q	Energy	J
R	Ideal gas constant	$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
r	Reaction rate	mol s^{-1}
T	Temperature	K
t	Time	s
u	Specific internal energy	kJ kg^{-1}
V	Volume	m^3
v	Volumetric flow rate	$\text{m}^3 \text{ s}^{-1}$
X	Conversion	—
x	Mole fraction (usually liquid phase)	—
y	Mole fraction (usually vapour phase)	—

Greek

ν	Stoichiometric coefficient	—
ξ	Extent of reaction	mol

Chapter **1**

Material Balances

Contents

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1.1 Introduction

A balance can be written for any conserved quantity (e.g. total mass, mass of a particular species, energy, momentum etc.), and the general balance equation has five terms. The balance equation must be set up for a particular system, the boundaries of which must be defined.

? Question

For example in 2017, 97,100 people moved into the Greater Manchester (the system), 46,700 people moved out, 33,700 were born, and 26,200 died. What is the change in the population of Greater Manchester? The annual change corresponds to the increase in the population after one year and has units of persons per year.

In solving this problem we used the general balance equation,



General Balance Equation

$$\begin{array}{ccccccc}
 \text{Input} & - & \text{Output} & + & \text{Generation} & - & \text{Consumption} = \text{Accumulation} \\
 \left[\begin{array}{c} \text{Enters} \\ \text{through} \\ \text{system} \\ \text{boundaries} \end{array} \right] & - & \left[\begin{array}{c} \text{Leaves} \\ \text{through} \\ \text{system} \\ \text{boundaries} \end{array} \right] & + & \left[\begin{array}{c} \text{Produced} \\ \text{within} \\ \text{system} \end{array} \right] & - & \left[\begin{array}{c} \text{Consumed} \\ \text{within} \\ \text{system} \end{array} \right] = \left[\begin{array}{c} \text{Build-up} \\ \text{within} \\ \text{system} \end{array} \right] \\
 & & & & & & (1.1)
 \end{array}$$

This is the only equation needed to solve material balance problems. In most cases we can eliminate some of the terms in the equation. For example if we consider the case of a system with no reaction we can eliminate the consumption and generation terms. If we also assume the process is a steady state, i.e. no change, then there is no accumulation

1.2 Classification of Process Operations

In addition to the terms in the material balance, the way that we set up the material balance will depend on how the process is operated:

Continuous Operation in which all materials enter and leave continuously throughout the operating period. Therefore, we do not start with a given amount of material as there is a continuous flow of feed. We use balance equations on the rates of flow of material (e.g. rate of input etc.). This is called a differential balance.

Batch Operation in which materials are put in at a certain time, the process takes place for some time, and the materials are then removed. In this case, we will use balance equations between two instants in time. We will thus be balancing the amount of the accumulated quantity between the beginning and the end of the operation. This is called an integral balance.

Semi-batch is all other combinations of continuous and batch operation, e.g. Semi-continuous, Open batch, etc.

Steady State is when a process can be considered to be operating with no change in variables (i.e. flowrates, compositions, temperatures, and pressures of all streams) with time. Operations for which this is not true are classified as transient.

1.3 Material Balance for a Simple Continuous Process

Let us consider a process that is continuous and at steady state with no reaction. As stated above the generation, consumption, and accumulation terms are therefore all zero. This means that the balance equation, equation 1.1, can be simplified to:

$$\text{Input} = \text{Output} \quad (1.2)$$

1.3.1 Step 1 - Drawing a Flowchart

The first step is to draw a flowchart of the process, with boxes or other symbols to indicate process operations (reactors, mixers, distillation columns etc.), and lines with arrows to indicate inputs and outputs. For example, let's think about a distillation column, which takes a feed of 2500 kg h^{-1} of 35 % ethanol and 65 % water. The distillation column separates this feed into two streams, one of 85 % ethanol with 15 % water and one of 5 % ethanol with 95 % water.

With this information the streams can be labelled with the amount or flow rate of each component. To do this we must first choose a basis for the calculation. A basis of calculation is an amount or flow rate of a stream or component we decide we want to fix (see Infobox 1). For this example, a sensible basis would be the total flow rate of the feed as then we don't need to scale anything. The system can be drawn as in Figure 1.1.

1.3.2 Step 2 - Setting up the Balance Equations

As the process is non-reactive we can set up balance equations simply as equation 1.2. Balance equations can in principle be set up for each component as well as a total balance. However, the total balance will be a sum of the component balances, so the number of independent balances (i.e. the number of simultaneous equations) is equal to the number of components involved (this is only true for a non-reactive system).

Before we can set up the material balance we must define the system. We do this simply by drawing its boundaries on the flow diagram, the dashed boundary in Figure 1.1.

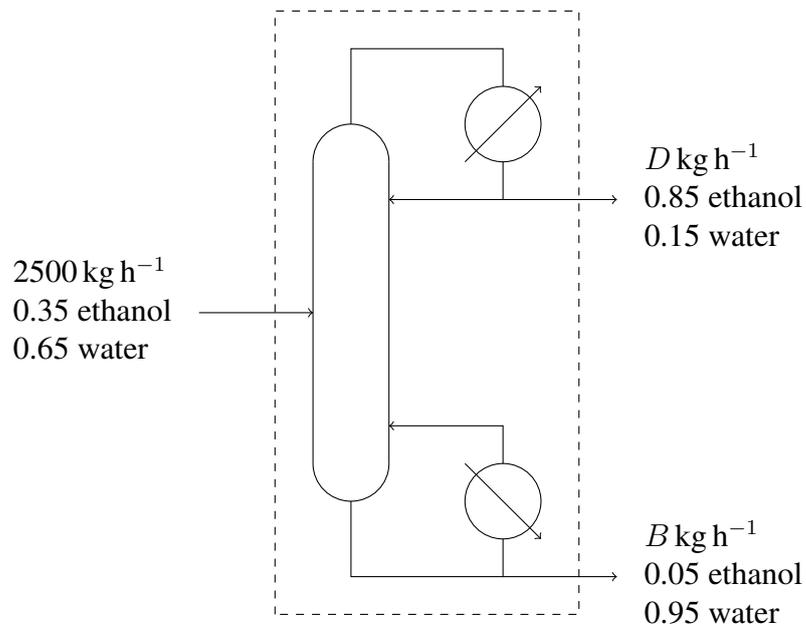


Figure 1.1: Mass balance for a simple distillation column.

We only need to consider the flow of material across the system boundary, and we can write differential material balances equations for the total mass, ethanol, and water,

$$\begin{aligned} \text{Input} &= \text{Output} \\ \text{Total mass: } F &= 2500 = D + B \\ \text{Ethanol: } 0.35F &= 0.35(2500) = 0.85D + 0.05B \\ \text{Water: } 0.65F &= 0.65(2500) = 0.15D + 0.95B \end{aligned}$$

This gives us three equations, with only two unknowns to determine (D & B). However, one of these equations is redundant. If we sum the last two equations, we obtain the first equation, i.e. the sum of the mass fractions in each stream being unity. In general for an operation involving N components, N independent material balance equations can be obtained. Solving the two simultaneous equations allows calculation of D and B .

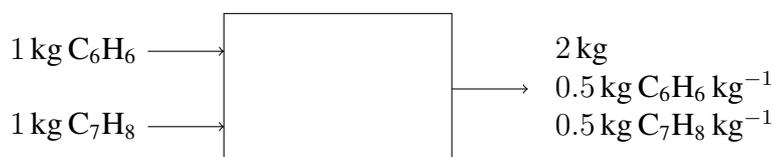
$$\begin{aligned} \text{Total: } 2500 &= D + B \\ B &= 2500 - D \\ \text{Ethanol: } 875 &= 0.85D + 0.05B \\ &= 0.85D + 0.05(2500 - D) \\ &= 0.8D + 125 \\ 750 &= 0.8D \\ D &= 937.5 \text{ kg h}^{-1} \\ B &= 1562.5 \text{ kg h}^{-1} \end{aligned}$$

Infobox 1: Scaling and Basis of Calculation.

Since a material balance can always be scaled, a material balance calculation can be performed on the basis of any convenient stream amount or flow rate, and the results can afterwards be converted to units on a time basis. Thus, the first step is always to choose the basis of calculation. The choice of the basis of calculation is arbitrary; any choice should lead to a correct solution. However, an appropriate choice may make the problem simpler to solve.

This means that a balanced flowsheet, for which material balances for all components are satisfied, can be scaled up or down. A balanced process can be scaled up or down by increasing the amount or flow rate of all streams proportionately, while keeping the composition of all streams constant.

For example: 1 kg of benzene is mixed with 1 kg of toluene to produce 2 kg of mixture. The composition of the mixture is obviously 50 %w/w benzene and 50 %w/w toluene.



This is a balanced process as the material balances for both components are satisfied. The process can be scaled up or down and by multiplying the amount or flow rate of each stream by a constant factor, e.g. multiply by 300,



One of the flowrates needs to be known per unit time in order to convert all other flows to a time basis. For instance, if 500 kg of total feed is to be processed per hour, then the flowrates can be converted to kg/hr with multiply by 250 hr⁻¹,



1.4 Material Balances for Reactive, Single Stage Processes

If reaction occurs, a balance for a species involved in any reaction(s) must include the generation and/or consumption terms. Conservation of mass is one of the fundamental laws of the universe, along with conservation of energy, except where nuclear reactions are involved, in which case mass can be converted to energy via the equation,

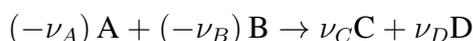
$$E = mc^2 \quad (1.3)$$

Because c is such a large term, a very small amount of mass is converted into vast amounts of energy - this is why nuclear energy is such an attractive prospect. But in most process industries, except the nuclear industry, we don't get nuclear reactions occurring, so we can take it as fundamentally true that mass is conserved.

When tackling problems which involve reactions we must always perform our balance with molar quantities and not masses. If data is provided in terms of mass (e.g. composition as %w/w), the first step is to convert compositions and flows to a molar basis. We need to use molar quantities as these are balanced across reactions.

Balances can be written for species or for atomic elements. Atomic balances don't have generation or consumption as atomic species can't be created or destroyed in chemical reactions (see Infobox 2). Species balances must account for any consumption or generation associated with reactions. This can be achieved either using reaction stoichiometry or considering an 'extent of reaction'. It is important to note that in a reaction the number of moles does not have to be conserved.

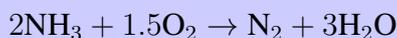
Consider a simple reaction,



where ν_A , ν_B , ν_C , and ν_D are called stoichiometric coefficients. Note that stoichiometric coefficients are negative for reactants and positive for products.

? Question

Consider the reaction,

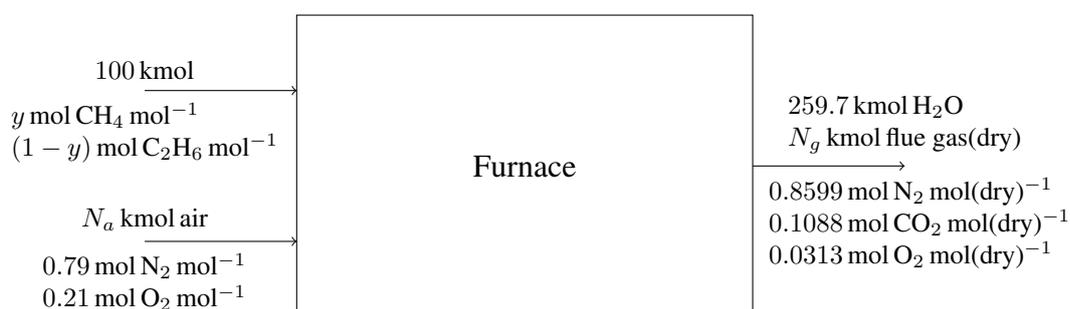


What are the stoichiometric coefficients for the components in the reaction? Initially 4.8 moles of NH_3 and 3.8 moles of O_2 are present. Which is the limiting reactant?

Infobox 2: Atomic Balances.

All balances on atomic species take the form input = output since atomic species can neither be generated or consumed in chemical reactions. It is simplest to carry out separate species balances for inert stream components (i.e. those not involved in any reaction) and exclude these species from the atomic balances. The method is best explained by considering an example.

A furnace, as shown below, burns a mixture of methane (CH_4) and ethane (C_2H_6) in air. The composition of the flue gas is measured on a dry basis (ignoring H_2O) and the amount of water in the flue gas is measured. What is the fraction of methane in the feed and the amount of air needed?



First set up material balances for all atomic elements involved in the reaction, and species balances for any non-reacting inerts (N_2 in this case). For this problem we set up material balance equations for C, H, O and N_2 . For the input of C into the system we have 1 kmol of C per kmol of CH_4 and 2 kmol of C per kmol of C_2H_6 . As atomic species are conserved, there is no generation or consumption, and assuming the process is steady state the balances become,

Input = Output

$$\text{C: } 1 \times 100y + 2 \times 100(1 - y) = 1 \times 0.1088N_g$$

$$\text{H: } 4 \times 100y + 6 \times 100(1 - y) = 2 \times 259.7$$

$$\text{O: } 2 \times 0.21N_a = 1 \times 259.7 + 2 \times 0.0313N_g + 2 \times 0.1088N_g$$

$$\text{N}_2: 1 \times 0.79N_a = 1 \times 0.8599N_g$$

This produces four balance equations,

$$200 - 100y = 0.1088N_g$$

$$600 - 200y = 519.4$$

$$0.42N_a = 259.7 + 0.2802N_g$$

$$0.79N_a = 0.8599N_g$$

The balance equation for H yields immediately the fraction of CH_4 in the feed. Solving the equations gives, $y = 0.403$, $N_g = 1467.8$ kmol, and $N_a = 1597.7$ kmol.

Remember: We cannot use an overall balance equation to help solve the problem as the total number of moles is not conserved in the reaction system.

Note that for atomic balances we do not have to consider what reactions occur or the reaction stoichiometry.

For a general reaction, for each reactant the ratio of the change in the number of moles present, dN_i , to the stoichiometric coefficient, ν_i , for the reactant is the same in each case, and this ratio is called the extent of reaction, ξ ,



Extent of Reaction

$$\xi = \frac{dN_i}{\nu_i} = \frac{N_{i,0} - N_i}{\nu_i} \quad (1.4)$$

The extent of reaction can be used in material balance calculations, if the number of moles of a species i present before the reaction is $N_{i,0}$, then the number of moles after the reaction can be found using,

$$N_i = N_{i,0} + \nu_i \xi \quad (1.5)$$

This can also be written in terms of a molar flow as,

$$\dot{n}_i = \dot{n}_{i,0} + \nu_i \xi \quad (1.6)$$

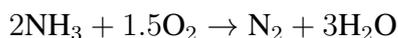
In many cases reactions will not proceed to completion, due to equilibrium limitations or reaction kinetics. The conversion is often used as an indication of how far a reaction has proceeded. Conversion, X_i , is the fraction of a specified reactant which is consumed by the reaction,



Conversion

$$X_i = -\frac{dN_i}{N_{i,0}} = -\frac{\xi \nu_i}{N_{i,0}} \quad (1.7)$$

For example, let's think about a reactor with the following reaction taking place,



Suppose we initially have 10.0 moles of NH_3 and 8.0 moles of O_2 . If the conversion of NH_3 is 0.75, we can work out how many moles of each of the four species exit the reactor.

The extent of the reaction can be calculated from the conversion using equation 1.7,

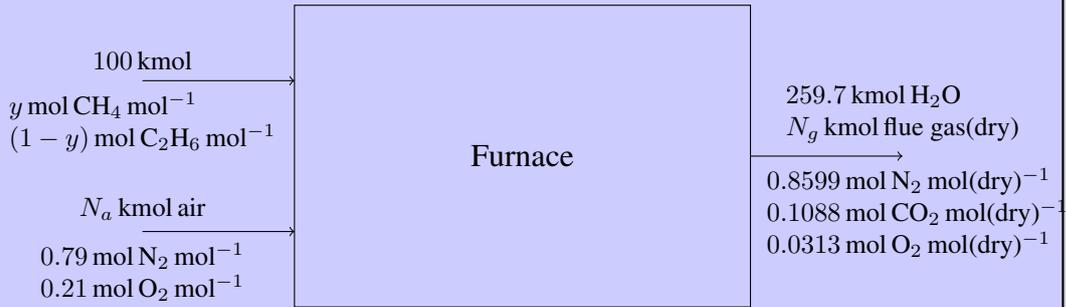
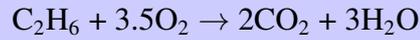
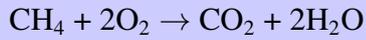
$$\xi = -\frac{X_{\text{NH}_3} n_{\text{NH}_3,0}}{\nu_{\text{NH}_3}} = -\frac{(0.75)(10.0)}{(-2)} = 3.75$$

Thus using equation 1.1 where the accumulation is zero due to being at steady state, produces,

	Input +	(Generation – Consumption)	=	Output	
NH_3 :	10.0 +	$(\xi \nu_{\text{NH}_3} = (3.75)(-2) = -7.50)$	=	2.50	mol
O_2 :	8.0 +	$(\xi \nu_{\text{O}_2} = (3.75)(-1.5) = -5.625)$	=	2.375	mol
N_2 :	0.0 +	$(\xi \nu_{\text{N}_2} = (3.75)(1) = 3.75)$	=	3.75	mol
H_2O :	0.0 +	$(\xi \nu_{\text{H}_2\text{O}} = (3.75)(3) = 11.25)$	=	11.25	mol

? Question

A furnace, as shown below, burns a mixture of methane (CH_4) and ethane (C_2H_6) in air. The composition of the flue gas is measured on a dry basis (ignoring H_2O) and the amount of water in the flue gas is measured. Assuming complete combustion, thus the reactions below, what is the fraction of methane in the feed and the amount of air needed?



1.5 Processes with Recycle

Many chemical processes involve a recycle stream, where unreacted material is separated from products and returned to the reactor. In order to avoid the build up of inerts in the recycle stream, a small flow rate purge stream is often removed from the recycle, as in Figure 1.2.

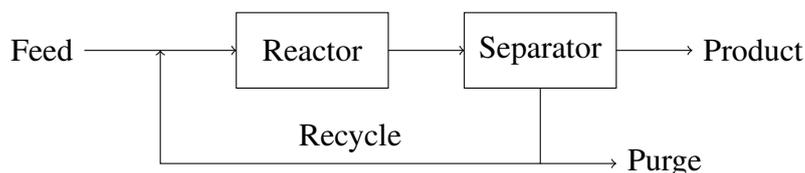


Figure 1.2: Recycle stream for a reactor.

The presence of a recycle can complicate material balance calculations as the composition of the reactor feed will depend on the composition of the reactor output. The solution of this type of problem is the same as for any multistage process. We can define system boundaries in a number of different ways, for example Figure 1.3.

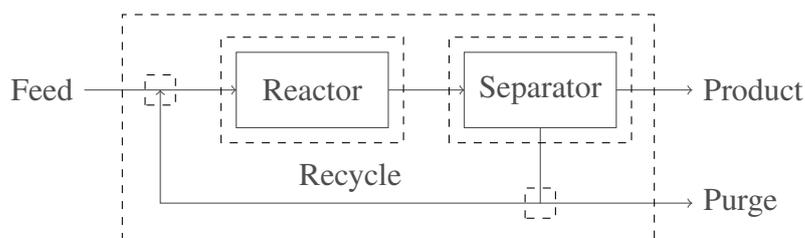


Figure 1.3: Some example system boundaries for a recycle stream for a reactor.

Usually problems of this type can be solved most efficiently using an overall balance along with a combination of balances around the reactor, separator, mixing point and splitting point.

The definition of conversion can often cause confusion for problems involving a recycle stream.

Normally 'conversion' refers to the overall conversion i.e.

$$X_O = \frac{\text{Reactant consumed in the process}}{\text{Reactant supplied in the feed}} \quad (1.8)$$

This may be different to the conversion across the reactor, which is sometimes called the 'conversion per pass' i.e.

$$X_R = \frac{\text{Reactant consumed in reactor}}{\text{Reactant fed to reactor}} \quad (1.9)$$

Thus the overall conversion is the conversion between the feed and product and the conversion per pass is the conversion between the inlet and the outlet of the reactor.

Consider a simple problem where a reactant A is fed to a process at a rate of 100 kmol h^{-1} . The feed is mixed with a recycle stream and fed to a reactor where a product B is produced

by the reaction $A \rightarrow B$, Figure 1.4. Most of the unreacted A is separated from the reactor product stream and recycled. If the overall conversion is 90% and the conversion per pass is 20%, determine the composition and flow rate of all streams, assuming that there is no B in the recycle stream.

The overall conversion of the system is 0.9, which means that,

$$\xi_O = - \frac{X_{A,O} \dot{n}_{A,1}}{\nu_A}$$

$$\xi_O = - \frac{(0.9)(100)}{(-1)} = 90 \text{ kmol h}^{-1}$$

Therefore the outlet flow rate, \dot{n}_4 is given by,

Output = Input + (Generation – Consumption)

$$\begin{aligned} \dot{n}_{A,4} &= \dot{n}_{A,1} + \nu_A \xi_O \\ \dot{n}_{A,4} &= (100) + (-1)(90) &&= 10 \text{ kmol A h}^{-1} \\ \dot{n}_{B,4} &= \dot{n}_{B,1} + \nu_B \xi_O \\ \dot{n}_{B,4} &= (0) + (1)(90) &&= 90 \text{ kmol B h}^{-1} \end{aligned}$$

We know that there is no B in the recycle stream, so the amount of B in stream 4 is equal to stream 3. Also, as there is no B in the recycle or the feed, the flowrate of B in stream 2 is also 0. Therefore we have,

	①	②	③	④	⑤
A kmol h ⁻¹	100	?	?	10	?
B kmol h ⁻¹	0	0	90	90	0

Now a balance around the reactor can be undertaken based upon the reactor conversion of 0.2,

$$\xi_R = - \frac{X_{A,R} \dot{n}_{A,2}}{\nu_A}$$

$$\xi_R = - \frac{0.2 \dot{n}_{A,2}}{-1} = 0.2 \dot{n}_{A,2}$$

Therefore the reactor outlet flow rate, \dot{n}_3 is given by,

Output = Input + (Generation – Consumption)

$$\begin{aligned} \dot{n}_{A,3} &= \dot{n}_{A,2} + \nu_A \xi_R \\ \dot{n}_{A,3} &= \dot{n}_{A,2} + (-1)(0.2 \dot{n}_{A,2}) &&= 0.8 \dot{n}_{A,2} \text{ --- --- --- --- --- 1} \\ \dot{n}_{B,3} &= \dot{n}_{B,2} + \nu_B \xi_R \\ \dot{n}_{B,3} &= \dot{n}_{B,2} + (1)(0.2 \dot{n}_{A,2}) &&= \dot{n}_{B,2} + 0.2 \dot{n}_{A,2} \text{ --- --- --- --- --- 2} \end{aligned}$$

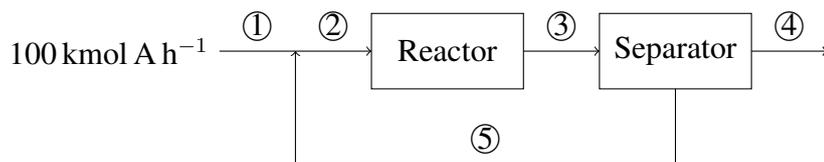


Figure 1.4: Example reactor with reactor and separator with recycle.

From 2,

$$\begin{aligned}\dot{n}_{B,3} &= \dot{n}_{B,2} + 0.2\dot{n}_{A,2} \\ \dot{n}_{A,2} &= \frac{\dot{n}_{B,3} - \dot{n}_{B,2}}{0.2} \\ \dot{n}_{A,2} &= \frac{(90) - (0)}{0.2} = 450 \text{ kmol A h}^{-1}\end{aligned}$$

and from 1,

$$\begin{aligned}\dot{n}_{A,3} &= 0.8\dot{n}_{A,2} \\ \dot{n}_{A,3} &= 0.8(450) = 360 \text{ kmol A h}^{-1}\end{aligned}$$

A final balance on the separator allows calculation of the amount of A recycled in stream 5,

Input = Output

$$\dot{n}_{A,3} = \dot{n}_{A,4} + \dot{n}_{A,5}$$

$$\dot{n}_{A,5} = \dot{n}_{A,3} + \dot{n}_{A,4}$$

$$\dot{n}_{A,5} = (360) + (10) = 370 \text{ kmol A h}^{-1}$$

Therefore we have,

	①	②	③	④	⑤
A kmol h ⁻¹	100	450	360	10	370
B kmol h ⁻¹	0	0	90	90	0

Chapter **2**

Reactor Design

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2.1 Introduction

Before describing the reactors, we need to first discuss how to provide mathematical expressions for the rate at which reactions occur using rate laws.

2.1.1 Definitions of Reaction Rate

The reaction rate represents how fast a chemical component is converted into another by a chemical reaction. More specifically, the reaction rate, r_i , is the moles of i formed (or appearing) per unit volume per unit time ($\text{mol}_i \text{m}^{-3} \text{s}^{-1}$). The reaction rate is negative when the moles of i are being consumed by the reaction (as occurs for reactants before any product has been formed). The reaction rate is positive when the moles of i increase with time due to the reaction (as occurs for products before any product has been formed).



Reaction Rate

The reaction rate can be positive or negative for any component of a reaction depending on the direction of the equilibrium from the initial compositions.

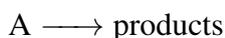
2.1.2 Reaction Equation or Rate Law

A reaction equation is an algebraic equation that is solely a function of the properties of the reacting materials and reaction conditions (e.g. species concentration, temperature, pressure, or type of catalyst) at any point in the system.



Rate Law

The rate equation is independent of the type of reactor (e.g. batch or continuous flow) in which the reaction is carried out.



The reaction rate may be a linear function of concentration, i.e. $-r_A = kC_A$ or may be some other algebraic function of concentration, such as $-r_A = kC_A^2$ or $-r_A = (k_1C_A) / (1 + k_2C_A)$.

For a given reaction, the concentration dependence of the rate must be determined from experimental observation. Typical examples of reaction rates are a first order reaction given by,

$$-r_A = kC_A \quad (2.1)$$

or a second order reaction,

$$-r_A = kC_A^2 \quad (2.2)$$

where k is called the rate constant, which varies with temperature. The order of the reaction with respect to a component i corresponds to the exponent of concentration i in the rate law. Note that the reaction rate, r , corresponds to a rate of formation. For

a reactant, the rate of formation is going to be negative as the reactant is consumed by the reaction, hence the negative sign in Equations 2.1 and 2.2. Usually the order of the reaction provides some insight into the molecular mechanism for the reaction. A first order reaction corresponds to a uni-molecular process, whereas a second order reaction corresponds to reaction controlled by collisions between molecules. These rules are only strictly true when the reaction is an elementary step. Most reactions are combinations of elementary steps, which can lead to more complicated rate laws. In addition, the rate law can depend on the relative concentrations of the components. For instance, rate laws are independent of the concentrations of components, which occur at a large excess relative to another component (e.g. water).

2.1.3 Rate Equations in terms of Extent of Reaction

Consider the simple reaction $A \longrightarrow B$, if this is first order, then the rate can be given by equation 2.1,

$$-r_i = kC_i$$

where C_i is the concentration of i and can be related to the number of moles, N_i , by,

$$N_i = C_i V \quad (2.3)$$

for a constant volume reactor, V , or, to the molar flow rate, \dot{n}_i , by

$$\dot{n}_i = C_i v \quad (2.4)$$

for a constant volumetric flow rate, v , reactor. This means that for a constant volumetric flow rate reactor with a first order reaction, we can write,

$$-r_i = \frac{k}{v} \dot{n}_i \quad (2.5)$$

From equation 1.6, we know that the number of moles in terms of the extent of reaction is,

$$\dot{n}_i = \dot{n}_{i,0} + \nu_i \xi$$

Substituting this into equation 2.5 gives,

$$-r_i = \frac{k}{v} (\dot{n}_{i,0} + \nu_i \xi) \quad (2.6)$$

This can also be carried out for other reaction rate functions.

2.2 Mole Balance for Reactors

Ideal reactors normally refer to simplified models of reactors, in which various approximations are made. These approximations allow us to describe the behaviour of the reactor using simple mathematical expressions.



Reactor Mole Balance

The mole balance is used to determine either the time (for a batch reactor) or the reactor volume (for a flow reactor) required to convert a specified amount of reactants into products.

The mole balance for a reactor can be written as equation 1.1,

$$\text{Input} - \text{Output} + (\text{Generation} - \text{Consumption}) = \text{Accumulation}$$

$$\dot{n}_{i,0} - \dot{n}_i + G_i = \frac{dN_i}{dt}$$

where \dot{n}_i is the molar flowrate of species i (with units of moles sec^{-1}) and N_i is number of moles of component i in the reactor. The above mole balance is performed over a volume element in the reactor over which all the system variables (e.g. temperature, concentration) are spatially uniform. In this case, the production rate in a reaction G_i (mol s^{-1}) over a given volume element, V , Figure 2.1, can be calculated from the rate of formation of i , r_i , by:

$$G_i = r_i V \quad (2.7)$$

Note that the production rate is negative when a reactant is being consumed.

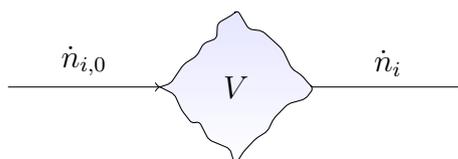


Figure 2.1: Schematic representation of the design of a reactor volume.

2.3 Mole Balance Applied to Plug Flow Reactor

Plug flow reactors (PFR) are mainly used for gas phase reactions and may be packed with catalyst. A schematic representation of a PFR is shown in Figure 2.2. The reactants are continuously fed into a cylindrical tube, while the products are continuously withdrawn. The reaction occurs as the stream flows through the reactor; the amount reacted increases with the distance down the cylindrical tube. The length needs to be chosen such that the desired conversion can be achieved. The PFR is operated under steady-state conditions except for the start-up and shut down of the reactor. The analysis below is only given for the steady state condition, which is used for sizing the reactor.

In order to model a PFR, a few assumptions need to be made. The PFR is not well-mixed, as the conversion increases with the distance down the tube. However, a well-mixed assumption is applied, in the radial direction only, that is, we assume that there are no gradients of composition or temperature in the radial direction. Thus, a slice of the reactor (i.e. ΔV in Figure 2.3 below) contains a homogeneous distribution of temperature and composition. Having no radial variation also requires that the velocity distribution in the PFR is flat, which is better approximated under turbulent flowing conditions¹. Lastly, we assume that there is no axial mixing; this allows us to omit terms due to diffusion or dispersion in the mole balance.

¹High velocity and low viscosity, e.g. a gas

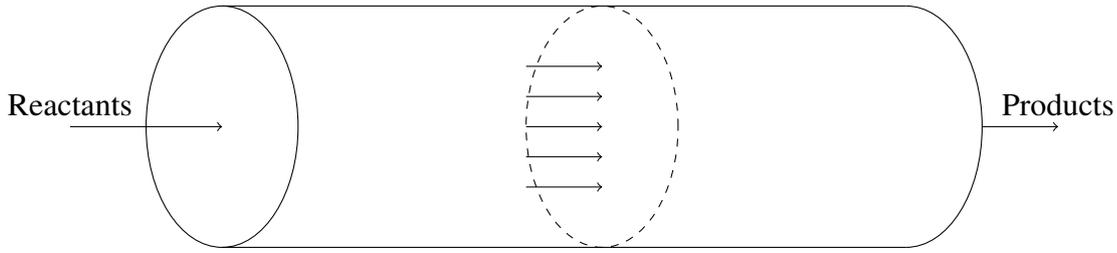
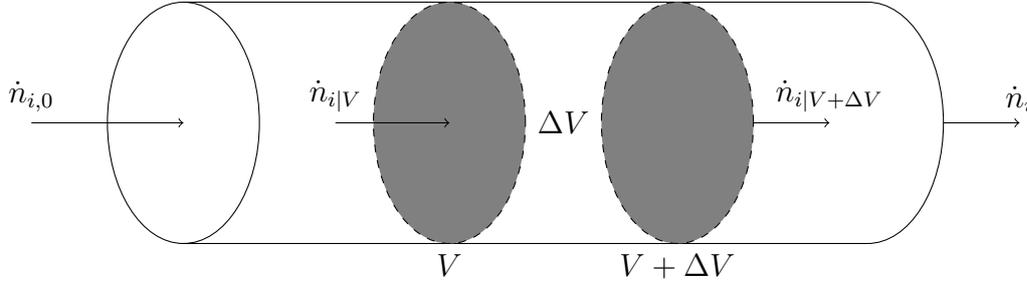


Figure 2.2: Schematic representation of a PFR.


 Figure 2.3: Mole balance of component i in a differential segment of ΔV .

Remember that the mole balance needs to be done over a volume element that has a uniform distribution of temperature and composition. This corresponds to the volume element shown in Figure 2.3. Consider the mole balance on i in a differential segment of reactor volume ΔV . Applying the mole balance,

$$\begin{array}{rcccl} \text{In} & - & \text{Out} & + (\text{Generation} - \text{Consumption}) & = \text{Accumulation} \\ \dot{n}_{i|V} & - & \dot{n}_{i|V+\Delta V} & + r_i \Delta V & = 0 \end{array} \quad (2.8)$$

and rearranging for the rate of reaction gives,

$$\frac{\dot{n}_{i|V+\Delta V} - \dot{n}_{i|V}}{\Delta V} = r_i \quad (2.9)$$

Now if we take the limit as $\Delta V \rightarrow 0$, then

$$\frac{d\dot{n}_i}{dV} = r_i \quad (2.10)$$

From equation 1.6 we know that the number of moles in terms of the extent of reaction, is given by,

$$\dot{n}_i = \dot{n}_{i,0} + \nu_i \xi$$

For a very small change in moles, $|\dot{n}_{i,0} - \dot{n}_i| \rightarrow 0$, we can write,

$$\frac{d\dot{n}_i}{d\xi} = \nu_i \quad (2.11)$$

Combining equations 2.10 and 2.11 gives,

$$\frac{d\xi}{dV} = \frac{r_i}{\nu_i} \quad (2.12)$$

Integrating with limits of $\xi = 0$ when $V = 0$ (the inlet) and $\xi = \xi_R$ when $V = V_R$ (the outlet) gives,

$$V_R = \int_0^{\xi_R} \nu_i \frac{d\xi}{r_i} = \nu_i \int_0^{\xi_R} \frac{d\xi}{r_i} \quad (2.13)$$

Consider the reaction $A \longrightarrow B$ as a first order reaction, where we know that the rate can be given by equation 2.6,

$$-r_i = \frac{k}{v} (\dot{n}_{i,0} + \nu_i \xi)$$

The reactor volume, V_R , necessary to gain a desired extent of reaction, ξ_R , is therefore given by substituting the above into equation 2.13,

$$V_R = -\frac{\nu_i v}{k} \int_0^{\xi_R} \frac{d\xi}{(\dot{n}_{i,0} + \nu_i \xi)} \quad (2.14)$$

Therefore, upon integration we find,

$$\begin{aligned} V_R &= -\frac{\nu_i v}{k} \left[\frac{1}{\nu_i} \ln(k(\dot{n}_{i,0} + \nu_i \xi)) \right]_0^{\xi_R} \\ V_R &= -\frac{v}{k} \ln \left(\frac{\dot{n}_{i,0} + \nu_i \xi_R}{\dot{n}_{i,0}} \right) \\ V_R &= -\frac{v}{k} \ln \left(1 + \frac{\nu_i \xi_R}{\dot{n}_{i,0}} \right) \end{aligned} \quad (2.15)$$

Figure 2.4 shows a plot of the molar flowrates for A and B as a function of the reactor volume.

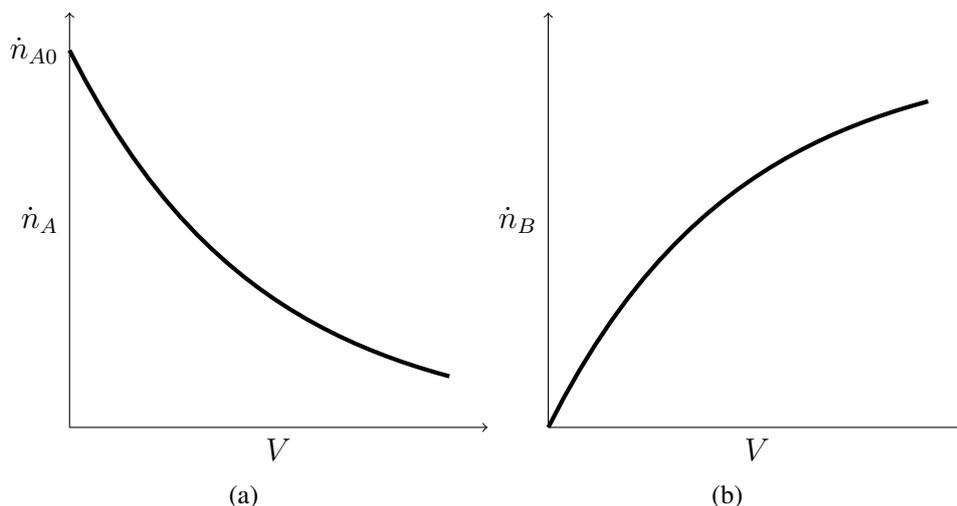


Figure 2.4: Molar flowrate of component A and B as a function of volume in a PFR.

Note that in deriving Equation 2.15 we have assumed that the volumetric flowrate, v , of the gas is independent of the position in the PFR. The conditions when v is a constant can be deduced from considering the ideal gas law, $v = \dot{n}_t RT/P$ (assuming that a gas is being reacted in the PFR), where \dot{n}_t is the total molar flowrate. Thus, the temperature, pressure, and total molar flowrate must be constants for v to be a constant. In the reaction

of A going to B, for each mole of A consumed, one mole of B is formed so that indeed the total molar flowrate is a constant. However, if the number of moles reacted does not equal the moles consumed, we would need to account for the change in v as a function of the change in mole number along the reactor. In addition, if the reactor is not isothermal, we would also have to consider how v depends on T . How T depends on position in reactor would be determined from a differential energy balance.

? Question

Substitute the second order rate equation $-r_A = kC_A^2$ into Equation 2.13 and find the answer for V_R . Assume no change in the total number of moles.

? Question

Consider the liquid phase cis-trans isomerisation of 2-butene which can be written symbolically as

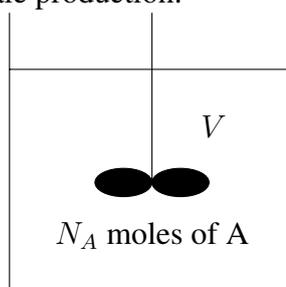


The first order ($-r_A = kC_A$) reaction is carried out in a tubular reactor in which the volumetric flow rate, v , is constant, i.e. $v = v_0$.

Determine the reactor volume necessary to reduce the exiting concentration of A to 10 % of the entering concentration when the volumetric flow rate is $5 \text{ m}^3 \text{ min}^{-1}$ and the specific reaction rate constant, k , is 0.23 min^{-1} .

Infobox 3: Mole Balance Applied to Batch Reactors.

A batch reactor is a reactor in which reactants are mixed together and the reaction is allowed to proceed for a given time in a closed vessel with no inlet or outlet flows, as below. Provision for mixing, heating, or cooling of the reactants may be required. Batch reactors are normally used for small-scale operations, testing new processes, the manufacture of expensive products, and processes difficult to convert to continuous. The advantage is that high conversions can be achieved due to leaving the reactants in reactor. The disadvantages are high labour costs, variability of products (batch to batch), and they are difficult to operate/automate for large-scale production.



In order to model a batch reactor, we need to make the assumption that at any given time the reactor is well-mixed so that the composition, temperature, and pressure are the same everywhere in the reactor. When the reaction takes place in a liquid (or sometimes solids), very often the reacting component occurs at a much lower concentration than the principal component of the liquid (i.e. the solvent). In this case, a good approximation is that the volume of the liquid and pressure in the reactor remain constant with time as there is only a small change in the density of the liquid during the reaction.

From equations 2.7 and 2.7 we have the general balance,

$$\text{Input} - \text{Output} + (\text{Generation} - \text{Consumption}) = \text{Accumulation}$$

$$\dot{n}_{i,0} - \dot{n}_i + r_i V = \frac{dN_i}{dt}$$

As we have no input or output, $\dot{n}_{i,0} = \dot{n}_i = 0$, therefore we can simplify the equation to be,

$$r_i V = \frac{dN_i}{dt} = \nu_i \frac{d\xi}{dt}$$

Integrating with limits $\xi = 0$ when $t = 0$ (i.e. the initial condition) and $\xi = \xi_R$ when $t = t_R$ (i.e. the reaction time),

$$t_R = \int_0^{\xi_R} \frac{\nu_i}{r_i V} d\xi$$

Now we need to substitute in a rate law for the reaction, for example equation 2.6,

$$-r_i = \frac{k}{V} (N_{i,0} + \nu_i \xi)$$

$$t_R = -\frac{\nu_i}{k} \int_0^{\xi_R} \frac{1}{(N_{i,0} + \nu_i \xi)} d\xi$$

$$t_R = -\frac{\nu_i}{k} \left[\frac{1}{\nu_i} \ln(N_{i,0} + \nu_i \xi) \right]_0^{\xi_R}$$

$$t_R = -\frac{1}{k} \ln \left(\frac{N_{i,0} + \nu_i \xi_R}{N_{i,0}} \right) = -\frac{1}{k} \ln \left(1 + \frac{\nu_i \xi_R}{N_{i,0}} \right)$$



Chapter 3

Energy Balances

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3.1 Introduction

Energy is expensive. Energy is also what makes things happen, the agent of change, and therefore something that is needed in a process (processes bring about change and therefore require energy). So energy is central in the process industries, but it is expensive. We therefore need to make sure we are using energy appropriately, but that we are not using too much.

Typical problems that a process engineer might be required to solve include:

- How much power is required to pump water from a storage vessel to a process unit? (The answer determines the size of the pump.)
- How much heat is required to convert water at 30 °C into steam at 180 °C? How much coal will this require each day?
- What is the total energy requirement for a process? How much will this energy cost? How can the process be designed to minimise the total energy requirement by maximising energy recovery?

These questions are answered by performing an energy balance, which accounts for all the energy entering and leaving a system.

3.2 Energy

Before we consider energy balances, it is important that we remind ourselves very clearly that energy has a variety of forms. If we overlook one of the forms of energy entering or leaving the system, we will not calculate the energy balance correctly.

Forms of energy include:

Kinetic energy - energy arising from motion. This is important if the system is rapidly moving, such as a bullet. Most processes are fairly stationary, so the kinetic energies involved are negligible and can be ignored in the energy balance. But this might not be true if, for example, a stream enters or leaves the system with high velocity, such as a jet from a nozzle.

Potential energy - energy arising from being moved against gravity. Most processes occur at or near the Earth's surface, so potential energy is not a major consideration in an energy balance. However, when liquids are pumped to several meters above the ground, the energy requirement to pump them may be substantial, and certainly is the energy that you would need to consider in sizing the pump motor.

Internal energy - the energy of molecular motion (translation, vibration, and rotation) and of intermolecular attraction and repulsion. This is related to enthalpy, which we will talk about later, and is usually obtained from tables.

Heat and work - in many ways these are the forms of energy most familiar to us. In an important sense, heat and work are different from the other forms of energy described above, in that they are energy in transit, i.e. energy being transferred from one body to another. Possibly this is why they seem familiar to us. Looking at a brick, it is not evident that it contains internal energy, but if you drop it on your foot, the work it does on your foot is felt quite evidently.

It is the interchange of energy that causes changes and is therefore at the heart of processes. So heat and work, which are forms of energy being interchanged between materials, are therefore at the heart of energy balances.

3.2.1 Heat

Heat is the most familiar form of energy. We know that a stove feels hot and ice feels cold. To describe this familiar phenomenon more carefully, what happens is that when we touch a stove, heat flows from the stove to our hand, and it therefore feels hot (relative to our hand). When we touch an ice cube, heat flows from our hand to the ice cube, and it feels cold (relative to our hand). From these familiar notions we can formulate two important ideas:

- Heat is a form of energy that flows, or as we often say, is transferred from one object to another or between a system and its surroundings. Because of this heat flow, one object loses some energy, and the other object gains this energy. When we hold an ice cube, heat flows from our hand to the ice cube. So our hand loses some of its energy content, as shown by the decrease in its temperature. Conversely, the energy content of the ice cube increases, as shown by the fact that the ice cube melts (or increases in temperature).
- In order for there to be a flow of heat, there must be a temperature difference or gradient (heat, like water, will only flow “downhill” i.e. from hot to cold).

From these two ideas, we can define heat as “the form of energy which flows from one object or system to another as the result of a temperature difference”. And it is one of the laws of thermodynamics, and something that we know from our everyday experience, that the direction of the flow is from hotter bodies to colder bodies.

3.2.2 Enthalpy

We noted earlier the concept of Internal Energy, that is, the energy that a material possesses as a result of the motion and attractions and repulsions of its molecules. This energy depends on the composition of the material and its state, which is determined by its temperature and pressure. Related to the internal energy is the enthalpy, which is defined as,

$$h = u + Pv \quad (3.1)$$

where h is specific enthalpy (enthalpy per unit mass, units kJ kg^{-1}), u is specific internal energy (kJ kg^{-1}), P is pressure (Pa), and v is specific volume ($\text{m}^3 \text{kg}^{-1}$).

The properties of enthalpy are as follows:

- For a given material, at constant pressure, the enthalpy depends only on the material’s temperature and physical state. So, for example, water at 100°C has less energy and less enthalpy than steam at 100°C .
- At constant temperature and physical state, the change of enthalpy with pressure is negligible for gases, and very small for liquids and solids. This means that for liquids, if you know the enthalpy at a given temperature and the corresponding vapour pressure (the pressure at which the liquid would boil), then this is close enough for

other pressures. Tables often give enthalpy data at a particular temperature and the corresponding vapour pressure.

- The enthalpy of a substance at a specific set of conditions (T , P and physical state) is independent of the route taken to reach those conditions. In addition enthalpy is an extensive quantity, i.e. the total enthalpy of a component is just given by the number of moles of that component times molar enthalpy h .

3.2.3 Specific heat capacity

When you heat up a material, its enthalpy increases as the temperature increases. The amount of energy needed to raise the temperature of a material by $1\text{ }^\circ\text{C}$ varies. For water, for example, it takes about 4200 J to raise the temperature of 1 kg by $1\text{ }^\circ\text{C}$, while for air, it takes only about 1000 J (less than a quarter) to achieve the same temperature rise.

The amount of energy required to heat up a kilogram of a material by $1\text{ }^\circ\text{C}$ is called its specific heat capacity, C_p (“specific” refers to the fact that we are dealing with a kilogram - if we were talking about the energy to heat up a mole of material, we would use the molar heat capacity). The units of specific heat capacity are $\text{J kg}^{-1}\text{ }^\circ\text{C}^{-1}$ i.e. the amount of energy in Joules to raise the temperature of 1 kg by $1\text{ }^\circ\text{C}$.

The specific heat capacity is the slope of the graph of enthalpy against temperature (provided the material does not change its phase),

Specific Heat Capacity

$$C_p = \frac{dh}{dT} \tag{3.2}$$

The above equation can be integrated to calculate the amount of energy required to raise the temperature of 1 kg (or 1 mol) of a pure substance from T_1 to T_2 .

$$Q = \Delta h = \int_{T_1}^{T_2} C_p dT \tag{3.3}$$

Note that this approach only works when there is no phase change during the heating process. In order to evaluate the integral, we need to know how heat capacity depends upon temperature.

Often, the specific heat capacity depends on the temperature, thus it is common to provide it as a general expression, for example,

$$C_p = A + BT + CT^2 + DT^3 \tag{3.4}$$

where A , B , C , and D are experimentally measured, empirical constants that depend on the molecule type.

3.2.4 Phase Change

Water at atmospheric pressure boils when it reaches 100 °C, to form steam at 100 °C. Both are at the same temperature, but steam contains more energy than water. To put it another way, it takes energy to convert water into steam.

The amount of energy required to convert water into steam is called the latent heat of vapourisation. Similarly, when steam gives up this energy and condenses into water, this is called the latent heat of condensation. The magnitude of the energy change is the same whether we are evaporating water or condensing steam. For water/steam at 100 °C and atmospheric pressure, the latent heat of vaporisation/condensation is 2257 kJ kg⁻¹. Comparing this with the enthalpy difference between water at 0 and 100 °C of 419.2 kJ kg⁻¹, we can see that it takes a lot more energy to convert water into steam than it does to heat water from 0 to 100 °C.

Similarly, it takes energy to melt ice, and water turning to ice gives up energy. This is called the latent energy of melting or fusion, and has a magnitude of 333.5 kJ kg⁻¹ at 0 °C.

Figure 3.1 below shows the change in enthalpy with temperature for water, as it changes from ice to liquid water to steam, showing that the largest change arises due to the latent heat of vaporisation.

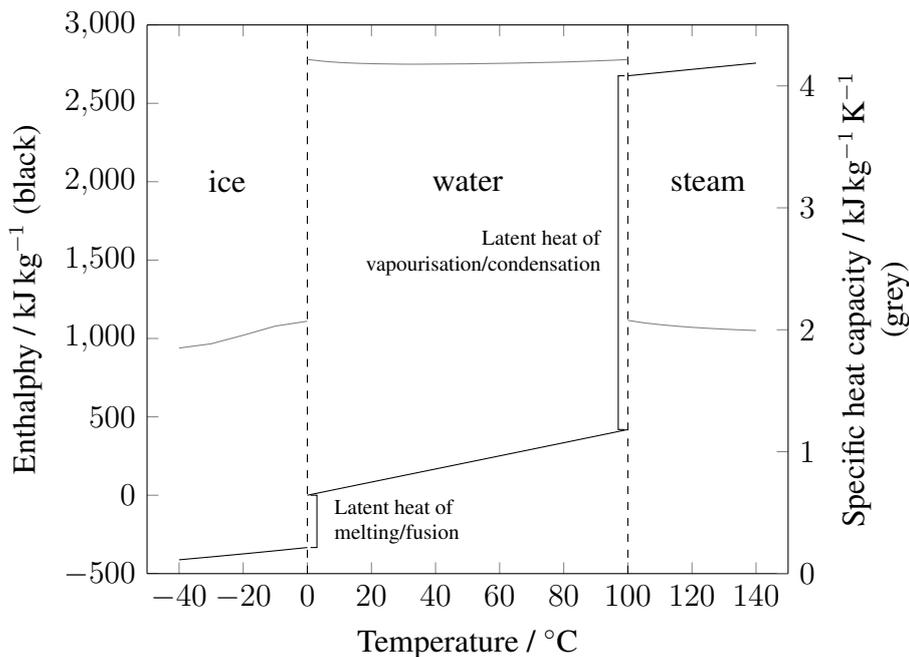


Figure 3.1: Variation with temperature of enthalpy (black lines, left axis) and specific heat capacity (grey lines, right axis) of ice, water, and steam at atmospheric pressure.

? Question

Air at 25 °C is able to “carry” a maximum of 0.0202 kg water per kg air (at which point the air is considered saturated). Calculate the temperature drop of dry air that would cause it to end up at 25 °C and 10% saturated with water, and therefore the initial temperature of the air.

Latent heat of vapourisation of water at 25 °C is 2442 kJ kg⁻¹, and the specific heat

capacity of air can be taken as $1.005 \text{ kJ kg}^{-1} \text{ K}^{-1}$.

3.3 Energy balances on non-reacting systems

Conservation of energy is one of the fundamental laws of the universe, along with conservation of mass, except where nuclear reactions are involved, in which case mass can be converted to energy via equation 1.3, as discussed in Section 1.4.

But in most process industries, except the nuclear industry, we don't get nuclear reactions occurring, so we can take it as fundamentally true that both energy, and mass, are conserved independently. This means that all the energy that enters a system must leave, one way or another, or else must accumulate in the system, i.e. the same balance as in equation 1.1,

$$\text{In} - \text{Out} + \text{Generation} - \text{Consumption} = \text{Accumulation} \quad (3.5)$$

Just as with mass balances, this applies to overall plant balances, to individual unit operations, and to small elements within equipment. Applying this law to conservation of energy within process equipment results in sets of equations, either algebraic or differential, which describe the variation of temperature or heat flow within the equipment.

We must remember to include **all** forms of energy involved, and recognise that a particular form of energy is not necessarily conserved, as energy can be transformed, e.g. from mechanical work into heat.

For the continuous system in Figure 3.2, at steady state (i.e. no accumulation) where there is no shaft work (i.e. no compressors or turbines), the energy balance, equation 3.5, can

be written as,

$$\left[\begin{array}{c} \text{Enthalpy} \\ \text{of inputs} \end{array} \right] + \left[\begin{array}{c} \text{Heat transfer} \\ \text{to process} \end{array} \right] = \left[\begin{array}{c} \text{Enthalpy} \\ \text{of outputs} \end{array} \right] + \left[\begin{array}{c} \text{Heat transfer} \\ \text{from process} \end{array} \right] \quad (3.6)$$

$$\dot{m}_{\text{in}} h_{\text{in}} + \dot{Q}_{\text{in}} = \dot{m}_{\text{out}} h_{\text{out}} + \dot{Q}_{\text{out}}$$

In this case the change in the kinetic and potential energy of the flowing stream have been neglected, as they are likely small in comparison to the enthalpy and heat change.

Therefore to allow us to perform the energy balance, we need to establish equations for the enthalpy of the various components flowing into and out of the system. The enthalpy of any component in phase β at the given temperature and pressure needs to be calculated. Usually a reference enthalpy is taken as the heat formation, Δh_f , i.e. the enthalpy change when one kg (or kmol) of a species is formed from its elements in its usual physical phase α (i.e. vapour, liquid, or solid) at 25 °C and 1 atm,

Component Enthalpy

$$h_{\beta}(T) = \Delta h_{f,\alpha} + \int_{25}^{T_p} C_{p,\alpha} dT + \Delta h_{\beta\alpha}(T_p) + \int_{T_p}^T C_{p,\beta} dT \quad (3.7)$$

where T_p corresponds to the temperature of phase change from α to β .

For example, lets think about a system that is used to heat water, as in Figure 3.3. How much energy does it take heat this water? The enthalpy of formation of water at 25 °C is $-285.83 \text{ kJ mol}^{-1}$, the latent heat of vapourisation at 100 °C is $40.68 \text{ kJ mol}^{-1}$, the molar heat capacity of water is $75.30 \text{ J mol}^{-1} \text{ K}^{-1}$, and the molar heat capacity of steam is $36.50 \text{ J mol}^{-1} \text{ K}^{-1}$.

To solve this problem we need to use equation 3.6, where we can calculate the values of the enthalpy from equation 3.7.

$$\begin{aligned} h_l(25) &= \Delta h_{f,l}(25) \\ &= (-285.83) = -285.83 \text{ kJ mol}^{-1} \end{aligned}$$

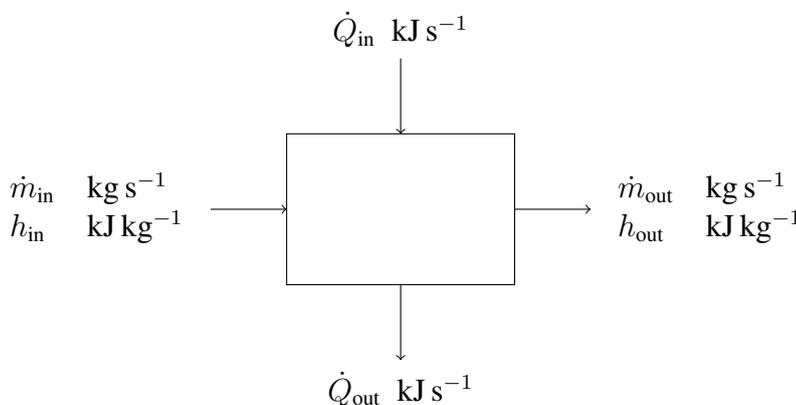


Figure 3.2: Energy balance for a simple continuous system.

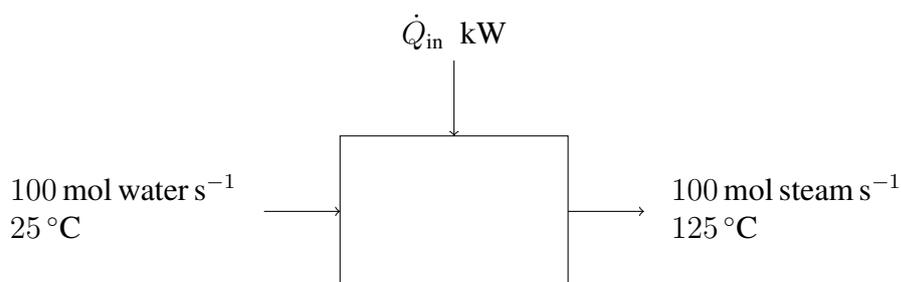


Figure 3.3: Example water heater calculation system.

$$\begin{aligned}
 h_v(125) &= \Delta h_{f,l}(25) + C_{p,l}(100 - 25) + \Delta h_{vl}(100) + C_{p,v}(125 - 100) \\
 &= (-285.83) + (75.30/1000)(100 - 25) + (40.68) + (36.50/1000)(125 - 100) \\
 &= -238.59 \text{ kJ mol}^{-1}
 \end{aligned}$$

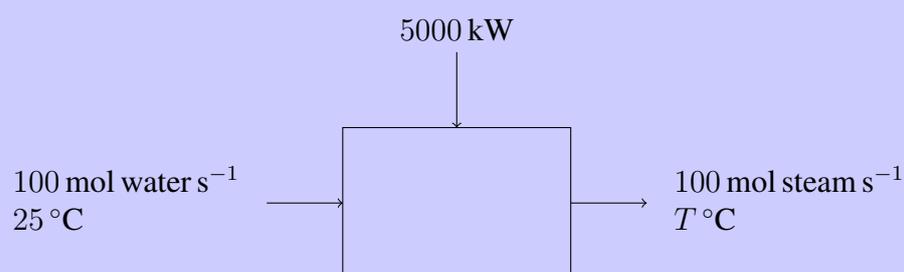
Thus

$$\begin{aligned}
 \dot{m}_{in}h_{in} + \dot{Q}_{in} &= \dot{m}_{out}h_{out} + \dot{Q}_{out} \\
 (100)(-285.83) + \dot{Q}_{in} &= (100)(-238.59) + (0) \\
 \dot{Q}_{in} &= (-23,859) - (-28,583) = 4,724 \text{ kW}
 \end{aligned}$$

? Question

A heater heats water as in the figure below and turns it into steam. What is the temperature of the exiting steam?

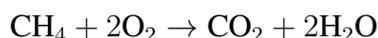
The enthalpy of formation of water at 25 °C is $-285.83 \text{ kJ mol}^{-1}$, the latent heat of vapourisation at 100 °C is $40.68 \text{ kJ mol}^{-1}$, the molar heat capacity of water is $75.30 \text{ J mol}^{-1} \text{ K}^{-1}$, and the molar heat capacity of steam is $36.50 \text{ J mol}^{-1} \text{ K}^{-1}$.



3.4 Energy balances involving chemical reactions

When chemical reaction occurs we must account for the enthalpy change associated with the reaction. The general approach for this is to use the standard heat of formation for each component as we did when there was no reaction.

Let us take the example of methane at 25 °C being supplied to a furnace, Figure 3.4, where it is burned in air supplied at 250 °C, as in,



The reaction goes to completion with simultaneous heat transfer within the furnace from the product gases. The gases then leave at 1000 °C. Determine the amount of heat transferred per kmol of methane.

The standard heats of formation (25 °C and 1 atm) are,

$$\text{CH}_{4(\text{g})} = -74,900 \text{ kJ kmol}^{-1}$$

$$\text{CO}_{2(\text{g})} = -393,800 \text{ kJ kmol}^{-1}$$

$$\text{H}_2\text{O}_{(\text{l})} = -286,000 \text{ kJ kmol}^{-1}$$

$$\text{Elements in standard form} = 0 \text{ kJ kmol}^{-1}$$

the molar heat capacities are,

$$\text{O}_{2,25 \rightarrow 250} = 29.58 \text{ kJ kmol}^{-1} \text{ K}^{-1}$$

$$\text{O}_{2,25 \rightarrow 1000} = 33.29 \text{ kJ kmol}^{-1} \text{ K}^{-1}$$

$$\text{N}_{2,25 \rightarrow 250} = 29.58 \text{ kJ kmol}^{-1} \text{ K}^{-1}$$

$$\text{N}_{2,25 \rightarrow 1000} = 31.35 \text{ kJ kmol}^{-1} \text{ K}^{-1}$$

$$\text{H}_2\text{O}_{,25 \rightarrow 1000} = 38.66 \text{ kJ kmol}^{-1} \text{ K}^{-1}$$

$$\text{CO}_{2,25 \rightarrow 1000} = 49.85 \text{ kJ kmol}^{-1} \text{ K}^{-1}$$

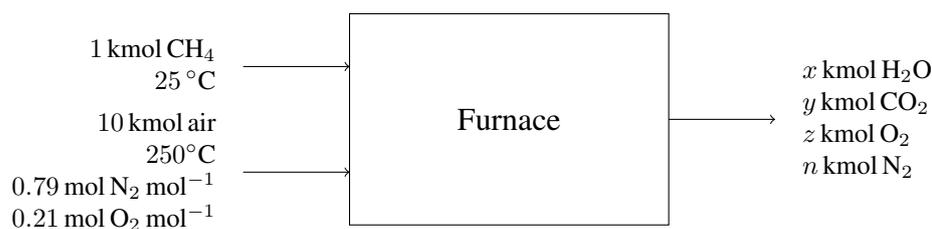


Figure 3.4: Example water heater calculation system.

and the latent heat of vaporisation of water at $25\text{ }^\circ\text{C} = 44,000\text{ kJ kmol}^{-1}$.

Firstly a mass balance must be undertaken for the system, as in equation 1.1 where the accumulation is zero due to being at steady state, and the extent of reaction, ξ is equal to the number of moles of CH_4 into the furnace, as the reaction goes to completion,

	Input	+ (Generation – Consumption)	= Output	
CH_4 :	1	+ $(\xi\nu_{\text{CH}_4} = (1)(-1) = -1)$	= 0	mol
O_2 :	0.21×10	+ $(\xi\nu_{\text{O}_2} = (1)(-2) = -2)$	= 0.1	mol
N_2 :	0.79×10	+ $(\xi\nu_{\text{N}_2} = (1)(0) = 0)$	= 7.9	mol
H_2O :	0.0	+ $(\xi\nu_{\text{H}_2\text{O}} = (1)(2) = 2)$	= 2	mol
CO_2 :	0.0	+ $(\xi\nu_{\text{CO}_2} = (1)(1) = 1)$	= 1	mol

Now the mass balance has been completed, we can undertake the energy balance. The enthalpy in is,

	$N\Delta h_f(25)$	+ $NC_p(T - 25)$	= Total	
$\text{CH}_4(25)$:	$(1)(-74,900)$	+ 0	= -74,900	kJ
$\text{O}_2(250)$:	$(0.21 \times 10)(0)$	+ $(0.21 \times 10)(29.58)(250 - 25)$	= 13,977	kJ
$\text{N}_2(250)$:	$(0.79 \times 10)(0)$	+ $(0.79 \times 10)(29.58)(250 - 25)$	= 52,578	kJ
Total:			= -8,345	kJ

The enthalpy out is,

	$N\Delta h_f(25)$	+ $N\Delta h_{vl}(25)$	+ $NC_p(T - 25)$	= Total	
$\text{O}_2(1000)$:	$(0.1)(0)$	+ 0	+ $(0.1)(33.29)(1000 - 25)$	= 3,246	kJ
$\text{N}_2(1000)$:	$(7.9)(0)$	+ 0	+ $(7.9)(31.35)(1000 - 25)$	= 241,473	kJ
$\text{H}_2\text{O}(1000)$:	$(2)(-286,000)$	+ $(2)(44,000)$	+ $(2)(38.66)(1000 - 25)$	= -408,613	kJ
$\text{CO}_2(1000)$:	$(1)(-393,800)$	+ 0	+ $(1)(49.85)(1000 - 25)$	= -345,196	kJ
Total:				= -509,090	kJ

Thus the total energy balance for the system is,

$$N_{\text{in}}h_{\text{in}} + Q_{\text{in}} = N_{\text{out}}h_{\text{out}} + Q_{\text{out}}$$

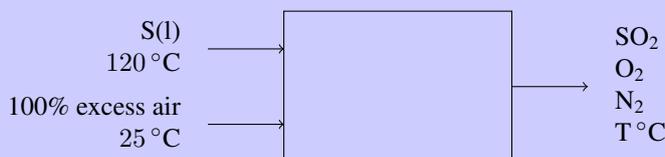
$$(-8,345) + (0) = (-509,090) + Q_{\text{out}}$$

$$Q_{\text{out}} = (-8,345) - (-509,090) = 500,745\text{ kJ}$$

Thus 500,000 kJ is released by the furnace for every kmol of CH_4 burned.

? Question

The first stage of sulfuric acid production is the adiabatic (no energy added/lost) combustion of liquid sulfur with 100% excess air. This produces sulfur dioxide gas at a high temperature. The sulfur dioxide is then reacted with more air to form sulfur trioxide in the contact process; this is then further reacted with water to form sulfuric acid. What is the temperature of the sulfur dioxide gas after the combustion (adiabatic means no heat given or lost from the system)?



Enthalpy of fusion (melting) for sulfur, $\Delta h_{l,s,S}(120\text{ }^\circ\text{C}) = 2000\text{ kJ kmol}^{-1}$

Standard heat of formation of SO_2 , $\Delta h_{f,\text{SO}_2} = -297,000 \text{ kJ kmol}^{-1}$

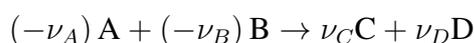
Molar heat capacities:

$$\begin{aligned} \text{S}_{(s)} &= 26.0 \text{ kJ kmol}^{-1} \text{ }^\circ\text{C}^{-1} \\ \text{SO}_{2(g)} &= 51.0 \text{ kJ kmol}^{-1} \text{ }^\circ\text{C}^{-1} \\ \text{O}_{2(g)} &= 33.3 \text{ kJ kmol}^{-1} \text{ }^\circ\text{C}^{-1} \\ \text{N}_{2(g)} &= 31.5 \text{ kJ kmol}^{-1} \text{ }^\circ\text{C}^{-1} \end{aligned}$$

Infobox 4: Solving energy balances by heat of reaction.

An alternative approach to solving energy balances is to use the standard heat of reaction. The standard heat of reaction is defined as the amount of heat removed for a process when the extent of reaction is 1 mole and the reactants and products enter and leave the process at 25 °C and in their usual state (i.e. the state at that temperature and pressure).

Consider a simple reaction,



As the products of a reaction must be made up of the same elements as the reactants, we can determine the standard heat of any reaction from the standard heats of formation of the reactants and products,

$$\Delta h_R^0 = \nu_A \Delta h_{f,A} + \nu_B \Delta h_{f,B} + \nu_C \Delta h_{f,C} + \nu_D \Delta h_{f,D} = \sum_i \nu_i \Delta h_{f,i}$$

The enthalpy for the reaction at the actual temperature can then be calculated by summing the three parts,

- i enthalpy change to take the reactants from their initial temperature and state (gas, liquid, or solid) to 25 °C and their usual state,

$$\Delta H_1 = \sum_i m_i C_{p,i,\beta} (25 - T_{in}) + \sum_i m_i \Delta h_{\alpha\beta,i,25}$$

- ii heat of reaction term given by multiplying the extent of reaction by standard heat of reaction

$$\Delta H_2 = \sum_r \xi_r \Delta h_{R,r}^0$$

- iii enthalpy change in taking the products from 25 °C and their usual state to their final temperature and final state.

$$\Delta H_3 = \sum_i m_i C_{p,i,\beta} (T_{out} - 25) + \sum_i m_i \Delta h_{\beta\alpha,i,25}$$

so that the total enthalpy is given by,

$$\Delta H_R = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Conversion of Landfill Gas to Town's Gas

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4.1 Introduction

Landfill gas (LFG) is produced by anaerobic decomposition of general waste and contains mainly Methane and Carbon Dioxide. The LFG may also contain other components, which tend to be the factors that cause the gas to be un-useful in its untreated form. These other components can include inerts, such as Nitrogen, potential poisons and toxins, such as Hydrogen Sulphide and Mercury, or compounds that hinder the treatment of the gas, such as Oxygen and Vanadium. The treatment of LFG is often complex as the concentration and type of these contaminants vary with not only the landfill site, but also with time in one particular landfill. One of the uses of LFG is the conversion to Town's Gas (TG).

TG tends to contain Methane and Hydrogen along with some other inert components, such as Nitrogen and Carbon Dioxide. The important parameters for TG are the calorific value and the flame speed. These will determine the correct amount of energy that can be received from burning the Towns Gas, so that it can be lit and kept burning.

Product gas Property	Range	Normal Value
H ₂	46.3 – 50.3 mol% (dry)	49.0 mol% (dry)
CH ₄	28.2 – 30.7 mol% (dry)	28.5 mol% (dry)
CO ₂ + N ₂	18.8 – 21.0 mol% (dry)	19.5 mol% (dry)
CO	3.0 mol% (dry) maximum	3.0 mol% (dry)
H ₂ S	0 – 3.5 ppmv	0 ppmv
THT Odorant	16.0 – 24.0 mg Nm ⁻³	20.0 mg Nm ⁻³
Calorific Value	17.10 – 17.44 MJ m ⁻³	17.27 MJ m ⁻³
Specific Gravity	0.50 – 0.54	0.52
Wobbe Index	23.2 – 24.8 MJ m ⁻³	24.0 MJ m ⁻³
Flame Speed	33.0 – 37.0 ft s ⁻¹	35.0 ft s ⁻¹
Pressure	7 barg	
Temperature	10 – 40 °C	25 °C
Dew Point	0 °C at 7 barg	

4.2 Process Description

The general process for turning LFG into TG can be seen as a block flow diagram as Figure 4.1. Data for some of the streams is known, which is given as Table 4.1.

4.2.1 Pre-treatment

The LFG is firstly pre-treated, this involves removing the trace amounts of impurities, such as:

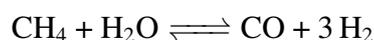
- organosulphur, organochlorine and organofluorine – reacted with hydrogen over a cobalt molybdate catalyst to hydrogen sulphide
- hydrogen sulphide – removed by reaction with Zinc Oxide or the Claus process
- hydrogen chloride and hydrogen fluoride – adsorbed with Na₂O
- mercury – adsorbed with sulphur doped activated carbon

- oxygen – burned with small amounts of added hydrogen
- vanadium, lead, and arsenic – adsorbed onto the cobalt molybdate catalyst

The treated LFG is also pressurised using a series of compressors up to the process pressure of 2835 kPa, this pressurisation also causes the treated LFG to heat up to 660 K.

4.2.2 Reformer

After the pre-treatment the LFG is sent to the reformer. Steam reforming is the process by which methane can be reacted with water to produce carbon monoxide and hydrogen. This is usually carried out by contacting a mixture of methane and steam at high temperature, with an activated Nickel Oxide catalyst. This process was conducted under a pressure of up to 4000 kPa and at temperatures up to close to 1225 K. The main steam reforming reaction is,



This reaction is highly endothermic and requires an external source of heat and an initial source of steam. This is generally carried out by preheating the steam – Methane mixture in heat exchangers or fired heaters to around 1000 K and then heated during the reaction over the nickel catalyst in tubes with a fired furnace. Some of the LFG is diverted to be burned in this furnace, in this case it is 18.8 % of stream 3.

Methane is only partially converted to Hydrogen determined by the equilibrium of reaction, which is in turn determined by the steam:methane ratio, pressure, temperature, etc. In this case steam (1000 K and 2785 kPa) is added at 2.2 times the flow rate of methane into the reformer.

In this case as we are producing TG we don't need to convert all the methane to hydrogen. Steam reformers have the ability to work at high conversion, therefore it is more economical to only send part of the LFG to the reformer and bypass some of the methane rich LFG. The fraction of LFG sent to the reformer is x .

If carbon monoxide is also present in the feed, or as it is produced in the reformer, a secondary reaction can take place in which this is too converted to carbon dioxide and hydrogen, as,



Depending on the exact temperature, this reaction may proceed in reverse.

Table 4.1: Known stream compositions and flow rates for Figure 4.1.

Value	Stream						
	1	2	3	4	5	6	7
Mole Fraction							
CH ₄	0.4994	0.4999	0.4999	0.0285			
CO ₂	0.3520	0.3523	0.3523				0.1858
CO	0.0000	0.0000	0.0000				
H ₂ O	0.1477	0.1478	0.1478	0.3052	0.1741		
H ₂	0.0000	0.0000	0.0000				
Impurities	0.0009	0.0000	0.0000				
Total / mol hr ⁻¹	1000000	999100	999100	896618		1402163	1032254

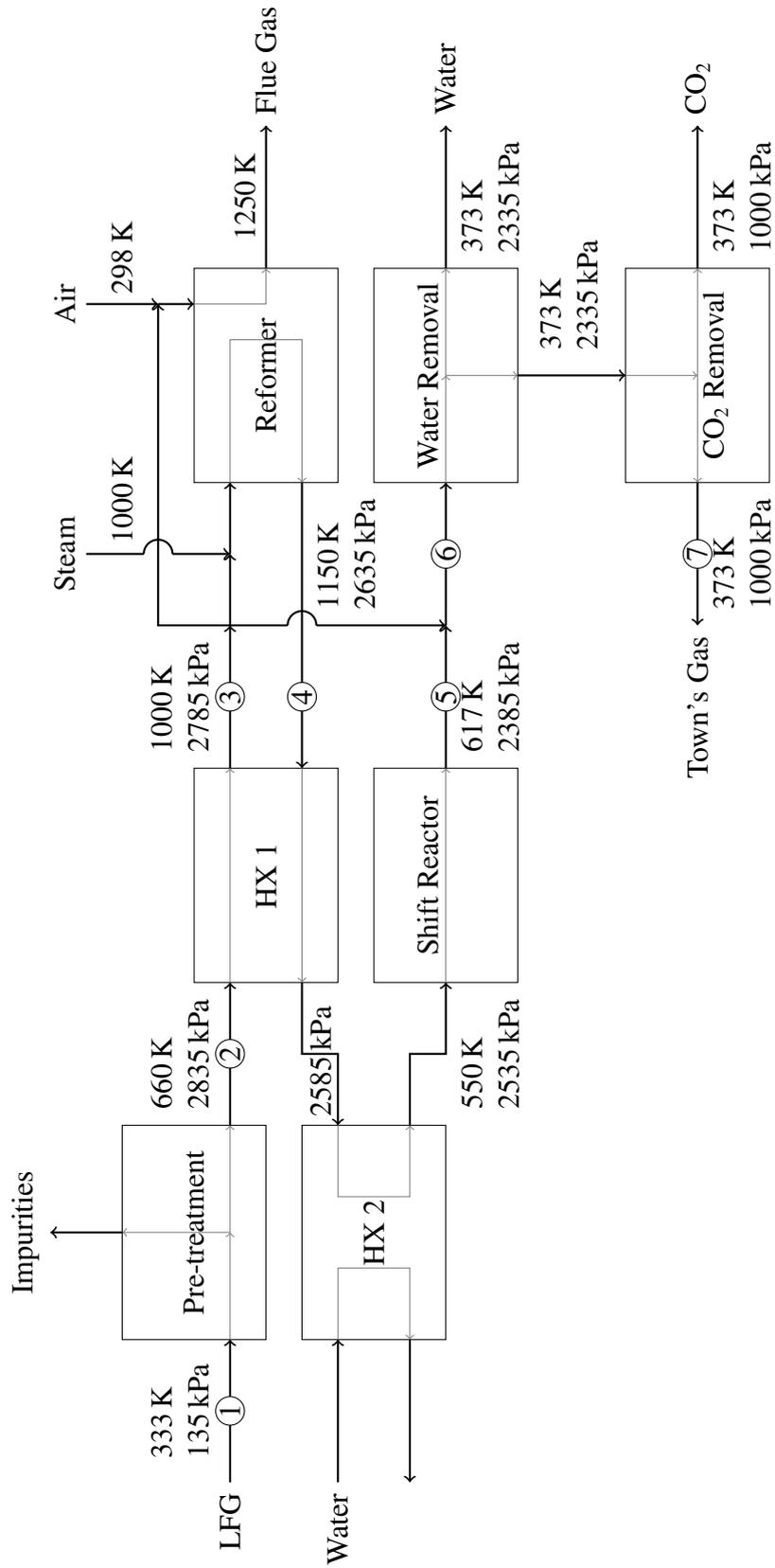


Figure 4.1: Block flow diagram for the conversion of land fill gas to town's gas.

4.2.3 Shift Reactor

After the reformer there can be a large amount of carbon monoxide present. This needs to be removed, which can be undertaken using the shift reaction,



This is usually carried out by contacting a mixture of carbon monoxide and steam in a two step process, the first at high temperature and the second at a reduced temperature. The first phase of this process is generally carried out at around 600 K. This process is carried out with an iron oxide catalyst, and can be used to reduce carbon monoxide concentrations to around 1-2 %. The second phase of this process is generally carried out at around 470 K and uses a copper based catalyst and can further reduce the carbon monoxide concentration to around 0.1-0.2 %. In this case this second process will not be needed as we only need to reduce the concentration of carbon monoxide to around 3 %.

As the temperature of the shift reactor is much lower than the temperature at the exit of the reformer heat needs to be removed from the process stream. This can be cooled using a heat exchanger with cooling water; however, the some of this heat can be used to heat up the entrance stream to the reformer. This is called process integration and saves energy, in this case we save the heat energy needed to heat the stream to the reformer and save the cooling water needed to cool part of the ext stream.

4.2.4 Post-Treatment

Before the TG can be used, some of the water and carbon dioxide needs to be removed to match the specification. As we do not need perfectly dry gas, this means that the method of cooling the gas and using a gas-liquid separator is perfectly adequate. The amount of water separated on cooling is dependent on the vapour pressure of the water, $p_{\text{H}_2\text{O}}^o$, at that temperature, T , and the gas pressure, P . The mole fraction of water, y , in the gas phase is given by,

$$y_{\text{H}_2\text{O}} = \frac{p_{\text{H}_2\text{O}}^o}{P} \quad (4.1)$$

If we know the mole fraction of water in the gas at the initial temperature and the fraction at the final temperature we can calculate the amount of water removed. The vapour pressure of water, in Pa, can be calculated by using, where T is in K,

$$p_{\text{H}_2\text{O}}^o = \exp \left[73.649 - \frac{7258.2}{T} - 7.3037 \ln T + 4.1653 \times 10^{-6} T^2 \right] \quad (4.2)$$

Carbon dioxide can be removed from the process gas in a number of positions within the process. The best position to do this will be after the reforming and shift reactions have taken place, as these produce carbon dioxide. A number of methods are available to remove carbon dioxide from the gas stream, for example adsorption or membranes; however, for this case the exact method is not important. These separation methods are however not perfect and often have a low separation, espeacilly if the separated gas is kept pure. In this case we only need a low separation to acheive the product specification.

4.3 Design

During the process some data about the stream flow rates and compositions are collected, given in Table 4.1. Using this data the compositions of all the streams can be calculated for the process.

1. What is the extent of the 2 reactions in the reformer and the reaction in the shift reactor?
2. What is the temperature of the stream between HX 1 and HX 2?
3. What is the final specification of the TG, does it meet what is needed?

Some useful data can be seen in Table 4.2.

Table 4.2: Vapour phase properties of key components. *liquid water enthalpy of formation is $-285.83 \text{ kJ mol}^{-1}$ and the enthalpy of vapourisation is 44 kJ mol^{-1} .

Component	$\Delta H_f \text{ kJ mol}^{-1}$	$C_p \text{ kJ mol}^{-1} \text{ K}^{-1}$
CH ₄	-74.6	0.0432
CO ₂	-393.5	0.044
CO	-110.5	0.028
H ₂ O	-241.8*	0.108
H ₂	0	0.029
N ₂	0	0.028
O ₂	0	0.032
Impurities	-37.4	0.0741

